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Multilayer Flexible Packaging

Technology and Applications for the Fodd, Personal Care and Over-The-Counter Pharmaceutical Industries

John R. Wagner Jr.

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Preface

In the beginning of this project, I had expected to complete it in less than a year. Now, four years later, it has finally come to completion. Along the road, the pressures of limited resources and conflicting objectives changed the time line and contributors.

This book had ambitious goals set. What has resulted is an incomplete description of multilayer films and the technology to produce them. It is a snapshot that gives a comprehensive view of multilayer film designs and technology used. As in any evolving system, things change and what we can describe today may be somewhat different tomorrow. The value this book brings is that it will help interested parties to understand what is being made and how it is produced. This will help them deal with current problems and issues and move forward to invent new products and processes that will meet future challenges.

The authors who have contributed their time and extensive knowledge are industry experts and respected educators from around the world. They have shared their thoughts and ideas with you so that you can better understand this important technology and improve your contributions in your area of expertise.

The book is organized as follows:

Introduction
Raw materials

- Resins
- Additives
- Rheology

Die Design

- Flat
- Blown

Process Considerations
Technologies

- Blown film, cast film and lamination processes
- Machine direction orientation process
- Biaxial orientation
- Blending
- Coating technologies
- Vacuum deposited coating

Multilayer Film Designs

- PE based film
- Oriented films

Appendix: Writing guide for describing multilayer film structures.

As the technology of multilayer films is constantly developing, it is virtually impossible to have an up-to-the minute description of every multilayer film and technology used. So, this book, by definition, is only a snapshot of what is available. By reading this book, whether you are a manager, purchasing agent, user, engineer or technician, you can improve your knowledge and insight into this important technology that provides safety, freshness and visual appeal for point of sale awareness.

The introduction starts by presenting a historical perspective of the materials used to produce flexible plastic films. Then a look at how the markets for flexible plastic films have grown along with an extrapolation to 2020. The main body of this book is divided into three sections:

- materials
- hardware and processes
- multilayer film designs with applications.

In the materials section, there are chapters about polyethylene and polypropylene, the two major materials used for flexible film, a comprehensive chapter on additives used to make polymers functional and then a chapter on rheology which presents important concepts needed to understand non-Newtonian viscoelastic flow.

The hardware and process section begins with a chapter that describes the dies used to produce multilayer film. Annular dies are used for blown processes. The several ways multilayer dies can be designed are presented. Flat dies are used for cast and oriented films. Multilayer structures can be produced with multicavity dies, feedblocks and by combining feedblocks with multicavity dies.

There is a special chapter on process engineering and how important this function is to producing multilayer films that meet specifications and cost targets.

Then there follow chapters about the technologies used to produce multilayer films. The areas covered are production of multilayer films, laminating films to produce a structure that cannot be produced in a single step and coating processes. The chapter on blending is especially useful as blending technology is widely used and not always easy to understand.

The last section presents PE based and oriented film based multilayer structures. In these two chapters, you will learn about many different structures and their applications.

The Appendix presents a nomenclature or shorthand language that can be used to describe multilayer films.

Read. Learn. Enjoy.

Acknowledgement

This book has been a long time in the making. This project would not have been possible without the dedicated efforts of the authors who have contributed their time and knowledge. Before you, the readers, get to read this book there were just blank pages. Now you can hear the author's thoughts across distance and time. It is my hope and desire that the knowledge presented in these pages will help you do your jobs more effectively and efficiently. Therefore, I dedicate this book to the authors who have contributed their time and you the reader who can learn from its contents and perhaps write your own book which will foster and add to our scientific and engineering knowledge.

For me, knowledge is the only thing I know that one can give away and still retain and in the giving enhance what you have.

Best regards,
John R. Wagner, Jr

Contributors

Joachim Bayer

Joachim Bayer joined Songwon in June 2007 as director of technical sales for Europe and Middle East. Joachim has 13 years of experience in antioxidants, UV additives, dispersing agents and antistats. Joachim acquired key competences in physical forms and polymer conversion processes. He held various positions in R&D, TS, Marketing and Sales. Before Songwon, he worked for Hoechst (D), Clariant (D), Great Lakes (CH) and Chemtura (CH).

Charles A. Bishop

Charles left school at 16 and completed an engineering apprenticeship as a toolmaker. He took a degree in Materials Technology at Loughborough University. He then moved to the Physics Department and completed his Masters and Doctorate degrees by research into vacuum deposition onto polymer webs. After a brief time as a post doctoral researcher and consultant, he moved into industry working for ICI and DuPont for 15 years before setting up his own consultancy business in 1998.

He authored the book '*Vacuum deposition onto webs, films and foils*' and authored or co-authored over 60 papers and 5 patents. He jointly runs a vacuum training website (www.VacuumCoatingTraining.com) and edits the AIMCAL Blog www.vacuumcoatingblog.com and is on their panel of 'Experts' to answer problems members send in. He received the SVC Mentor Award 2008.

Jürgen Breil, PhD

Dr Jürgen Breil graduated from the Rheinisch-Westfälische Technische Hochschule (RWTH) Aachen in 1980. He remained at RWTH Aachen and was employed in the field of science and industrial projects in the faculty of Mechanical Engineering. He focused on automating extrusion lines and received his PhD from the Institute for Plastic Processing (IKV).

At Krauss Maffei Kunststofftechnik, Munich, he worked on automating injection-molding machines. He joined Brückner Maschinenbau GmbH in 1986 and worked on several automation projects. He was promoted to department leader for technology and automation and, in 1993, he became responsible for the Research and Development department. Since 2002, he has been the head of division Process Technology and R&D.

Dr Breil is the author of 14 papers and nine patents on orientation technologies.

Thomas Butler

Thomas I. (Tom) Butler received his BS in Chemical Engineering from New Mexico State University. He has over 39 years of experience in the development of application and products for the plastics and chemical industry. Tom now provides consulting services with his company Blown Film Technology, LLC. Tom retired from The Dow Chemical Company in 2004 where he made significant contributions in the development of polyethylene polymers and processing technology while in the Polyethylene Technical Service and Development Group. His interests include expertise in extrusion process design and control, coextrusion technology and blown film process technology. He has been involved in film application development for film liners, stretch cling, grocery sacks, adhesive resins, sealant resins, skin packaging, snack food applications, processed meat packaging, hygiene applications and produce packaging.

Allison Calhoun, PhD

Dr Allison Calhoun is an Associate Professor of Chemistry and teaches courses in general and physical chemistry and the applications of physical chemistry in environmental and polymeric systems at Whitman College in Washington state. Prior to joining the faculty at Whitman, she worked for five years in the polymer industry and holds three patents for the use of mineral additives in polymeric thin films. She is the co-author of a polymer science textbook and her current research projects examine the oxidation of polyolefins and the impact of this oxidation on the interface of minerals in polymers. She received her PhD from the University of Georgia with a focus in physical chemistry. She sits on the Board of Directors for the Flexible Packaging Division of the Society of Plastics Engineering and is a member of the Physical Chemistry Test Writing Committee through the American Chemical Society.

Edward D. Cohen, PhD

Dr Cohen is a technical consultant in all aspects of the web coating process. He received a PhD from the University of Delaware and a BS in Chemical Engineering from Tufts University. His expertise is in the coating and drying of thin films, coating process development and scale-up, coating defects and new product development.

He has over 45 years' experience in coating research and manufacturing technology with the DuPont Company and as an independent consultant. He has extensive publications in coating drying technology. Currently, he is Technical Consultant for AIMCAL.

Edgar B. Gutoff

Edgar B. Gutoff, ScD, PE has been a consultant on coating and drying since 1988. He organized the first of the 14 International Coating Symposia at the AIChE Spring 1982 meeting and was the founding Secretary of the International Society for Coating Science and Technology, which now sponsors them. He has organized a number of coating courses and seminars and has co-authored *Coating and Drying Defects*, *Modern Coating and Drying Technology* and *The Application of Statistical Process Control to Roll Products*. In 1994, he was awarded the AIChE John A. Tallmadge Award for Contributions to Coating Technology. He is a Fellow of the AIChE and IS&T and is on AIMCAL's Technical Advisory Panel. He worked for Polaroid for 28 years and now is an Adjunct Professor at Northeastern University. He received an ScD and an SM from MIT and a BChE from CCNY.

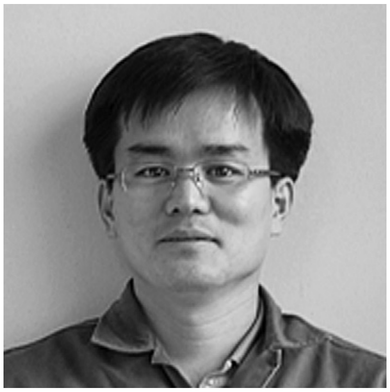
Eric Hatfield

Eric Hatfield is co-owner of MDO Engineering which specializes in Machine Direction Orientors (MDO). He just recently was a Partner and the Managing Director of Operations Technology at FlexTech Packaging Ltd, an MDO & high barrier based film company where he was responsible for Engineering and Process Technologies. Formally, Eric was the manager of Process and Equipment Development for James River's Flexible Packaging Group. Duties there included design of combining adapters, flat and round dies, MDOs and the creation and commercialization of process equipment and technologies. Eric has a BS in Chemical Engineering from the Illinois Institute of Technology and an MBA from Keller Graduate School. He also has several patents.

Duk-Suk Jung

Duk-Suk Jung received an education as chemist and process engineer in South Korea. Duk-Suk is team leader and the manager of the technical department in Songwon's homebase Ulsan (South Korea). His responsibility involves the process engineering of all synthesis plants. He has over 24 years' experience in technical service in Asian countries in antioxidants, UV absorbers, HALS and PVC stabilizers.

Sung-Leal Jung



Sung-Leal Jung received an education as chemist and process engineer in South Korea. Sung-Leal currently holds the position of manager of the Asian technical service group for PVC stabilizers, based in Ulsan (South Korea). For this product group, he has more than 15 years of experience. Before that, he was involved in the engineering of Songwon's stabilizer plants.

Klaus Keck-Antoine

Klaus Keck-Antoine studied Polymer Chemistry at FH Reutlingen in Germany until 1991. He joined Songwon in September 2007 after an extensive career in plastic stabilizers and additives. In the past 16 years, he worked on antioxidants, UV additives, inhibitors, dispersing agents and antistats for polyolefins, engineering resins and non-polymeric substrates. Before Songwon, he worked for Hoechst (Germany), Hoechst Celanese (USA), Clariant (USA), Great Lakes (USA and Belgium) and shortly for Chemtura (Belgium). Currently, he is in charge of implementing Songwon's Global Application and Technical Service Community (GATSC). GATSC is a global forum of and network for industry experts and scientific laboratories to enhance the systematic understanding of polymer additives and provide this service and knowledge to Songwon's customers. He holds various patents and has published frequently on above-mentioned topics.

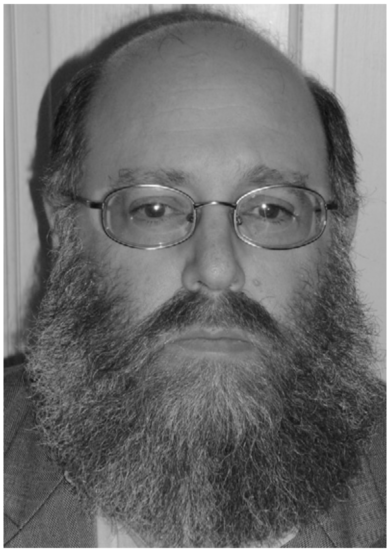
Els Lievens

Els Lievens is a professional bachelor of chemistry from the Karel De Grote Hogeschool in Hoboken (B). She started her career in 1992 with Shell Chemicals in the application research group for polypropylene (PP) in Louvain La Neuve (B), more particular PP film applications. In 1995, she started doing application development work on additives for PP throughout all applications. Later, after the merger of Shell into respectively Montell and Basell, she became responsible for the upscaling of new PP additives in the northern European plants and technical qualification of new additives. In 2002, she joint Great Lakes – later on Chemtura – to be project leader for application development of polymer stabilizers. Since 2007, she has held the position of chemical sourcing manager in the chemistry research department of Agfa Graphics in Mortsel (B).

John Mara

John Mara is the Technical Sales Manager for Songwon International – Americas, a position he has held since 2007. During this time, his primary responsibility has been to grow Songwon's polymer stabilizer business in the Americas providing commercial and technical support to a broad range of customers. Prior to joining Songwon, John managed the Advanced Polymer Technologies Group at Excel Polymers where his research focused on Rubber Nanocomposites. Prior to Excel, John provided technical support to BASF's Light Stabilizer Business, managed commercial and technical activities involving polymer stabilizers with Great Lakes Chemical Company and managed the Polymer Science Analytical Group at Chevron Chemical Company. John received his PhD in Polymer Science/Plastics Engineering from the University of Massachusetts-Lowell (1992) where he studied the synthesis and characterization of novel liquid crystalline polymers. John also holds a Six-Sigma Black belt from the University of Akron (2007) and has authored and co-authored over a dozen technical papers on polymer stabilization.

Scott B. Marks



Scott Marks was educated at Rutgers University where he earned degrees in Mechanical Engineering and Business Administration. He is employed by E.I. DuPont de Nemours & Company, starting initially as a Construction Engineer and then, in 1984, transferred into the Polymers business unit working in the Flexible Packaging industry. He has held Market Development and Technical Service positions concentrating on the Asia-Pacific and North American regions the majority of his career, but also has supported Latin American and Europe.

Scott's process expertise is in multilayer blown film, cast film, extrusion coating and sheet. He has also worked with adhesive lamination and thermal lamination. He has a broad packaging knowledge including meat, cheese, seafood, pharmaceutical and healthcare, personal care and industrial and consumer goods markets. In addition, he has worked with non-packaging applications such as composite building panels, cable shielding, cable sheathing and surf and boogie boards.

Scott's work is mainly with polyolefins, specializing in modified ethylene copolymers for sealants, adhesives and bulk layers in extrusions and laminations. In addition, he has worked with Nylon and ethylene vinyl alcohol coextruded with polyolefins and polyesters, polystyrenes and newer materials such as thermoplastic starch and polylactic acid.

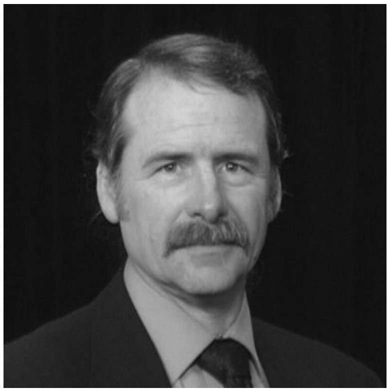
Scott has presented for TAPPI and SPE in North America and via other organizations in Singapore, Malaysia, Thailand, Taiwan, Australia and New Zealand.

He is active in TAPPI's PLACE division, having served in several officer positions including Division Chairman and division council advisor. He is an active member of the Flexible Packaging, Extrusion Coating, and Film Extrusion working committees and co-chairs the International Committee.

Barry A. Morris

Barry A. Morris is a senior technology associate with DuPont Packaging and Industrial Polymers. He received a BS in chemical engineering from the University of Virginia and a PhD from Princeton University. He also has an MBA from the University of Delaware. His research interests include polymer adhesion, blends, compounding, rheology, coextrusion and film and coating converting processes. He has over 20 years of experience in packaging technology and is widely published.

Eldridge M. Mount III



Dr Mount is an independent consultant in the extrusion, metallization and plastic film industries. Originally a chemist, he obtained ME and PhD degrees in chemical engineering at Rensselear Polytechnic in 1979 with the experimental and theoretical study of melting mechanisms and the modeling of polymer melting in single-screw extruders. Since graduation, Eldridge has worked for ICI Americas and ExxonMobil in the areas of biaxially oriented PET and OPP films. His work encompassed process and product design where he was responsible for new screw designs, increased output, coextrusion technology and the development of new metallized and other OPP film products. Eldridge has nine US patents and many publications in the area of metallized OPP films and extrusion. A Fellow and Honored Service Member of SPE, he has been active on the Executive Committee and the Extrusion Division Board and has been a speaker at ANTEC, TAPPI and AIMCAL as well as other professional societies in the areas of metallized films, extrusion and film processing. Since June 2000, Eldridge has been an independent consultant with EMMOUNT Technologies. In his spare time he is a long standing adult Boy Scout Leader and Silver Beaver recipient. He enjoys hunting, hiking and camping.

David Strutt

Dr David Strutt earned his PhD in chemical engineering from the University of Waterloo in 1998, in the area of simulation of mixing in reactive flows of polypropylene in co-rotating twin-screw extruders. He has held several industrial and consulting positions related to plastics processing and currently works in process development for thermoplastic composite tapes at Baycomp Ltd. He is the author of 10 papers on single- and twin-screw extrusion and a co-author of chapters in two SPE books.

John Vlachopoulos

John Vlachopoulos was educated at NTU, Athens, Greece (Dipl Ing) and at Washington University, St Louis, Mo(MS, DSc). He subsequently started teaching and doing research at McMaster University, Hamilton, Canada on polymer processing, applied rheology and computer-aided methods for the solution of flow problems. He is the author of more than 250 publications, frequent lecturer at conferences and consultant to the polymer processing industry worldwide. He is currently Professor Emeritus of Chemical Engineering and President of Polydynamics, Inc. a company specialized in process simulation software.

John R. Wagner Jr

John R. Wagner Jr is President of Crescent Associates, Inc., a consulting firm that specializes in plastic films and flexible packaging. He graduated from the University of Notre Dame with a BS and MS in chemical engineering. His career began with B.F. Goodrich Chemical Co. working on PVC manufacturing from monomer production through polymerization and compounding. He then worked for Mobil Chemical Co. Films Division doing research and development on oriented polypropylene films (OPP) for the food packaging industry. His areas of expertise included product and process development and optimization, processing equipment troubleshooting/improvement and applying statistical methods to improve the efficiency and effectiveness of experimental investigations. He currently holds 23 patents on flexible packaging films and coating technology.

John has presented several papers at local, national and international technical and scientific meetings. He has authored book chapters and co-edited three books: *The SPE Guide on Extrusion Technology and Troubleshooting*; *The Plastics Technician's Toolbox – Extrusion*; *Extrusion – The Definitive Processing Guide and Handbook*. He is also co-editor of the *Journal of Plastic Film and Sheeting*.

An SPE member since 1969, he has been a member of the Extrusion Division Board of Directors since 1984, ANTEC Technical Program Chair 1995, Board Chair 1996–97 and elected Fellow of the Society in 1998. He has served as treasurer for the SPE Extrusion Division Board of Directors since 2001. He was Technical Program Co-Chair for Flexible Packaging Conference 2004 and was on the technical program committed for Flexible Packaging Conference 2005. He is on the Flexible Plastics Packaging Division Board of Directors and has served as Treasurer since 2007.

Chapter 1

1

Introduction

John R. Wagner Jr[1] and Scott B. Marks[2]

[1] *Crescent Associates, Inc.*
[2] *E.I. du Pont de Nemours & Co*

Materials: A historical perspective

Today, we have many clear plastic packaging films. Jacques E. Brandenberger invented the first common clear film, ‘Cellophane’ in 1908. Jacques was a Swiss textile engineer who first thought of the idea for a clear, protective, packaging layer in 1900. He was seated at a restaurant when a customer spilled wine onto the tablecloth. As the waiter replaced the cloth, Brandenberger decided that he would invent a clear flexible film that could be applied to cloth, making it waterproof.

He experimented with different materials and tried applying liquid viscose (a cellulose product known as rayon) to cloth, but the viscose made the cloth too stiff. His idea failed but he noted that the coating peeled off in a transparent film. Like so many inventions, the original use was abandoned and new and better uses were found. By 1908, he developed the first machine for the manufacturing of transparent sheets of regenerated cellulose. By 1912, Brandenberger was making a saleable thin flexible film used in gas masks. He obtained patents to cover the machinery and the essential ideas of his process [1]. The rights to the production of cellophane were then obtained by E.I. du Pont de Nemours & Co, who began to produce and refine further the process for producing cellophane. Breakthrough improvements included adding a moisture barrier layer to the cellophane, in the form of a nitrocellulose coating. This allowed for better stiffness retention in the cellophane and facilitated use of the film as an overwrap film for foods. This coating was then refined to make it heat sealable as well, creating the first readily sealable transparent packaging film. Later on, other coatings were applied to cellophane including PVdC (polyvinylidene chloride), which added oxygen barrier and moisture barrier to the cellophane, resulting in the original non-metal barrier film for food packaging.

Today, we have many polymers such as PE (polyethylene), PP (polypropylene), PET (polyester) and PS (polystyrene) that are used to produce clear films for packaging. While these aforementioned polymers are commonly used in monolayer format, they are also used in multilayer films produced by coextrusion and/or lamination processes. There also exists a broad variety of specialty polymers and compounds which sometimes are used monolithic, but are more commonly used in coextrusions.

Polyethylene was first synthesized by the German chemist Hans von Pechmann who prepared it by accident in 1898 while heating diazomethane. When his colleagues Eugen Bamberger and Friedrich Tschirner characterized the white, waxy substance that he had created, they recognized that it contained long -CH_2- chains and termed it polymethylene [2].

The first industrially practical polyethylene synthesis was discovered (again by accident) in 1933 by Eric Fawcett and Reginald Gibson at the ICI works in Northwich, UK. Upon applying extremely high pressure (several hundred atmospheres) to a mixture of ethylene

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and benzaldehyde, they again produced a white, waxy material. Because the reaction had been initiated by trace oxygen contamination in their apparatus the experiment was, at first, difficult to reproduce. It was not until 1935 that another ICI chemist, Michael Perrin, developed this accident into a reproducible high-pressure synthesis for polyethylene that became the basis for industrial low-density (LD)PE production beginning in 1939 [2].

Subsequent landmarks in polyethylene synthesis have revolved around the development of several types of catalyst that promote ethylene polymerization at more mild temperatures and pressures. The first of these was a chromium trioxide-based catalyst discovered in 1951 by Robert Banks and J. Paul Hogan at Phillips Petroleum. In 1953, the German chemist, Karl Ziegler, developed a catalytic system based on titanium halides and organoaluminum compounds that worked at even milder conditions than the Phillips catalyst. The Phillips catalyst is less expensive and easier to work with, however, and both methods are used in industrial practice.

By the end of the 1950s, both the Phillips and Ziegler type catalysts were being used for high-density (HD)PE production. Phillips initially had difficulties producing an HDPE product of uniform quality and filled warehouses with off-specification plastic. However, financial ruin was unexpectedly averted in 1957 when the hula hoop, a toy consisting of a circular polyethylene tube, became a fad among youth in the USA.

A third type of catalytic system, one based on metallocenes, was discovered in 1976 in Germany by Walter Kaminsky and Hansjörg Sinn. The Ziegler and metallocene catalyst families have since proven to be very flexible at copolymerizing ethylene with other olefins and have become the basis for the wide range of polyethylene resins available today, including very low-density polyethylene and linear low-density polyethylene. These new catalysts have allowed creation of some very special polyethylene resins. One such example is the polymer used to produce DSM's 'Dyneema' fiber, an ultra high strength material that competes with aramid based fibers in a variety of applications where high strength is needed, but not where high temperature resistance is also needed. As it has always been, new materials find their useful niches in the market.

Until recently, the metallocene systems were the most active single-site catalysts for ethylene polymerization known – new catalysts are typically compared to zirconocene dichloride. Much effort is currently being exerted on developing new, single-site (so-called post-metallocene) catalysts that may allow greater tuning of the polymer structure than is possible with metallocenes. Recently, work by Fujita at the Mitsui Corporation (among others) has demonstrated that certain salicylaldimine complexes of Group 4 metals show substantially higher activity than the metallocenes [2].

Dr Karl Rehn at Hoechst AG in Germany first polymerized polypropylene in 1951 and did not recognize the importance of his discovery. It was then rediscovered on March 11, 1954, by Giulio Natta [3]. Biaxially oriented polypropylene (BOPP) was introduced in the 1960s. Initially, it was developed in a blown film process and the first commercial production was started by DuPont in Iowa, USA. Eventually, other companies started to produce BOPP in a cast sheet/orientation process which made the film production more economical. This change was instrumental in replacing cellophane, as it was lower cost and more environmentally friendly to produce. As BOPP usage gained in the industry, there was a corresponding decline in cellophane usage and production. Today, cellophane production is a mere fraction of what it once was.

British chemists, John Rex Whinfield and James Tennant Dickson, employees of the Calico Printer's Association of Manchester, patented 'polyethylene terephthalate' (also called PET or PETE) in 1941, after advancing the early research conducted by Wallace Carothers of DuPont. They saw that Carothers' research had not investigated the polyester formed from ethylene glycol and terephthalic acid. Polyethylene terephthalate is the basis of synthetic fibers such as generic polyester fiber and specialty fibers such as Invista's 'Dacron'. Whinfield and Dickson along with inventors W.K. Birtwhistle and C.G. Ritchie also created the first polyester fiber called 'Terylene' in 1941 (first manufactured by Imperial Chemical Industries or ICI). The second polyester fiber was DuPont's 'Dacron' (now a product of Invista Corp.) [4].

Polystyrene was discovered in 1839 by Eduard Simon [5], an apothecary in Berlin. From storax, the resin of the Turkish sweet gum tree (*Liquidambar orientalis*), he distilled an oily substance, a monomer which he named styrol. Several days later, Simon found that the styrol had thickened, presumably from oxidation, into a jelly he dubbed styrol oxide ('Styroloxyd'). By 1845, English chemist John Blyth and German chemist August Wilhelm von Hofmann showed that the same transformation of styrol took place in the absence of oxygen. They called their substance metastyrol. Analysis later showed that it was chemically identical to Styroloxyd. In 1866, Marcelin Berthelot correctly identified the formation of metastyrol from styrol as a polymerization process. About 80 years went by before it was realized that heating of styrol starts a chain reaction which produces macromolecules, following the thesis of German organic chemist Hermann Staudinger (1881–1965). This eventually led to the substance receiving its present name, polystyrene.

The company I.G. Farben began manufacturing polystyrene in Ludwigshafen, Germany, about 1931, hoping it would be a suitable replacement for die-cast zinc in many applications. Success was achieved when they developed a reactor vessel that extruded polystyrene through a heated tube and cutter, producing polystyrene in pellet form.

In 1959, the Koppers Company in Pittsburgh, Pennsylvania, developed expanded polystyrene (EPS) foam [5].

Other polymers used in the packaging industry have had similar stories of invention ranging from purely accidental discovery to hard wrought research.

Markets: A global economy

The dynamics of the industrialized nations post World War II have lead to a plethora of applications for many polymers from the mid-20th century continuing into the 21st century. The flexible packaging industry has been one significant part of this engine of growth and adoption for use in many applications has expanded into a global economy, as many newly industrialized nations have become global players in trade.

Looking at recent years only in the USA, Table 1-1 [6] shows the flexible plastic packaging films market (in million lb) in the USA for three packaging films for the years 2002 and 2007.

Fig. 1-1 plots these data and shows a trend line for the total film market. This exponential fit trend line calculates a 4.5% growth rate from the 2002 to 2007 data. At this growth rate, the US flexible packaging film market could be over 20 billion pounds in 2020.

Selected data from the US census office for the NAICS code 26112 (Unsupported plastics packaging film & sheet mfg) is shown in Table 1-2 [7]. In addition to these selected data, the total value shipments have been adjusted to 1997 dollars using data from the Misery index web site [8].

Fig. 1-2 plots the data in Table 1-2 for employees, total value shipments and the adjusted total value shipments to 1997 dollars versus year. The exponential curve fits, calculate the total value shipment growth rate at 9.16% and the employee growth rate at 6.96%. When the total value shipments are adjusted to 1997 dollars the calculated growth rate is 6.73%. This suggests that the market was growing at a 7% rate over this time period and it closely followed the employee growth rate. If one were to do a more rigorous estimate of future growth, one would have to have good historical sales and population data. Market growth is a function of market penetration, i.e. pounds of material used per person and number of people. Looking at global data one would find that there are countries with minimal market penetration, some with average market penetration and some where the value of flexible plastic packaging is highly recognized and are leaders in taking advantage of the benefits flexible films give.

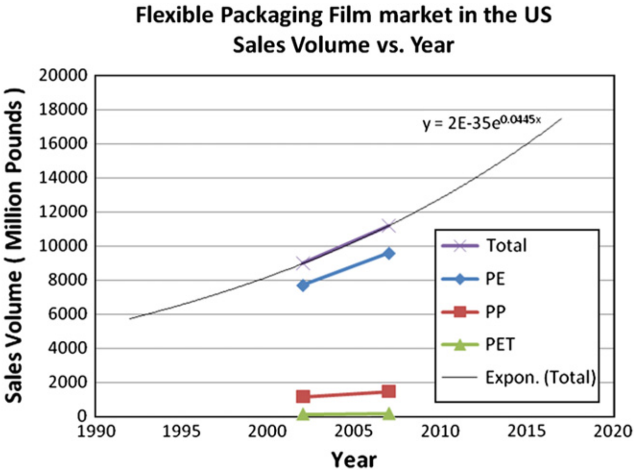

Fig. 1-1 Flexible packaging film market in the USA – sales volume versus year.

Table 1-1 Flexible plastic packaging films market in the USA: breakdown of volume sales by material type for the years 2002 and 2007 (in million lb)

Flexible plastic	2002	2007
Packaging film type		
Polyethylenes	7676.6	9584.3
Polypropylene	1160.3	1449.2
Thermo plastic polyesters	131.2	170.0
Total	8968.1	11203.5

Table 1-2 Selected data from the US census office for the NAICS code 26112 (Unsupported plastics packaging film & sheet mfg)

Year	Companies	Employees	Total value shipments ($1000)	Total 1997 value shipments ($1000)
1997	131	15 428	3 638 911	3 638 911
1998		15 288	3 998 678	3 937 645
1999		16 447	4 813 330	4 638 284
2000		17 327	4 823 210	4 495 845
2001		16 875	4 782 978	4 335 645
2002	207	23 418	6 203 922	5 535 676

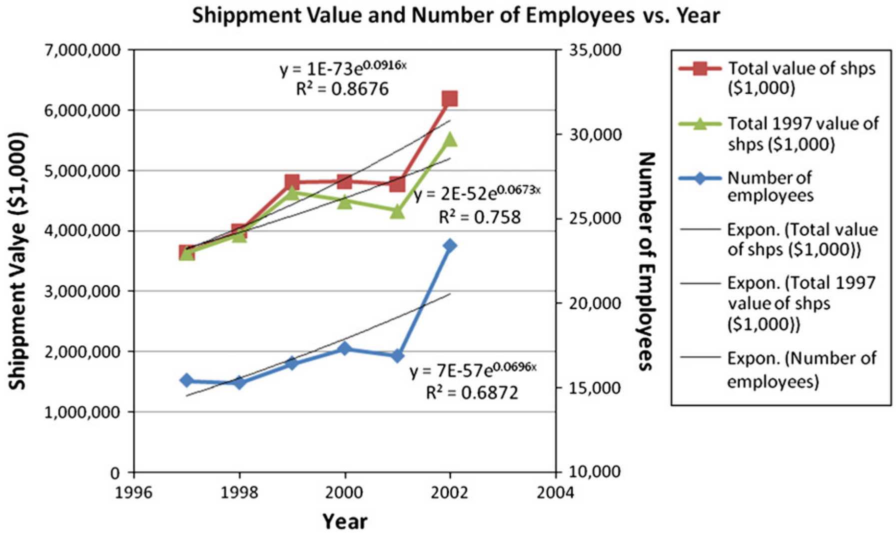

Fig. 1-2 Shipment value and number of employees versus year.

Processes, materials, needs

Coextrusion is used in the following processes:

- blown film
- cast film (<10 mils or <250 μm)
- cast sheet (>10 mils or >250 μm)
- blow molding
- tubing and sheathing
- extrusion coating and laminating
- profile.

Fig. 1-3 is a flow diagram of a coextrusion feedblock where three extruders are employed to produce a three-layer asymmetrical structure. This particular design has the barrier on the outside with a tie layer to provide adhesion to the core resin.

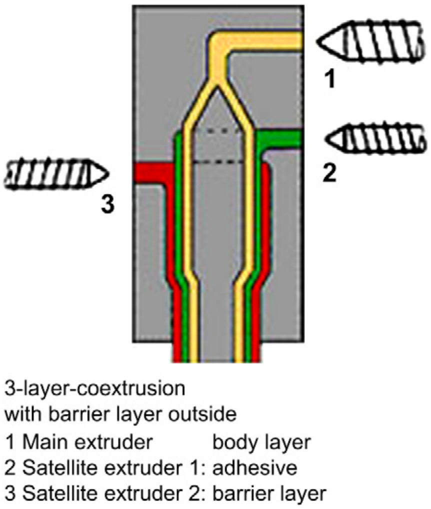

Fig. 1-3 Flow diagram of a coextrusion feed block where three extruders are employed to produce a three-layer asymmetrical structure.

While a large majority of polymer extrusion is done in monolithic form, the world of coextruding polymers has been growing now for half a century. The whole concept of polymer extrusion grew from the already existing technology for extrusion of processed foods, ranging from cereals to meats. Likewise, coextrusion was being practiced in the food industry before it was practiced using molten polymers. Without realizing it, every reader of this manuscript has likely consumed some type of coextruded food in the form of candy, bakery items, cereals or processed meats.

Some considerations as to why we may wish to coextrude polymers are:

- to bring the desired properties of differing materials into one structure
- to reduce emissions from solvents used in adhesive lamination processes
- to process multiple materials in one pass into a structure to save process steps, cost and time.

Coextruding polymers is no simple matter. In the food industry, they have their compatibility issues and, in the polymer industry, we take the complexity to a higher level. We must consider the three main scientific property arenas related to moving a polymer from solid form to liquid form and back to solid form of a differing shape, which are:

- thermal
- fluid
- mechanical [9].

Thermal considerations are important because the processes are non-isothermal. The science of fluid flow is important because the fluids are non-Newtonian viscoelastic with non-linear temperature dependent viscosities. These fluids have interfacial boundaries that depend on the fluids' viscosity and normal stress difference. Mechanical considerations are important because the metal that contains the fluid flow is subjected to internal pressure forces which distort the metal. The metal has to be shaped properly and has thermal mass and chemical resistance characteristics, which interact with the flowing fluids.

However, the benefits of combining materials in coextrusion far outweigh the challenges associated with such an endeavor. Coextrusion provides solutions to meet product functionality. There is a variety of film properties that need to be taken into consideration when designing a packaging film. Some properties relate to the surface characteristics while others relate to the entire thickness/body of the film. Surface characteristics typically include coefficient of friction (COF), gloss, haze (surface induced) and sealability, as well as surface tension and chemical receptivity, which are important for materials to be printed. 'Body' characteristics include tensile properties, elongation, haze (internally induced), transparency, color, impact strength and a variety of other parameters.

Additionally, packaging requirements may also include gas and aroma barrier, chemical resistance, puncture resistance, formability and shrink properties. In a world where energy prices keep rising, the biggest challenge is to have a structure that includes all the desirable properties in the most economical way. This requires that processors have a good understanding of the material properties, as well as a good grasp of polymer rheology to achieve an optimal formulation especially when attempting to coextrude [10].

In designing a coextruded film one has to consider the world of needs including [11]:

- physical properties
  - tensile, elongation, flexure, stiffness
  - hardness, toughness, puncture, COF
  - sealability, peelability, etc.
- barrier properties
  - oxygen, moisture, oil, chemical
  - aroma/fragrance, carbon dioxide, etc.
- additives
  - colors, mineral fillers, COF modifiers, melt fracture inhibitors, scavengers, etc.

A typical coextruded structure will have a bulk layer, a barrier layer, a sealant layer and, often, an adhesive layer to join incompatible layers. Reclaim also has to be considered and can be put back into its own layer or into the bulk layer [12].

Common choices for the bulk layer are usually from the following groups [12]:

- PE (polyethylene)
  - HD (high density), LLD (linear low density), LD (low density), VLD (very low density)
- PP (polypropylene)
  - HoPP (homopolymer PP), CoPP (ethylene-propylene copolymer), Ter-PP (ethylene-propylene-butene terpolymer)
- Acrylates
  - EMA (ethylene methyl acrylate)
  - EBA (ethylene butyl acrylate)
  - EEA (ethylene ethyl acrylate)
  - PMMA (poly(methyl methacrylate))
  - EMMA (ethylene/methylmethacrylate)
- EVA(ethylene vinyl acetate)
  - low %, med %, high % VA
- PS (polystyrene)
  - HIPS (high impact PS), GPPS (general purpose PS).

The criteria that are important to consider are:

- cost
- adhesion
- flexibility
- softness
- stiffness, etc.

Resin selection criteria are:

- melt index – MW and MWD (physical properties tensile strength, organoleptics)
- density – crystallinity (opticals, permeability, modulus – i.e. LDPE)
- molecular branching – (melt strength, processing parameters)
- comonomer content – all properties
- melt point – crystallinity (seal initiation temp., thermoforming).

Following is a list of generic names for extrudable resins. When the brand/grade of a polymer is unknown, it can be referred to in this fashion to help communicate better about the nature of the material [12]:

- Polyethylenes
  - HDPE – high density polyethylene
  - HMW-HDPE – high molecular weight HDPE
  - MDPE – medium density polyethylene
  - LDPE – low density polyethylene
  - LLDPE – linear low density polyethylene
  - VLDPE – very low density (linear) polyethylene (also VLLDPE)
  - ULDPE – ultra low density polyethylene (also ULLDPE)
  - mPE – metallocene polyethylene, generic.

    - mLMDPE – metallocene linear medium density polyethylene
    - mLLDPE – metallocene linear low density polyethylene
    - mVLDPE – metallocene very low (linear) density (sometimes referred to as a 'plastomer')
- Polypropylenes
    - PP – polypropylene (generic indication when minimal information is known)
    - CoPP – copolymer polypropylene
    - HoPP – homopolymer polypropylene
    - Ter-PP – terpolymer polypropylene
- Acid copolymer resins
    - ACR – acid copolymer resin, generic name for EAA and EMAA resins
    - EAA – ethylene acrylic acid copolymer, such as DuPont Nucrel®, Dow Primacor® and ExxonMobil Escor®
    - EMAA – ethylene methacrylic acid copolymer, such as DuPont Nucrel®
    - Ionomer – generic name for ionomeric copolymer resins, such as DuPont Surlyn®, and ExxonMobil Iotek®
- Acrylates
    - Acrylate – generic name for various acrylate copolymers, such as DuPont Elvaloy AC®, Arkema Lotryl®, Westlake EMAC®, ExxonMobil Optema®
    - EBA – ethylene butyl acrylate
    - EEA – ethylene ethyl acrylate
    - EMA – ethylene methyl acrylate
    - EMMA – ethylene methyl methacrylate
    - EiBA – ethylene iso-butyl acrylate
    - EnBA – ethylene normal-butyl acrylate
- Ethylene vinyl acetates
    - EVA – ethylene vinyl acetate; examples: DuPont Elvax®, AT Plastics Ateva®, Equistar Ultrathene®, ExxonMobil Escorene Ultra®
- Polystyrenes
    - PS – polystyrene
    - EPS – expanded (or foamed) polystyrene
    - HIPS – high impact polystyrene
    - GPPS – general purpose polystyrene
- Polyvinyl chlorides
    - PVC – polyvinyl chloride
    - PVdC – polyvinylidene chloride. Most commonly seen as a coating on a film, but there are also extrudable grades, such as Dow Saran® and SolVin Ixan®
- Terpolymers
    - EVACO – terpolymer of ethylene, vinyl acetate and carbon monoxide
    - EnBACO – terpolymer of ethylene, normal-butyl acrylate and carbon monoxide
    - EiBAMAA – terpolymer of ethylene, isobutyl acrylate and methacrylic acid
    - (there are various other terpolymers in the industry)
- Grafted resins
    - EVA-gMAh – ethylene vinyl acetate with a graft of maleic anhydride
    - LLDPE-gMAh – LLDPE with a graft of maleic anhydride
    - (there are various other grafted resins in the industry)
- Others
    - Peel Seal or Easy Peel – generic name for a peelable sealant resin of unknown brand and grade. Example brand names include: DuPont Appeel®, Mitsui-DuPont CMPS®, Yasuhara Hirodyne® or Toyo Topco®
    - TPS – generic name for 'thermoplastic starch' resin. These are a new family of materials in the market, for example, Plantic® TPS or DuPont Biomax® TPS.

Materials and barrier

When one talks about 'barrier', please note that there are differences in interpretation of what this relates to. For some it may be related to oxygen, while for others moisture barrier may be more important. Barrier to other parameters may also be of greater or lesser importance including carbon dioxide, oils, acids, flavors, aromas, fragrances, solvents and other chemicals. Each polymer has its own unique characteristics and properties and, thus, will have differing 'barrier' performance. Which polymer or combination of polymers you may wish to coextrude will depend upon whether you need a barrier for oxygen, water, oil, aroma or something else and to what degree for each property. Some common resins that can be used for certain barriers are [12]:

- Nylon, polyamide, (PA)
    - oxygen barrier, aroma barrier, and some oil barrier
- EVOH
    - oxygen barrier, flavor/aroma barrier
- PET
    - moisture barrier, some flavor/aroma barriers and some chemical barrier needs
- PVdC
    - Good for moisture, oxygen, flavor, aroma, and some chemical
- HDPE
    - moisture barrier
- PP
    - moisture barrier
- ionomer
    - oil barrier, some chemical barrier.

When choosing one or more of these resins to coextrude, in addition to the barrier properties, you must also understand the criteria for flex durability, clarity and other physical parameters related to each material and how it adds or diminishes from the needs of the overall coextrusion.

Following here is some general information on Nylon. This is a material that is used broadly in coextrusions, but has some unique properties related to processing, so cannot be dropped into any extruder at will [12, 13].

Nylon or polyamide common types:

- Nylon 6: melting point (MP)=220°C (430°F)
  - The most common grade used in flexible packaging coextrusions
- Nylon 66: MP=250°C (480°F)
- Nylon 6/66: MP=210°C (410°F)
- Amorphous Nylon
  - used mainly in blends with Nylon 6 or 66, but occasionally is used pure
- Nylon 11 and 12: MP=180°C (360°F).

It is important to note that extrusion screws for Nylon are generally very different in design versus PP, PE and ethylene copolymer screws. Thus, do not just try extruding Nylon resin through a screw not known to be designed for Nylon. Please consult with the equipment manufacturer for advice. Without doing so, you run the risk of damaging equipment including but not limited to the screw, gearbox and drive motor on the extruder.

There are a number of extrusion grade Nylon resin producers who supply globally:

- Honeywell
- BASF
- Bayer
- DuPont
- EMS
- Mitsubishi
- Ube, etc.

The features that one can obtain with Nylon are:

- good gas barrier
- good thermoformability
- good toughness, abrasion resistance, tensiles
- good optics
- good oil resistance.

The extrusion issues for consideration with Nylon are:

- crystalline melt point
- flow properties change rapidly from solid to melt and back to solid. SAFETY!
- moisture sensitivity
- various types, so need to choose extrusion temperature profiles carefully
- ‘high’ extrusion temperature needed
- almost always processed in coextrusion.

Ethylene vinyl alcohol, commonly known as ‘EVOH’, has grown into a very useful barrier resin in the flexible packaging industry. Ethylene vinyl alcohol began its life in the 1950s as an offshoot of research into polyvinyl alcohol adhesive polymers. Ethylene vinyl alcohol was originally developed and patented by the DuPont Company, but the polymer did not have properties of value as an adhesive. In the 1950s, there was no barrier film coextrusion market, so looking at the barrier properties of the polymer was not even something of consideration. The technology for EVOH was eventually sold to the Monsanto Company. Monsanto, in turn, later sold it to a Japanese corporation and, by this time, coextrusion was in swing and barrier films containing Nylon were becoming prevalent. The oxygen barrier properties of EVOH were studied and found to be very interesting if you keep the polymer dry, protecting it from moisture by other polymers in coextruded films [12, 13]. Today, there are three major suppliers of EVOH:

- Kuraray Eval®
- Evalca Eval® (subsidiary of Kuraray in the USA)
- Nippon-Gohsei Soarnol®.

Ethylene vinyl alcohol characteristics are:

- good oxygen barrier when dry
- almost always run in coextrusion
- needs tie layers (except to Nylon)
- moisture sensitive
- thermal sensitivity
  - needs short, smooth flow paths when designing extrusions systems
- good optical properties
- high stiffness
- flex crack sensitivity.

Polyester has been previously discussed in this introduction with regards to its history.

There are many types of polyester and the most important one for films/sheet is PET (polyethylene terephthalate). Polyethylene terephthalate is typically oriented to provide strength, clarity and barrier properties. Polyethylene terephthalate for extrusion coating is more challenging to process compared to common polyolefins, such as PE and PP, and requires special equipment. Coextrusion makes it easier to run, but will require use of in-line dryers and proper PET screw designs [12,13]. Suppliers of film and extrusion coating resins in the USA would be:

- Eastman
- DuPont
- M&G (formerly Shell).

Polyester type polymers found in the packaging industry include:

- PET – generic extruded polyester. Could be monolayer or in a coextrusion
- PET ext.ctg. – generic extrusion coating of polyester
- APET – amorphous polyester
- CPET – crystalline polyester
- PET or PETE – polyethylene terephthalate
- PETG – polyester copolymer with glycol
- PBT – polybutylene terephthalate
- PPT – polypropylene terephthalate
- PTT – polytrimethylene terephthalate
- PEN – polyethylene napthalate
- PLA – polylactic acid
- PGA – polyglycolic acid
- PHA – polyhydroxyalkanote.

Other resins that can be considered to provide a barrier of some type are:

- PAN – polyacrylontrile, sometimes written as ‘ACN’
- SAN – styrene acrylonitrile copolymer
- AN-MA — acrylonitrile methyl acrylate copolymer (such as Innovene, Barex®)
- ABS – acrylonitrile butadiene styrene copolymer
- LCP – liquid crystal polymer
- COC – cyclic olefin copolymer, such as TAP Topas® or Mitsui Apel®
- PUR – polyurethane, extrudable type when seen in a coextrusion, for example
- SBC – styrene butadiene copolymer (such as ChevronPhilipps K-Resin®).

Materials and sealing

When assembling a coextruded film for the flexible packaging industry, most films require that they be sealable. The most common seal method is thermal, using a constant temperature sealer or a variable temperature impulse sealer. Other seal methods include:

- radiofrequency
- high frequency
- ultrasonic
- pressure sensitive.

Given that thermally created seals are the most common, following is an overview of what to consider when considering a material for the sealing layer.

The sealant layer choice should be made considering the application needs, since each parameter does not need to be maximized in order to perform in the given end use. What is important is finding the appropriate balance with properties such as:

- hot tack strength
- heat seal strength
- seal initiation temperature
- sealing speed
- coefficient of friction
- ability to seal through a given contaminant
- chemical resistance to the material to be contained
- economics, etc.

The most common sealant layer resins range from high performance to commodity performance. Inherent property differences in the polymers will affect the sealing performance and, since there is such a broad range of polymer grades in each family, it is best to consult with polymer suppliers to match your given needs to the performance of a given resin such as:

- ionomers of acid copolymers
- acid copolymer (EAA or EMAA)
- mVLDPE (very low density)
- EVA or EMA blends with LLDPE
- CoPP/TerPP, EVA, EMA, LLDPE, mLLDPE
- LDPE or PP.

Bringing things together

When assembling coextrusion structures, some materials will bond to other materials. However, the adhesion level may be insufficient for the durability needs of the given application. In order to create a more robust structure, it is required to use a material designed specifically to bond one material to another with improved interlayer adhesion. The family of polymers that will work as a ‘facilitator’ in this case is commonly called ‘tie resins’. They are designed to act as glue and provide adhesion between the incompatible layers. These ‘coex tie’ resins are designed to provide both mechanical and/or chemical bonding to other polymers when in a molten state. The adhesive strength obtained will be a function of the tie resin formulation and the coextrusion process parameters. It should be recognized that the extrusion process can have a significant impact in generating interlayer adhesion. For example, taking the same structure from a blown film process to a cast film process using the same resins, usually will not translate into obtaining the same interlayer adhesion. This is a complex topic for another discussion [12].

To achieve higher bond strengths than attainable with a base polymer, resins are formulated with a variety of materials including grafted functional groups and/or are compounded with an array of modifiers. Proper choice of the correct ‘tie’ resin is based on many variables including, extrusion processing parameters and material end use parameters. Your ‘tie’ resin supplier can provide helpful recommendations [12,13].

Base resins typically used for tie layers are:

- LDPE, LLDPE, HDPE
- EVA, PP
- acrylate copolymers
- acid copolymers.

Common modifiers used are:

- maleic anhydride
- olefinic tougheners
- tackifiers
- rubbers.

Some tie resin suppliers include:

- DuPont
- Mitsui
- Equistar
- Mitsubishi
- Arkema
- Rohm & Haas
- Dow
- DSM and several others.

When selecting a coextrudable adhesive resin, it is always useful to choose the correct resin for a given process and/or end-use application. If an EVA resin is selected care must be paid to temperature limitations of the extrusion process since EVA should not be processed over 235°C (455°F). For all resins, the tie layer rheology must match with adjacent materials to assure good layer uniformity with no 'interfacial instability'. Some materials have a minimum temperature that is necessary to generate adhesion via chemical and/or mechanical interaction. Extrusion 'process time' is also an important factor and related to the time between the polymers exiting the die and solidification. This relates to the 'cooling' and 'drawing' of the polymers and internally induced stresses during production. Coextrusion feedblock and die design are also influential in how a 'tie resin' may be able to generate interlayer adhesion [12].

This book is an attempt to provide a snapshot of multilayer flexible films and where they are used. Like any still picture, this book cannot describe the future and the innovative uses, applications and film designs that will drive these products to fill the needs of consumers.

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Chapter 2

2

PE Processes

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Introduction

When we talk about polyethylene (PE) today, we have to specify whether it is high density or low density, what catalyst was used, what comonomer was used to lower the density and how much it was lowered, what process was used and what molecular structure resulted and molecular weight distribution. This chapter will cover:

- low density polyethylene (LDPE)
- linear low density polyethylene (LLDPE)
- metallocene linear low density polyethylene (m-LLDPE)
- high density polyethylene (HDPE)
- very low density polyethylene (VLDPE)
- enhanced polyethylene (EPE)

and the manufacturing processes to make them.

Low density polyethylene

Low density polyethylene (LDPE) was first discovered by Imperial Chemical Company (ICI) in 1932 while researching ethylene reactions at high temperatures and pressures. The first commercial plant was built in 1939 [1]. Today, LDPE is still produced using similar chemistry and reactors. There are two reactors used to produce LDPE:

- autoclave reactors
- tube reactors.

The basic raw material for polyethylene is the monomer ethylene. Ethylene (Fig. 2-1) is a colorless gas with a slightly sweet smell and is obtained by cracking (thermal decomposition) ethane at high temperatures (800°C) in a cracker or steam furnace. Ethane is found in natural gas or can be obtained from oil or naphtha. The ethylene is compressed to high pressure and, at the right temperature and with an initiator, polyethylene (PE) molecules are produced.

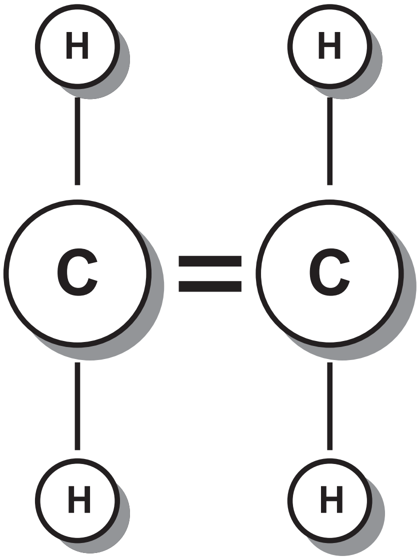


Fig. 2-1 Ethylene molecule (C_2H_4: molecular weight = 28).

Multilayer Flexible Packaging; ISBN: 9780815520214

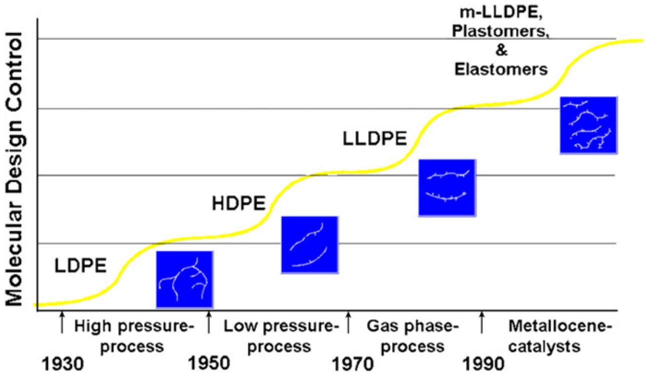


Fig. 2-2 History of polyethylene.

In 1953, Carl Ziegler and Giulio Natta each developed a new catalyst system (known today as Ziegler–Natta, Z/N) using transition metal chemistry that allowed PE production at low temperatures and pressures. High density (HD) PE polymers were introduced with these new processes. In 1973, the Z/N catalyst efficiency was dramatically improved using a supported catalyst technology. In 1978, linear low density polyethylene (LLDPE) polymers were introduced using Z/N catalyst technology and adding an alpha-olefin comonomer. The latest new technology was introduced in 1993 as single site catalyst technology (also called metallocene catalyst) and has resulted in several new polyethylenes being introduced commercially (Fig. 2-2).

Polyethylene resin selection is, in general, based on the physical properties required for the product or end-use. Polyethylene is typically characterized by melt index and density.

Melt index

Melt index (MI) or melt flow index (MFI) refers to the grams/10 minutes pushed out of a die of prescribed dimensions according to an ASTM D-1238 under a specified load as shown in Fig. 2-3. Condition E is typically used for polyethylene grades with a 2.16 kg piston load and the die dimensions are D = 0.0825 in and L = 3.149 in (D = 2.095 mm and L = 80 mm). The test is carried out at 190°C.

Polymer MI is reported as grams/10 minutes of flow or (dg/min). Blown film PE grade polymers typically will range from 0.01 to about 30 dg/min (Fig. 2-4).

The inverse relationship between MI and the average molecular weight (M_w) (as measured by gel permeation chromatography) is shown in Fig. 2-5 for LLDPE polymers (made via Z–N cat.). Lower MI polymers have higher molecular weight. Long-chain branching (LCB) effects are not shown, but they will shift the M_w down at the same MI.

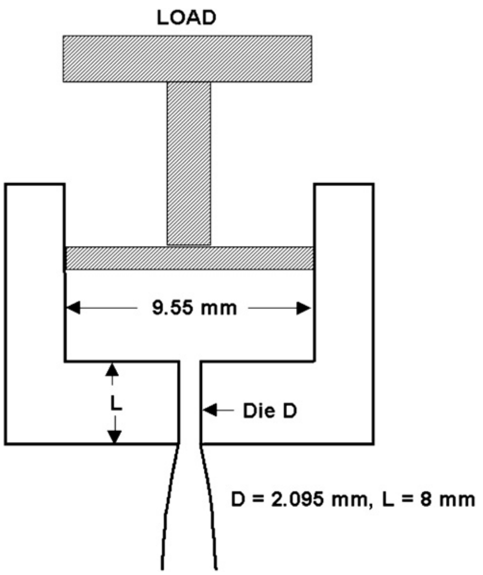


Fig. 2-3 Schematic of a melt indexer. ASTM D-1238 Under the conditions of the melt index measurement with the 2.16 kg load, the wall shear stress can be calculated to be $\tau_W = 1.94 \times 10^4$ Pa ($=2.814$ psi) and the wall shear rate approximately $\dot{\gamma} = (1838/\rho)$ MI where ρ is the melt density. Assuming $\rho = 766\ \mathrm{kg/m^3}$ for a typical PE melt at 190°C, we get $\dot{\gamma} = 2.4 \times \mathrm{MI}$.

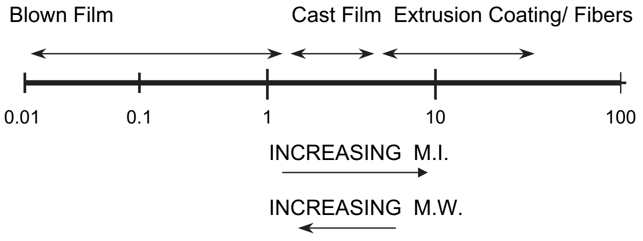


Fig. 2-4 Melt index of PE polymers used for various extrusion processes.

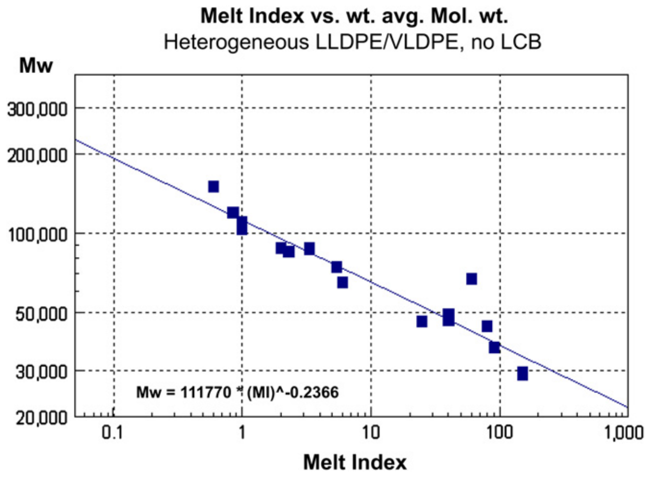


Fig. 2-5 Melt index as a function of M_W.

Density

Short-chain (SCB) and LCB branch concentration controls resin density. Short-chain branch is how much alpha olefin comonomer is incorporated into LLDPE. Fig. 2-6 shows how resin density decreases as octene comonomer level is increased for homogeneous polymers.

Higher polyethylene resin density increases crystallinity and, therefore, the modulus at ambient conditions. Fig. 2-7 shows crystallinity as a function of density for polyethylene polymers.

The relationship between density and weight % crystallinity (X_w) for polyethylene is expressed in equation (2.1). The volume % crystallinity (X_v) is calculated using equation (2.2).

$$X_w = \frac{\rho - \rho_a}{\rho_c - \rho_a} \bullet \frac{\rho_c}{\rho} \bullet 100$$

$$X_w = [(\rho - \rho_a)/(\rho_c - \rho_a)] \bullet (\rho_c/\rho) \bullet 100 \qquad (2.1)$$

$$X_v = \frac{1/\rho - 1/\rho_a}{1/\rho_c - 1/\rho_a} \bullet 100$$

$$X_v = [(1/\rho) - (1/\rho_a)/(1/\rho_c - 1/\rho_a)] \bullet 100 \qquad (2.2)$$

where:

ρ	=	polymer density
ρ_a	=	amorphous density (0.853 g/cc)
ρ_c	=	crystalline density (1.000 g/cc)

Many polymers contain some crystalline structure when they are solidified. These polymers are referred to as semicrystalline since not all polymer chains are incorporated into the crystalline structure (Fig. 2-8). For these polymers, the chain segments that are not crystallized make up a second phase known as the amorphous phase. Linear low density polyethylene resins are common semicrystalline polymers and have solid densities ranging from about 0.9 to 0.935 g/cm^3. Resins with higher solid densities contain higher crystallinity. For LLDPE, the crystallinity level is, in general, controlled by the comonomer content, i.e. the percent alpha olefin reacted into the polymer chain.

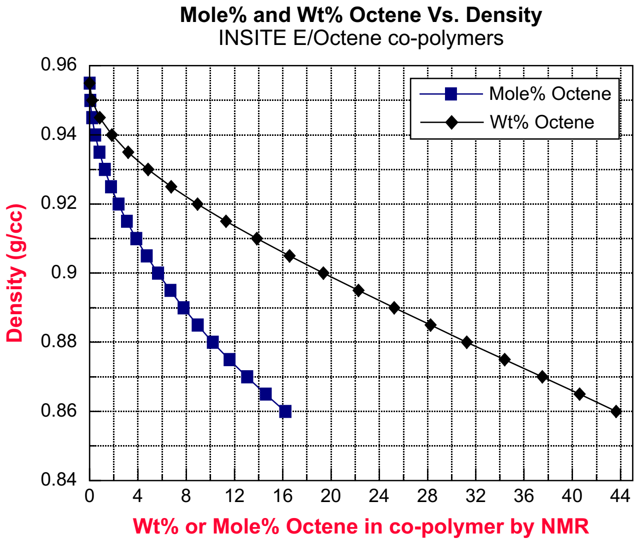


Fig. 2-6 Density as a function of comonomer level.

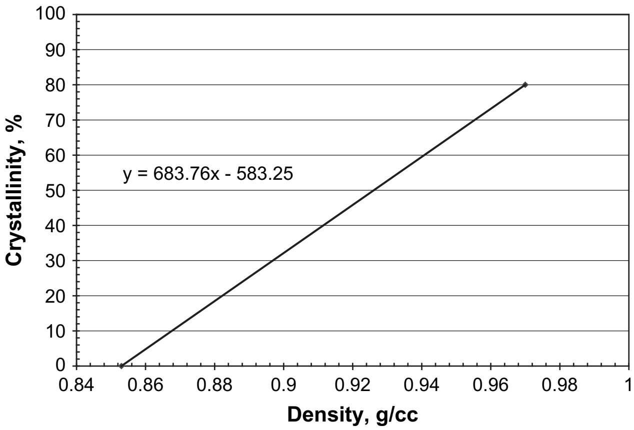


Fig. 2-7 PE polymer weight percent crystallinity as a function of density.

Gel permeation chromatography (GPC)

Polymerization gives rise to a molecular weight distribution as individual polymer chains end up with a repeat unit distribution. Gel permeation chromatography technology measures the molecular weight distribution in a polymer. The polymer molecules are dissolved in a solvent and processed through columns packed with gel particles that separate the molecules, which are detected as they emerge from the column (Fig. 2-9).

Due to this chain length distribution and, thus, molecular weight distribution, it is not possible to describe the resin using a single molecular weight.

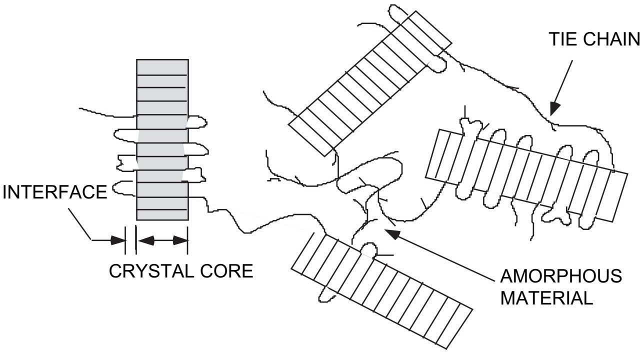


Fig. 2-8 Crystalline and amorphous regions of a semicrystalline polymer.

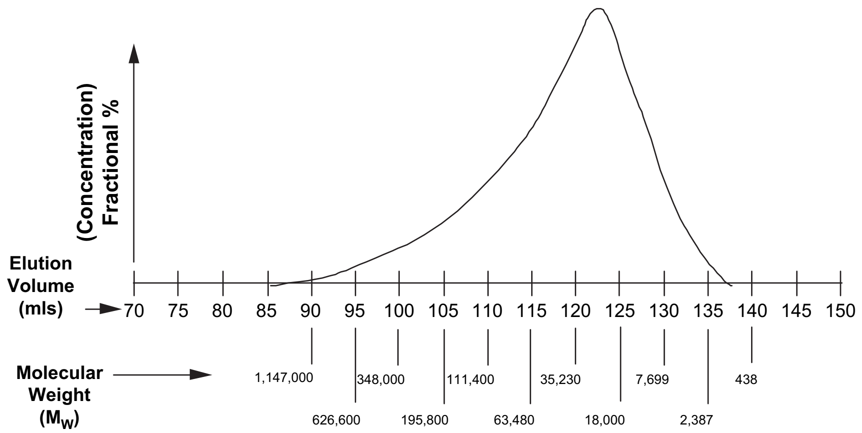


Fig. 2-9 GPC curve showing concentration of various molecular weights of a polymer.

Numerous methods have been developed with the two most common being the number-averaged molecular weight (M_n) (equation (2.3)) and the weight-averaged molecular weight (M_w) (equation (2.4)).

$$M_n = \frac{\sum n_i M_i}{\sum n_i} \tag{2.3}$$

$$M_w = \frac{\sum n_i M_i M_i}{\sum n_i M_i} = \sum w_i M_i \tag{2.4}$$

where:

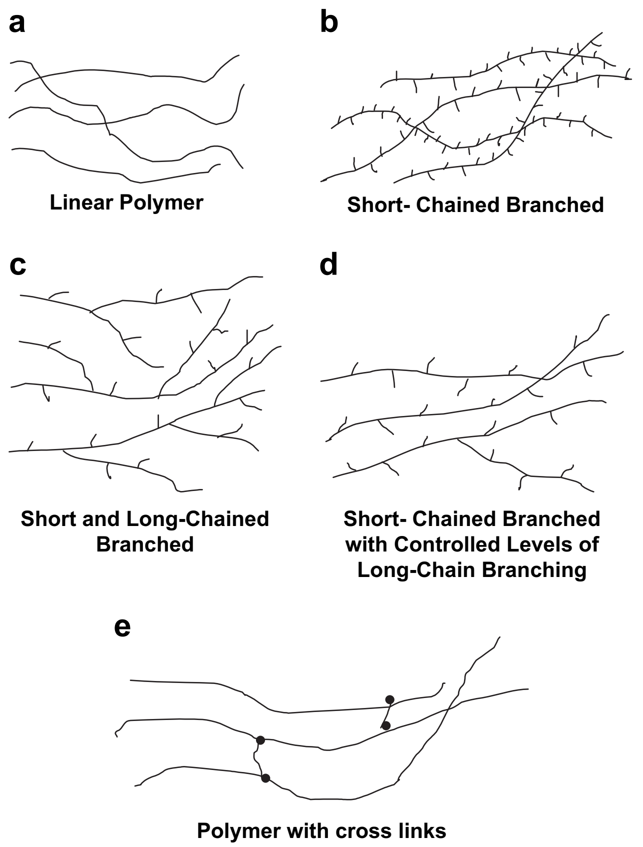
n_i	=	the number of molecules with a molecular weight of M_i
w_i	=	the weight fraction of molecules with a molecular weight of M_i.

Molecular weights can range from several thousand to several million. Another common descriptor for a resin is the polydispersity or molecular weight distribution (MWD). The MWD is given by the ratio of M_w to M_n (equation (2.5)).

$$MWD = \frac{M_w}{M_n} \tag{2.5}$$

The MWD of a resin depends on how it was produced, i.e. the catalyst type, reactor conditions, etc. Molecular weight distribution can range from between 2 and 20 and, typically, for LLDPE, MWD are between 3.5 and 4.0 for single reactor polymers. Bimodal polymers (produced using multiple reactors) can increase the MWD up to 20. Single site (homogeneous) catalyst polymers will have MWD from 2 to 3.

Polyethylene resins have five common molecular structures (Fig. 2-10). The most common polymer structure is linear (see Fig. 2-10a), where the repeating units are connected one after another. Common linear polymers include HDPE, polystyrene (PS), polycarbonate (PC) and polyamide (PA) (although branching can be designed into these materials). Some polymerization processes add a comonomer that results in short-chain branches (see Fig. 2-10b). The most common polymer with short-chain



Linear Polymer

Short- Chained Branched

Short and Long-Chained Branched

Short- Chained Branched with Controlled Levels of Long-Chain Branching

Polymer with cross links

Fig. 2-10 Schematic of common polymer chain structures. (a) Linear polymer; (b) short-chained branched; (c) short- and long-chained branched; (d) short-chained branched with controlled levels of long-chained branching; (e) polymer with cross links.

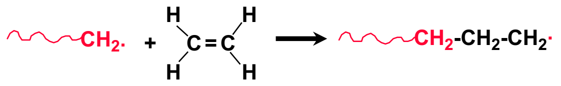


Fig. 2-11 Chain propagation mechanism for free radical polymerization.

branches is LLDPE. This polymer is produced by incorporating an alpha-olefin, like 1-butene, 1-hexene or 1-octene into ethylene. Low density polyethylene produced by a high-pressure process has both short- and long-chain branches and has a chain structure like that in Fig. 2-10c. Patented catalyst systems [4] have been developed to control both long- and short-chain branches (see Fig. 2-10d), tailoring both the physical and processing properties to the desired process and end-use. As will be discussed later, the polymer structure and chain length highly influence its rheological properties [3]. When two or more polymer chains are connected through a chemical bond, the resin is said to contain cross-linked segments. A schematic for a cross-linked polymer chain is given in Fig. 2-10e.

Free radical processes

The free radical propagation mechanism is shown in Fig. 2-11. A free radical is generated with an initiator (either a peroxide or oxygen is injected into the reactor). The free radical then reacts with an ethylene molecule being inserted into the polymer chain. The free radical is transferred to the end of the just inserted ethylene molecule and the reaction continues to grow the polymer chain.

The free radical molecule is also capable of transferring the radical to another carbon molecule on another polymer molecule (Fig. 2-12). Then the free radical will start another polymer chain growing at the site of the free radical. Typically, when the branch is greater than 30 carbon atoms it will be designated as a LCB.

A third important free radical reaction for the insertion of SCB is shown in Fig. 2-13. The active center is transferred through a 'back-biting' mechanism. In the example shown, a butyl branch (4 carbon SCB) will be created when the new free radical continues to grow the polymer chain.

Autoclave reactor

The autoclave is a stirred cylindrical reactor (Fig. 2-14). These reactors are typically about 6.1 m (20 ft) long and 0.38–0.91 m (15–36 in) in diameter. Ethylene is introduced into the primary compressor along with the low pressure recycled gas from the recovery units. The compressed gas is then further compressed in the hypercompressor up to the target pressures of the reactor (15 000–30 000 psi/100–200 MPa) and is cooled to remove the heat. The peroxide initiator is injected with the fresh ethylene. Ethylene polymerization is an exothermic reaction. The heat of reaction must be removed by the incoming cool gas to maintain the target reactor temperature. Proprietary baffle designs partition the reactor into discrete zones enabling better molecular reaction control. This will control the polymer's M_w, MWD and density.

Fig. 2-12 Mechanism for insertion of LCB in free radical polymerization.

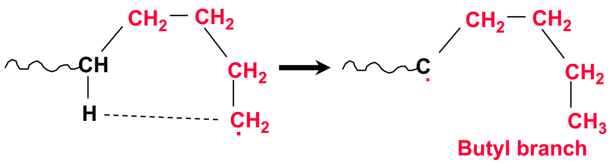


Fig. 2-13 Mechanism for insertion of SCB in free radical polymerization.

The autoclave reactor enables the gas/polymer to be efficiently back-mixed. The reactor walls have to be very thick to accommodate the high pressures. Typical ethylene conversion to polyethylene is about 22% per reactor pass. When the polymer/gas exits the reactor, it passes through separators where the unreacted ethylene is recycled and the molten polymer is prepared for injection of additives and then pelletized [4]. Typical production rates for autoclave reactors output capacities are 150–450 M lb/year (75–225 kT/year).

Tube reactor

The tube is a long pipe reactor (Fig. 2-15). These reactors are typically about 1.25 km (1 mile) long and

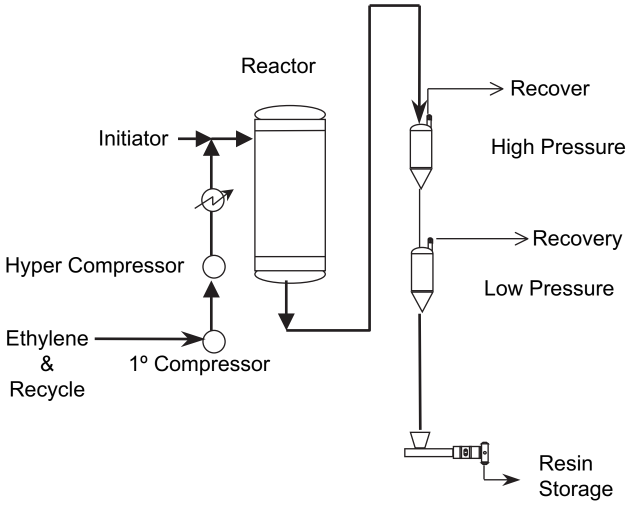


Fig. 2-14 Autoclave reactor (simplified).

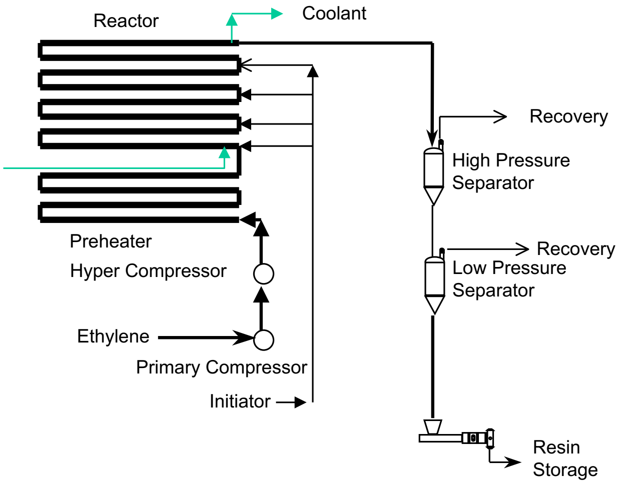


Fig. 2-15 Tube reactor (simplified).

2.5–7.6 cm (1–3 in) in diameter. Ethylene is introduced into the primary compressor along with the low pressure recycled gas from the recovery units. The compressed gas is then further compressed in the hyper-compressor up to the target pressures of the reactor (20 000–50 000 psi, 140–350 MPa). The oxygen or peroxide initiator is injected with the fresh ethylene, sometimes at multiple points along the tube. The heat of reaction is removed with cooling jackets to maintain the target reactor temperature profile. This will control the polymer's M_w, MWD and density.

The tube reactor has poor back-mixing. Typical ethylene conversion to polyethylene is about 35% per reactor pass. When the polymer/gas exits the reactor, it passes through separators where the unreacted ethylene is recycled and the molten polymer is prepared for injection of additives and then pelletized. Typical production rates for tube reactors output capacities are 200–500 M lb/year (100–250 kT/year).

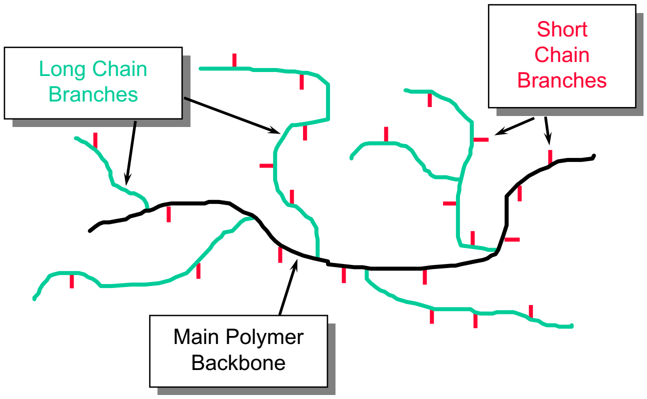


Fig. 2-16 LDPE homopolymer with LCB and SCB in the molecule.

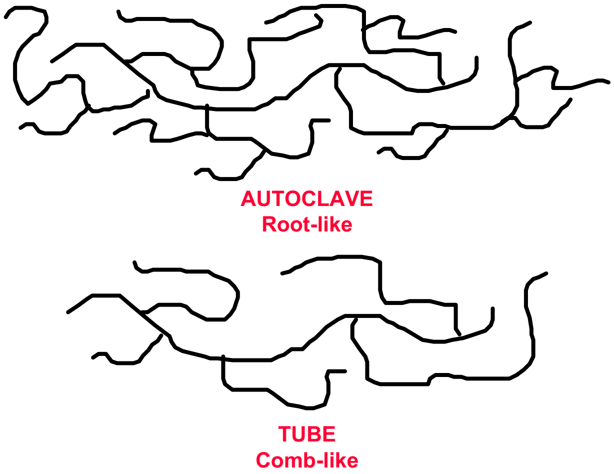


Fig. 2-17 Branching for autoclave and tube LDPE polymers.

LDPE Homopolymer

Low density polyethylene polymers are called homopolymers because they are produced with only one monomer (ethylene). The branching controls the polymer density. The free radical process allows both LCB and SCB to be incorporated into the polymer molecule (Fig. 2-16). The SCB creates a defect when the polymer molecule crystallizes, forcing smaller lamella to form (which lowers density).

There are some subtle differences in the branching distributions for autoclave and tube polymers (Fig. 2-17). The autoclave process typically will produce a branching distribution that is more root-like, while the tube process produces a distribution that is more comb-like.

Polyethylene density is directly related to the polymer crystallinity (Fig. 2-18).

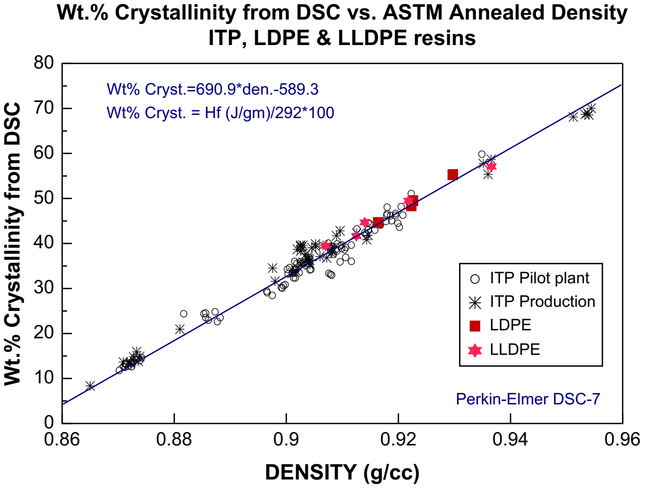


Fig. 2-18 Density versus crystallinity for PE polymers.

Copolymers of PE

There are several copolymers of polyethylene that are of commercial significance:

- ethylene vinyl acetate (EVA)
- ethylene methyl acrylate (EMA)
- ethylene acrylic acid (EAA)
- ethylene methyl acrylic acid (EMAA)
- ethylene butyl acrylate (EBA)
- ethylene carbon monoxide (ECO)
- ionomers (ION).

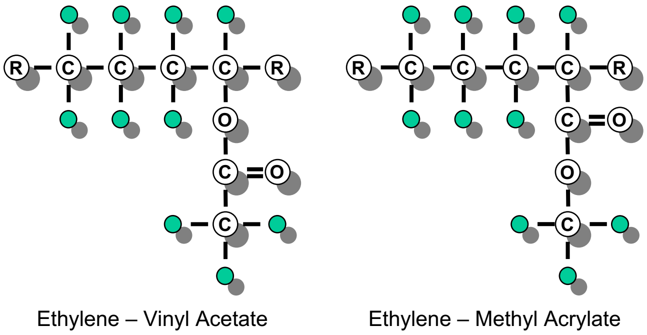
The largest volume of these is the ethylene vinyl acetate (EVA) copolymer. Similar free radical polymerization processes used for LDPE homopolymers produce the EVA polymers. The vinyl acetate (VA) functionality is randomly distributed along the polymer backbone and branches (Fig. 2-19). The vinyl acetate and methyl acrylate copolymers both exhibit polar functionality. The low crystallinity gives the polymer adhesive characteristics as well as low seal initiation temperatures.

The VA is denser than the ethylene monomer and it disrupts the polymer crystallinity such that, as VA levels increase, density increases but crystallinity decreases (Fig. 2-20).

Ethylene acrylic acid copolymers (EAA) and ethylene methyl acrylic acid (EMAA) use acids as a copolymer (Fig. 2-21). These polymers, in addition to having a polar comonomer, also have the ability to hydrogen bond with the acid functionality. These characteristics make these copolymers good adhesive polymers for metals and polyamides.

Fig. 2-22 illustrates the relationship of crystallinity to density for EAA polymers, similar to EVA, the crystallinity decreases as comonomer levels increase.

Ionomers are produced from acid copolymers (usually EMMA) and the acid functionality is neutralized using bases of sodium or zinc (Fig. 2-23). The neutralization creates ionic clusters that act like cross-linked networks.



Ethylene – Vinyl Acetate   Ethylene – Methyl Acrylate

Fig. 2-19 Polar copolymers of ethylene EVA and EMA.

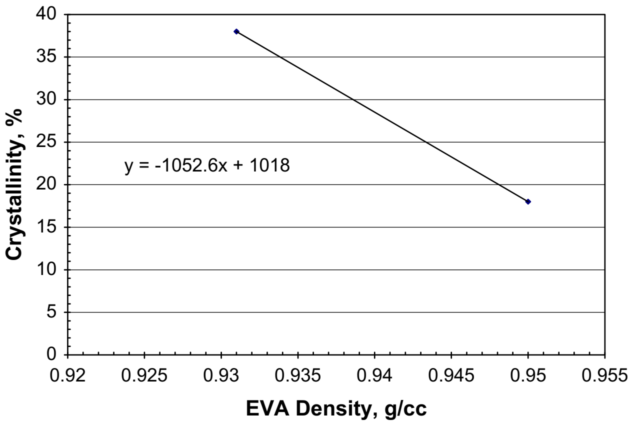
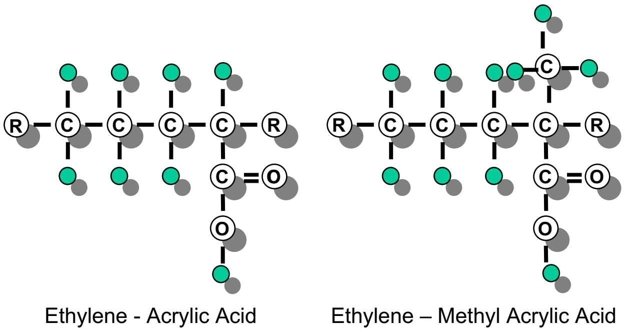


Fig. 2-20 EVA crystallinity as a function of density.



Ethylene - Acrylic Acid   Ethylene – Methyl Acrylic Acid

Fig. 2-21 Acid copolymers of ethylene.

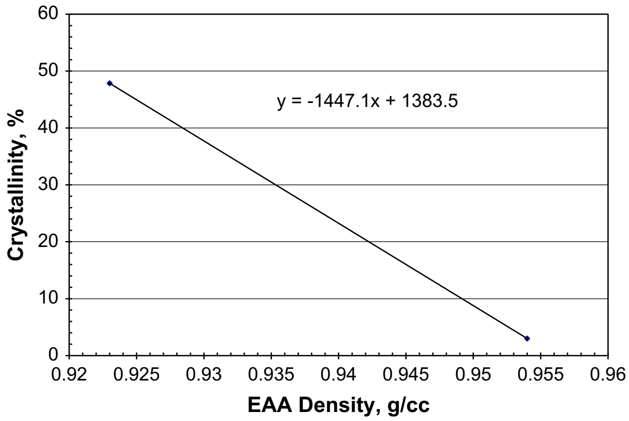
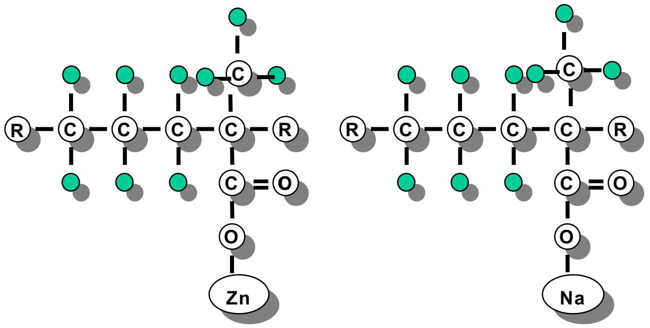


Fig. 2-22 EAA crystallinity as a function of density.

The MI is decreased as the degree of neutralization increases. This results in a polymer that has a very high effective melt strength and provides a polymer that has excellent heat seal and hot tack strength.



Zinc Ionomer

Sodium Ionomer

Fig. 2-23 Zinc and sodium ionomers.

Transition metal catalyst polymerization processes

The transition metal catalyst chemistry developed by Zeigler and Natta led to several processes that produce linear PE molecules. The processes are characterized by the low pressures (compared to the free radical processes) where they operate. These processes are:

- gas phase
- solution
- loop slurry
- slurry.

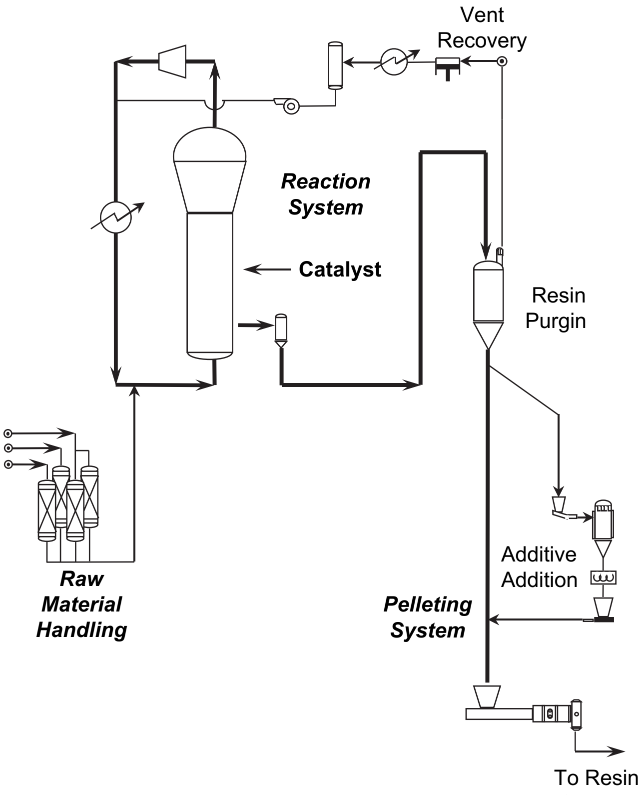
The first PE made with Z–N catalyst was high density polyethylene (HDPE) in 1953. The Z–N catalyst produces a linear molecule (a carbon chain than has very few branches (short or long)). In the late 1970s, linear low density polyethylenes (LLDPE) were introduced by copolymerizing with alpha olefins to create SCB.

Gas phase process

The gas phase process operates in the gaseous ethylene state and, as the PE molecule is polymerized, it precipitates as a solid (powder) dispersed as a fluid bed in the reactor (Fig. 2-24). Raw materials include: ethylene, hydrogen, comonomer, catalyst and cocatalyst. The gas is circulated through the polymerizing fluidized bed. The reactor temperature must be kept (<115°C) to allow the powder to remain solid. The pressure is typically 350 psi (2.4 MPa). The gas recycles through the reactor, while the polymer is removed from the reactor bed into a separator to recover the gas. Then additives and catalyst kill are added and the polymer is pelletized.

There are three main catalysts used in gas phase reactors and come in many variations:

- Ziegler–Natta
- chrome based
- metallocene.



Credit: Univation Technologies

Fig. 2-24 Gas phase process (simplified).

The heat of reaction is removed by injecting a cooled gas stream. The polymer density is controlled by the alpha olefin comonomer content. The comonomers used are butene, hexene or octene. Increasing the comonomer content lowers the polymer density. The reactor conditions are controlled to produce a target melt index, density and MWD. Single reactors or products from multiple reactors can be formulated to produce a product. A single catalyst or multiple catalysts can be used to produce a wide range of MWD products (Fig. 2-25).

The gas phase process can produce a wide variety of PE products from very high M_w to moderately low M_w, densities from 0.91 to 0.96 and MWD from 3.2 to 30.

Solution process

The solution process operates with the ethylene and polymer in a liquid state (Fig. 2-26). Raw materials include: ethylene, hydrogen, comonomer and catalyst. The ethylene, hydrogen and a comonomer are dissolved in an organic hydrocarbon fluid which is used as the diluent. The reactor temperature must be kept (>150°C) to keep the polymer in solution. The pressure is typically 500 psi

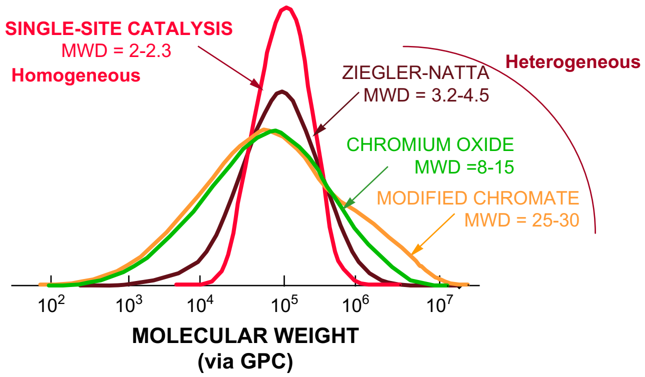


Fig. 2-25 Range MWD for polymers from gas phase process.

(3.5 MPa). The gas recycles through the reactor or reactors. The heat of reaction is removed by the cool fresh ethylene injected into the reactor. The polymer solution is removed from the reactor into a series of separators to recover the gas and cool the molten polymer. Then catalyst kill agents and other additives are injected and the polymer is pelletized.

There are two catalysts systems used in solution reactors and come in many variations:

- Ziegler–Natta
- metallocene.

The polymer density is controlled by the alpha olefin comonomer content. This is typically octene, but also could include a number of other alpha olefin comonomers. The more comonomer used, the lower the polymer density. The reactor conditions are controlled to produce a target melt index, density and MWD. Single reactors or products from multiple reactors can be formulated to produce a product. A single catalyst or multiple catalysts can be used to produce a wide range of MWD products.

The solution process can also produce a wide variety of PE products ranging from moderate M_W to very low M_W, densities range from 0.89 to 0.96 and MWD from 3.4 to 30.

Slurry processes

The loop slurry process operates with two phases. The liquid phase contains the ethylene and the diluent fluid and the solid phase is the polymer (Fig. 2-27). Raw materials include:

- ethylene
- hydrogen
- comonomer
- catalyst
- cocatalyst.

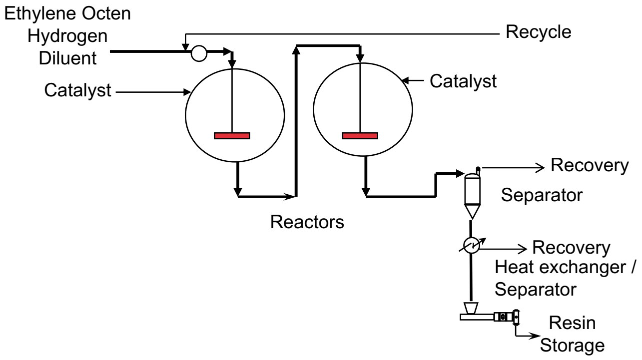


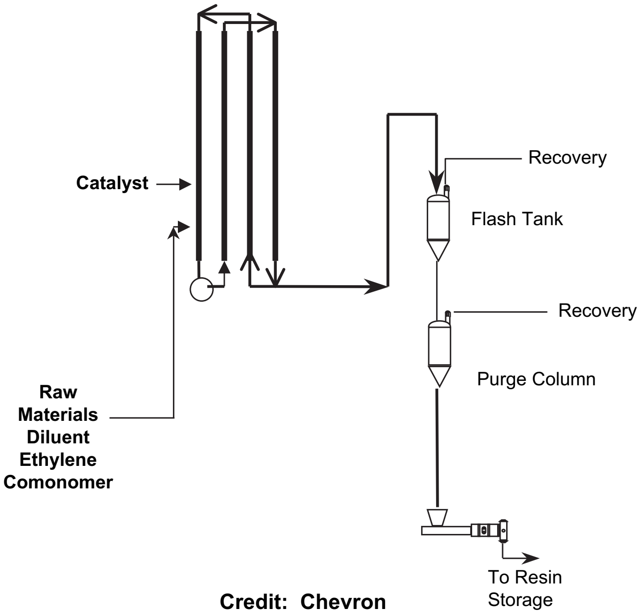
Fig. 2-26 Solution process (simplified).

The ethylene, hydrogen and a comonomer are dissolved in an organic hydrocarbon fluid which is used as the diluent. The reactor temperature must be kept (<90°C) to keep the polymer solid. The pressure is typically <300 psi (2 MPa). The gas recycles through the reactor. The heat of reaction is removed by a jacket cooling the loop. The polymer slurry is removed from the reactor into a flash tank to recover the ethylene. Then catalyst kill agents and other additives are injected and the polymer is pelletized.

There are three main catalysts used in slurry reactors and come in many variations:

- Ziegler–Natta
- chrome-based
- metallocene.

The polymer density is controlled by the alpha olefin comonomer content. This could include several alpha



Credit: Chevron

Fig. 2-27 Slurry loop process (simplified).

olefin comonomers. The more comonomer used, the lower the polymer density. The reactor conditions are controlled to produce a target melt index, density and MWD. A single catalyst or multiple catalysts can be used to produce a wide range of MWD products.

The slurry process can also produce a wide variety of PE products from ultra high M_w to moderate low M_w, densities from 0.91 to 0.96 and MWD from 3.5 to 30.

Catalyst chemistry

Ziegler–Natta

The early Z–N catalysts (Fig. 2-28) had a PE yield about 1000 lb polymer/lb Ti. This is low compared to today's catalysts.

In 1973, the catalyst technology advanced to a supported catalyst system (Fig. 2-29). This increased the efficiency 1000× to 1 000 000 lbs polymer/lb Ti.

The supported catalyst has multiple active sites that produce slightly different polymers as shown in Fig. 2-30. Site A on the catalyst support produces low M_w polymers with high levels of comonomer incorporation. Site B will produce a medium M_w polymer with a medium level of branches on the backbone. Site C on the catalyst produces polymers of high M_w, but with only low levels of branching due to low levels of copolymer incorporation.

The original Z–N and also the supported Z–N catalysts can control both the MWD and the branching distribution (Fig. 2-31).

$$Al(C_2H_5)_3 + 2TiCl_4 \longrightarrow [2TiCl_3 + Al(C_2H_5)_2Cl] + C_2H_5Cl$$

“Catalyst”

Yield ~ 1000 lbs. Polymer/lb. Ti (1964-1973)

Fig. 2-28 Typical Z–N catalyst (low efficiency).

“Supported Catalyst” $MgCl_2 + Ti(OR)_4 + Al(C_2H_5)Cl_2$

1,000,000 lbs. Polymer/lb. Ti (1973- present)

Fig. 2-29 Supported Z–N catalyst technology (1973 to present).

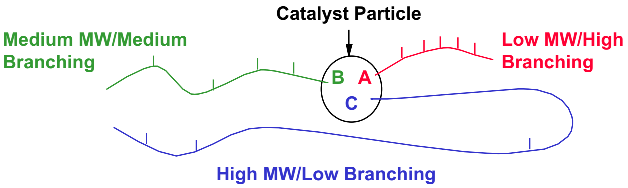


Fig. 2-30 Multiple site Z–N catalyst.

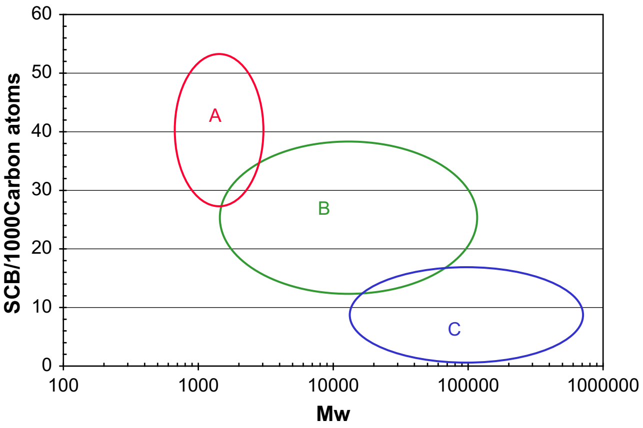


Fig. 2-31 Branching distribution and M_w of a multiple site Z–N supported catalyst producing a heterogeneous polymer.

When semicrystalline polymers are heated in a differential scanning calorimetry (DSC), the melt temperature (T_m) is where the highest crystal melting energy is required. Fig. 2-32 shows the DSC curves of an LLDPE (heterogeneous polymer) 1.0 MI, 0.920 g/cc, octene copolymer. The LLDPE melting point is 122.6°C. The melting point is directly related to the crystalline lamella thickness. As the polymer melts, the heat of fusion (H_f=area under the DSC curve) is determined and the weight percent crystallinity can be calculated (100% crystallinity=292 J/g). This heterogeneous LLDPE has a broad energy distribution for melting the crystalline structure. This indicates a broader crystalline lamella thickness distribution, thus a broader branching distribution for this LLDPE. It should be pointed out that Z–N catalyst chemistry variations and different process conditions will produce different heterogeneous characteristics.

The broad distribution of this heterogeneous LLDPE polymer reflects a broad distribution of comonomer incorporation into the polymer molecules. The higher density crystalline section of the polymer melts at a higher temperature, while the low density components of the polymer melt at lower temperatures.

The peak melting point of various polymers is a function of the crystallinity of the polymer (Fig. 2-33). Low density polyethylene, EVA, SSC (all homogeneous polymers) have a similar relationship of peak melting point and crystallinity. The heterogeneous polymers LLDPE and ultra low density polyethylene (ULDPE) shown here are polymers made on a solution process with a Z–N catalyst and octene comonomer that are designed to provide high impact and tear properties. Notice that the melting curve for the heterogeneous polymers does not follow the same relationship as the homogeneous polymers.

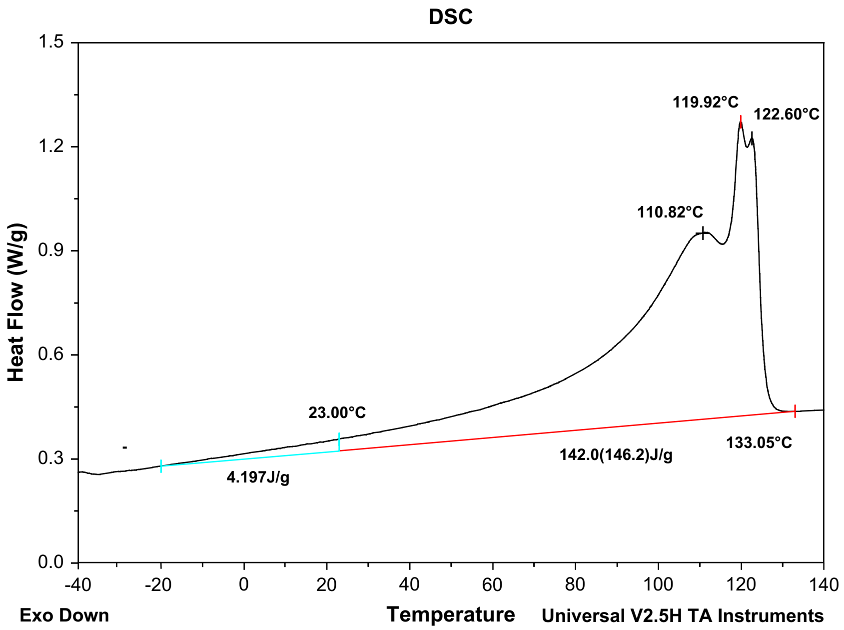


Fig. 2-32 DSC for LLDPE solution process octene heterogeneous copolymer.

Fig. 2-33 shows the differences in the peak melting temperature as a function of crystallinity for homogeneous PE homopolymers and copolymers and related octene solution copolymers. The heterogeneous curve will shift slightly depending upon the specific Z–N catalyst characteristics and comonomer employed. Ziegler–Natta catalyst systems that produce a more random branching distribution than the one shown here and using different comonomers could shift the heterogeneous curve 2 to 4 degrees lower for a similar crystallinity/density [5].

Variations in catalyst design can also produce significant differences in film properties obtained from polymer produced on these processes/catalyst systems. Fig. 2-34 compares the dart impact strength for two gas phase Z–N catalyst systems using hexene as the comonomer and two solution processes using different Z–N catalyst systems with octene as the comonomer. The two effects demonstrated here are from the comonomer difference and the different comonomer distribution (CD).

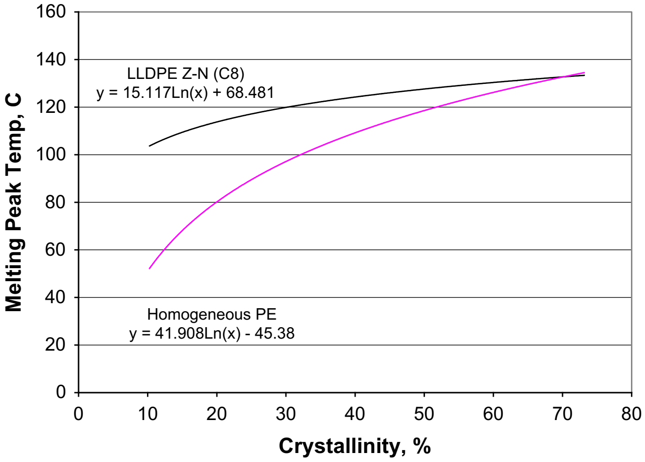


Fig. 2-33 Peak melting temperature for homogeneous PE versus crystallinity is compared to heterogeneous LLDPE octene copolymers from a solution process.

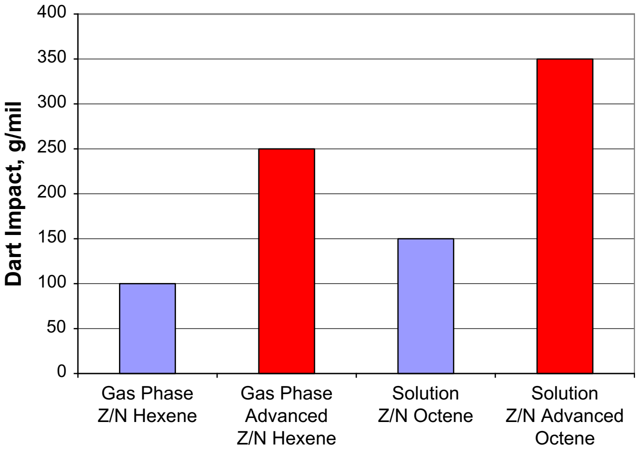


Fig. 2-34 Comparison of different Z–N catalyst systems in both gas phase and solution process on dart impact strength.

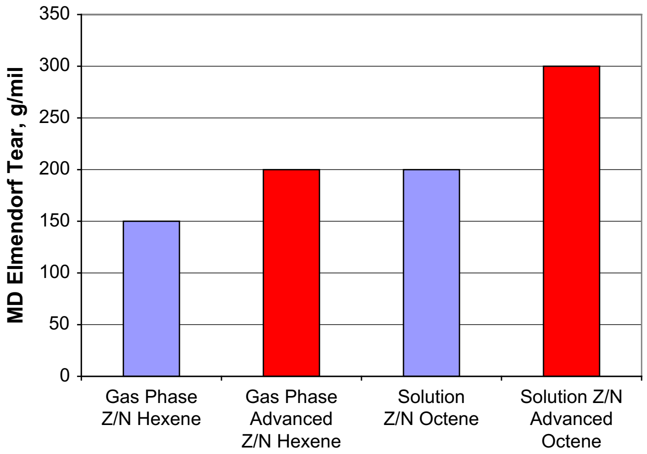


Fig. 2-35 Comparison of different Z–N catalyst systems in both gas phase and solution process on MD Elmendorf tear strength.

A similar effect for MD Elmendorf tear strength is shown in Fig. 2-35. The CD has a significant effect on the tear strength. These advanced Z–N catalyst systems have led to improved film properties that can be obtained.

Table 2-1 shows how different alpha olefin comonomers affect film properties. The SCB length is directly related to the comonomer used. The higher alpha olefins have longer branches and this leads to improved film properties such as dart impact tear strength, and tensile strength.

The polymer density is a function of the comonomer incorporated (Fig. 2-36). The higher the alpha olefin used, the more effective it is in achieving a target density.

Chrome-based catalysts

Chrome-based catalysts are used for both slurry and gas phase processes. Chrome-based catalysts can produce very high molecular weight polymers. These polymers are used in high melt strength applications such as:

- blown molding
- pipe
- thermoforming
- high stalk blown film.

In some cases, the chrome-based catalyst technology may incorporate some LCB into the polymer structure, further improving melt strength and processability. Broad MWD polymers are produced with chrome-based systems. Bimodal distributions are produced with multiple reactors.

Table 2-1 Influence of comonomer type on film properties

Melt index (dg/min)	1.0	1.0	1.0
Density (g/cc)	0.919	0.919	0.920
Comonomer	Butene (C4)	Hexene (C6)	Octene (C8)
Dart impact (g/mil)	100	200	335
MD Elmendorf tear (g/mil)	100	300	400
CD Elmendorf, tear (g/mil)	300	650	710
MD tensile (Mpa)	33.1	36.5	46.9
CD tensile (Mpa)	25.5	31.0	44.1

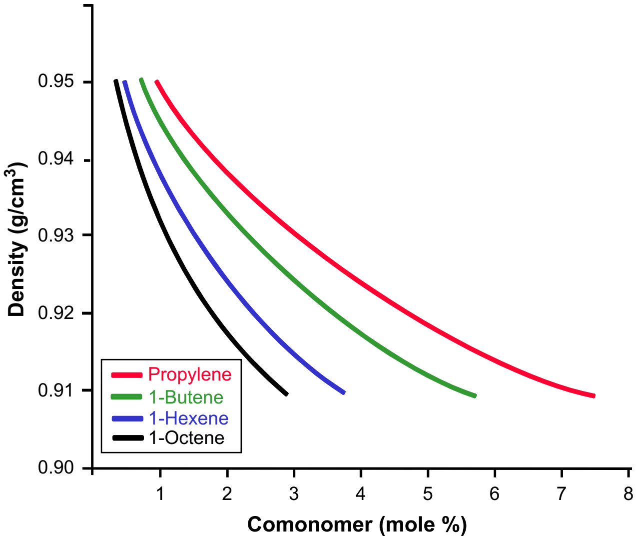


Fig. 2-36 Comonomer versus density for various alpha olefins.

Single site catalyst (Metallocene)

Single site catalysts (SSC) have evolved since 1992 when they were introduced. Some fall into a subset technology called metallocene catalysts (Fig. 2-37).

All these catalyst technologies are characterized by a uniform reactive site that very accurately controls the ethylene and the comonomer insertion into the polymer backbone (Fig. 2-38). The polymers produced using SSC technology will typically have very narrow MWD and CD.

Fig. 2-39 compares an SSC MWD to a typical Z–N LLDPE MWD at similar MI and density. Typically, a single site catalyst will produce a 2.0–2.5 M_w/M_n MWD. The narrow MWD distribution provides:

- increased film strength
- lower extractables
- better optical properties.

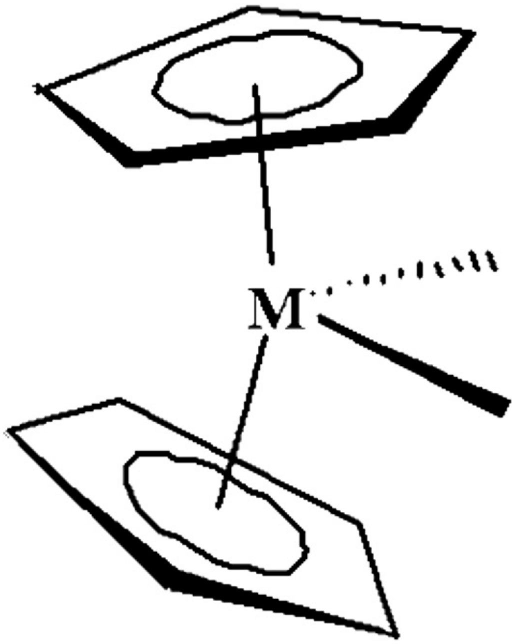


Fig. 2-37 Metallocene catalyst typically contains a metal atom (zirconium) stabilized with, in this case, two cyclopentyldienenyl rings.

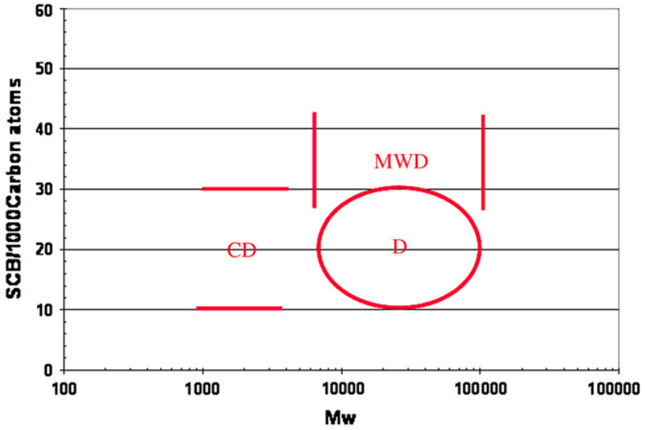


Fig. 2-38 Single site catalyst.

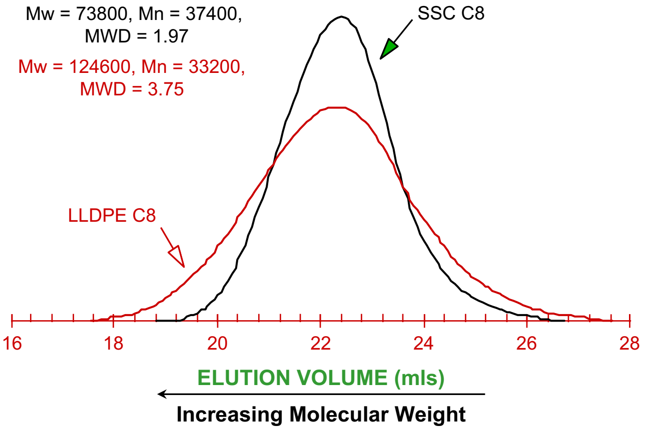


Fig. 2-39 MWD comparison between Z–N LLDPE and SSC octene copolymers of similar MI and density (1.0 MI, 0.920 g/cc).

However, the narrow MWD will make these polymers more difficult to process, in that they require higher amps and generate higher temperatures and pressure.

The CD distribution for SSC polymers is also very narrow compared to Z–N polymers. From the DSC curves shown in Fig. 2-40, one notes that the solution phase octene LLDPE and VLDPE copolymers with different density (0.92 and 0.905 g/cc) have very similar DSC curves. The HD peaks differ only in the relative amounts, while the lower density peak for the 0.905 polymer is at a lower temperature (lower density component). The Z–N catalyst used for these polymers produces a very heterogeneous CD as shown by the DSC curves. The SSC (INSITE process (ITP)) all have narrower DSC curves and the peak melting temperature is proportional to density.

The SSC polymers shown here have LCB incorporated into the molecular structure. The reactor conditions can be varied to increase or decrease the LCB. Table 2-2 shows the relationship between polymers with increased LCB and the I_{10}/I_2 ratio for 1.0 MI HDPE polymers produced using the INSITE technology. Higher I_{10}/I_2 means that the viscosity shear sensitivity is greater which makes these polymers easier to process.

Fig. 2-41 compares Z–N LLDPE octene polymers with no LCB to SSC with LCB and without LCB on

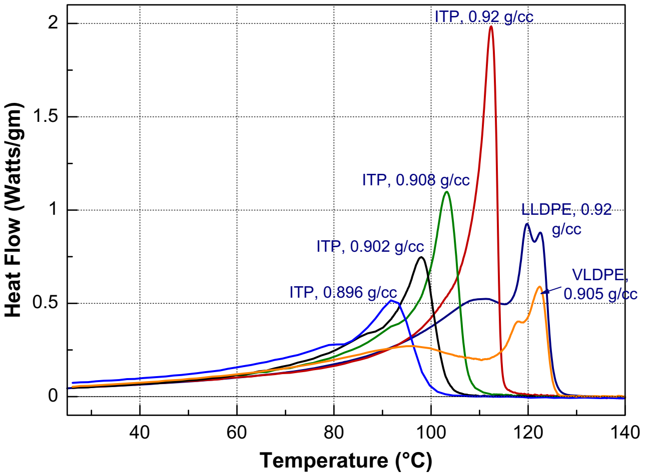


Fig. 2-40 DSC curves comparing Z–N LLDPE and SSC octene copolymers (ITP).

Table 2-2 I_{10}/I_2 relationship to LCB for four SSC polymers

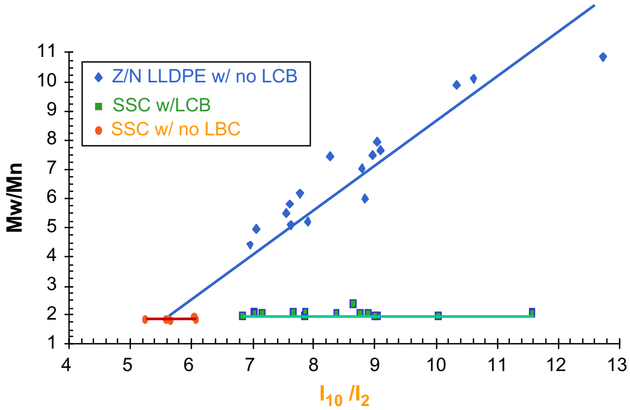
Polymer #	NMR LCB/Chain	I_{10}/I_2
1	0.2	8.89
2	0.44	10.63
3	0.53	11.85
4	0.66	16.07

a plot of M_wM_n versus I_{10}/I_2. For the Z/N LLDPE, the shear sensitivity can be significantly increased as the MWD is increased. Single site catalyst polymers with no LCB fall on the lower extrapolation of the LLDPE curve. Notice that the SSC polymers with LCB show significant shear sensitivity even though they have a very narrow M_w/M_n.

Enhanced polyethylenes (EPE)

Molecular architecture modification enhances PE properties. Film solid state properties can be optimized by controlling the MWD and CD. Fig. 2-42 illustrates the crystalline and amorphous components of semicrystalline polyethylene. The crystalline lamella size distribution is determined by the comonomer distribution. Larger lamella thickness indicates higher density components (few comonomer insertions along the molecule backbone).

The amorphous polymer molecules have high comonomer levels. Included in the amorphous component are the tie molecules. A tie molecule is an amorphous molecule that has been restrained either by having its ends embedded in the lamella or by entanglement with other amorphous molecules. The tie molecule will significantly improve toughness and tear properties by providing improved energy dissipation capability when the film is put into in high stress by puncture or fracture.



- Higher I_{10}/I_2 means easier processability at a given melt index.

Fig. 2-41 Comparison of LLDPE, m-LLDPE and SSC w/LCB on the relationship of MWD and I_{10}/I_2.

Tie chain concentrations are difficult to measure in polyethylene. Fig. 2-43 shows the probability of tie molecules in homogeneous (single site catalyst) polymers as a function of density for octene comonomers. Not shown in Fig. 2-43 is the tie molecule interaction and the lamella size. As density is reduced, tie molecule concentration increases up to about 0.915 g/cc density. Lamella thickness decreases as density decreases, so the tie molecules are less restrained by smaller lamella at lower density. This reduces the tie molecule effectiveness for improving toughness. Therefore, an optimum density exists that provides the best properties as shown in Fig. 2-44 with intrinsic tear as a function of density for octene, pentene

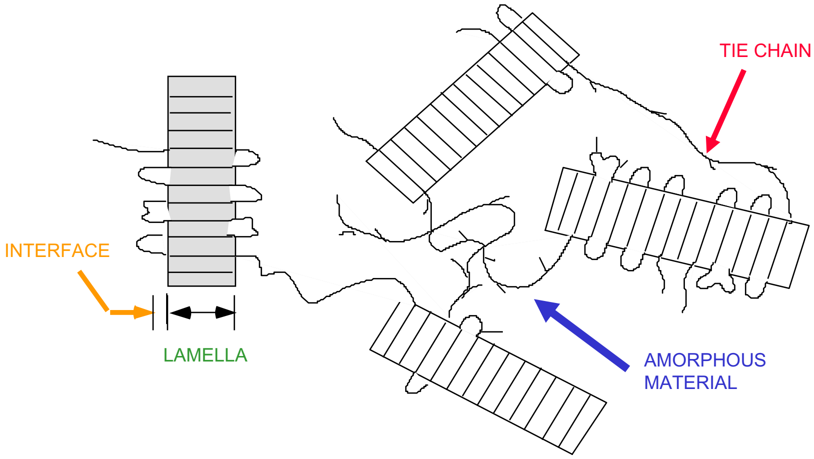


Fig. 2-42 Crystalline and amorphous regions of polyethylene.

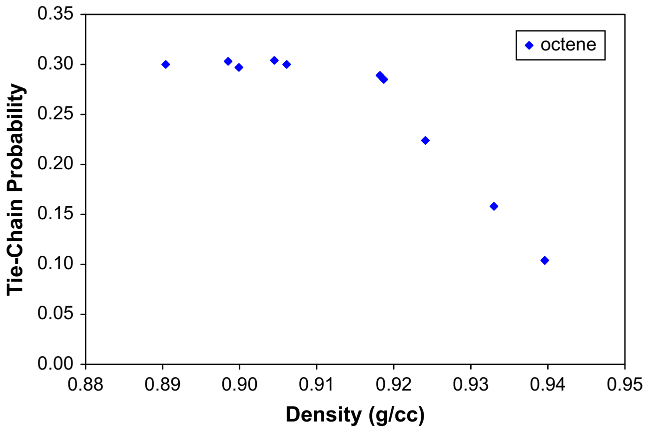


Fig. 2-43 Probability of tie molecules in homogeneous octene copolymers as a function of density.

and butene copolymers. All polymers had a similar melt index (1.0 dg/min).

The EPE polymers are designed to provide improved properties such as:

- impact
- tear
- sealability
- optical
- or modulus

compared to either LLDPE or m-LLDPE polymers. The MWD and CD are key attributes in designing these polymers. Fig. 2-45 shows how a polymer can be formulated to adjust the MWD of an EPE polymer. This could be accomplished by using multiple reactors, mixed catalyst system or by blending.

The CD can be adjusted similar to MWD (Fig. 2-46). Here, DSC curves show how a heterogeneous CD can be obtained for EPE polymers that provide high levels of tie molecules and high density molecules (thick lamella).

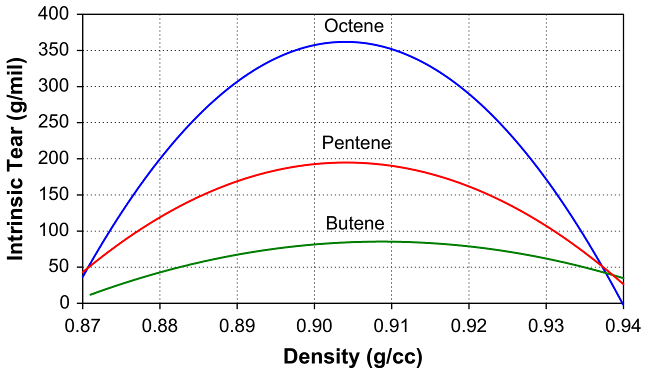


Fig. 2-44 Intrinsic tear as a function of density for octene, pentene and butene copolymers.

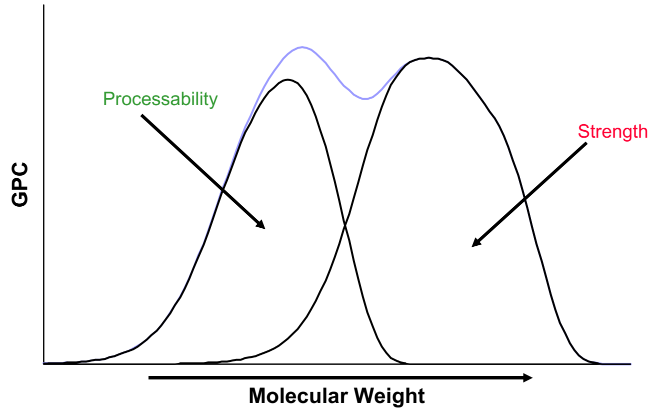


Fig. 2-45 Enhanced molecular design using MWD.

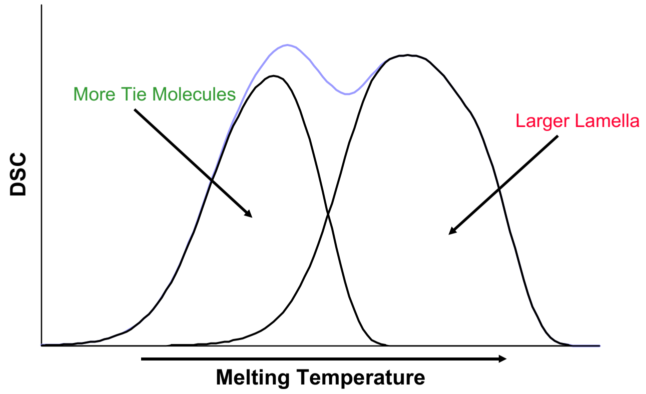


Fig. 2-46 Enhanced molecule design using CD.

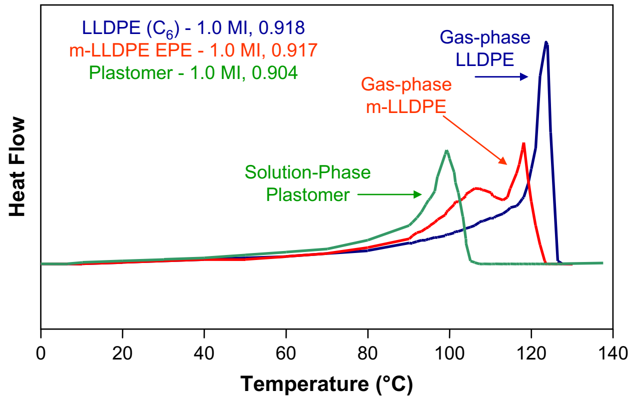


Fig. 2-47 DSC curves for a SSC plastomer, an EPE m-LLDPE and an LLDPE (C_6).

Fig. 2-47 compares DSC curves for a solution-phase plastomer, an enhanced PE (EPD) gas-phase m-LLDPE and a gas-phase LLDPE hexane comonomer. The solution-phase plastomer and the gas-phase LLDPE (C_6) have relatively narrow melting curves and the EPD gas-phase m-LLDPE has a broader melting curve with two distinct peaks. The lower peak is from the abundance of low density molecules which are the tie molecules. The higher peak is from thick lamella forming high density molecules.

The EPE resins can be optimized with catalyst parameters and process conditions. As there are many variables to choose from, this becomes a complex problem to provide the optimum resin for the desired film properties and optimum performance.

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Chapter 3

Polypropylene

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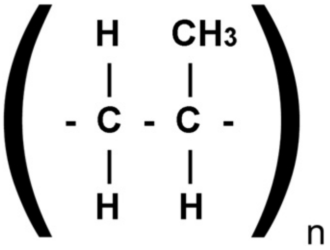
Managerial overview

Polypropylene is found in a wide variety of films and multilayer film structures as a result of its strength, toughness and high melting point [1]. Additionally, when formulated with the proper additive packages, polypropylene (PP) resins can exhibit excellent processability. The homopolymer chemical structure is rather simple, a methyl group located on every other methylene unit (Fig. 3-1).

The placement of this methyl group around the stereocenter during polymerization creates different tacticities (Fig. 3-2).

Methyl groups placed consistently on one side of the polymer chain generate an isotactic polypropylene. When these methyl groups alternate from one side to the other, the polymer is known as syndiotactic. A random ordering of the methyl groups creates an atactic polymer. The polymer tacticity partially defines the polymer's properties. Molecular weight distribution, degree of crystallinity and the polymerization method also define the polymer properties. Further chemical alterations, via copolymerization with monomeric units, such as ethylene and butylenes, create an even more comprehensive library of physical properties for specific applications.



$$\left(-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}- \right)_n$$

Fig. 3-1 The polypropylene monomer unit. The subscript n indicates that this is a repeating unit that is connected to n other monomeric units.

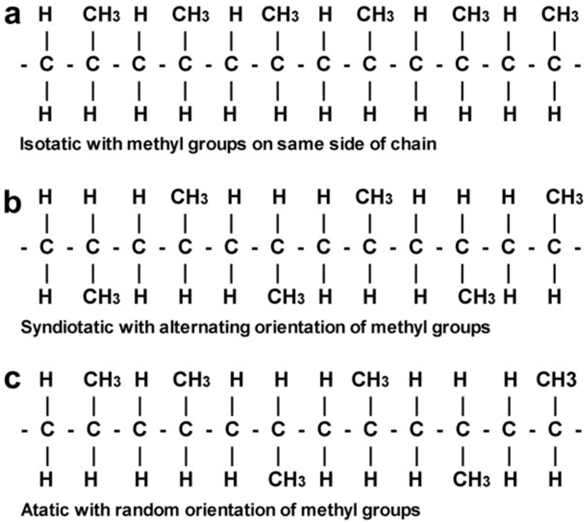


Fig. 3-2 A schematic of polypropylene tacticities: (a) isotactic with all methyl groups on the same side of the chain; (b) syndiotactic with methyl groups alternating above and below the chain; (c) atactic with methyl groups in a random orientation.

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Polymerization

Initial research investigating polypropylene polymerization relied on high pressures and radical initiators [2]. This technology produced low molecular weight oligomers with little commercial value. The Ziegler–Natta catalyst technology allowed manufacturing of commercially viable polypropylene. The resulting product was predominantly an isotactic polypropylene and could be manufactured at high molecular weight. Metallocene catalysts were the next generation catalysts and led to creating both isotactic and syndiotactic high polymer with highly controlled molecular weight distributions and tacticities.

Ziegler–Natta catalyzed polypropylene

Ziegler–Natta catalyzed polypropylenes exhibit a relatively broad molecular weight distribution with a weight average molecular weight divided by the number average molecular weight (M_w/M_n) or polydispersity approximately equal to 3.5 [3, 4]. These isotactic polymers comprise a large majority of the commodity grade resins used in film manufacture today.

The Ziegler–Natta catalysts developed for propylene polymerization generally consist of $TiCl_3$ and trialkyl aluminum. High weight average molecular weights are achievable with this chemistry, around 4×10^6 g/mol, creating a polymeric material that can be processed into cohesive films. To improve this catalyst system, specifically better to control molecular weight distribution and polymer tacticity as well as to improve the catalyst efficiency, chemists have modified the crystal structure of the $TiCl_3$, purified the catalysts, introduced transition metal compounds and/or a Lewis base to act as an electron donating species.

Ziegler–Natta catalyst chemistry allows polymerization in four unique polymerization systems: slurry, liquid propylene, solution and gas phase.

Slurry process polymerization of polypropylene

In slurry polymerization, chain growth occurs as monomers dissolved in a hydrocarbon solvent add to growing chains also dissolved in the solvent. Two fractions result from polymerization: one fraction is soluble in the solvent while the other is not. The two fractions are separated by centrifugation, thereby creating two product streams. The insoluble fraction creates the slurry phase and is predominantly isotactic material. The soluble components are either low molecular weight oligomers or highly atactic polypropylene that precipitates from solution when the solvent is boiled off at high temperatures. Unreacted monomer is also released as a gas when the solvent boils off. This monomer is then recycled back into the monomer stream.

Liquid propylene polymerization of polypropylene

Another way to achieve polymerization utilizes the liquid monomer as the polymerization solvent. This process has an advantage over the slurry method because the high monomer concentration increases the reaction rate. Runaway reactions, uncontrolled reactions that arise from hot spots in the reaction medium, are prevented by the fact that the monomer itself can absorb excess heat as it vaporizes. The gas phase monomer then can be condensed and reintroduced to the reactor. As in the slurry process, high molecular weight PP and atactic PP form an insoluble phase in the condensed monomer. This insoluble phase contains both the atactic and isotactic fractions which are isolated from the liquid propylene at the same time. A second separation step removes the solvent soluble atactic fraction by using an appropriate organic solvent resulting in a pure isotactic polypropylene product.

Solution polymerization of polypropylene

During solution polymerization, the monomer, catalyst and solvent enter a reactor held at a temperature between 175 and 250 °C. Polymerization in the solvent creates a viscous polymer solution. A pump removes the solution from the reactor and the solution is filtered to remove any residual catalyst, if necessary. Vacuum drying removes the solvent from the polymer, leaving behind isotactic and atactic polymer.

Gas phase polymerization of polypropylene

Gas phase polymerization passes gaseous monomer through a fluidized bed containing polymer granules and inert-media supported catalyst. Some monomer reacts within the bed to create polymer and the remainder passes through where it is collected and recycled. The high polymer granules are removed from the bottom of the fluidized bed along with some of the inert-media supported catalyst. The catalyst is replenished in the reactor at the same time.

Metallocene catalyzed polymerization of polypropylene

Once manufacturers recognized the benefits of polypropylene in composite film structures, there was an increased demand for tightly controlled polypropylene materials with low polydispersity and controlled tacticity. The Ziegler–Natta catalysts were unable to meet these market needs. Additionally, there was a need for improved catalyst performance which would reduce residual catalyst levels in the final polymer, thereby enhancing the polymer's stability. The most effective way to achieve these goals found to date is to use metallocene catalysts. Metallocene catalysts control the polymerization by permitting only those monomers that approach with a specific orientation to attach to the growing chain. This results in increased tacticity control in the final polymer. In addition, the metallocene catalysts have only one active polymerization site, which results in a narrower molecular weight distribution than achieved by Ziegler–Natta catalysts ($M_w/M_n \approx 2.0$). These catalysts introduce their own special defects which actually result in a slightly lower melting temperature than can be achieved with the best Ziegler–Natta catalysts.

Metallocenes are homogeneous catalysts that are often soluble in organic solvents. Therefore, polymerization can occur via a solution process with a non-polar diluent dissolving the propylene gas, the catalyst and the co-catalyst system. They can also be adsorbed onto an inert substrate which acts as part of the fluidized bed for gas phase polymerization processes.

General classes of polypropylene resins

Atactic polypropylene

Atactic polypropylene, though the first manufactured polypropylene, finds little commercial use in the film industry. The random methyl group placement creates a polymer with low crystallinity. It is a soft and tacky material with low strength. It has high vapor and gas permeability and little solvent resistance. Commercial applications are very limited, however, it can be found as a component in adhesives and roofing systems.

Isotactic polypropylene

Isotactic polypropylene produced through current catalyst technology can be more than 95% isotactic as defined by the percent isotactic pentads in the polymer chain. This method, typically accomplished through nuclear magnetic resonance (NMR) spectrometry determines the fraction of five adjacent units with methyl groups all on the same side of the polymer chain relative to the total number of pentads in the polymer. The advantages isotactic polymer has relative to the syndio- and atactic polypropylene arise from its high crystallinity. Typical isotactic polypropylenes range from 40 to 70% crystallinity. The resulting polymer has a higher melting point (160–180 °C), higher density and higher strength relative to the syndiotactic and atactic forms.

In general, isotactic homopolymer polypropylene has a high degree of crystallinity thereby creating a material that is strong, with low permeability to vapor or solvents and high chemical resistance. Isotactic polypropylene – with the exception of the mesomorphic crystalline form – is typically opaque, due to the high concentrations of crystalline regions.

Isotactic polypropylene exhibits four crystalline structures: alpha, beta, gamma and mesomorphic [3, 5]. Each of these structures forms under specific processing conditions and defines the properties of the polypropylene. In polypropylene containing the alpha, beta and gamma structures, the final material is typically opaque due to the light scattering by spherulites with sizes similar to the wavelength of visible light.

Alpha crystallinity

Alpha crystallinity arises from a helical conformation of the polymer chains described by a monoclinic unit cell. This structure represents the most thermodynamically stable structure and forms readily as the polypropylene cools below its crystallization temperature. The helices align to form crystallites which then associate to form sheet-like lamellae. Cross-hatching microstructure arises as secondary lamellae grow perpendicularly off the primary lamellae. These secondary lamellae create a supermolecular structure by connecting the neighboring primary lamellae. The secondary lamellae can further associate to create spherulites (Fig. 3-3).

Another way to look at the spherulites and the lamella arrangement in the spherulite is shown in Fig. 3-4.

Fig. 3-5 [6] is a picture of a PP spherulite grown between glass slides on a microscope hot stage.

Polypropylene crystallites can be the size of the wavelength of light and therefore tend to refract light and be translucent with high haze and low transparency. There are several additives that can promote nucleation, reduce the spherulite size below the wavelength of light and make the quenched PP more transparent. Fig. 3-6 [7] is an optical micrograph that shows the effect of a nucleating agent on spherulite size.

Beta crystallinity

Beta crystallinity is observed when the polymer is cooled quickly below its melting point. The polymer chains do not have the time required to form the thermodynamically stable alpha crystallinity. Beta crystalline polymer has a lower density and lower melting point than alpha crystals. Once the polymer is heated or placed under strain, the beta crystallinity will revert to the alpha structure.

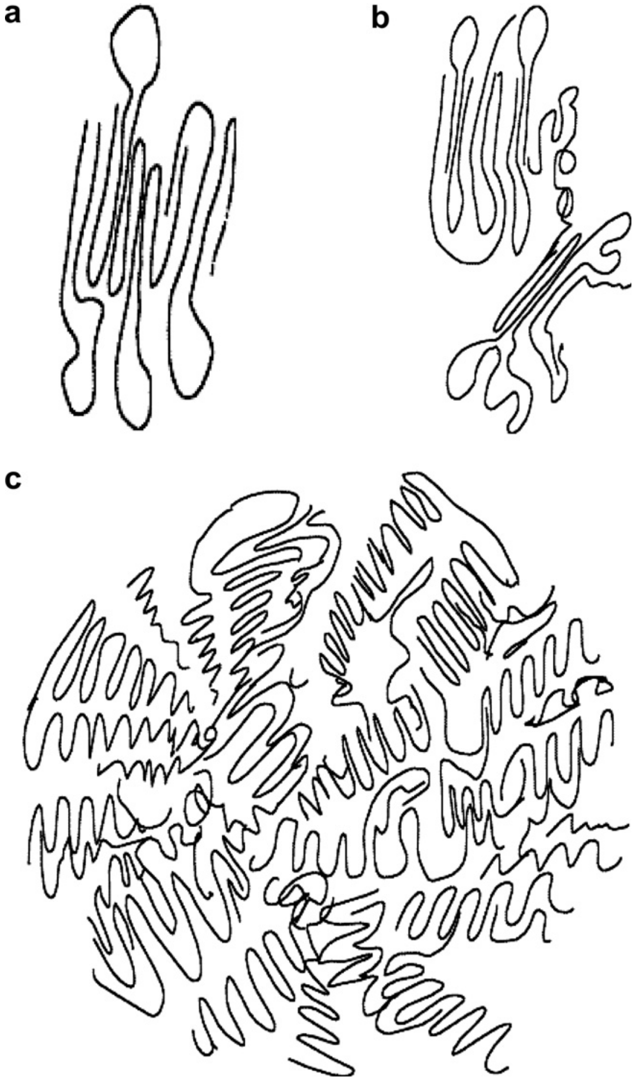

Fig. 3-3 Semicrystalline structure of polypropylene. (a) crystallite formed from polymer chains associating; (b) secondary crystallization associating crystallites to form lamellae; (c) formation of spherulites from long range structuring of lamellae.

Gamma crystallinity

Isotactic polypropylene also can exhibit gamma crystallinity, though this form rarely arises from processing under standard conditions. The gamma crystallites form a cross-hatched structure just as seen in alpha crystallinity. However, the crystallites grow in two directions at the same time, resulting in a highly crystalline, high density material. The mechanism for the formation of gamma crystallinity is believed to rely on shearing an alpha crystalline polymer, which creates a more uniform crystal structure.

Smectic or mesomorphic crystallinity

Rapidly quenched isotactic polypropylene exhibits an additional form of crystallinity. Rapid cooling prevents large crystalline domains from forming. Therefore, the crystalline regions are small with poor alignment between the individual crystallites. The properties of a smectic crystalline polypropylene lie between those of alpha crystalline and atactic polypropylene. The polymer will be transparent and will revert to an alpha crystalline structure upon heating.

Syndiotactic polypropylene

With the introduction of single-site catalysts, syndiotactic polypropylene became commercially available, however, its use is not widespread in multilayer film manufacture. Until this time, syndiotactic polypropylene was not a viable commercial product as its manufacture was not feasible with the prior catalyst technologies [3, 5]. The syndiotacticity of the single site catalyst produced polymer rarely exceeds 75%, based on pentad sequences. The polymer, relative to isotactic polypropylene, has a lower melting point (approximately 138°C relative to approximately 155–160°C) and a lower density (0.89 g/cm^3 relative to 0.93 g/cm^3). The crystallites that form in syndiotactic polypropylene are more complex than those formed in the isotactic polymer. This complexity reduces the rate at which the crystallites can form, meaning that the polymer crystallizes very slowly. [8, 9]

Processing

Polypropylene's excellent strength, low surface energy, low gas and liquid permeability and relative ease of processing make it an attractive option for use in

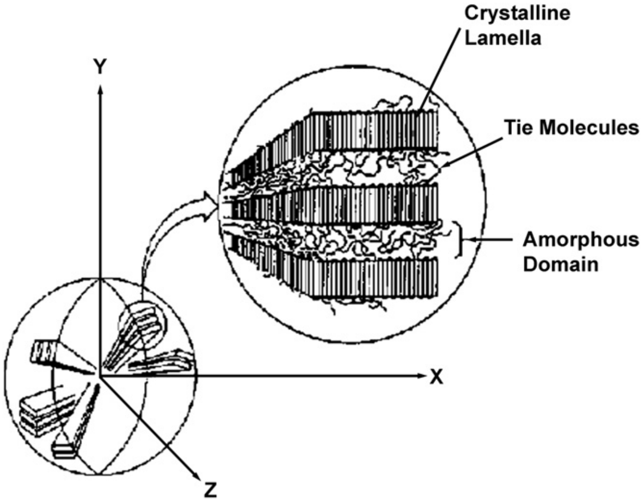

Fig. 3-4 Spherulite crystal morphology showing the lamella, tie molecules and amorphous domain.

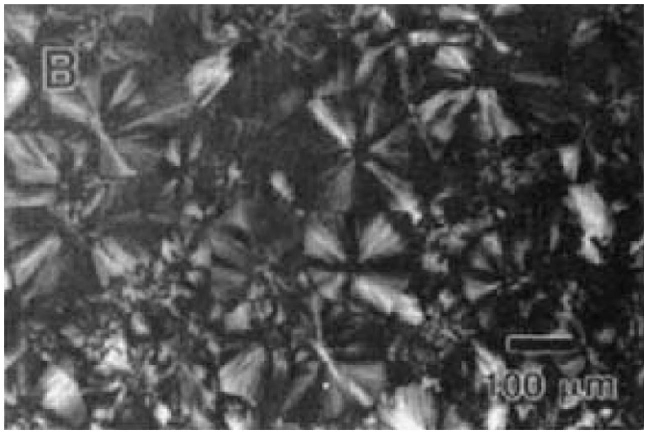

Fig. 3-5 A Maltese cross pattern of birefringence obtained using optical microscopy under crossed polarizers. Polypropylene was isothermally crystallized at a pressure of 100 MPa.

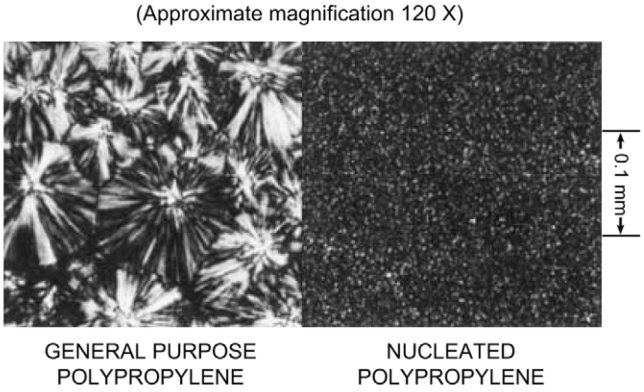

Fig. 3-6 Two optical micrographs show the effect of a nucleating agent on spherulite size. In nucleated polypropylene, right, spherulites are smaller and more numerous than in unnucleated polypropylene, left.

multilayer films. However, its opacity may be a detriment for packaging applications.

To overcome the issues of opacity, orientation breaks up the spherulitic structure thereby resulting in a transparent film. Additionally, orientation improves tensile properties, impact strength and reduces gas permeability.

Polypropylene may be used to manufacture single layer films or as a component in multilayer films via both cast and blown film processing. In multilayer films, polypropylene can serve as the major layer to provide structural integrity to the film or it may be used as a minor layer for specific functionality. In either blown or cast film processing of multilayer films, coextrusion generates the individual layers. Processors accomplish adhesion between the layers by using pressure to create intimate contact between the layers when they are still hot. In blown and cast film processes the layer joining is usually done inside the die. However, in some blown film processes a hot nip can intentionally block the collapsing bubble together and double the number of layers minus one.

One functional application of polypropylene as a non-structural layer is found when a polypropylene copolymer, including ethylene- and ethylene, butylene-propylene copolymers, is used as the skin layer of a multilayer film. These copolymers exhibit lower melting points thereby promoting a good heat seal during conversion of the film into functional packaging.

Challenges of using polypropylene

The challenges associated with using polypropylene in film applications are mostly centred on the fact that it is an intrinsically unstable polymer that degrades via oxidative, thermo-oxidative and ultraviolet degradation processes [10, 11]. Manufacturers of these resins recognize this issue so they generally stabilize them well before sending them to their customers. However, stability may be a considerable issue if the stabilizer is ineffective for the processing conditions or is used up during processing or use.

The most common degradation during manufacturing is that of thermo-oxidative degradation. In this process, oxygen and high temperatures create an autocatalytic reaction which promotes the formation of double bonds in the polymer chain, creates chain scissions and generates low molecular weight volatile products. The double bonds end up conjugated on the chains which leads to off color resin with a yellow tint. The low molecular weight volatile materials can lead to holes in the film (under very extreme conditions) or thin spots where the volatiles flashed off at the die. Another issue associated with degradation is molecular weight reduction induced by the chain scission events which reduces the polymer melt viscosity. This can lead to ineffective mixing and pumping of the polymer thereby changing the final film properties.

To prevent this degradation from occurring, processors need to confirm that the stabilizer works under the processing conditions including residence time, shear conditions and temperature regime that the polymer will experience. This becomes especially critical when recycled material is introduced to the process. The stabilizer will already be depleted in this recycled material which can lead to additional problems during its reprocessing.

Another processing concern is that polypropylene's melt strength may be inadequate to sustain a stable bubble during blown film processing. This means that the bubble may sag or dance under its own weight resulting in uneven film thicknesses across the bubble. A recent improvement to this resin family includes a polypropylene which contains long-chain branching. This branching increases entanglements among the polymer chains promoting greater cohesion of the polymer. This, therefore, increases the melt strength.

Summary

Polypropylene provides the film manufacturer with strength, toughness, high melt temperature and ease of processing that makes it a star among the polyolefin resins. Films produced with this polymer find a wide range of applications in many different arenas. Consumable and medical packaging, labels, stickers, personal hygiene and construction films all have been made with this versatile resin.

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Chapter 4

4

Additives to design and improve the performance of multilayer flexible packaging

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[3] *Songwon International, Switzerland*
[4] *Songwon International Americas, USA*

Introduction

In order to design tailor-made properties for an end application, the characteristics of the principal substrate must be modified. The properties of a polymeric substrate can be modified in a variety of different ways. The two principal approaches are:

- structural modification of the polymer
- incorporation of additives.

Structural modification of the polymer includes different polymerization processes for the same polymer (see Chapters 2 and 3), copolymerization, polymer alloys and the entire substitution of one polymer by another.

Additives are chemical substances that are incorporated into the polymeric substrate in order to stabilize, modify or enhance the initial performance of the substrate. The general term ‘additive’ can be subdivided into:

- stabilizer
- modifier
- filler.

Stabilizers are added to maintain the substrate’s original molecular architecture (mechanical, optical and organoleptic properties) during storage, conversion and service life.

Modifiers, such as slip agents, antistats, antiblocking agents, lubricants, processing aids, etc. improve or alter polymeric substrates’ performance and properties.

Fillers, having a different surface to volume ratio and being added at significantly higher amounts than the additives mentioned before, improve the physical properties or cost-dilute the polymeric substrate (e.g. talc, chalk, etc.). In most cases, additive combinations are used to modify the polymeric substrate for a particular end-use.

Overview

Organic substrates can be modified significantly by incorporating additives. In order to achieve an optimum effect, the incorporation method and the additive chemistry must be considered.

Additive incorporation has two general possibilities for multilayer films. First, the additives can be incorporated into the organic substrate after synthesis (see Appendix 4.2, Tables A4.2.1–4). Second, the additives can be incorporated into the layers of a multilayer film (see Appendix 4.1, Table A4.1-1).

The different effects and how to influence those are summarized below. The general comments on additives should also be considered.

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Additive handling, addition and dosing

Modifying polymer properties via additives requires incorporating them into the polymer. Additives can be incorporated at various points during the life time of a polymer.

The specific additive and its most appropriate physical form have an impact on the most appropriate addition point during a substrate's life cycle. Fig. 4-1 is a generic representation that shows the principal addition points in the life cycle of a polymeric substrate from the monomer stage through to the end article (e.g. film) [1, 2].

Depending on the substrate, additives can or already have been incorporated into the monomer (addition point (A)). Selected additives (e.g. inhibitors for vinyl chloride (VCM), the monomer for polyvinylchloride (PVC)) are designed to be depleted or physically lost during further operations. Depending on the polymerization technology and the substrate, additives can be incorporated at various points during the synthesis, either into the reactor (B) or during immediate post-reactor operations, e.g. immediately into the reactor discharge, solvent flash off or polymer drying (C–E). Only occasionally, additives are incorporated into the storage silo (F). Later on, additives are incorporated via extrusion to yield basic grades (G). Compounds equipped for specific end-use applications or conversion processes are manufactured during a compounding step (H). This compounding step can either be integrated into the polymer manufacture or can be independent. In the first case, addition points (G) and (H) can be identical. The last possibility to incorporate additives is at the actual conversion step, e.g. the film manufacturing step (I). If the end article is recycled, further additives can or might have to be added (K).

Especially for polyolefins, it is possible either to use fully formulated grades or, alternatively, to use basic additive grades and top-up additives during the conversion step. In the latter cases, it should be noted that knowledge about additives that are already present in the organic substrate is imperative in order to avoid overdosing or undesirable interactions between different additives or additive classes.

Any process to handle, add or dose additives must be designed to ensure accurate dosing and accurate dispersion of, in most cases, numerous additives within the organic substrate. Insufficient dispersion typically results in a significant additive performance loss, especially on an industrial scale. Insufficient performance often is corrected by overdosing the corresponding additive in order to improve its performance. It should be noted that the physical form and chemical characteristics of individual additives can span a wide range. In many cases, the additive's basic physical form is not very suitable for an optimum homogenization in the organic substrate.

It is important to match the additive's physical form that will be used in handling and dosing to the industrial plant requirements. Various different physical forms are suitable for addition during synthesis of the organic

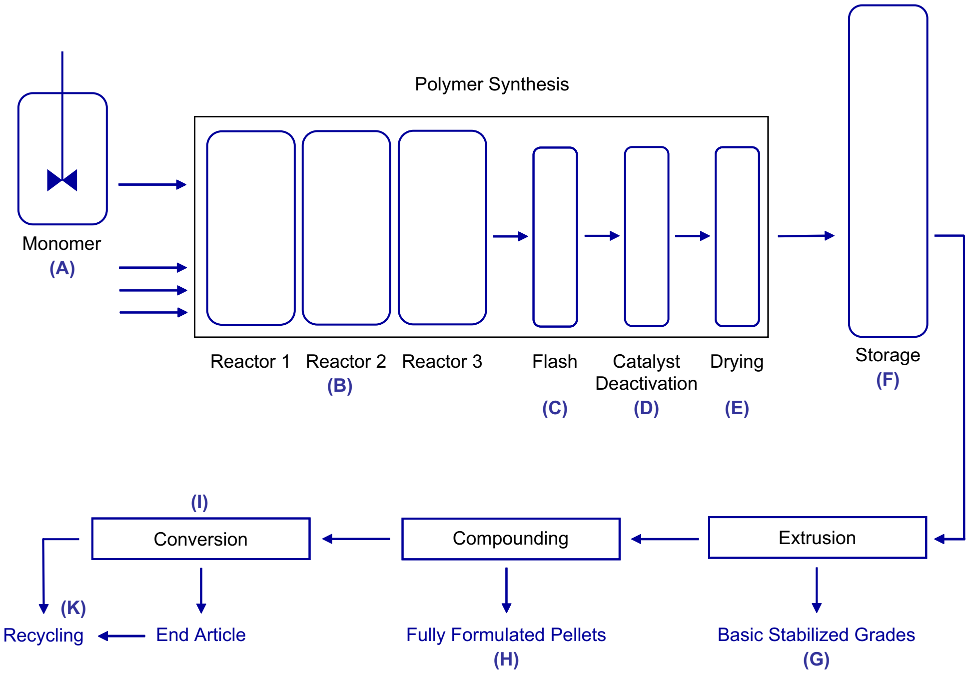

Fig. 4-1 Addition points for additives during the life time of a substrate (modified from [1]).

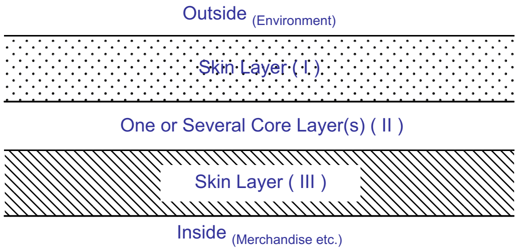

Fig. 4-2 Generic multilayer film.

substrate (depending on which addition point (A) through (F) [3, 4]) is used. After synthesis, addition is predominantly via extrusion (G–K). The dominant physical forms used are:

- masterbatch (20–50% active ingredients in a carrier compatible with the organic substrate)
- one pack (100% active ingredient without a carrier)

When manufacturing multilayer films, it should be highlighted that not every additive needs to be added to every layer of the construct. Some additives, like UV additives, need only to be added to the skin layer (Fig. 4-2). Appendix 4.1 provides an overview of the necessity to equip the individual layers of a multilayer film with which type of additive.

In the case when additives are added to selected layers only, migration effects must be considered. Like in any heterophasic (co-) polymer system, the additive solubility in the different phases results in a partition coefficient which, together with the concentration difference, determines the (potential) additive migration from one phase to the other. Thus, although additives might only be added to one layer, migration into neighboring layers may occur. This effect will decrease the additive concentration in the initial layer.

Additive types and principal mode of action

For practical reasons, additives are mainly classified according to the technical effect that should be achieved. This technical effect is generally referred to as *primary effect*. While a simple and practical classification, the approach struggles with additives that can be used for various effects. Nevertheless, this approach is used here. As mentioned earlier, additives can be subdivided into:

- stabilizers
- modifiers
- fillers.

Stabilizers can be further subdivided into:

- antioxidants
- UV stabilizers.

The specific *modifier* classes discussed in this chapter are:

- optical brighteners
- slip additives
- antiblock additives
- antistats
- others.

Additives will be selected based on the primary effect desired. It is advisable to modify this initial ranking based on secondary effects. The obtained ranking should be further ‘thinned out’ according to the permanence in the substrate and industrial suitability needed. Last, but not least, the regulatory guidelines or ‘approval’ status should be considered. General requirements for additive selection are listed below. For any given additive class and substrate, these requirements can be described in more detail. The relative importance of any of the listed requirements can vary case by case. Although this is a technical discussion, the requirement *cost* has been added because, in industrial practice, it is an important selection criterion.

- Activity (primary effect)
  - ○ efficiency
  - ○ molar activity (selected additive classes)
  - ○ concentration
  - ○ ‘process window’
- Interactions (secondary effect)
  - ○ side effects at excessive concentrations
  - ○ discoloration
  - ○ chemical reactions with other additives
  - ○ physical–chemical effects with other additives
- Permanence in the substrate
  - ○ solubility
  - ○ diffusion rate
  - ○ thermal stability (e.g. at processing temperature)
  - ○ volatility
  - ○ chemical stability
- Industrial suitability
  - ○ addition point
  - ○ physical form
  - ○ physical–chemical characteristics (e.g. melt point)
  - ○ storage stability
  - ○ end application
- Cost
- Regulatory status
  - ○ registration (local and global)
  - ○ EHSA, FDA
  - ○ indirect food contact.

The effect of an additive can be influenced by its concentration. Most additives exhibit a concentration dependency (Fig. 4-3). This behavior is characterized as a *saturation curve*. In phase (B), the primary effect

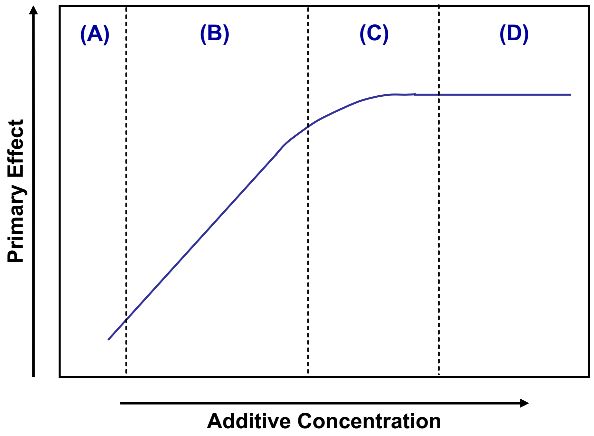

Fig. 4-3 Concentration dependency of the primary effect of additives.

increases with increasing concentration. In phase (C), the primary effect 'flattens-out'. Then, in phase (D), there is no further improvement. Within phase (B), the primary effect can be predicted semiquantitatively as a function of additive concentration. Within phase (D), the primary effect is not further improved despite a continued increase in the additive concentration. One might think that incorporating excess additive ('a lot helps a lot') is an acceptable approach. However, in phase (D), secondary effects have a negative impact on the overall additive performance. One secondary effect is exceeding the additive solubility limit, which results in plate-out and blooming. Additionally, the cost increases without any beneficial effect.

The actual concentration should be situated in phases (B) or (C) with a particular emphasis on the required safety margin relative to the (in-) accuracy of additive dosing on an industrial scale.

Phase (A) describes an often experienced phenomenon of a lower critical additive concentration, below which no measurable effect is detected. Phase (A) can be due to real scientific considerations (a real lower critical concentration limit) and/or dosing and dispersion limits on an industrial scale plant operation.

The additive classes will now be discussed by first outlining the principal mode of action, followed by substrate specific considerations.

Antioxidants and other stabilizers

Effect

For the purpose of this discussion, the term 'antioxidant' is used to describe all stabilizer classes that are utilized to protect organic substrates from thermal and thermo-oxidative degradation during storage, processing or conversion and service life in the absence of ultraviolet light (sunlight) and maintain its initial properties (e.g. molecular architecture, appearance and organoleptic properties). The complex degradation chemistry is generally described in [5]. Substrate specific degradation patterns can be found in [6].

The effect of antioxidants is essentially a bulk effect although, during service life, degradation will start where the organic substrate contacts the environment (oxygen diffusion).

Principle

On one hand, for any given organic substrate, the requirements for antioxidants used during processing or conversion are quite different and sometimes contrary to the requirements during service life. On the other hand, the degradation pattern strongly depends on the organic substrate. Therefore, the antioxidant (or stabilizer classes) needed vary considerably for polyolefins (polypropylene, polyethylene), polyester, polyvinylchloride and polyamide (to mention only the major substrates for flexible packaging).

A very generic principle is outlined in Fig. 4-4. During processing and conversion, the initial properties of the synthesized organic substrate start to deteriorate immediately if the organic substrate is neither intrinsically stable nor stabilized (case (A)). An ideal stabilizer retains the properties of the organic substrate throughout the entire processing or conversion step (B). In reality, most stabilizers or stabilizer combinations are only able to delay the onset of measurable degradation and slow down the degradation rate in order to maintain the organic substrate within specifications throughout the processing or conversion step (C).

Influencing the substrate stability during processing or conversion

Adjusting the processing stability is necessary when the organic substrate degrades at the processing conditions in

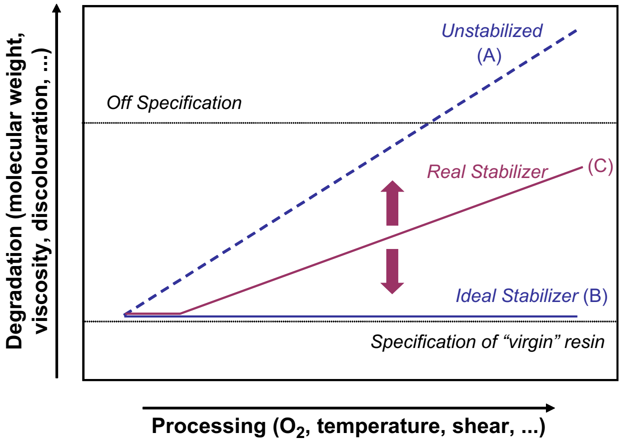

Fig. 4-4 Principle of the utilization of antioxidants (and other stabilizers) during processing or conversion.

the selected equipment (Table 4-1). If no changes occur during processing or conversion, a stepwise reduction of the antioxidant and stabilizer concentration might be possible within the limitations outlined in Fig 4-3. It is important to understand the complete chain of use for the material and have a product that will perform properly during its projected life span.

Protecting the organic substrate during service life is illustrated in Fig. 4-5. The gray area represents the service life in general. The area is limited by time (expressed in days, weeks and eventually months) and a defined acceptable deterioration of properties. Both time and properties are mainly determined by the end application. Stabilizer addition (case (C)) typically results in an induction period during which no or only minor changes in the organic substrate are detectable. As the stabilizer is depleted, changes occur until the specification limit of the end article is reached. The slope of these changes can, in selected cases, be lower compared to the unstabilized case (A).

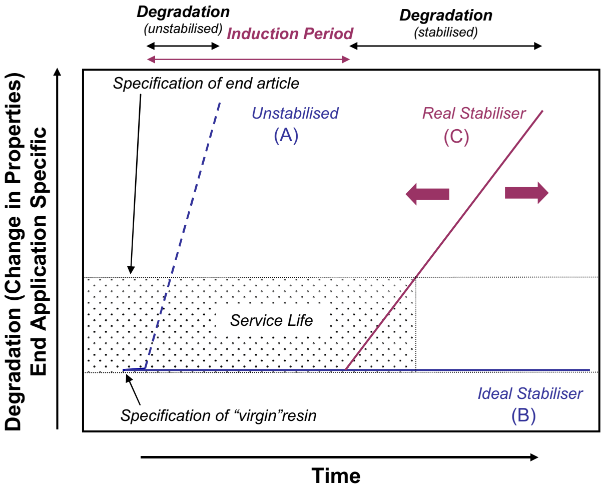

Fig. 4-5 Principle for the utilization of antioxidants (and other stabilizers) during service life (modified and improved from [5]).

Influencing the substrate stability during service life

The life time of the organic substrate should match (including a safety margin) the desired service life of the plastic article. Table 4-2 highlights several alternatives, involving stabilizers or other option, to adjust the life time to the requirements.

The detailed stabilization strategies applied during processing or conversion need to be discussed substrate by substrate.

Polyolefins (polypropylene and polyethylene)

The term polyolefin (PO) comprises polypropylene (PP, mainly homopolymers and also random copolymers) and the different polyethylenes (PE), namely high density (HDPE), linear low density (LLDPE) and low density (LDPE). Although all polyolefins degrade in a thermo-oxidative pattern only, the intrinsic stability varies [5]. The general ranking is:

$$\text{PP} < \text{HDPE} \approx \text{LLDPE} < \text{LDPE}$$

It should be noted that PP and some PE types degrade exclusively via a molecular weight reduction, while other PE grades show both molecular weight reduction and cross-linking (molecular weight increase). In industrial practice, the intrinsic stability depends on the specific polymerization process and catalyst system used.

Polyolefin degradation is counteracted by using antioxidants. The fundamentals of antioxidants are summarized in [7].

Table 4-1 'Quick reference guide' to influence processing stability

Issue/observation	Corrective action
High change in molecular weight	• Lower processing temperature and shear • Eliminate/reduce oxygen • Use an organic substrate with different initial molecular weight • Increase stabilizer concentration (until saturation) • More efficient stabilizers (substrate specific) • Synergistic stabilizer mixtures (substrate specific)
High discoloration	• Substrate specific • Use of optical brightener

Table 4-2 'Quick reference guide' to influence the service life of plastic articles

Issue/observation	Corrective action
Time to mechanical property deterioration insufficient	• Increase thickness of plastic article • Surface coating • Substitute with intrinsically more stable substrate • Increase stabilizer concentration (until saturation) • More efficient stabilizers (substrate specific) • Synergistic stabilizer mixtures (substrate specific)
High discoloration	• Substrate specific

Table 4-3 Stabilizer selection for polyolefin extrusion grades

Antioxidant	PP	HDPE	LLDPE	LDPE	Remark
AO-1	●	○			Multipurpose
AO-2		○	●	●	Multipurpose, good solubility
AO-3	●	●			Reduced color
AO-4	●				Low water-carry-over
AO-37				●	Multipurpose
HYA-1	○	○	●		Excellent color
P-1	●	●	●		Multipurpose
P-2			●		Multipurpose, liquid
P-3	○	○	○	○	Excellent color, related stability P-4 & P-5
Others					

● Filled circles indicate a recommended use or application; ○ open circles indicate limited, partial or conditional use
Note: For the antioxidant codes used in this chapter, Table 4-17 lists their chemical name, commercial name and a selection of suppliers.

Requirements

Apart from the general requirements, low discoloration of both substrate and antioxidant is desirable. For film or tape manufacturing processes that use a water bath to quench the film with water rather than chill rolls, antioxidants with low water-carry-over (w-c-o) effect are required. The stabilizer's thermal stability can vary depending on the conversion conditions which are defined by the polyolefin type and the conversion process (blown versus cast film).

Antioxidant chemistry

Extrusion grade polyolefins are stabilized using the synergistic effect between a phenolic antioxidant (AO) and a phosphite (P). The antioxidant's main purpose is to protect the organic substrate during processing or conversion including the stretching step. The phenolic antioxidant concentration present for processing or conversion usually is enough to extend the organic substrate life time beyond the service life-time requirement. The physical form of all antioxidants recommended in Table 4-3 is solid unless otherwise stated.

Depending on the catalyst system used, acid neutralizers must be added in order to avoid long-term corrosion effects in the processing equipment and improve stability during service life.

Influencing the antioxidant effect

Case (A) in Table 4-4 can be considered as typical multipurpose film stabilization, e.g. biaxially oriented polypropylene (BOPP) double bubble and cast film. In the BOPP tenter process, organic substrates with high molecular weight are used, requiring a better stabilization package. This is achieved by increasing the overall concentration and shifting the phenolic antioxidant to phosphite ratio from 1:1 to 1:2. Better color is achieved by choosing a low discoloring phenolic antioxidant (AO-3) combined with reducing the stabilizer responsible for the discoloration (phenolic antioxidant; (C)). It must be pointed out that (C) can only be effective instead (and not on top of) (A) and/or (B). Therefore, knowledge of antioxidants already present in the organic substrate is crucial.

Table 4-4 Recommendations for polypropylene extrusion grades

Case	Effect	Additive	Load level (ppm)	Remark
A	General purpose	AO-1 P-1	750 750	• Robust multipurpose blend
B	Severe processing	AO-1 P-1	750 1500	• Increased stabilizer concentration • Balance shifted to processing
C	Reduced color	AO-3 P-1	500 1000	• Low discoloring phenolic antioxidant • Balance shifted to processing
D	Low water-carry-over	AO-4 P-1	1000 500	• Balance shifted towards antioxidant • with lowest water carry over
E	Severe processing (Top-up during conversion)	AO-1 P-3	1000 1000	

Indicative starting point formulations from [8]

Table 4-5 Recommendations for LLDPE extrusion grades

Case	Effect	Additive	Load level (ppm)	Remark
F	General purpose	AO-2 P-1 / P-2	300 1200	• Robust multipurpose blend • Blown film
G	Severe processing	AO-2 P-1 / P-2	750 1500	• Cast film
H	Excellent color	HYA-1 P-1	750 750	• Non-discoloring stabilizer

Indicative starting point formulations from [8]

Low water-carry-over can be achieved by utilizing as much as possible a stabilizer not causing w-c-o (AO-4), which needs to be balanced with an increase in color (D). Case (E) is designed as top-up formulation at the conversion step in case an insufficient stability of the organic substrate is encountered at the film manufacturer level.

The recommendations for HDPE are essentially identical.

PE, in particular LLDPE, is stabilized differently for blown film (F) versus cast film (G). The increased stabilizer concentration is a result of the higher cast film processing temperature. The low discoloring phenolic antioxidant AO-3 has a very high melting point and is not very soluble in LLDPE. As a consequence, excellent color can only be achieved by using an intrinsically non-discoloring stabilizer (HYA-1, (H)). Table 4-5 gives an overview.

As LDPE is the most stable polyolefin type, lower antioxidant levels are suitable (Table 4-6).

Incorporation

Antioxidants are typically incorporated during the extrusion step directly after polymerization (addition point (G) in Fig. 4-1). As a major exception, formulation (E) from Table 4-4 should be used at the conversion step (addition point (I)) in masterbatch form or to stabilize the masterbatch carrier itself (see Appendix 4.2).

Polyester

The polyester group comprises polyethylene terephthalate (PET), polybutylene terephthalate (PBT) and, more recently (although scientifically not entirely correct), the biodegradable polylactide (PLA, polylactic acid). In general, PET is considered a bit more stable against degradation during conversion and service life than PBT. Both show the following degradation pattern in descending order of importance:

- hydrolysis
- thermal (mainly during conversion)
- thermo-oxidative (conversion and service life in particular at high temperatures).

During processing, the hydrolysis reaction kinetics are significantly faster than the thermal and thermo-oxidative degradation kinetics. Hydrolysis is defined as the ester bond decomposition due to the moisture and water which leads to a significant (melt) viscosity and molecular weight decrease. Hence, the primary stabilization strategy for polyester during processing is to suppress hydrolysis. Hydrolysis can be retarded by adding chemicals such as:

- epoxide (a cyclic ether with only three ring atoms)
- carbodiimide (functional group consisting of the formula $N{=}C{=}N$)
- phosphorus acid ester.

However, the most efficient way to prevent hydrolysis does not involve additives but simply good drying.

Thermal decomposition during conversion also results in lower molecular weight, lower viscosity and more end-standing carboxyl groups. End-standing carboxyl groups

Table 4-6 Recommendations for LDPE extrusion grades

Case	Effect	Additive	Load level (ppm)	Remark
I	General purpose	AO-2	500	• Multipurpose and high solubility
K	Severe processing	AO-37	500	

Indicative starting point formulations from [8]

Table 4-7 Recommendations for polyester grades

Substrate	Stabilizer	Load level (ppm)	Remark
PET	P-3 AO-1 P-1	3000 600 2400	• Phenol free
PBT	AO-2 P-1	800 3200	

Indicative starting point formulations from [8]

have a strong negative impact on hydrolytic stability. Thermal degradation is strongly influenced by metal compounds used as catalysts during the synthesis of the organic substrate. Hence, organic phosphorus compounds are used as complexing agents. Selected molecules include among others:

- bis-stearyl-pentaerythritol-diphosphite (additive code P-7)
- triphenylphosphate (P-10)
- trimethylphenylphosphate (P-11).

Discoloration during processing or conversion is very difficult to control and often only possible with the help of optical brighteners (see below).

PET is sufficiently stable against *thermo-oxidative* degradation during processing, so that no antioxidants (as outlined above) need to be added. In contrast, PBT benefits from the addition of phenolic antioxidants (e.g. additive code AO-2) and phosphite (P-1).

Top-up stabilization during processing or conversion is recommended (Table 4-7).

Requirements

No specific requirements other than mentioned above need to be considered.

Incorporation

Chemicals to retard hydrolysis are added during compounding. Complexing agents to guard against thermal decomposition during processing and conversion are most efficiently added during synthesis. Appendix 4.2 compiles an overview.

Polyvinylchloride

Flexible PVC is, of all the substrates that are discussed in detail in this chapter, the most complex and the most difficult to stabilize against degradation mainly during processing or conversion and, to a certain degree, during service life. Even non-industrial, artificially pure PVC must be considered intrinsically unstable. Polyvinyl chloride as an organic substrate degrades via various mechanisms. For flexible PVC, the plasticizer stability must be considered as well. On top of that, (flexible) PVC stabilizer packages tend to be more customer and equipment specific than stabilizer packages for other organic substrates.

(Flexible) PVC degrades according to the following mechanism:

- dehydrochlorination in the absence of oxygen
- thermo-oxidative degradation (resulting in dehydrochlorination) in the presence of oxygen
- secondary degradation reactions.

The degradation mechanisms of (flexible) PVC are described extensively in [9]. An effective stabilizer needs to either react with one of the key intermediates in the dehydrochlorination (allylic chloride) and/or scavenge liberated hydrochloric acid (HCl). The following chemical families are available:

- lead based
- tin based
- mixed metal based
- metal-free.

Mixed metal-based heat stabilizers are the most used in flexible packaging film. They can be further broken down into:

- barium/zinc stabilizers
- barium/cadmium stabilizers
- calcium/zinc stabilizers.

While barium/zinc-based stabilizers are a valid alternative to cadmium-based stabilizer systems, they can be further replaced by calcium/zinc-based systems in order to be completely heavy-metal free. These systems are often liquid. The performance of a barium/zinc-based stabilizer package is dependent on the proper choice of co-stabilizer (synergist). These synergists are:

- phosphites
- epoxy compounds
- antioxidants.

Lubricants play an important role in the stabilization of PVC during processing or conversion. Due to the complexity of the formulations, Table 4-8 can only give a very rough guidance for a flexible PVC stabilizer system. Other formulations are possible.

Plasticizers are incorporated into PVC in order to make it flexible. The plasticization mechanism is described in [10]. There are many chemical families available to achieve this effect, such as:

- phthalates (most common)
- trimelliates
- aliphatic dibasic esters
- polyesters
- epoxides.

A degrading plasticizer will impact the overall properties of flexible PVC and hence needs to be stabilized. The

Table 4-8 Generic recommendations for flexible PVC

Effect	Additive	Load level (ppm)	Remark
Heat stabilizer	BZ	35000	• Liquid, formulated system
Co-stabilizer	ESBO	30000	
Lubricant	Stearic acid	5000	

Plasticizer content up to 60% (indicative starting point formulations from [8])

stabilization strategies employed depend on the plasticizer chemistry. The most common plasticizers are listed in Table 4-9 together with suggested starting point formulations for both processing or conversion and storage stabilization.

Incorporation

Due to the complexity of the formulations, the potential interactions between the components and the trend for customer specific formulations, all ingredients related to stabilization must be added at the same point, e.g. during compounding (addition point (G) in Fig. 4-1).

Polyamide

Polyamide (PA) can be divided into aromatic and aliphatic polyamide and the latter further into:

- PA 6
- PA 6,6
- PA 4,6
- PA 11
- PA 12.

These notes on preventing degradation during processing or conversion and service life are limited to PA 6 and PA 6,6. Like polyester, PA exhibits the following degradation pattern:

- hydrolysis
- thermal
- thermo-oxidative.

Concerning hydrolysis, the same recommendations apply as for polyester. Polyamide used for film applications does not need to be specifically stabilized during processing. The intrinsic stability of PA against thermal and thermo-oxidative degradation is mainly influenced by the amount of carboxylic acid present in place of primary amino end groups. A further improvement can be achieved with lubricants. To a certain degree, yellowing must be controlled during processing via phosphites or optical brighteners (Table 4-10).

Stability during service life can, in principle, be improved by three alternative stabilizer and/or antioxidant classes:

- copper salts (combined with halogen ions or phosphorus compounds)
- aromatic amines
- phenolic antioxidants (e.g. AO-21).

Table 4-10 'Quick reference guide' to improve processing stability of PA

Issue/observation	Corrective action
High change in molecular weight	• Decrease carboxylic end groups • Increase amino end groups • Incorporate lubricants
High discoloration	• Incorporate phosphite (P-1 or P-10) • Incorporate optical brightener
Hydrolysis	• Improved drying • Incorporate hydrolysis inhibitor, e.g. polymeric carbodiimide)

Table 4-9 Recommendations for PVC plasticizers

Plasticiser		Stabilizer		
Code	**Family**	**Type**	**Load level (ppm)**	**Remark**
DOP	Phthalate	AO-2	1500	• General purpose
DINP	Phthalate	AO-8	1500	• Improved regulatory status
DINA	Adipate	AO-2	2000	• Improved low temperature brittleness
DOA	Adipate	AO-2	2000	• Food packaging

Indicative starting point formulations from [8]

Table 4-11 Recommendations for polyamide extrusion grades

Case	Effect	Additive	Load level (ppm)	Remark
A	Color suppression (processing)	P-1 P-10	2000 2000	• Multipurpose • Multipurpose, low volatility
B	Good balance processing & service life	AO-21 P-1	1000 1000	

Indicative starting point formulations from [8]

While the first two stabilizer classes are very effective (primary effects), both impart negative secondary effects which prohibit their use in packaging applications. For the modest service life stability needed in packaging film applications, phenolic antioxidant AO-21 offers a good balance of properties. A detailed differentiation of the three stabilizer classes is given in [5, 6]. Table 4-11 summarizes the recommendations.

Incorporation

Phosphites are typically added during compounding (addition point (H) in Fig. 4-1). The phenolic antioxidant is best added during polycondensation (B) or as additional top-up stabilization during compounding (H).

UV-stabilizers

Effect

Organic substrates tend to degrade during service life due to various mechanisms. Along with thermal, thermo-oxidative (induced by oxygen and heat) and hydrolysis initiated degradation (discussed above), UV light can initiate oxidation. Organic substrates which are used outdoors or exposed to lamps emitting UV radiation are subject to photo-oxidative degradation. An overview over photo-oxidation is provided in [11]. UV-stabilizers are one of several tools to prevent and retard photo-oxidation.

Photo-oxidative degradation is a non-homogeneous effect that always starts at the surface (at the side exposed to UV light) and propagates throughout the sample.

Using antioxidants can lead to an improved resistance against photo-oxidation. It must be further noted that a suitable stabilization during processing or conversion is mandatory for optimum stability against photo-oxidation.

Principle

Although four principal classes of UV-stabilizers exist, only two (in italics) are suitable for flexible packaging applications:

- *UV absorption*
- *free radical scavenging*
- *excited state quenching*
- *hydroperoxide decomposition.*

Ultraviolet absorption (UVA) stabilizers follow a physical principle and essentially depend on the substrate thickness, not the substrate type. As the name implies, UV absorbers absorb UV light and dissipate it as less harmful longer wavelength radiation (heat). Ultraviolet absorption can be used to stabilize the packaging material and the merchandise that it protects.

Free radical scavenging follows a chemical principle that is related to antioxidants. It is substrate dependent and, in particular, suitable for substrates that degrade by a free radical auto-oxidative mechanism. This is the only mechanism that can be used to stabilize the organic substrate used as packaging material.

The principle, illustrated in Fig. 4-5, also applies to UV-stabilizer utilization during the service life of an organic substrate.

Requirements

No specific requirements other than mentioned above need to be considered.

Chemistry

Ultraviolet absorber additives are either pigments/dyes, which absorb in the visible and the UV light spectrum or organic UV absorbers that absorb mainly in the UV range. The specific pigment or dye can have a positive or negative effect on the photo-oxidative stability of an organic substrate. A particular pigment worth mentioning is carbon black, which imparts high UV stability and limits the ability to manufacture non-colored and/or transparent packaging material. Another way to absorb UV energy is with *h*indered *a*mine (*l*ight) *s*tabilizers (HA(L)S), hydroxybenzoates and selected antioxidants to provide free radical scavenging.

Not every additive class can be used in every substrate discussed in this chapter. Table 4-12 gives an overview.

Table 4-12 Use and purpose of UV stabilizers

Class	Subclass	PP	PE	PVC	PA	PET	Substrate protection	Content protection
UV absorption	Pigment	●	●	●	●	○	○	●
	Dye	○	○	●	●	○		
	UVA	●	●	●	●	●	●	●
Radical scavenger	HA(L)S	●	●	○	●		●	
	Hydroxybenzoate	●	●	○		○	●	
	Antioxidant	○	○		○		●	

● Filled circles indicate a recommended use or application; ○ open circles indicate limited, partial or conditional use

Influencing the stability against photo-oxidation

Apart from increasing the UV stabilizer concentration up to the saturation limit, stability against photo-oxidative degradation can be increased by:

- thicker sample (film)
- best possible protection during processing or conversion
- surface coating with a protective layer (skin layer (I) in Fig. 4-2).

Table 4-13 summarizes starting point formulations for various substrates. It should be noted that stability requirements against photo-oxidation in packaging applications are often low.

Incorporation

UV stabilizers are typically added during the compounding step as top-up stabilization of a base grade (addition point (H) in Fig. 4-1) or even later during the conversion step (I). Ultraviolet stabilizers can be added evenly into all layers of a multilayer film. Alternatively, a skin layer (I) can be heavily loaded with UV absorber, thus filtering out UV radiation in the top layer, thus lower layers do not need to be stabilized. This second approach does not work well for very thin films.

Appendices 3.1 and 3.2 give an overview over the addition of UV stabilizers (excluding pigments and dyes).

Optical brighteners

Effect and principle

Organic substrates that impart a slight yellowish color can be modified to appear whiter and brighter by increasing reflected bluish light (in the range of 400–600 nm). One of several options is to utilize additives

Table 4-13 UV recommendations for various substrates

		UV Stabilizer			
Substrate	Expected service life (months)	Type	Molecule	Load level (ppm)	Remark
PP	≤ 12	HA(L)S	HAS-3	1000	• Multipurpose
	≤ 12	HA(L)S	HAS-3	600	• Improved UV & reduced secondary effects
		HB	HB-1	400	
	≤ 12	HA(L)S	HAS-5	800	• Protection of content
		UVA	HBP-1	1200	
PE	≤ 12	HA(L)S	HAS-5	1000	• Multipurpose
	≤ 12	HA(L)S	HAS-5	1000	• Protection of content
		UVA	HBZ-1	1000	
PET	≤ 12	UVA	HBZ-7	3000	• Protection of content
PVC	≤ 12	HA(L)S	HAS-7	1000	• Multipurpose
		UVA	HBZ-5	1000	
PA	≤ 12	HA(L)S	HAS-3	1000	• Multipurpose
		UVA	HBZ-7	1000	

Indicated starting point formulations from [8] based on geographical regions with an annual radiation of 70–90 Kly/a) that absorb in the UV range and re-emit the energy at higher wavelength. This effect is called fluorescence and the additives achieving this effect are called optical brighteners or fluorescent whitening agents.

Fluorescent whitening of organic substrate is a surface effect. Optical brighteners are a defensive tool to mask unpreventable discoloration of the organic substrate (or any additive component).

Requirements

Optical brighteners are partially efficient at rather low load levels ($\leq$10 ppm). Requirements for homogenization and dispersion are very high. Therefore, optical brighteners tend to be added along with other materials if technically feasible. Limited compatibility and limited photo-stability lead to a limited service life of the additive and the achieved effect.

Due to the difficult handling and limited stability, optical brighteners should be considered only after approaches described above are not successful in reducing discoloration.

Chemistry

Various chemical classes are available.

Influencing the effect

The effect of optical brighteners is concentration dependent and the saturation level is reached at low load levels. The performance depends on the processing or conversion conditions and is substrate specific. Additives that absorb UV light (UV absorbers and selected pigments) will decrease the efficiency of optical brighteners.

Table 4-14 proposes some starting point formulations.

Incorporation

Due to the (very) low concentrations used, the techniques used to incorporate optical brighteners vary considerably. Adding the additive alone should be avoided wherever possible. For polyester, selected optical brighteners are incorporated into the monomer, while for flexible PVC, optical brightener is added preferably pre-dispersed in the plasticizer which is added during compounding.

Slip additives

Slip is when polymeric films slide parallel over each other. Slip is a surface effect.

Slip is quantified via the coefficient of friction (COF). If films have a high COF, individual film layers have a high surface friction and tend to stick together instead of sliding over one another. The films do not ‘slip’. This phenomenon typically makes the handling, use and conversion of films rather difficult. It can result in decreased line speeds (lower productivity) and/or wrinkled film (higher waste). In order to overcome this issue, slip agents are added.

Principle

Slip additives can be divided in two fundamental classes:

- migrating
- non-migrating.

Migrating slip additives are by far the most common class and must be used above their solubility limit in the polymeric substrate. Slip agents have a part that is soluble in the organic substrate and a part that is insoluble. During processing (in the molten phase), slip additives (as overall effect) are soluble and homogeneously dispersed in the organic substrate. Upon crystallization, the solubility limit is exceeded and the slip additive migrates from the matrix towards the surface.

Initially, the slip additive is homogeneously dispersed in the film and, consequently, its surface concentration is low (Fig. 4-6; Phase A) and the COF is high. Due to the limited compatibility with the organic substrate, the slip

Table 4-14 Recommendations for optical brighteners

		Optical brightener		
Substrate	**Pigmentation**	**Type**	**Load level**	**Remark**
PP / PE	Transparent	FWA-1	10	• Compatibility is critical
PET	Transparent	FWA-1	200	
PVC	Transparent	Various	75	• Solubility and migration in plasticizer to be considered
	TiO_2	Various	$\leq$1000	
PA	Transparent	FWA-1	200	

Indicative starting point formulations from [8]

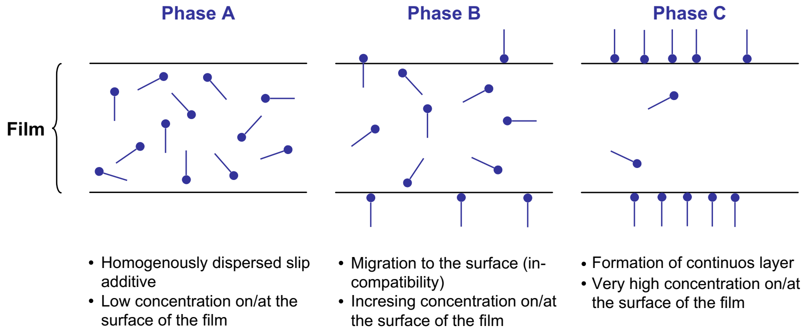

Fig. 4-6 Principal mode of action of slip additives.

additive migrates to the surface, thus the concentration at/on the film surface increases (Phase B) and the COF decreases. At equilibrium (Phase C) a continuous coating of at least one layer of slip additive molecules is formed at/on the film surface and the COF reaches its minimum value. The two major performance criteria are the migration speed to the surface (time until slip effect occurs) and the slip effect achievable (minimum COF). These two criteria are determined by:

- the polymeric substrate (crystallinity)
- slip additive (in-) compatibility (aliphatic chain lengths for fatty acid)
- slip agent concentration
- temperature.

Non-migrating slip additives are only used in very specific cases. These slip additives are applied externally. An immediate slip effect is achieved; reducing the principle outlined in Fig. 4-6 to 'Phase C'. Typical applications are very tacky substrates and the outer layer of multilayer films. Due to its limited applicability, this principle is not discussed further.

Requirements

Apart from the general additive requirements, migrating slip additives must have a designed low compatibility with the polymeric substrate. Chemically, migrating slip additives are mainly fatty acid amides that are derived from natural sources (vegetable or animal based). As with every additive derived from natural sources, purity (manifested as odor, flavor and color) needs to be defined.

Chemistry of slip additives

Most commonly, migrating slip agents are fatty acid amides. Various structural modifications are available, differing mainly in the aliphatic chain length, (un-)saturation and the amide (primary, secondary or bisamide). Oleamide (O) and erucamide (E) are most often used. However, for multilayer films, fatty acid amides with longer aliphatic chains and correspondingly slower migration speed are favored, e.g. ethylene bis-oleamide (EBO), stearyl erucamide (SE) and oleyl palmitamide (OP). Table 4-15 shows a comparison.

Chemically, migrating slip additives are high molecular weight organic materials such as poly-siloxane. While not migrating, upon prolonged contact, the additive can nevertheless transfer onto a neighboring layer.

Influencing the slip effect

In general, slip additives should always be tested in the presence of the entire additive package in the film.

Table 4-15 Classification of different fatty acid amides

	Amide type	Migration speed	Low COF achievable	Thermal stability	Other effects/notes
Erucamide (E)	P	++	+++	++	AB (limited)
Oleamide (O)	P	+++	++	+	
Ethylene bis-oleamide (EBO)	S, B	+	+	+++	AB in polar polyolefin copolymers; multilayer film
Stearyl erucamide (SE)	S	+	+	+++	AB Multilayer film
Oleyl palmitamide (OP)	S	+	+	+++	Multilayer film

P: Primary amide; S: secondary amide; B: bisamide; AB: anti-block effect. +++ very good; ++ medium; + poor but established

Various co-additives influence the performance of slip agents. When combining slip additives and antiblock additives, there can be an interaction where increasing one additive actually enhances the effect of the other additive.

The slip effect is influenced by the slip additive concentration. Increasing the concentration will reduce the COF until an equilibrium state is obtained. At (too) high concentrations, slip additives plate onto process equipment and negative interactions with adhesion and lamination operations might be observed. Further, an increased film haze will likely be observed.

The slip properties can also be improved by:

- decrease in film thickness
- antiblocking agents (low concentration)
- fast migrating substances (e.g. antifogging agents and selected antistats provide a carrier effect).

The slip properties can be negatively affected by several interactions. Interactions affecting slip properties can occur through:

- polar additives (chemical interaction)
- other surface modifying agents (e.g. stearates or antifogging agents; competition for space on the film surface)
- too high slip additive concentration (deposits on processing equipment, printing issues)
- changing the substrate polarity
- increase in film thickness
- insufficient thermal stability of slip additive at processing temperature.

Starting point formulations are given in Table 4-16.

Incorporation

Slip additives can alternatively be added during the extrusion, compounding or conversion step (see Fig. 4-1; addition points G, H and I). The most suitable physical form depends on the selected addition point. Migrating slip additives should be added mainly to the skin layer but sometimes as well to the core layer, while non-migrating slip additives are added to the skin layer only (see Appendix 4.1).

Antiblock additives

Effect

Blocking is when adjacent film layers (made of organic substrate) stick to one another. Blocking is a surface effect.

The effect is quantified via the force needed to separate two film layers under controlled conditions. A high force results in more difficult opening of blown film tubes after extrusion (lower productivity) and layer separation after storage (re-blocking) [12]. In order to overcome this issue, antiblock additives are added.

Principle

Antiblock additives can be divided into two fundamental classes:

- inorganic
- organic.

Chemically inert, inorganic antiblock additives are most commonly used. Inorganic antiblock additives migrate to the film surface, partially stick out and create a micro-roughness of the film surface. Fig. 4-7 illustrates this principle.

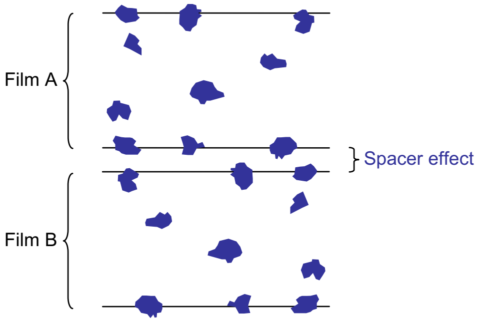

Fig. 4-7 Principal mode of action of inert, inorganic antiblock additives.

Table 4-16 Recommendations for slip additives

Substrate	Effect	Additive type	Load level	Remark
PP	Multipurpose Metallized film	Erucamide —	900 —	 • Interaction with surface treatment
PE	Multipurpose	Erucamide	1000	
PET	Multipurpose	Various	2000	
PVC	Multipurpose	Erucamide	2000	

Indicative starting point formulations from [8]

Table 4-17 Selection guide for antiblock additives used in packaging

	Silica				
Substrate	Synthetic	Natural	Talc, chalk china clay, $CaCO_3$	Organic antiblock	Others
PP	●			●	● Spherical silicon ● Spherical MMA
PE	○	●	●		
PET	●				● Zeolithes
PVC	●				● Alumosilicates
PA					

● Filled circles indicate a recommended use or application; ○ open circles indicate limited, partial or conditional use

The detailed mechanism of how organic antiblock additives work is not yet understood. It is thought that a barrier layer is formed on the plastic film surface, thus inhibiting the two adjacent plastic film layers' adhesion. Their usage is limited. Organic antiblock additives were partially discussed above and will not be further mentioned here.

Requirements

Apart from the general additive requirements, inorganic antiblock additives must be chemically inert with the organic substrate. Particle size and homogeneous dispersion has a major influence on the antiblock effect. The right balance between particle size and optical properties (low haze) is crucial. Abrasion effects to the surface of processing or conversion equipment need to be considered as well.

Chemistry

Several chemical classes of inorganic antiblock additives are available. Every class has its own performance profile. Table 4-17 selects the antiblock additives for the major organics substrates used in packaging. Table 4-18 recommends load levels for selected antiblock additives.

Influencing the antiblock effect

Apart from the concentration, the antiblock properties will additionally be improved by:

- best possible dispersion
- larger particle size (although too large particles will cause film defects)
- addition of selected slip additives.

The antiblock properties can be negatively affected by several interactions. Interactions related to antiblock properties can occur through:

- additive agglomeration
- increased film haze at too high load level of antiblock additive
- static charges
- high temperatures (during film storage)
- high contact pressure.

Table 4-18 Recommendations for antiblock additives

Substrate	Effect	Additive type	Load level (ppm)	Remark
PP	Multipurpose High quality	Synthetic silica Spherical MMA	2000 3000	 ● Multilayer
PE	Multipurpose	Talc	5000	
PET	Multipurpose	Synthetic silica	2000	
PVC	Multipurpose	Alumosilicates	4000	

Indicative starting point formulations from [8]

Incorporation

Antiblock additives are typically added during the extrusion and/or compounding step or sometimes even at the conversion step (see Fig. 4-1; addition points (G), (H) and (I)). However, for PET, the additive is added to the monomer (addition point (A)). (See Appendix 4.1 for an overview.)

Antiblock agents must be very well dispersed in order to obtain a good effect.

Antistats

Effect

When two (organic) substrates are in contact with each other such that friction occurs, electrostatic charges can built up. Electrostatic charges can impact plastic parts in several ways; one of the most annoying being the attraction of dust particles. One way to counter this effect is to use antistats (or antistatic additives).

This effect is principally a surface effect, although one potential counter measure (conductive fillers) converts it into a bulk effect.

Principle

Tools that decrease electrostatic charges and hence increase the conductivity of an organic substrate can be classified as:

- external antistat (surface effect)
- conductive filler (bulk and surface effect)
- internal antistat (surface effect).

An external antistat is applied via a carrier medium to the surface of the plastic part. The same considerations and limitations apply as with non-migrating slip additives. A conductive filler is incorporated into the organic substrates and builds up a conductive network on a molecular level. While both approaches are used in organic substrates, they are not the most common.

An internal antistat is compounded into the organic substrate and migrates to the plastic part surface. The same principle considerations apply as for migrating slip additives (see Fig. 4-6). However, it has to be mentioned that the molecule's orientation is inversed relative to migrating slip additives, meaning that the polar part of the antistat sticks out. It is moisture attracted by the polar functionalities that leads to the build up of a very fine water layer on the plastic part surface, which is capable of dissipating electrostatic charges. In the following, the focus will be only on internal antistats.

Requirement

The same requirements as for migrating slip additives apply. Based on the mechanism for static dissipation, typical antistats only function at a high enough relative humidity. For low humidity applications, special chemistries need to be applied.

Chemistry

Internal antistats can be divided into chemical families of which only two are of importance for the scope of this section [13]:

- non-ionic
- cationic
- anionic
- amphoteric.

The subclass of non-ionic antistats can further be subdivided into:

- fatty acid ester
- ethoxylated alkylamine
- diethanolamine
- others.

Fatty acid esters migrate quickly (in their major application area polyolefins) and are also quickly depleted. Ethoxylated alkylamines migrate slower and the effect remains longer. For optimum performance, mixtures are employed.

Influencing the antistatic effect

A concentration increase will (initially) increase the antistatic effect. However, certain fatty acid esters do not follow the previously described saturation curve behavior. In those cases, the effect declines beyond an optimum concentration. The antistatic properties will additionally be improved by:

- higher relative humidity
- use of more fatty acid ester versus ethoxylated alkylamine in blends (initial effect).

The antistatic properties can be negatively affected by interactions. Interactions related to antistats can occur through:

- lower relative humidity
- incorporation of filler (lower migration speed)
- recrystallization of (surface of) organic substrate
- volatility
- migration inside the plastic part
- increased surface orientation.

Incorporation

Antistats are mainly incorporated during the compounding step (addition points (G) and/or (H) in Fig. 4-1). However, as the chemicals are mainly low melting or liquid, antistats are often added separate from solid additives (e.g. antioxidants, UV stabilizers, etc.).

Table 4-19 Additives discussed in Chapter 3

Additive code	Chemical name	Commercial name	Supplier
AO-1	Tetrakis (methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)methane	Irganox 1010 Songnox 1010	Ciba Songwon
AO-2	Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	Irganox 1076 Songnox 1076	Ciba Songwon
AO-3	Tris (3,5-di-tert-butyl-4-hydroxybenzyl)iso- cyanurate	Irganox 3114 Songnox 3114	Ciba Songwon
AO-4	1, 3, 5-Trimethyl-2,4,6-tris (3,5-di-tert-butyl-4- hydroxybenzyl) benzene	Ethanox 330	Albemarle
AO-8	Tri(butylcresyl) butane	Topanol CA	Vertellus
AO-21	N,N’-Hexamethylenebis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide)	Irganox 1098 Songnox 1098	Ciba Songwon
AO-37	4-Ethyl-2,6-di-tert-butylphenol	BHEB	Chevron Phillips chemical Nanging Datang chemical Clariant
HYA-1	N,N-distearylhydroxylamine	Irgastab FS 042	Ciba
P-1	Tris(2,4-di-tert-butylphenyl) phosphite	Irgafos 168 Songnox 1680	Ciba Songwon
P-2	Trisnoylphenyl phosphite	Weston 399	Chemtura
P-3	Bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite	Ultranox 626 Songnox 6260	Chemtura Songwon
P-7	Distearyl pentaerythritol diphosphite	Weston 618 Songnox 6180	Chemtura Songwon
P-10	Triphenylphosphate	TPF	Bayer
P-11	Trimethylphenylphosphate		
DOP	Di (2-ethylhexyl-)phthalate	DEHP	BASF, LG chem.
DINP	Di (isononyl-)phthalate	DINP	BASF, LG chem.
DINA	Di (isononyl-)adipate	DINA	BASF
DOA	Di (2-ethylhexyl-)adipate	DEHA	BASF, Songwon
BZ	Barium/zinc mixed metal stabilizer system		Songwon
ESBO	Ethoxidzed soybean oil	ESBO/ESO	Chemtura Arkema
HAS-3	Poly[(6-[(1,1,3,3-tetramethyl butyl)amino]-s-triazine-2,4-dinyl][(2,2,6,6-tetramethyl-4-piperidyl) imino] hexamethylene [2,2,6,6-tetramethyl-4-piperidyl] iminol]	Chimassorb 944 Songlight 9440	Ciba Songwon
HAS-5	Polymer of dimethyl succinate and 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol	Tinuvin 622 Songlight 6220	Ciba Songwon
HAS-7	Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate	Tinuvin 770 Songlight 7700	Ciba Songwon
HB-1	Hexadecyl-3,5-di-tert-butyl-4-hydroxybenzoate	Cyasorb UV 2908 Songsorb 2908	Cytec Songwon

(*Continued*)

Table 4-19 Additives discussed in Chapter 3—*cont'd*

Additive code	Chemical name	Commercial name	Supplier
HBP-1	2-Hydroxy-4-n-octoxybenzophenone	Cyasorb UV 531 Chimassorb 81	Cytec Ciba
HBZ-5	2-(2'-Hydroxy-5'-methylphenyl) benzotriazole	Tinuvin P Songsorb 1000	Ciba Songwon
HBZ-7	2-[2'-Hydroxy-3',5'-di(1,1-dimethylbenzyl) phenyl]-2H-benzotriazole	Tinuvin 234 Songsorb 2340	Ciba Songwon
FWA-1	2,5-thiophenediylbis(5-tert-butyl-1, 3-benz- oxazole)	Uvtex OB	Ciba

Others

Various other additives, like nucleating agents, oxygen scavengers and fillers can be used in multilayer packaging film.

Neutralizers and acid scavengers will not be covered systematically in this section. However, it should be mentioned that polyolefins synthesized with Ziegler–Natta catalysts need acid scavengers due to acidic residues. In general, metal soaps (mainly calcium stearate) are preferred for cost reasons. For metallizable and printed film, metal soaps interfere antagonistically with the surface treatment and are therefore substituted by hydrotalcite. Hydrotalcite, being a superior acid scavenger, is used at lower load levels than metal soaps.

Lubricants will also not be covered systematically. However, their importance for the processing and/or conversion of PVC and PA should be mentioned.

Adhesive compounds are not classified as additives and should be considered separately.

Suppliers and contacts

Several additives mentioned in this chapter are described with additive codes. Table 4-19 gives their chemical name, commercial name and a selection of suppliers.

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Appendix 4.1

Table A4.1-1 Incorporation of additives into various layers of multilayer film constructs

	Generic film construct		
	Skin layer (I)	**Core layer (II)**	**Skin layer (III)**
Antioxidants and heat stabilizers	●	●	●
UV-stabilizers			
UV absorber	●	○	○
HA(L)S	●	○	○
Optical brighteners	●		
Slip additive			
Migrating	●	○	●
Non-migrating	●		●
Antiblock additives	●		●
Antistats	●		●
Neutralizers	●	●	●
Others	○	○	○

Definitions see Fig. 4-2. HA(L)S: hindered amine (light) stabilizers. ● Filled circles indicate a recommended use or application; ○ open circles indicate limited, partial or conditional use

Appendix 4.2

Table A4.2-1 Addition points of additives for polyolefins

	Addition point										
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**K**	**Other**
Phenolic antioxidant							●		●	○	
Phosphite							●		●	○	
UV absorber							●		●	○	
HA(L)S							●		●	○	
Optical brightener							●				
Slip additive							●		●		
Antiblock additive							●		●		
Antistats							●	●			
Neutralizers							●				

Addition points refer to Fig. 4-1. (HA(L)S): hindered amine (light) stabilizers; ● Filled circles indicate a recommended use or application: ○ open circles indicate limited, partial or conditional use

Table A4.2-2 Addition points of additives for polyester

	Addition point										
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**K**	**Other**
Anti-hydrolysis agent							●	○			
Complexing agent		●		○							
Phenolic antioxidant							●				
Phosphite							●				
UV absorber							●		●	○	
Optical brightener	○						●				
Slip additive		●									
Antiblock additive	●										
Antistat							●				

Addition points refer to Fig. 4-1. ● Filled circles indicate a recommended use or application: ○ open circles indicate limited, partial or conditional use

Table A4.2-3 Addition points of additives for polyvinylchloride

	Addition point										
	A	B	C	D	E	F	G	H	I	K	Other
Heat stabilizer							●	●			
Co-stabilizer							●	●			
UV absorber							●		●	○	
HA(L)S							●		●	○	
Optical brightener							●	●			
Slip additive							●		●		
Antiblock additive							●		●		
Antistat							●				
Lubricant							●	●			

Addition points refer to Fig. 4-1. (HA(L)S): hindered amine (light) stabilizers; ● Filled circles indicate a recommended use or application: ○ open circles indicate limited, partial or conditional use

Table A4.2-4 Addition points of additives for polyamide

	Addition point										
	A	B	C	D	E	F	G	H	I	K	Other
Phosphite								●		○	
Phenolic antioxidant		●						●		○	
UV absorber							●		●	○	
HA(L)S							●		●	○	
Optical brightener							●				
Slip additive							●		●		
Antiblock additive							●		●		
Lubricant		●						●	○	○	

Addition points refer to Fig. 4-1. (HA(L)S): hindered amine (light) stabilizers; ● Filled circles indicate a recommended use or application: ○ open circles indicate limited, partial or conditional use

Chapter 5

Rheology of molten polymers

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Introduction

The term 'rheology' was coined by E.C. Bingham in 1929, from the Greek verb *rheo* (= flow) and was defined as the study of deformation and flow of matter. The Society of Rheology was formed in 1929 by Bingham and other prominent scientists and engineers from both Europe and the USA, with its motto '*panta rei*' (all things flow, Heracleitus 6th century BC). The birth of rheology as a separate branch of engineering science coincides with the time when the flow behavior of materials like rubber, plastics, paints, clays, human blood and other biological fluids started to attract considerable attention.

A central concept in rheology is that force applied to materials results in deformations for solids or flow for fluids. The relative deformation is called *strain* and the applied force per unit area is called *stress*. The main objective of rheology is measurement, examination and development of relations between stresses and the corresponding strains and the change of strains per unit time (strain rates). Such knowledge is absolutely necessary for problem solving in polymer processing.

Although all materials are composed of molecules, in rheology, we rely heavily on the *continuum hypothesis*, according to which, a material, solid or fluid is considered as an infinitely divisible substance. For molten polymers, we first try to measure the flow properties making use of the continuum concept and, subsequently, we try to find relations between the flow properties and the molecular structure.

In the study of flow, we assume that a fluid adjacent to a solid surface cannot slip relative to the surface. In other words, all fluids at a point of contact with a solid take on the velocity of the solid surface ($V_{fluid} = V_{wall}$). This assumption is one of the cornerstones of fluid mechanics and has been shown to apply for air and water over a very wide range of flow conditions. We will see later on in this chapter under what conditions molten polymers can actually slip on the solid walls of process equipment.

The flow properties of polymers depend on their molecular weight and molecular architecture. In subsequent sections, reference will be made to *linear polymers* (with monomeric units linked linearly, like high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS)) and *branched polymers* (with side chains attached to the backbone chain like low density polyethylene (LDPE)). Since the polymer chains in a given polymer sample are not of the same molecular weight or same length, we define average molecular weights. The *number average molecular weight*, M_n, is the sum of the individual molecular weights divided by their number. The *weight average molecular weight*, M_w, is the sum of the squares of the weights divided by the sum of the molecular weights. Because of the squares involved in the calculation of M_w, its value is shifted towards the higher molecular weights. The *polydispersity index* (PDI) M_w/M_n (weight average/number average) would be 1.0 if all chains had exactly the same length (only theoretically possible). Usual grades of polymers have PDI values from 1.5 to 30.

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With the advent of metallocene catalysts, it is possible to make controlled molecular weight and molecular architecture polyolefins. Generally, metallocene catalyzed polyolefins have more narrow molecular weight distributions (lower PDI values) than those catalyzed with Ziegler–Natta catalysts. It will be shown later on in this chapter how rheological properties relate to average molecular weight and molecular weight distributions.

Viscosity and melt flow index

Viscosity is the most important flow property [1]. It represents the resistance to flow. Strictly speaking, it is the resistance to shearing, i.e. flow of imaginary fluid slices like the motion of a deck of cards. Referring to Fig. 5-1, we can define viscosity as the ratio of the imposed *shear stress* (force F, applied tangentially, divided by the area A) and the shear rate (velocity U, divided by the gap h)

$$\eta = \frac{\text{SHEAR STRESS}}{\text{SHEAR RATE}} = \frac{F/A}{U/h} = \frac{\tau}{\dot{\gamma}}$$

The Greek letters τ (tau) and $\dot{\gamma}$ (gamma dot) are conventionally used to designate the shear stress and shear rate, respectively.

This relation is known as *Newton's law of viscosity.* When the viscosity is independent of the shear rate, a fluid is called Newtonian. Small molecule fluids like air, water, mercury and glycerin are Newtonian. Molten polymers, polymer solutions and other complex fluids have viscosities dependent on shear rate and are called non-Newtonian.

The viscosity in SI is reported in units of Pa·s (Pascal·second). Before the introduction of SI, poise was the most frequently used unit (1 Pa·s = 10 poise). Here are some other useful conversion factors:

$$\begin{aligned} 1\ \text{Pa}\bullet\text{s} &= 1.45 \times 10^{-4}\ \text{lb}_\text{f}\text{s/in}^2 \\ &= 0.67197\ \text{lb}_\text{m}\text{/s ft} = 2.0886 \times 10^{-2}\ \text{lb}_\text{f}\text{s/ft}^2 \end{aligned}$$

The viscosity of water is 10^{-3} Pa·s, while the viscosity of most polymer melts during their processing may vary from 10^2 Pa·s to 10^5 Pa·s. The shear stress is measured in units of Pa = (N/m^2) or psi (pounds (lb$_\text{f}$) per square inch) and the shear rate in reciprocal seconds (s^{-1}).

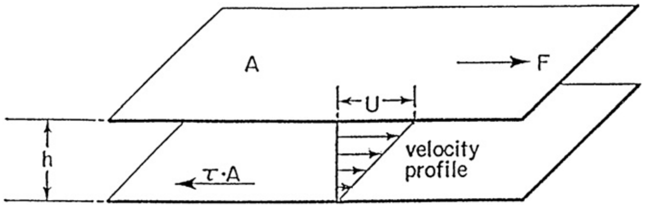

Fig. 5-1 Simple shear flow.

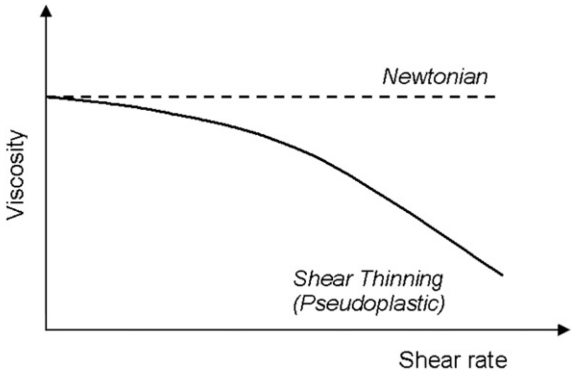

Fig. 5-2 Newtonian and shear-thinning viscosity behavior.

One remarkable property of polymeric liquids is their *shear-thinning* behavior (also known as pseudo-plastic behavior). If we increase the shear rate (i.e. extrude faster through a die), the viscosity decreases (Fig. 5-2). This reduction of viscosity is due to molecular alignments and disentanglements of the long polymer chains. It has been said: 'polymers love shear'. The higher the shear rate, the easier it is for polymers to flow through dies and process equipment.

The most frequently used model to express the shear-thinning behavior of polymers is the power law:

$$\eta = m\dot{\gamma}^{n-1}$$

This expression is a straight line when plotted on double logarithmic coordinates as shown in Fig. 5-3. The value of the consistency index m can be obtained

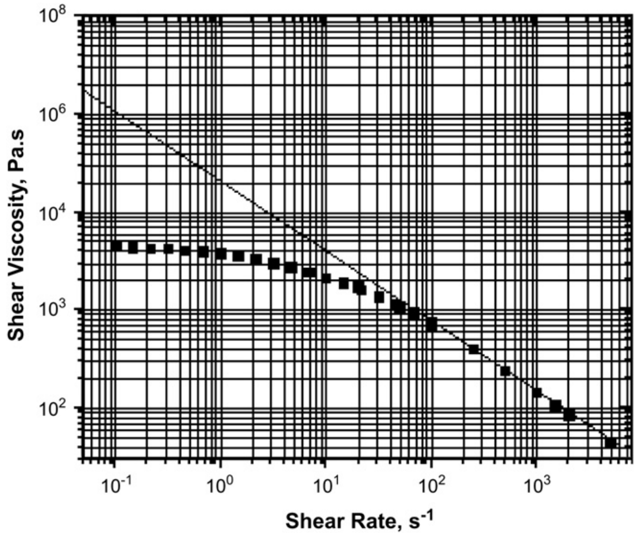

Fig. 5-3 Double logarithmic plot of shear viscosity versus shear rate. The straight line is the power law fit which fails at low shear rates. For this graph the coefficients for the straight line are: m ≈20 000 Pa·s^n; n ≈ 0.3.

from the intercept at $\dot{\gamma}=1$. The exponent $n-1$ is the slope, because

$$\log \eta = \log m + (n-1) \log\dot{\gamma}$$

For $n=1$, the power-law model reduces to Newton's law (constant viscosity). As n decreases, the polymer becomes more shear thinning.

The power-law exponent varies between 0.8 (for polycarbonate (PC)) and 0.2 (for rubber compounds). For various polyethylene (PE) grades, the range is $0.3<n<0.6$ and depends on molecular weight and chain branching. The consistency m for molten polymers varies between 1000 $\text{Pa}\cdot\text{s}^n$ (for some polyethylene terephthalate (PET) resins) to 100 000 $\text{Pa}\cdot\text{s}^n$ for highly viscous rigid polyvinylchloride (PVC). The value depends on chain mobility and molecular weight and varies exponentially with temperature.

During single-screw extrusion, shear rates may reach 200 s^{-1} in the screw channel near the barrel wall and much higher between the flight tips and the barrel. At the die lip or exit, the shear rate can be as high as 1000 s^{-1}. During cavity filling in injection molding, shear rates can reach 10 000 s^{-1}. Low shear rate on a die wall implies slow polymer melt movement over the metal surface. Some die designers try to design dies for cast film or blown film operations not having wall shear rates less than, say 10 s^{-1}, to prevent the molten material from hanging up. When the wall shear stress exceeds 0.14 MPa, sharkskin (i.e. surface mattness) occurs in capillary viscometer measurements using various HDPE grades. At very high shear rates, a flow instability known as melt fracture occurs [2,3].

Melt index (MI), melt flow index (MFI) or melt flow rate (MFR) (for polypropylene) refers to the grams per 10 minutes pushed out of a die of prescribed dimensions according to an ASTM Standard [4] under the action of a specified load (Fig. 5-4). For PE (ASTM D-1238), the load is 2.16 kg and the die dimensions are D = 2.095 mm and L = 8 mm. The experiment is carried out at 190°C. For PP, the same load and die dimensions are used, but the experiment is carried out at 230°C.

When measuring the melt index with a 2.16 kg load, the wall shear stress can be calculated to be $\tau_w = 1.94 \times 10^4$ Pa (2.814 psi) and the wall shear rate approximately $\dot{\gamma} = (1838/\rho) \times \text{MI}$ where ρ is the melt density in kg/m^3. Assuming $\rho = 766\ \text{kg/m}^3$ for a typical PE melt, we get $\dot{\gamma} = 2.4 \times \text{MI}$. Low melt index means a high molecular weight, highly viscous polymer. A high melt index means low molecular weight, low viscosity polymer. When the melt index is less than 1, the material is said to have a fractional melt index. Such materials are used for film extrusion. For some film grades, MI can be less than 0.1. Most extrusion PE grades seldom exceed MI = 12, however, for injection molding, MI is usually in the range of 5–50.

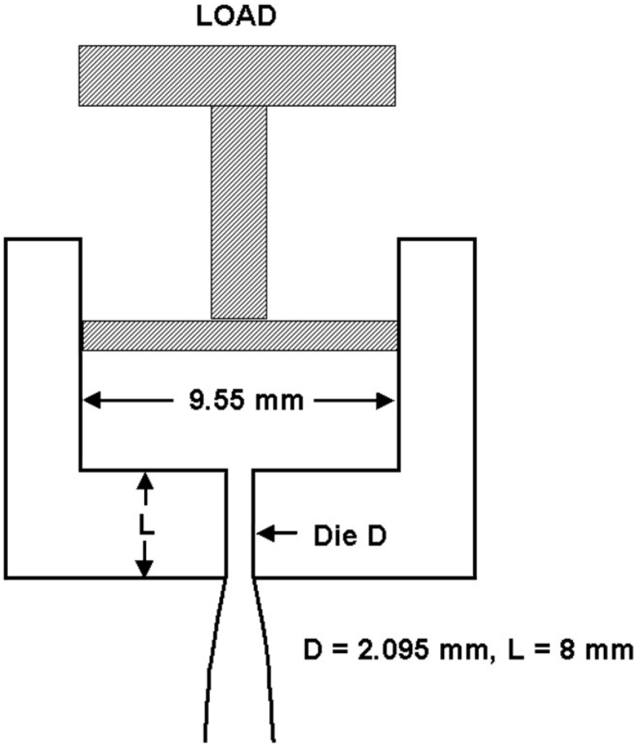

Fig. 5-4 Schematic of a melt indexer.

An approximate calculation of both m and n can be carried out by using two melt index values (MI and HLMI). MI refers to standard 2.16 kg weight and HLMI to high load melt index (frequently 21.6 kg or 10 kg). By manipulating the appropriate equations for pressure drop, shear stress and flow rate [1], we have:

$$\text{Power} - \text{law exponent}\ \ n = \frac{\log(\text{HL}) - \log(\text{LL})}{\log(\text{HLMI}) - \log(\text{MI})}$$

$$\text{Consistency}\ m = \frac{8982 \times (\text{LL})}{\left[\frac{1838}{\rho} \times \text{MI}\right]^{n}}$$

where:

LL	=	low load (usually 2.16 kg);
HL	=	high load (usually 21.6 kg or 10 kg);
ρ (kg/m^3)	=	the melt density at the test temperature;
n	=	dimensionless exponent;
m	=	parameter with dimensions of Pa s^n.

Intrinsic viscosity, frequently designated as IV, is a relative number that measures the average molecular weight through the Mark-Houwink equation:

$$[\eta] = K M_v^a$$

where:

M_v	=	the (viscosity) average molecular weight;
K	=	constant depending on the polymer solvent system;
a	=	constant depending on the polymer solvent system.

For example, for PET, IV is determined by dissolving PET at less than 1% in a solvent and measuring the time required for a certain volume of the solution to flow through a capillary. By extrapolating to 0% concentration, the intrinsic viscosity is obtained. The intrinsic viscosity has the dimensions of inverse concentration. The American units are 100 cm^3/g and the European units are cm^3/g, usually expressed as dl/g or ml/g. The IV for bottle grade PET resins is usually between 0.70 and 0.85 dl/g. This number is of relative importance. High IV means higher average molecular weight and higher melt viscosity.

Polyvinyl chloride polymers are often graded according to their K-value, which is a measure of their molecular weight. It is obtained from intrinsic viscosity measurements in cyclohexanone solution. K-values vary between 35 and 80. Low K-values imply low molecular weight (which is easy to process, but has inferior properties) and high K-values imply high molecular weight which is difficult to process and has outstanding properties.

Mathematical relations

For unidirectional flows, the shear rate is simply the derivative of velocity (V_x) with respect to distance y, perpendicular to the flow direction

$$\dot{\gamma} = \frac{dV_x}{dy}$$

For the drag flow shown in Fig. 5-1, the velocity profile is linear (due to the no-slip assumption at top and bottom plates)

$$V_x = \frac{U}{h} y$$

and the shear rate

$$\dot{\gamma} = \frac{dV_x}{dy} = \frac{U}{h}$$

For pressure driven axial flow (z direction) of a Newtonian fluid in a tube of radius R, the velocity profile is parabolic

$$V_z = V_{max}\left(1 - \frac{r^2}{R^2}\right)$$

and the absolute value of shear rate

$$\dot{\gamma} = \left|\frac{dV_z}{dr}\right| = \frac{2r}{R^2} V_{max}$$

varies between zero at the axis of symmetry ($r = 0$) to a maximum value at the wall $r = R$

$$\dot{\gamma}_w = \frac{2}{R} V_{max}$$

The relation between maximum and average velocity in tube flow is

$$V_{max} = 2V_{avg}$$

therefore

$$\dot{\gamma}_w = \frac{4}{R} V_{avg}$$

and since the volume flow rate Q is related to the average velocity by

$$Q = V_{avg}\pi R^2$$

we may write

$$\dot{\gamma}_w = \frac{4Q}{\pi R^3}$$

Although this relation is strictly valid for Newtonian fluids, it is also used for non-Newtonian fluids and it is referred to as the *apparent shear rate*.

A correction is necessary (Rabinowitsch correction) for shear thinning fluids. For the power-law model, the true (Rabinowitsch corrected) shear rate becomes

$$\dot{\gamma}_w = \frac{3n+1}{4n} \frac{4Q}{\pi R^3}$$

This means that for a material with power-law index $n = 0.4$ (very common), the relation between apparent and true shear rate is

$$\dot{\gamma}_{true} = 1.375 \times \dot{\gamma}_{apparent}$$

Capillary dies with a 1–2 mm diameter are usually used to measure viscosity. The shear stress is determined from the pressure drop by the equation

$$\tau = \frac{\Delta P}{2L} r$$

which varies linearly from zero on the capillary axis ($r = 0$) to a maximum value at the wall ($r = R$)

$$\tau_w = \frac{\Delta P}{2L} R$$

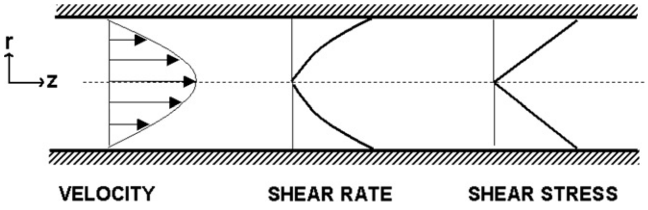

Fig. 5-5 Velocity, shear rate and shear stress profiles for pressure driven flow through a tube of radius R.

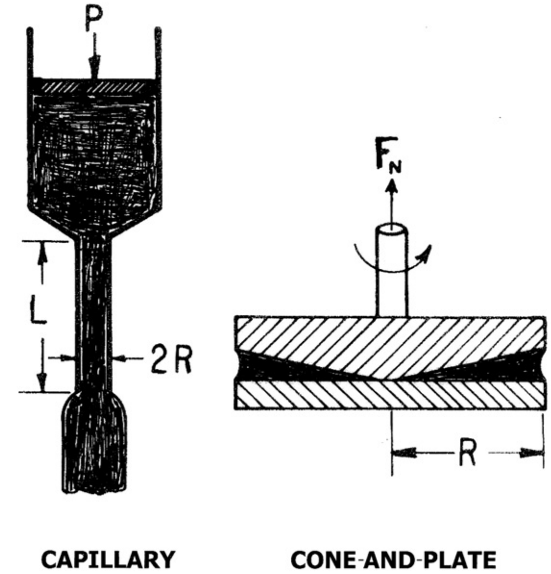

Fig. 5-6 Schematic representation of a capillary and a cone-and-plate viscometer.

The ratio of the measured wall shear stress and the corresponding wall shear rate gives the viscosity

$$\eta = \frac{\tau_w}{\gamma_w}$$

Fig. 5-5 shows schematically the variation of velocity, shear rate and shear stress for polymer melt flow in a tube. It should be noted that the shear stress is linear while the velocity profile is quasi-parabolic.

$$V_z = V_{max}\left[1 - \left(\frac{r}{R}\right)^{\frac{n+1}{n}}\right]$$

The pressure drop ΔP is measured in the reservoir (see Fig. 5-6) and at the entrance to the capillary there is an excess pressure drop ΔP_e. The easiest way to determine the excess pressure drop ΔP_e is to carry out the experiment using a twin bore viscometer having two capillaries. One of them has very short length ($L = 0$) and the pressure drop recorded is essentially the excess pressure due to the entrance (orifice). This correction is necessary when capillaries are relatively short ($L/R<50$) and is known as the Bagley correction [2,3]. The Bagley correction is usually expressed as

$$n_B = \frac{\Delta P_e}{2\tau_w}$$

The Bagley correction (n_B) may reach perhaps 20 when polymeric materials are extruded near the critical stress for sharkskin. For a Newtonian fluid the value for n_B is 0.587.

The Bagley corrected shear stress becomes:

$$\tau_w = \frac{\Delta P_{cap} + \Delta P_c}{2\left(\frac{L}{R} + n_B\right)}$$

To apply the Bagley correction, measurements with at least two capillaries are needed.

The Bagley entrance correction can be relatively large when one compares it to the pressure drop in the capillary

$$\Delta P_{cap} = 2\frac{L}{R}\tau_w$$

For a standard capillary of $L/R = 32$, we have $\Delta P_{cap} = 64\ \tau_w$. If we assume some sort of 'average' value $n_B = 10$ then $\Delta P_e = 20\ \tau_w$ or approximately 30% of the pressure drop in the capillary. Obviously, for shorter dies, the entrance pressure drop accounts for a large portion of the total pressure drop recorded from the reservoir to the exit of the capillary.

Without the Rabinowitsch and Bagley corrections there can be significant errors in viscosity data obtained from capillary instruments.

The power-law model discussed in the previous section is good for fitting the viscosity data at the high shear region (usually from 10 to 2000 s^{-1}). At the low shear region, there is a Newtonian (horizontal) plateau, as shown by the data points in Fig. 5-3.

Two other models are frequently used for better fitting of data over the entire shear rate range:

Carreau-Yasuda

$$\eta = \eta_o\left(1 + (\lambda\dot{\gamma})^a\right)^{\frac{n-1}{a}}$$

where η_o is the viscosity at zero shear and λ, a and n are fitted parameters;

Cross model

$$\eta = \frac{\eta_o}{1 + (\lambda\dot{\gamma})^{1-n}}$$

where η_o is the zero shear viscosity and λ and n are fitted parameters. Note that, in this model, when $\lambda = \frac{1}{\dot{\gamma}}$, $\eta = \frac{\eta_o}{2}$.

With rotational viscometers (cone-and-plate or parallel plate), the shear stress is determined from the applied torque and the shear rate from the rotational speed and the gap where the fluid is sheared.

For the cone-and-plate instrument of Fig. 5-6, the shear rate is given by

$$\dot{\gamma} = \frac{\omega}{\alpha}$$

and the shear stress by

$$\tau = \frac{3M}{2\pi R^3}$$

where

ω	=	rate of rotation;
α	=	cone angle (usually less than 5°);
M	=	torque;
R	=	radius.

Capillary viscometers are usually used for the shear rate range from 1 s^{-1} to 3000 s^{-1}. Rotational viscometers are usually used for the range 10^{-2} to 5 s^{-1}. At higher rotational speeds, secondary flows and instabilities may occur which invalidate the simple shear assumption. Simple shear means the slice-by-slice relative motion in a fluid as if it were composed of imaginary fluid slices, like a deck of cards. For more information about viscosity measurements, the reader is referred to Macosko [2].

The viscosity of polymer melts varies with temperature in an exponential manner

$$\eta = \eta_{ref} \exp(-b\,\Delta\,T)$$

The temperature sensitivity coefficient b is usually between 0.01 and 0.1°C. For common polyolefin grades, we may assume that b=0.015. This means that for a temperature increase ΔT=10°C (18°F), the viscosity decreases by 14%. For HDPE (linear polymer) the value of b is 0.01, while for LDPE $b = 0.03$.

The effects of factors such as shear rate, molecular weight distribution, pressure, filler, temperature and additives on viscosity are summarized in Fig. 5-7 following Cogswell [3]. Linear narrow molecular weight distribution polymers (metallocene catalyzed) are more viscous than their broad distribution counterparts. Fillers may increase viscosity (greatly). Pressure increases viscosity (negligible under usual extrusion conditions but important in injection molding). Various additives are available and are designed to decrease viscosity. The zero shear viscosity increases dramatically with the weight average molecular weight:

$$\eta_o = \text{const}M_w^{3.4}$$

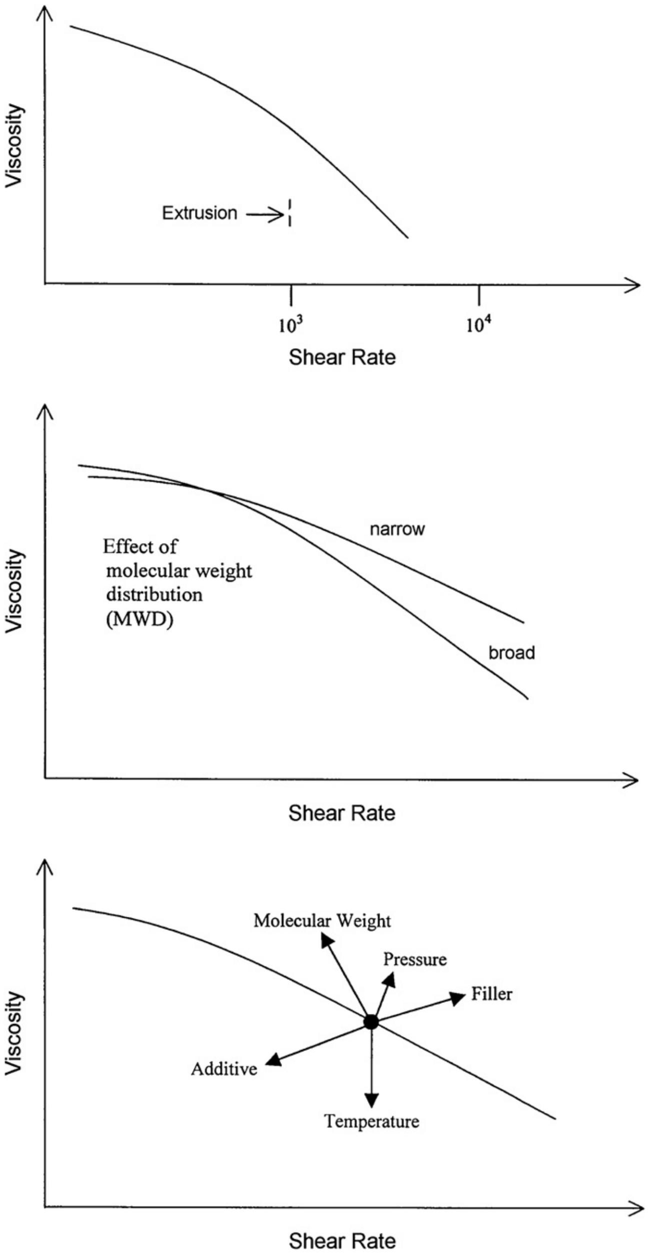

Fig. 5-7 The influence of various parameters on polymer viscosity.

For some metallocene catalyzed PEs with long chain branching, the exponent might be much higher (perhaps 6.0).

In the above discussion of viscosity measurements, the assumption is made that the no-slip condition on the die wall is valid. This is, however, not always the case. In fact, at shear stress levels of about 0.1 MPa for PE, slip occurs. Wall slip is related to the sharkskin phenomenon [5]. Wall slip is measured by the Mooney method [5,6] in which the apparent shear rate ($4Q/\pi R^3$) is plotted against 1/R for several capillaries having different radii. In the absence of slip, the plot is horizontal. The slope of the line is equal to 4 × (slip velocity), as explained by Dealy and Wissbrun [6].

Extensional viscosity and melt strength

Extensional (or elongational) viscosity is the resistance of a fluid to extension [2]. While stretching a low viscosity fluid like water is difficult to imagine, polymer melts exhibit measurable resistance. In fact, about 100 years ago, Trouton measured the stretching and shearing resistance of stiff liquids, including pitch, and found that the extensional to shear viscosity ratio is equal to 3.

$$\frac{\eta_e}{\eta} = 3$$

This relation, known as the Trouton ratio, is valid for all Newtonian fluids and has a rigorous theoretical basis that confirms Trouton's experiments.

Measuring elongational viscosity is considerably more difficult than measuring shear viscosity. One device used involves capillary extrusion and subsequent stretching with a pair of rollers. The maximum force required to break the extruded strand is referred to as *melt strength*. In practice, the terms extensional viscosity and melt strength are sometimes confused. Fig. 5-8 compares extensional viscosity as a function of stretch rate ($\dot{\varepsilon}$) and compares it to the shear viscosity as a function of shear rate ($\dot{\gamma}$). Melt strength is an engineering measure of resistance to extension. Several extrusion processes involve extension, such as film blowing, melt spinning and sheet or film drawing. The stretch rates in film blowing can exceed $10\,\mathrm{s}^{-1}$, while in entry flows from a large reservoir into a smaller diameter capillary, the maximum stretch rate is likely to be one order of magnitude lower than the maximum wall shear rate (e.g. in capillary viscometer, when $\dot{\varepsilon}_{\max}$ about $100\,\mathrm{s}^{-1}$, $\dot{\gamma}_{\max}$ is about $1000\,\mathrm{s}^{-1}$). Frequently, the extensional viscosity is plotted as a function of stretching time (increasing) without reaching a steady value (strain hardening).

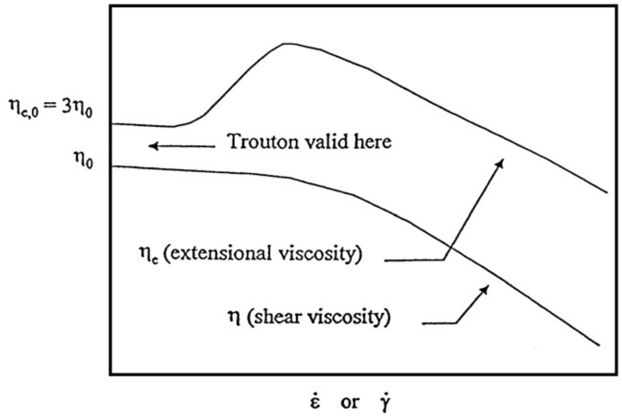

Fig. 5-8 Extensional and shear viscosity as a function of stretch and shear rate, respectively.

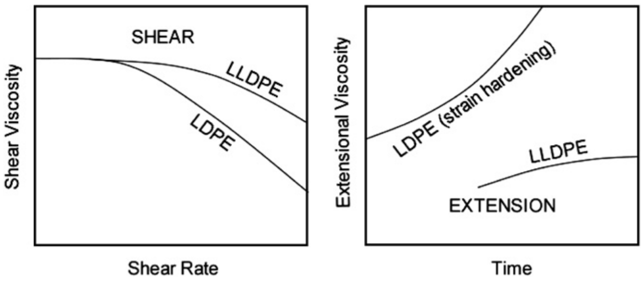

Fig. 5-9 Schematic representation of LDPE and LLDPE behavior in shear and extension.

The excess pressure drop encountered in flow from a large reservoir to a smaller diameter capillary is due to elongational viscosity. In fact, Cogswell [3] has developed a method for measurement of elongational viscosity η_e from excess pressure drop ΔP_e (i.e. the Bagley correction):

$$\eta_e = \frac{9(n+1)^2(\Delta P_e)^2}{32\eta\dot{\gamma}^2}$$

$$\text{at } \dot{\varepsilon} = \frac{4\eta\dot{\gamma}^2}{3(n+1)\Delta P_e}$$

Shear and extensional viscosity measurements reveal that linear low density polyethylene (LLDPE) is 'stiffer' than LDPE (branched) in shear, but 'softer' in extension. In extension, the linear LLDPE chains slide by without getting entangled. However, the long branches of the LDPE chains result in significantly larger resistance in extension. In the film blowing process, LDPE bubbles exhibit more stability because of their high extensional viscosity. Typical LDPE and LLDPE behavior in shear and extension is shown in Fig. 5-9. LDPE is often blended with LLDPE to improve the melt strength and consequently bubble stability in film blowing. Most PP grades are known to exhibit very low melt strength. However, recent advances in polymer chemistry have led to the production of some high melt-strength PP grades (with long chain branching).

Normal stress differences and extrudate swell

Stress is defined as force divided by the area on which it acts. It has units of $\mathrm{lb_f/in^2}$ (psi) in the British system or $\mathrm{N/m^2}$ (Pascal, Pa) in SI. When a force is acting tangentially on a surface, the corresponding stress is referred to as *shear stress*. When a force is perpendicular (normal) to a surface, it is termed *normal stress*. Pressure is a normal stress. When a fluid flows through a conduit, it is acted upon by the normal (pressure) forces and it exerts both normal and shear (stress) forces on the conduit walls. For flow through a planar die, the shear stress is zero at the midplane and maximum at the wall, while the corresponding velocity profile is quasi-parabolic.

Weissenberg discovered in the 1940s that polymer solutions and melts, when subjected to shearing, tend to develop normal stresses that are unequal in the x (direction of flow), y and z (normal directions) which are added to or subtracted from the local pressure. But, why are these elusive forces generated? They are generated because a polymer's long molecular chains exhibit anisotropic or non-uniform properties when they flow. Any further explanation of the physical origin of normal stresses is likely to be controversial. Here is perhaps an oversimplification: shearing means motion of a fluid in a slice-by-slice manner. If the imaginary slices were made of an extensible elastic material (like slices of rubber), shearing would also result in extension in the flow direction and uneven compression in the other two directions. So, when an (elastic) polymer solution or melt flows along a pressure gradient, it is less compressed in the direction of flow than in the other two normal directions.

The so-called First Normal Stress Difference N_1 is defined as the total normal stress in the direction of the flow (σ_{xx}) minus the perpendicular (σ_{yy}) stress.

$$\begin{aligned} N_1 &= \sigma_{xx} - \sigma_{yy} = (-P + \tau_{xx}) - (-P + \tau_{yy}) \\ &= \tau_{xx} - \tau_{yy} \end{aligned}$$

The Second Normal Stress Difference is

$$\begin{aligned} N_2 &= \sigma_{yy} - \sigma_{zz} = (-P + \tau_{yy}) - (-P + \tau_{zz}) \\ &= \tau_{yy} - \tau_{zz} \end{aligned}$$

We use normal stress differences rather than just normal stresses to remove the value of the pressure. Experiments show that N_1 is positive for usual polymers (i.e. extensive, while the compressive pressure forces are negative). N_2 is negative and of the order of 20% of N_1 for most common polymers. N_1 is very sensitive to the high molecular weight tail of a polymer. Broad molecular weight distribution polymers exhibit high N_1 values.

The normal stress differences can be very large in high shear-rate extrusion through lips of a die. Some authors suggest a variation for the normal stress difference at the wall in the form

$$N_{1w} = A\, \tau_w^b$$

The stress ratio

$$S_R = \frac{N_{1w}}{2\tau_w}$$

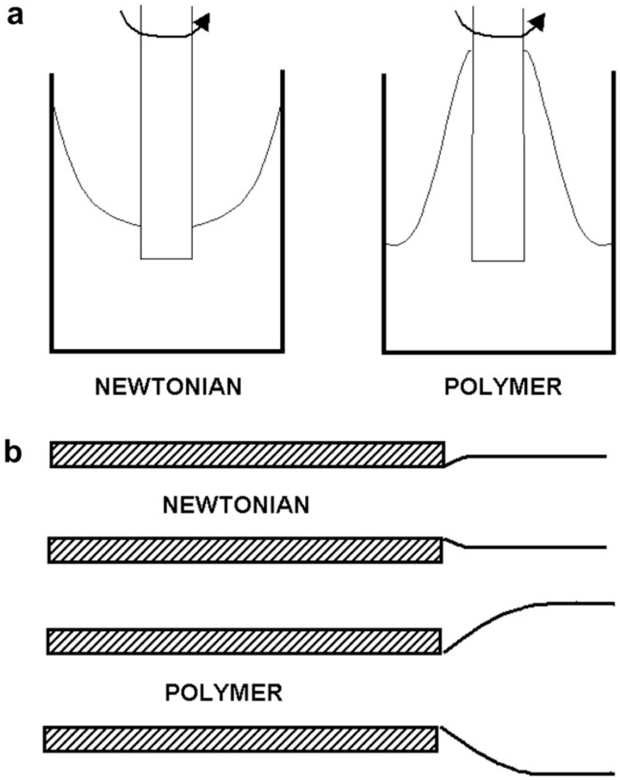

Fig. 5-10 (a) Rod climbing (Weissenberg) effect in polymeric fluids; (b) extrudate swell.

can reach a value of 10 or more at the onset of melt fracture.

The rod-climbing effect observed by Weissenberg (Fig. 5-10a) when a cylinder rotates in a polymeric liquid is due to some sort of 'strangulation' force exerted by the extended polymer chains, which results in an upward movement normal to the direction of rotation (normal stress difference). The extrudate swell phenomenon [7] (see Fig. 5-10b) is due mainly to the contraction of the exiting polymer that is under extension in the die due to N_1. The uneven compression in the various directions results in a number of unusual flow patterns and instabilities. The secondary flow patterns in square channels observed by Dooley and co-workers [8] are due to the second normal stress difference. Bird et al. [9] in their book state: 'A fluid that's macromolecular is really quite weird, in particular the big normal stresses the fluid possesses give rise to effects quite spectacular'.

In extrusion through dies, the extrudate diameter (d) is larger than the die diameter (D). Extrudate swell ratios (d/D) reach values of 400% or more, under certain conditions.

This phenomenon (also known as die swell) has been studied by several researchers. While the primary mechanism is release of normal stresses at the exit, other effects are also important. Extrudate swell is largest for zero length dies (i.e. orifices). It decreases for the same throughput with increasing die length due to fading memory as the residence time in the die increases. Even Newtonian fluids exhibit some swell upon exiting dies (13% for round extrudates, 19% for planar extrudates). This Newtonian swell is due to streamline rearrangement at the exit. The swell ratio can be influenced by thermal effects due to viscosity differences between the walls and die center. Maximum thermal swell can be obtained when a hot polymer flows through a die with colder walls. Swell ratio of about 5% on top of other mechanisms can be obtained from temperature differences. For linear polymers, the swell ratio increases as the molecular weight distribution broadens.

Several attempts have been made to predict extrudate swell through equations relating the swell ratio d/D (extrudate diameter/die diameter) to the first normal stress difference at the wall N_{1w}. Based on the theory of rubber elasticity, the following equation is obtained [7].

$$N_{1w} = 2\tau_w \left(3\left[\left(\frac{d}{D}\right)^4 + 2\left(\frac{d}{D}\right)^{-2} - 3\right]\right)^{1/2}$$

Based on stress release for a Maxwell fluid (described later in the chapter) exiting from a die, Tanner's equation can be derived [7]

$$N_{1w} = 2\sqrt{2}\tau_w \left[\left(\frac{d}{D} - 0.13\right)^6 - 1\right]^{1/2}$$

Although this equation has a more rigorous derivation and theoretical basis, the rubber elasticity theory is believed to give better predictions. Unambiguous evaluations are virtually impossible to carry out because there are no reliable methods for measuring N_{1w} at high shear rates and stresses. At low shear rates (up to perhaps $1\ s^{-1}$), the first normal stress difference can be determined by measuring the separation force that develops in a cone-and-plate instrument (see Fig. 5-6) due to the Weissenberg effect.

Stress relaxation and dynamic measurements

When flow stops, the stresses become immediately zero for small molecule Newtonian fluids like water or glycerin. For polymer melts, the stresses decay exponentially after flow stops. Stress relaxation can be measured in a parallel plate or a cone-and-plate rheometer by applying a given shear rate level (rotation speed/gap) and measuring the stress decay after the rotation is brought to an abrupt stop. Such tests, however, are not performed routinely, because of experimental limitations associated with abrupt stopping of strain and stress measurement decay over more than three decades with one transducer.

Dynamic measurements involve the response of a material to an imposed sinusoidal stress or strain on a parallel plate or cone-and-plate instrument. A perfectly elastic material that behaves like a steel spring, by imposition of extension (strain), would develop stresses that would be in-phase with the strain, because

$$\text{stress } (\tau) = \text{modulus } (G) \times \text{strain } (\gamma)$$

However, for a Newtonian fluid subjected to a sinusoidal strain, the stress and strain will not be in-phase because of the time derivative (strain rate) involved

$$\tau = \eta\dot{\gamma}$$

$$\tau = \eta\frac{d\gamma}{dt} = \eta\frac{d}{dt}(\gamma_o\, sin\omega t) = \eta\,\omega\,\gamma_o\, cos\,\omega\, t$$
$$= \eta\,\omega\,\gamma_o\, sin(\omega t + 90°)$$

where ω is frequency of oscillation. That is, a Newtonian fluid would exhibit 90° phase difference between stress and strain. Polymeric liquids that are partly viscous and partly elastic (viscoelastic) will be $0 \le \phi \le 90\,°$ out of phase.
We can define

$$G'(\omega) = \frac{\text{in-phase stress}}{\text{maximum strain}} \quad \begin{matrix}\text{storage}\\ \text{modulus}\\ \text{(elastic part)}\end{matrix}$$

$$G''(\omega) = \frac{\text{out-of-phase stress}}{\text{maximum strain}} \quad \begin{matrix}\text{loss}\\ \text{modulus}\\ \text{(viscous part)}\end{matrix}$$

where ω ranges usually from 0.01 to 10^3 rad/s. Larger G' implies more elasticity. Further, we can define

$$\eta' = \frac{G''}{\omega} \quad \text{the dynamic viscosity}$$

$$\eta'' = \frac{G'}{\omega}$$

and the magnitude of the complex viscosity

$$|\eta^*| = (\eta'^2 + \eta''^2)^{1/2}$$

An empirical relationship called the 'Cox-Merz rule' states that the shear rate dependence of the steady state viscosity η is equal to the frequency dependence of the complex viscosity η*, that is

$$\eta(\dot{\gamma}) = |\eta^*(\omega)|$$

The usefulness of this rule, which holds for most polymers, is that while steady measurements of shear viscosity

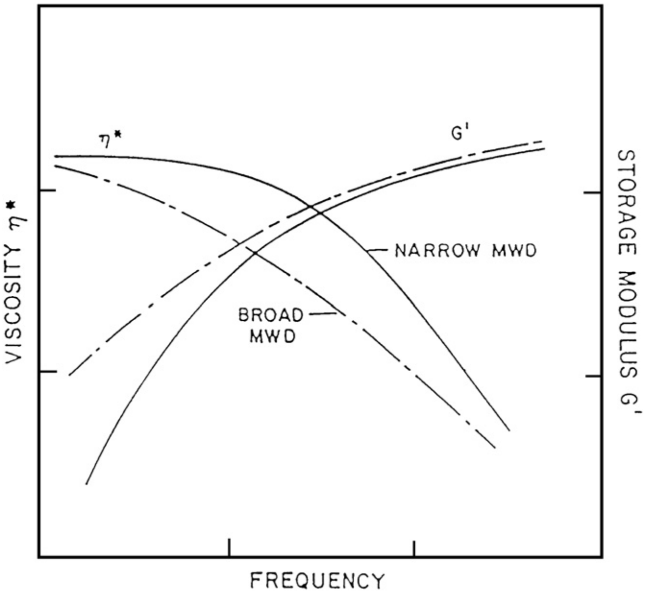

Fig. 5-11 Storage modulus G′ and dynamic viscosity η∗ behavior of broad and narrow molecular weight distribution polymers.

are virtually impossible above 5 s^{-1} with rotational instruments, the dynamic measurements can easily be carried out up to 500 rad/s (corresponds to $\dot{\gamma} = 500\,s^{-1}$) or even higher. Thus, the full range of viscosity needed in extrusion can be covered.

Some typical results involving narrow and broad molecular-weight-distribution samples are shown in Fig. 5-11. The relative behavior of G′ versus ω can be used to identify whether a sample is of narrow or broad molecular weight distribution [6]. In fact, from the 'crossover point' where G′ = G″, it is possible to get a surprisingly good estimate of the polydispersity M_w/M_n for PP [7]. For such experiments to be meaningful, the imposed strain amplitude must be low, so that the measured G′ and G″ values do not vary with the strain, but they are intrinsic properties of the polymer structure. This is the region of the so-called linear viscoelasticity.

Another interesting result is the relation between storage modulus and first normal stress difference at very small deformations ($\omega > 0, \dot{\gamma} > 0$)

$$2G' = N_1$$

It is possible to measure N_1 using a cone-and-plate rotational rheometer. The Weissenberg effect results in a separating force between the cone and the plate which can be measured to give N_1.

$$N_1 = \frac{2F_N}{\pi R^2}$$

where

N_1	=	first normal stress difference;
F_N	=	normal (separating) force;
R	=	cone radius in Fig. 5-6.

Instruments capable of measuring N_1 require high precision construction and very sensitive force gauges. However, measurement of G', the storage modulus, can be carried out more easily.

Constitutive equations

These are relations between stresses and strains (deformations). In its simplest form, the Newtonian equation is

$$\tau = \eta\dot{\gamma}_{fluid}$$

where

η	=	viscosity;
$\dot{\gamma}$	=	du/dy, the shear rate.

For a shear thinning material of the power-law type, we have

$$\tau = \eta\,\dot{\gamma} = m\,\dot{\gamma}^{n-1}\bullet\dot{\gamma} = m\,\dot{\gamma}^{n}$$

where m is consistency and n the power-law exponent.

However, the above expressions, when inserted into the equation of conservation of momentum, cannot predict viscoelastic effects such as normal stresses, stress relaxation or extrudate swell. The simplest way to develop viscoelastic constitutive equations is to combine a model for an elastic solid

$$\tau = G\gamma_{solid}$$

with that for a Newtonian fluid

$$\tau = \eta\dot{\gamma}_{fluid}$$

By differentiating the elastic solid equation and adding the two strain rates, we get

$$\frac{\dot{\tau}}{G} + \frac{\tau}{\eta} = \dot{\gamma}$$

or

$$\tau + \lambda\,\dot{\tau} = \eta\dot{\gamma}$$

where

$$\lambda = \frac{\eta}{G}$$

has dimensions of time (relaxation constant).

This is known as the Maxwell model and shows that the viscoelastic nature of polymers can be described by viscosity and a relaxation time. More advanced models require a spectrum of characteristic time constants to describe the complex molecular processes involved during stress relaxation.

The concept of stress relaxation is very important in material characterization and polymer processing. If in the simple shear flow experiment shown in Fig. 5-1 the force applied was abruptly stopped, the stress would become immediately zero if the fluid was Newtonian, like water. However, in polymeric fluids, the stress would require some time to relax (exponentially) to zero. Polymers with different molecular weight and molecular architecture would require different relaxation times. Those with higher molecular weight and broader molecular weight distribution would require longer relaxation times. In polymer processing, materials with long relaxation times would have larger frozen-in stresses whenever cooling results in rapid solidification.

The relaxation time is characteristic of the elastic nature of polymeric liquids. In rheology, we define the Deborah number as the ratio of a characteristic material time (λ) and a process time (θ).

$$\mathrm{De} = \frac{\lambda}{\theta}$$

The characteristic process time can be chosen as the inverse of the shear rate ($\theta = 1/\dot{\gamma}$), because it represents the time for a flow process to be completed, e.g. passage through the die lips or filling a mold cavity. For very small Deborah numbers, the material behaves as a purely viscous fluid and for very large Deborah numbers the material behaves as an elastic solid. In polymer processing, the Deborah numbers are usually neither too small nor too high, but somewhere in between and such behavior is called viscoelastic.

Choosing a characteristic material relaxation time is difficult. For example, some authors of publications involving blown film use the parameter λ in the Cross model of viscosity presented above, because it has dimensions of time. In fact, some attempts have been made to correlate final film properties to this parameter. This is a very poor choice of relaxation time not supported by either theory or experimental evidence. Actually, in the Cross model, λ is equal to the inverse of the shear rate at a value where the viscosity is half the zero shear viscosity. A spectrum of relaxation times is required to describe the viscoelastic nature of polymers, however, if only one constant is to be used, theory dictates the 'longest relaxation time' which is given for steady shear by:

$$\lambda = \frac{N_1}{2\eta\dot{\gamma}^2} \quad \text{for} \quad \dot{\gamma} \to 0$$

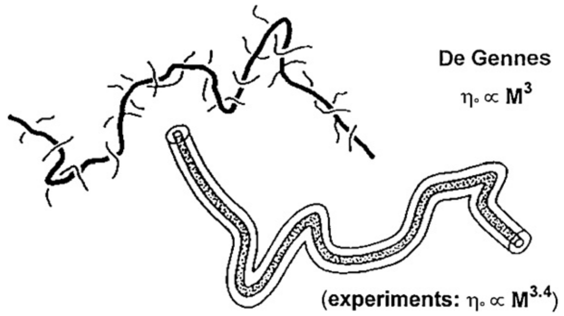

Fig. 5-12 Reptation model of polymer chain motion.

which can also be measured from dynamic experiments as

$$\lambda = \frac{G'}{G''\omega} \quad \text{for} \quad \omega \to 0$$

This result suggests that the elastic nature of polymers can be determined by measuring the storage and loss moduli at very low frequencies, preferably less than 10^{-3} (rad/s). Higher λ values mean more elastic polymers.

When describing polymer flow through channels and dies and for the subsequent stretching, orientation and solidification processes, the viscoelastic models must be expressed in three dimensions and in a proper mathematical frame of reference that moves and deforms with the fluid. The result is a very complicated expression involving dozens of derivatives [11, 12].

The most powerful constitutive equation is the so-called K-BKZ integral model that involves more than two dozen experimentally fitted parameters (see, for example, Mitsoulis [13]). Current trends involve the development of models based on macromolecular motions. De Gennes proposed the snake-like motion of polymer chains called reptation [2], illustrated in Fig. 5-12 and deduced from scaling relations that the zero shear viscosity must be $\eta_0 \approx M^{3.0}$, while experiments give $\eta_0 \approx M^{3.4}$ (M is the molecular weight). Based on the reptation concept, Doi and Edwards [14] developed a constitutive equation which leaves much to be desired before it can be used for predicting viscoelastic flow phenomena. Several attempts have been made to fix the Doi-Edwards theory. Perhaps the most advanced concepts have been proposed by Marrucci and coworkers (see, for example, Marrucci and Ianniruberto [14]).

The most talked about viscoelastic model recently is the Pom-Pom polymer model, developed by McLeish and Larson [15]. The motivation for its development was that the K-BKZ equation fails to predict the observed degree of strain hardening in planar extension when certain functions are adjusted to fit the observed degree of strain softening in shear. The failure to describe the rheology of long-chain branched polymers suggests that some new molecular insight is needed into the non-linear

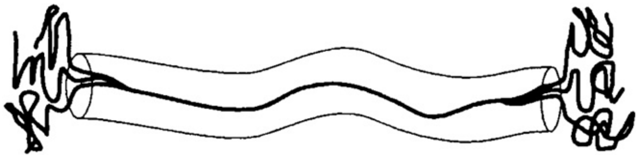

Fig. 5-13 The Pom-Pom polymer model.

relaxation processes that occur in such melts under flow. The Pom-Pom model uses an H-polymer structure, in which molecules contain just two branch points of chosen functionality and a 'backbone' which links the two pom-poms as shown in Fig. 5-13.

The Pom-Pom model exhibits rheological behavior remarkably similar to that of branched commercial melts like LDPE. It shows strain hardening in extension and strain softening in shear. It can describe both planar and uniaxial extension. The constitutive equation is integro-differential. For successful application at least 32 parameters must be obtained by fitting experimental rheological data. Of course, fitting 32 or more parameters in a complicated constitutive equation is a mathematical challenge.

Modeling polymer viscoelastic behavior has always been a very controversial subject. While viscoelastic constitutive equations have contributed towards understanding various deformation mechanisms and flow, they unfortunately have not provided us with quantitative predictive power. Very often the predictions depend on the model used for the computations and are not corroborated with experimental observations. Some viscoelastic flow problems can be solved with the appropriate constitutive equations, but this is still an area of academic research with very limited practical applications at the moment.

Sharkskin, melt fracture and die lip build-up

The term *sharkskin* is used when an extrudate loses surface gloss, also sometimes termed surface mattness. The surface usually exhibits a repetitious wavy or ridged pattern perpendicular to the flow direction. It occurs at a critical stress level of at least 0.14 MPa (21 psi) for most common polymers extruded through capillary dies. With some additives, lubricants, processing aids or die coatings, the onset of sharkskin can be shifted to higher throughput rates corresponding to higher levels of apparent shear stress.

The prevailing explanation is that sharkskin originates near the die exit and is due to stick-slip phenomena. A critical shear stress near the exit, in conjunction with a critical acceleration, results in skin rupture of the extrudate [16,17]. There was some disagreement over whether slip between the polymer and the die wall causes or helps avoid sharkskin [18]. However, it is now believed that it is slip which helps to postpone sharkskin to higher flow rates. Good adherence is also thought to be potentially beneficial, but stick-slip is always detrimental.

Fluorocarbon polymers, which can cost five to ten times as much as PE, are used in parts per million levels as processing aids with LLDPE. The proposed mechanism is that they deposit on the die surface and allow continuous slip. More recently, boron nitride has been introduced for the same purpose [19]. Other ways to reduce sharkskin and allow higher throughput rates involve heating the die lips to reduce the wall shear stress and polymer viscosity and adding a small exit angle (flaring) at the die exit. Also, special die lip coatings are known to result in sharkskin-free extrusions.

At higher throughput rates, extrudates usually become highly distorted and the pressure in a capillary viscometer shows significant fluctuations. This phenomenon is known as gross melt fracture.

Fig. 5-14 shows LLDPE extrudates for increasing shear rates, illustrating the progression from smooth surface to sharkskin and then melt fracture [20]. It is possible with some polymers (e.g. LDPE) to obtain melt fractured extrudates without sharkskin, i.e. the surface remains smooth and glossy but overall the extrudate is distorted.

Proposed mechanisms for melt fracture include entry flow vortex instability, elastic instability during flow in the die land for stress ratios ($N_{1w}/2\ \tau_w$) greater than about 10, stick-slip phenomena and other interactions between the polymer and the metal die wall. Probably more than one mechanism is responsible [5].

Die lip build-up (also known as die drool) refers to the gradual formation of an initially liquid deposit at the edge of the die exit which solidifies and grows and may partially obstruct the extrudate flow and/or cause defective extrudate surface. Depending on the severity of the problem, continuous extrusion must be interrupted every few hours or days and the solid deposit removed from the die lips. The causative mechanisms are not well known. Observations suggest that die lip build-up is not continuous but intermittent. Tiny droplets of material come out of the die or perhaps from a rupturing

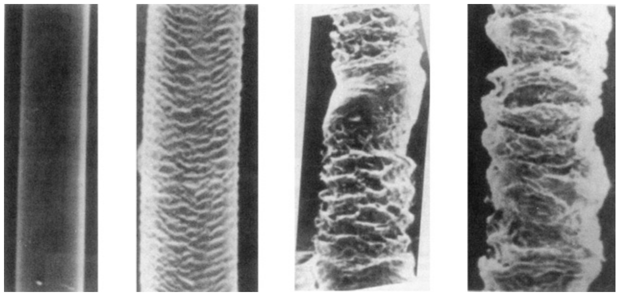

Fig. 5-14 LLDPE extrudates obtained from a capillary at apparent shear rates of 37, 112, 750 and 2250 s^{-1}.

extrudate surface. Some studies suggest that the build-up is rich in lower molecular weight polymer fractions, waxes and other additives [21].

Remedies for reducing die lip build-up include repairing missing plating and surface imperfections, removing moisture from the feed material, lowering the extrudate temperature and adding stabilizer to the resin. Fluorocarbon processing aids will sometimes also be helpful, as they are with sharkskin. Die lip exit modification by adding a small die exit angle (flaring) is also known to reduce build-up, for polyethylenes and polycarbonate.

Rheological problems in coextrusion

There are two rheological phenomena that manifest themselves during the flow of immiscible polymer melts through dies: layer non-uniformity and interfacial instability [22, 23].

Layer non-uniformity in coextrusion flows is caused mainly by the less viscous polymer going to the high shear region (i.e. the wall), thereby producing encapsulation. Fig. 5-15 illustrates this phenomenon for rod and slit dies [24]. Partial encapsulation can occur in common types and sizes of dies and complete encapsulation is possible for extremely long dies. Differences in polymer wall adhesion and viscoelastic characteristics can also be contributing factors. Weak secondary flows caused by viscoelastic effects (from the second normal stress difference) have been demonstrated to produce layer non-uniformities even when coextruding differently colored polymer streams of the same polymer [25]. This defect can be reduced by choosing materials with the smallest possible differences in viscosity and viscoelasticity (G′, G″, extrudate swell), or by adjusting the stream temperatures to bring the polymer viscosities closer to one another.

Layer non-uniformity can also arise in feedblock coextrusion, in which melt streams are merged into a single stream in a feedblock prior to entering the flat die. Uneven flow leakage from the flat die manifold to the downstream die sections can lead to encapsulation of the more viscous polymer by the less viscous, or even the reverse! Feedblock profiling is used to counteract the natural tendency for encapsulation due to viscosity differences [26]. This involves contouring the feedblock flow passages for regions of high or low volumetric throughput (Fig. 5-16). Feedblock profiling combined with eliminating uneven flow leakage from the feeding section of a flat die (or the use of this leakage to counteract the natural tendency for encapsulation) can be used to produce layer-to-layer uniformity in the extrudate. The problem is much more complex when coextruding many layers, as profiling for one layer will disrupt the other layers. The influence of a feedblock design change is virtually impossible to predict computationally at present, even with the use of the most powerful 3-D finite element flow simulation packages on powerful supercomputers.

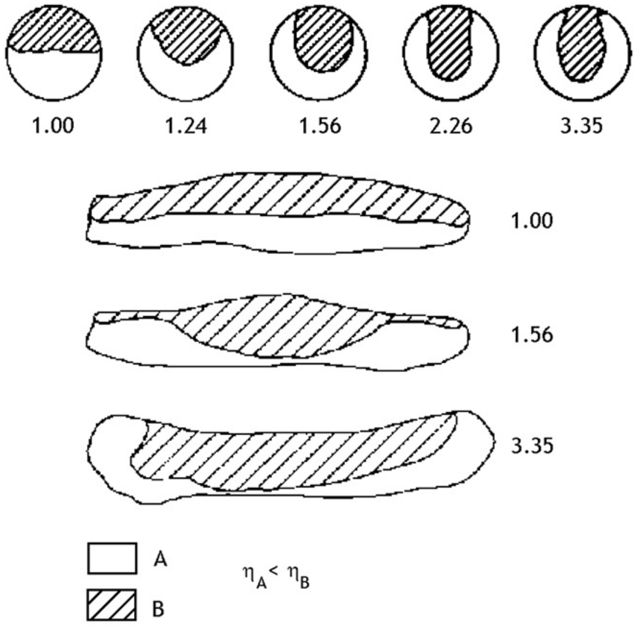

Fig. 5-15 Layer-to-layer flow rearrangement as a function of time.

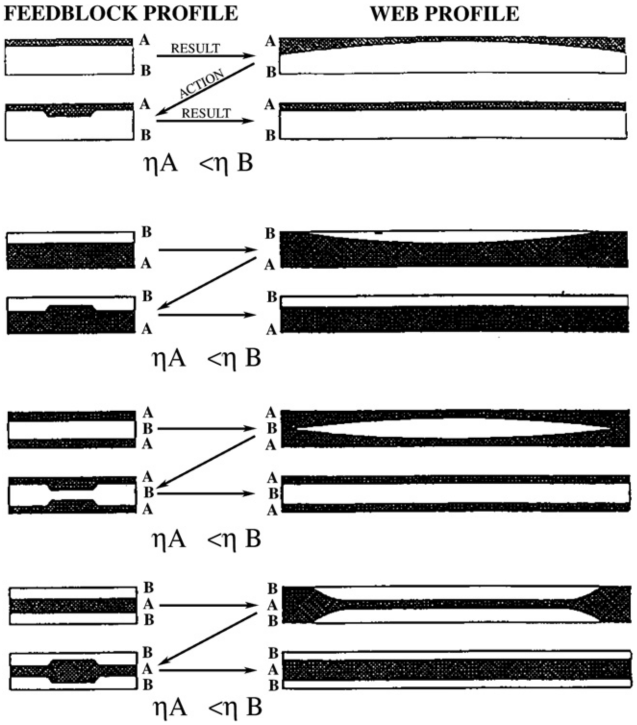

Fig. 5-16 Feedblock profiling and the resultant effects.

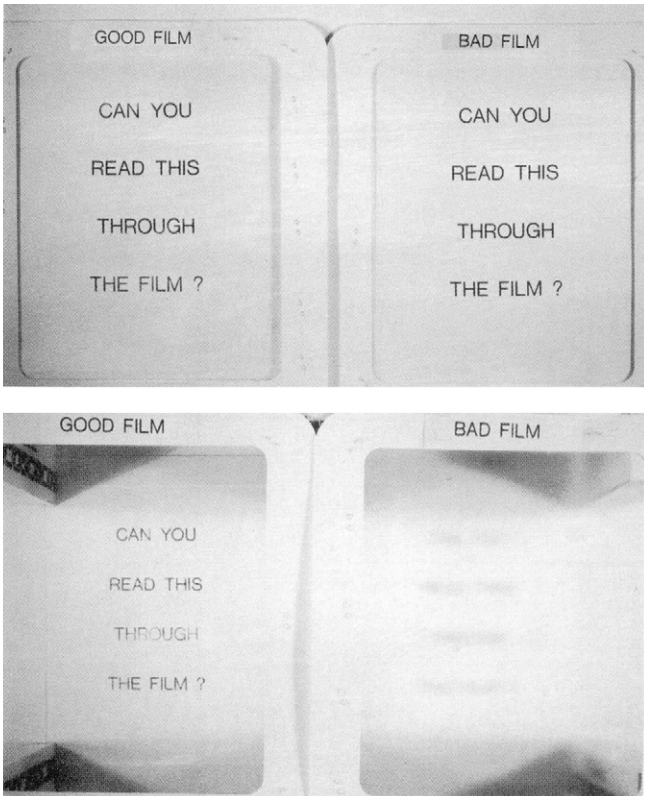

Fig. 5-17 The effect of interfacial stability on contact clarity of coextruded films (top) versus see-through clarity (bottom).

Interfacial instability in coextrusion refers to two common defects consisting of highly irregular or sometimes regular waviness which appears in coextruded structures at the polymer/polymer interface. The effect is to reduce significantly the optical quality of coextruded film. It is an internal defect, which distinguishes it from sharkskin, which is a surface defect.

The most frequently encountered interfacial instability is zig-zag (also known as die-land) instability, which appears as chevrons pointing in the flow direction. It is initiated in the die land and is characterized by a critical interfacial shear stress, in the range of 40–80 kPa (roughly ¼ to ½ of the critical wall shear stress level for sharkskin). Fig. 5-17 shows the effect of this instability on film clarity [27]. This problem can arise even if adjacent layers are the same material. The mechanism responsible has not been conclusively identified. Apparently, there is amplification of certain disturbance wavelengths under high stress conditions [28]. Viscoelasticity is probably a contributing factor, i.e. the interfacial normal stress difference is important [23]. Unfortunately, this is impossible to measure and difficult to calculate accurately. The most reliable means of diagnosing zig-zag instability at present is to calculate interfacial shear stress using simulation software.

Zig-zag instability problems are remedied by reducing interfacial shear stresses. The following actions are beneficial:

- decrease the total output rate (this reduces stresses everywhere)
- increase the skin layer thickness (this will shift the interface away from the wall where the shear stress is maximum)
- decrease the skin layer viscosity, e.g. by raising its temperature or by using a less viscous polymer (this reduces stresses everywhere)
- increase the die gap (this reduces stresses everywhere).

Matching layer viscosity is a popular remedy that does not always work. In fact, as recommended above, it is often advisable intentionally to mismatch the viscosities by using a lower viscosity resin for the skin layer [29].

The less common interfacial instability is ‘wave’ pattern instability, which appears as a train of parabolas spanning the width of the sheet and oriented in the flow direction. It occurs when a fast moving polymer stream merges with a much slower moving stream in a coextrusion feedblock. When the skin layer is thin relative to the second layer, the wave instability can be more pronounced. Large differences in extensional viscosities between adjacent layers can also make the defect more likely, as can a skin layer with a large extensional viscosity. The instability is aggravated by whatever flow or geometrical asymmetries might be present in the feedblock and die. As well, dies with larger lateral expansion ratios (die lip width divided by manifold entry width) and longer channel lengths (from feed slot vanes to die manifold) are more susceptible [30].

Rheometers

The commercially available instruments for measuring the various rheological properties can be classified into the following categories:

- melt indexers
- capillary viscometers
- rotational rheometers
- torque rheometers.

Melt indexers are inexpensive and they are used for quality control. Measurements with the standard load (2.16 kg) and a high load (usually 21.6 kg or 10 kg) can provide useful information into the polymer’s shear-thinning behavior and a rough estimate of power-law parameters as explained above.

Capillary instruments are equipped with one or two pistons for simultaneous measurements through a long and a very short (orifice) die. At least one vendor sells a three-bore instrument. Usually the shear rate is determined from the piston speed. The orifice die is used to measure the entrance pressure drop for calculating the Bagley end correction. These viscometers are usually accompanied by computer software for performing the Rabinowitsch and Bagley corrections. Also, the extensional viscosity according to Cogswell's method (from the entrance pressure drop) is easily calculated from two- or three-bore instruments. Performing the Bagley correction with single bore instruments is considerably more time consuming. Separate measurements must be carried out with three or preferably four capillaries with different L/D. Then, the pressure drop versus L/D lines must be extrapolated to obtain the Bagley correction [6]. Capillary viscometers may also be supplemented with a pair of rollers for measuring the melt strength.

Rotational instruments that have either cone-and-plate or parallel disk geometry are operated in either steady or dynamic (oscillatory) modes. The steady rotational speed measurements are limited to lower shear rates, (i.e. less than 5 s^{-1}) because, at higher shear rates, secondary flows or flow instabilities occur that violate the simple shear flow requirement. In dynamic mode, rotational instruments are used extensively for determination of storage modulus G', loss modulus G'' and complex viscosity $\eta*$, usually over a three decade frequency range with the same transducer. To extend the range, the so-called time–temperature superposition is used, in which measurements are carried out at different temperatures and the curves are shifted horizontally and vertically [6] and may cover usually an 8-decade frequency range from 10^{-4} to 10^{4}. The low frequency range is needed for determining relative elasticity levels, e.g. broad molecular weight distribution polymers exhibit higher values of G' at low frequencies. Torque rheometers utilize mixing rotors and the viscosity is determined from the measured torque and rotational speed [31]. Because the rotor blades have a complex geometry, neither the strain rate nor the temperature are uniform within the sample. These instruments are not suitable for accurate measurements and they are mainly used for quality control purposes.

Extensional viscosity measurements are difficult to carry out. Cogwell's method from entrance pressure drop in capillaries provides only a rough approximation. Several instruments became commercially available over the years but virtually all of them were plagued by miscellaneous complexities and experimental inaccuracies. Recently a device has been developed [32] that can be attached to conventional rotational rheometers and appears very promising.

A review of various commercially available instruments as well as the names of major suppliers has recently been published [33].

Concluding remarks

Polymer resins are frequently sold on the basis of density and melt index (MI). However, MI is only just one point on an (apparent) viscosity curve at low shear rate. Plastics extrusion involves shear rates usually up to 1000 s^{-1}, in cavity filling in injection molding, the shear rate can reach 10 000 s^{-1} and, in some coating operations, even higher shear rates are reached. For equipment and process design, troubleshooting or optimization, it is important that the polymer's shear thinning behavior be known. For a rough estimate of shear thinning, different loads in a melt indexer can be used. More accurate measurements require capillary and/or rotational rheometers. In capillary viscometry, the Rabinowitsch correction (for shear rate) and the Bagley correction (for shear stress) are usually necessary. At higher shear stress, around 0.1 MPa, wall slip occurs and slip velocity can be measured with the Mooney method.

Rotational rheometers (cone-and-plate or plate-plate) can also be used from very low shear rates of 10^{-2} s^{-1} to perhaps up to 5 s^{-1}. At higher values, the onset of secondary flows gives erroneous results. Rotational rheometers can be used in dynamic mode to yield storage (G') and loss moduli (G''). The complex viscosity versus frequency curve obtained from dynamic measurements coincides with the shear viscosity versus shear rate curve up to perhaps 1000 s^{-1}.

Other measurements might also be necessary to provide insight into a process or for differentiating polymers. These include the extensional viscosity and the first normal stress difference. Both these properties are difficult to measure and require special equipment. For extensional viscosity, the melt strength is an alternative and, for first normal stress difference, the storage modulus G' at low frequencies can be used.

Generally, rheological instruments are expensive and require knowledgeable people to run them. The engineer must understand his/her problem very well before deciding which rheological measurements are necessary for improving the understanding of the process or material behavior. Capillary viscosity measurements are perhaps more useful in understanding the processes, while dynamic measurements give more insight into the structure of polymer resins.

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Chapter 6

6

Coextrusion equipment for multilayer flat films and sheets

Eldridge Mount III

EMMOUNT Technologies

Designing and manufacturing multilayer flexible plastic films with multilayer coextrusion die technology

Overview

Several generations of coextrusion film dies exist for both tubular and flat dies, as well as several techniques for combining molten polymers for the production of multilayer polymer films. For this discussion we will focus solely on the production of flat sheets and films. The purpose of a film or sheet die is to produce a polymer film with uniform thickness dimensions across its width which is suitable for any subsequent film process. For a multilayer system, the production of uniform layer dimensions is added to the overall requirement of uniform total thickness. The number of polymers which can be combined is limited primarily by the ability to locate extruders to feed the molten polymers to the coextrusion system and will depend in part on the method used to perform the melt combination.

The most general configuration for coextrusion systems consist of the individual extrusion and melt systems used to prepare the molten polymers (extruders, filters and melt pumps), the melt pipes used to deliver the polymers from the extruders, the adapter to gather and route the melts from the extruders, a coextrusion feedblock to shape and combine the melts and a die to spread, thin and distribute uniformly the melt to form the coextruded film.

In producing flat multilayer films, there are two principal approaches, feedblock coextrusion and multicavity die coextrusion. In addition, it is possible and, oftentimes advantageous, to combine feedblock and multicavity dies together. In some instances, the adapter and feedblock can be combined together into a single structure and, if this is done, it becomes especially important to determine the adapter/feedblock size to permit future coextrusion system changes without disturbing the melt pipe and extrusion systems.

Because of this ability to combine sections and technologies for multilayer films and sheets together, there is a fair amount of strategy which must be developed when establishing a coextrusion system, especially in relationship to the number and thicknesses of the layers to be combined. Care should be taken to define adequately the products necessary or desired to be manufactured so that initial equipment choices do not inadvertently limit equipment changes for future products or prevent cost effective modifications to the equipment layout. It is of primary importance to size and locate properly the adapter used to collect and route the melt streams to the feedblock and/or die to permit the use of different feedblock and die combinations without the need to replace existing melt pipes or to disturb the existing extruder layouts. Changes which require new melt pipes and extruder relocations are costly and time consuming and potential costs or lost production may prevent the

Multilayer Flexible Packaging; ISBN: 9780815520214

changes from being made due to costs. To a large extent, the adapter can be viewed as a simple extension of the melt pipes, but adapters can also serve the function of routing various melt streams to various inlet locations on feedblocks or dies. This routing feature has been added to various adapter designs using interchangeable flow plates or selector plugs and adds a great deal of flexibility to coextrusion systems, especially when polymer specific extrusion systems are required. This feature permits changing a polymer from one surface layer to another surface or interior layer without the need to change extruders. This can be important, for instance, if the screw design or melt transfer pipes are optimized for the particular material being extruded and cannot be easily extruded with another screw or melt pipe design. The alternative to routing in the adapter would be to change the screw in the extrusion system, a more difficult and time consuming operation than changing an adapter system or adapter plate.

Introduction

Multilayer films have evolved over the last several decades as new polymers and processing technologies have become available. Originally, multilayer packaging structures were produced from single layer film products which were glued together by several lamination processes or were coated with additional polymer layers. Often times, the polymer films, such as cellophane, which were available were not melt extrudable and it was not possible to produce multilayer products directly as it is today by coextrusion. At times, the multilayer structures were produced containing non-polymer materials such as aluminum foil to supply the desired packaging properties such as light and gas barriers not available in polymer films.

Coextrusion of multilayer films became possible as new polymers were developed which expanded the available polymer properties and, as new copolymerization technologies were commercialized, the compatible polymers were increased. At the same time, new film manufacturing technologies were developed which further enhanced the polymer properties and permitted the production of thinner film combinations. As polymer layers became thinner, it became impractical to combine the layers together after they were produced as films and, in some cases, the required polymer thickness necessary for the layer was far less than would be practical to produce and handle as a single layer for subsequent lamination. In these cases, lamination resulted in more expensive combinations than were necessary. All of these factors drove early film developers to look for better ways to combine various polymers together without the need to produce individual free standing film layers for later combination and coextrusion was born.

Polymer processing of thermoplastic materials consists of transforming solid polymers in easy to transport pellet form into useful shapes and combinations and is most often performed by an extrusion-based process where the solid polymer is melted, mixed if necessary to form a homogeneous melt and then pumped to a die where it is shaped and, on exiting the die, is solidified by cooling. It is the shaping of the polymer by the die which differentiates the many polymer processes from each other and which is critically important in producing multilayer films. It should be noted at this point that once the polymer leaves the extruder and enters the coextrusion flow system the flow process is pressure flow or Poiseuille flow.

In this chapter, we will focus on the production of thin multilayer films. In some instances, the films will be later oriented and therefore the film passes through a relatively thick sheet stage as it exits the die after the coextrusion process. This cast sheet, which is formed as a precursor to the multilayer film orientation step, is, in many regards, similar to the multilayer sheets formed for subsequent thermoforming. Consequently, much of what is discussed here is applicable to the coextrusion of multilayer sheet products as well.

The molten polymers produced in extrusion are, in general, high viscosity fluids which exhibit low Reynolds numbers or a general description might be that of creeping, laminar flow in the various materials and flow geometries and therefore it would appear that the combinations of various polymer layers would be straightforward. However, the polymers are generally viscoelastic which will add some complexity to the flow of the polymer layer combinations and the choice of the layer combination methods. But, in general, the combination of polymer melts into layered flows is fairly straightforward and has been developed successfully over the years into a highly evolved set of techniques and equipment categories. In general, many polymer melts may be successfully combined before a single cavity film die followed by melt spreading in the die by what is known as feedblock coextrusion technology. Alternatively, the melts may be extruded in multicavity dies where the individual molten polymers are first spread and distributed prior to their combination. Both feedblocks and multicavity dies are common today and are also used in combination together; both technologies have their advantages and disadvantages in terms of cost and performance as well as process flexibility. Consequently, care should be taken to define the most appropriate technology or combination of technologies when establishing or modifying a coextrusion system so that future modifications in die and feedblock technology, product designs and infrastructure of the film lines are not compromised or excessively costly. Today, films with two to several hundred individual layers are common.

General coextrusion equipment overview

A coextrusion system is a combination of parts which takes molten polymer from two or more extruders, routes and shapes the melt and delivers it to the combination point where the melts are stacked and then delivered to a die for spreading to the final width (Fig. 6-1). In its most general configuration, the coextrusion system will consist of an adapter, a feedblock and a single or multicavity die. Each of these components and their functions will now be described in turn.

The adapter

The adapter is designed to collect and route the various melt streams to the feedblock and/or die used to produce the multilayer film and sheet. Consequently, the adaptor's selection is a key strategic decision in selecting a coextrusion system and of critical importance as it can be the key to future changes in coextruded product design because it can control the magnitude of the equipment change necessary. Adaptors can be stand alone parts or can be made integral with feedblocks or dies. The adaptor is the bridge between the extrusion system and the coextrusion system. The adaptor can be viewed as an extension of the melt system or as the coupling of the melt system to the coextrusion system.

The adaptor should be sized such that it permits the future addition of layers to an existing coextrusion system without the need to replace existing melt system components (melt pipes, filters, melt pumps etc.). For example, in the production of five-layer films and sheets by the use of a three-layer feedblock attached to a three-cavity die. In this case, the adapter should be physically sized such that it permits the future addition of two additional feedblocks to the system without the need to change the adaptor dimensions. If this is not done during the initial coextrusion system design, the larger physical dimensions, typical of a feedblock system for multiple die cavities, compared to a single cavity feedblock system, will generally require that new melt pipes be obtained to replace the existing melt pipes. An alternative to new melt pipes would be to relocate the extrusion or downstream equipment to accommodate the increased adaptor section dimensions. This can significantly increase the cost and installation time for an upgraded coextrusion system and, in some cases, makes the change economically unjustifiable.

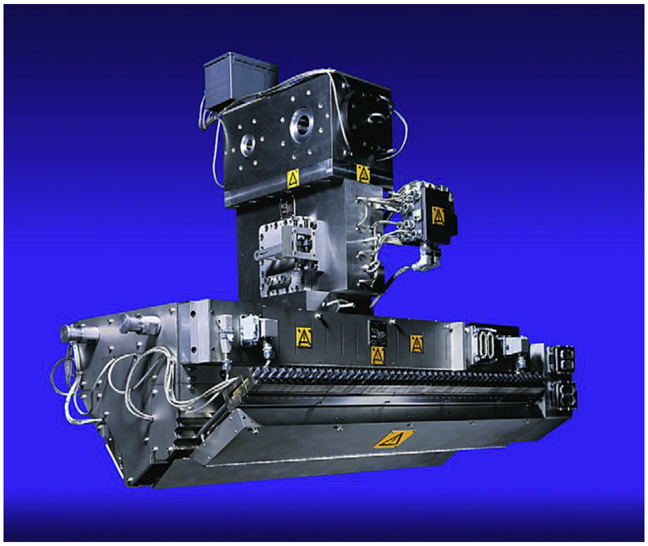

Fig. 6-1 General configuration the coextrusion system consisting of an adapter, a feedblock and a single or multicavity die (courtesy Cloeren Company).

Adaptors can have fixed flow channels or can be made such that they allow multiple flow paths of the melts between the adaptor inlet and the adaptor exit to the feedblock and/or die. This can be accomplished with segmented adaptors with interchangeable body segments to reroute flow or with removable plugs. The decision between fixed and interchangeable adaptors is a balance between product and process flexibility and melt stream integrity.

In fixed geometry adaptors (Fig. 6-2), there is little to no chance of melt stream cross contamination. However, changing polymer layer positions requires either a change in adaptor or changes in resin feed streams (and perhaps screw designs) to the extruders. Both require some down time to make the change and to re-establish the manufacture of acceptable product.

With interchangeable flow path adapters (Fig. 6-3), there is, perhaps, some possibility of cross-contamination between melt streams, but this is generally not a problem. However, the increase in ease of layer position changes can be dramatically increased depending on the adapter design.

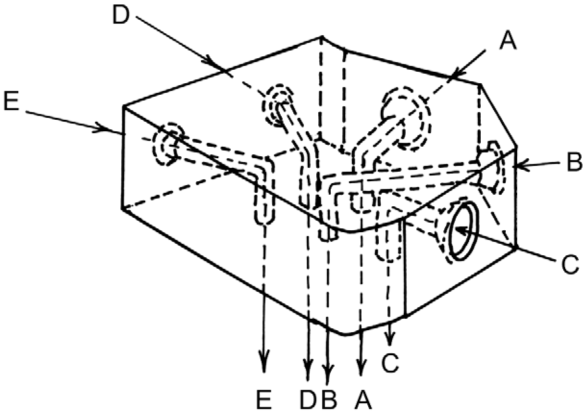

Fig. 6-2 Fixed geometry adapter showing inflow from extruders A, B, C, D and E and the outflow of each extruder to the feed block. The adapter flow locations cannot be changed without replacing the adapter.

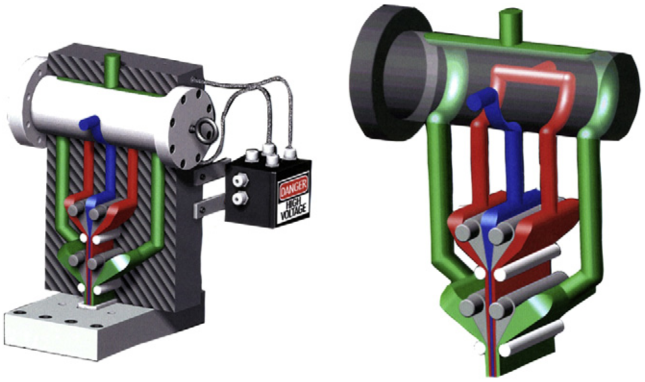

Fig. 6-3 Adapter with removable flow selector showing position in adapter and the polymer flow paths (Courtesy of Cloeren, Inc.).

For segmented adapters (Fig. 6-4), the change will require removal and rebuilding the adapter while adapters with interchangeable inserts will only require removal, some cleaning and reinsertion of the new flow insert and can be accomplished with minimal losses in production.

Therefore, as with adapter sizing, adapter flow path control is a strategic decision which is dependent on the expected number and frequency of product design changes, the sensitivity of layer polymers to extrusion (screw) technology, the infrastructure of the plant for resin rerouting and the ability of the die cavities to maintain acceptable layer dimensions across the film or sheet as polymers are changed.

The feedblock

The purpose of the feedblock is to shape and combine the multiple polymers entering from the adapter into a well-defined stack of polymers for delivery to the flat die. Feedblock technology exists in several basic geometries and combination philosophies ranging from the segmented flow of the Dow feedblocks (Fig. 6-5), the stepwise addition of the Welex modular designs (Fig. 6-6) with interchangeable cassette inserts and the Cloeren style feedblock with adjustable vane designs (Fig. 6-7).

Overall, these feedblock designs can be broken down into two design types: fixed geometry feed blocks, Dow and Welex and the variable geometry feedblock, Cloeren. All three feedblocks can be modified by the use of interchangeable parts, but only the Cloeren vane feedblock may be adjusted during operation.

Feedblock technology has evolved over the last several decades from simple beginnings to the current art where feedblocks are very flexible and effective. The understanding of the design goals for feedblocks has also evolved and a better understanding of how to accommodate interface migration and layer encapsulation, which is common in simple feedblocks, has evolved. While not a lot of analytical work has been published, recent experimental efforts are highlighting the impact of flow channel geometry and melt elasticity [1] and elongational viscosity [2] as key factors in maintaining layer integrity.

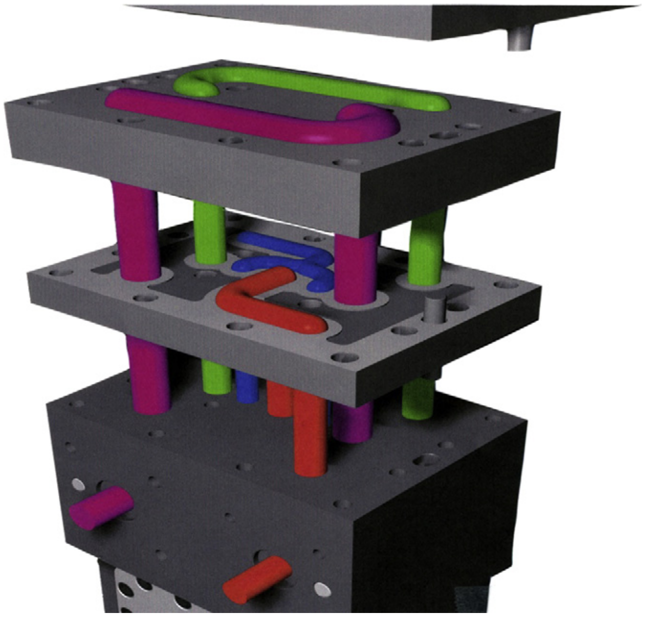

Fig. 6-4 Segmented adapter with removable programming plates for re-routing of melt flow from the adapter to the feedblock.

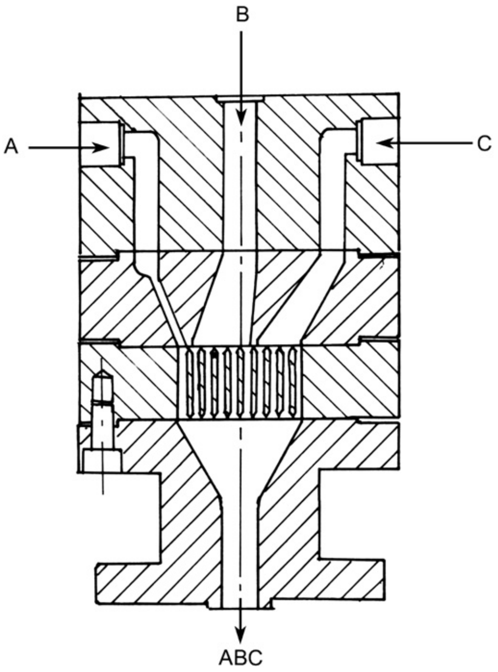

Fig. 6-5 Three-layer Dow feedblock showing segmented flow plates.

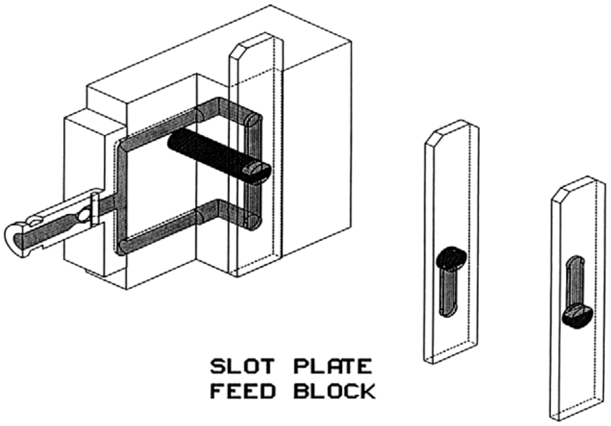

Fig. 6-6 WELEX modular adapter showing various interchangeable cassette inserts. Adapters may be combined sequentially to permit multiple layer addition. (Courtesy of Frank Nissel).

The die

As with feedblocks, the dies have evolved from simple forms to the modern coextrusion dies. In general, there are two principal approaches to coextrusion with dies: the single manifold die combined with a feedblock and the multimanifold coextrusion die. The multimanifold die may also be combined with a feedblock. Originally, the use of multimanifold dies was limited more by manufacturing methods and the difficulty in producing multiple die body sections, which greatly increased their costs relative to single manifold dies. However, with the revolution of multiaxis computer numerical controlled (CNC) machining capabilities, the machining difficulties have been greatly diminished and their availability has increased. The improved CNC capabilities also permit the machining of the die manifolds to the optimum flow design with fewer limitations imposed on manifold and preland geometry by the die manufacturer. This has led to the ready availability of multilayer dies with as many as five or more individual manifolds. The number of individual flow cavities in a die is somewhat limited by the die width as the cost and mechanical complexity of the die increases with each additional cavity.

Theoretical understanding of die and feedblock design parameters

Rheological background

There are several concepts which must be comprehended before the attempt is made to describe key die and feedblock design parameters. These concepts relate to the material science of polymer melts and the science of rheology. While a complete description of polymer melts and rheology is beyond the scope of this chapter, it should be possible to state and highlight the key concepts and the interested reader can then turn to the literature or textbooks on the subjects and find the derivations and background assumptions. Our first observation is that, within the scope of this chapter, we are dealing with fluids and that the fluids are forced to flow through the coextrusion equipment by pressure alone. Because the flow is a pressure-driven flow, we will be interested in the relationship between the volumetric output (Q) and the pressure or pressure drop (ΔP), required to sustain it. It will be from the solutions to the conservation equations (mass, energy and momentum) from which we obtain the various flow models used to design and trouble shoot coextrusion feedblocks and dies.

The development of the flow models also requires the use of a constitutive equation for the material and an equation of state if the material is compressible. The constitutive equation relates the material flow behavior in a stress field and defines the relationship between the stress components and the rate of strain (deformation) in the fluid. This constitutive relationship must be

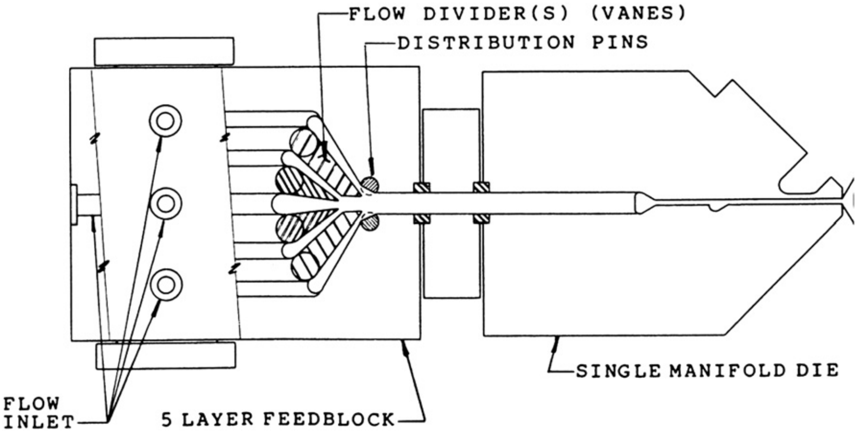

Fig. 6-7 Cloeren five-layer adjustable vane feedblock (courtesy of Cloeren, Inc.).

determined experimentally for each material and is generally depicted as the flow curve which plots the stress versus the rate of deformation or, more commonly, the shear rate. The shear rate is derived from the first invariant of the rate of deformation tensor which will be dependent on the geometry of the flow. For complex flows, the material behavior is difficult to measure and, therefore, it is common practice to use rheologically ‘simple’ flows to characterize the materials. Flows which meet this rheologically ‘simple’ requirement uniquely relate the stress (τ_{xy}) components in the fluid to the shear rate by a single material constant, the shear viscosity (η). The viscosity is defined as the ratio of the shear stress to the shear rate.

$$\text{Shear viscosity} = \frac{\text{Shear Stress}}{\text{Shear rate}} \qquad (6.1)$$

$$\eta = \frac{\tau_{xy}}{\dot{\gamma}}$$

Representative simple flows are the pressure flow in a tube (Poiseuille flow), the drag flow in a narrow gap between rotating cylinders (Couette flow) and the flow in a narrow gap between a flat plate and a low angle cone. These three flows form the basis for instruments used to measure material viscosity as a function of temperature and shear rate and each instrument has an effective range of shear rates over which it can operate. Shear rates of 0.0001 s^{-1} to 0.1 s^{-1} for a cone and plate, 0.001 s^{-1} to perhaps 10 s^{-1} for a Couette viscometer and 0.1 s^{-1} to 10 000 s^{-1} for a capillary rheometer.

As explained above, it is necessary to obtain the fluid flow behavior in order to perform the die design calculations as well as to derive the theoretical flow models used in the die design. Fig. 6-8 displays the flow curve, log shear stress versus log shear rate, for various types of flow properties found for real materials.

In Fig. 6-8, we see the flow curves for a shear thickening, or dilatent fluid ($n > 1$), a Newtonian fluid ($n = 1$) and a shear thinning ($n < 1$) or pseudoplastic material. Also noted in Fig. 6-8 is n, the power-law index which is the slope of the log (shear stress) versus log (shear rate) curve.

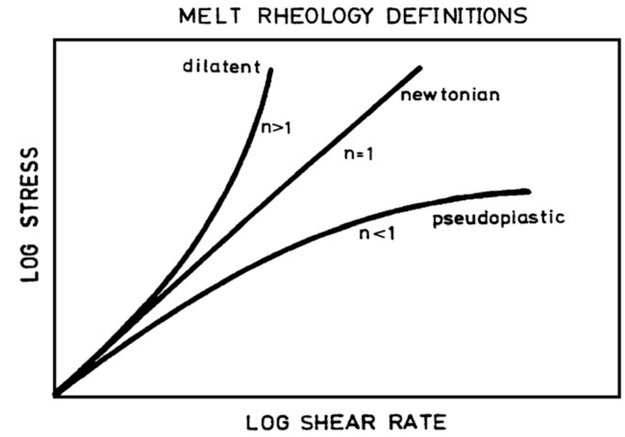

Fig. 6-8 Flow curves of ideal materials.

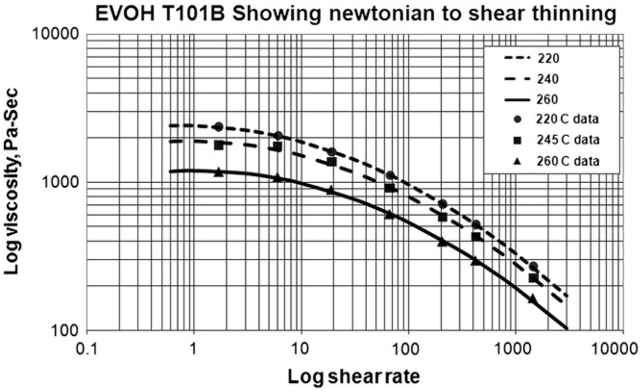

Fig. 6-9 Newtonian to pseudoplastis flow for EVOH polymer.

An example of a dilatent material would be wet sand or fluid–particle mixtures, such as ketchup, and the shear stress increases in a shear field due to the building or forming of an internal structure in the fluid which retards flow. Newtonian fluids, such as water, show a linear relationship between increasing shear stress and shear rate while pseudoplastic materials, representative of many polymer melts, show a shear thinning behavior where the shear stress decreases with increasing shear rate due to breakdown of the entangled chain molecular structure generally assumed for polymer melts. Real polymer melts show a Newtonian viscosity at very low or zero shear rates with a transition to a pseudoplastic behavior as the shear rate is increased (Fig. 6-9).

In general, the Newtonian, or zero shear viscosity, the shear rate where the transition to shear thinning behavior occurs, is different for different polymers and can occur at shear rates as low as 0.01 s^{-1} to as high as several hundred s^{-1} as shown for various materials in Fig. 6-10. As we will see later, this variation in apparent shear thinning between shear rates of 10 s^{-1} and 1000 s^{-1} will have an impact on successfully maintaining uniform

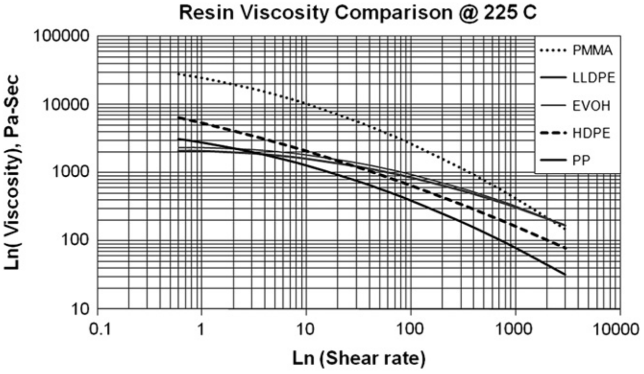

Fig. 6-10 Comparison of flow behavior of several resin types.

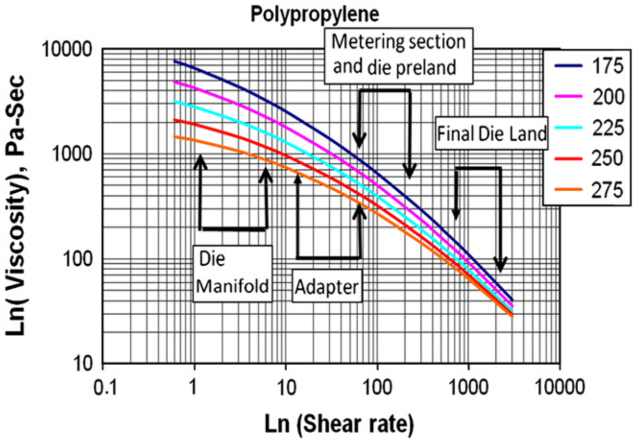

Fig. 6-11 Shear rate ranges in various locations in multilayer extrusion equipment.

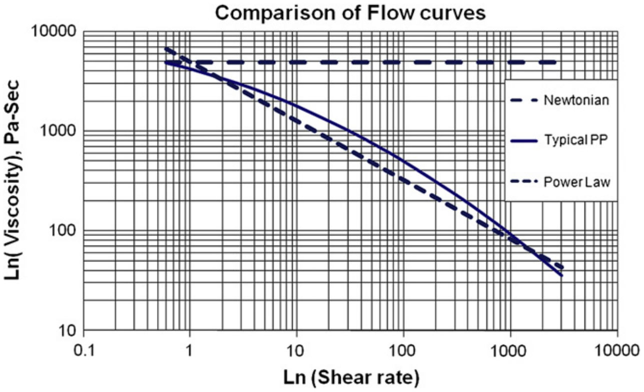

Fig. 6-12 The viscosity versus shear rate for a Newtonian, a power law and a typical polypropylene (PP) melt.

layer distribution and the interchangeability of polymers in existing dies and feedblocks.

In polymer melt processing, it is a common engineering practice to use the flow data collected from a capillary rheometer, because the shear rate range of the instruments, approximately $0.1\,\mathrm{s}^{-1}$ to $10\,000\,\mathrm{s}^{-1}$, covers the practical range of shear rates observed in most equipment (Fig. 6-11).

The capillary rheometer also permits the determination of the fluid viscosity without the need to assume its constitutive behavior by the use of the Rabinowitsch method or correction. Because of this, the Rabinowitsch correction should always be applied to capillary data, eliminating the need to use the apparent viscosity (assumed Newtonian fluid model). However, to characterize completely a polymer melt, it is necessary to obtain cone-and-plate as well as capillary data. Capillary data are generally available and the equipment is relatively easy to operate, but cone-and-plate experiments at low shear rates are extremely time consuming and not readily available. A useful approximation of the zero shear viscosity can be obtained using the method described by Gillespie [3] and would permit an engineering approximation of the zero shear viscosity from capillary data if it were not possible to measure the low shear rate data directly.

It has been a common practice in the development of polymer flow modeling to assume either a Newtonian or power law constitutive equation for the model development. Fig. 6-12 plots the viscosity versus shear rate for a Newtonian, a power law and a typical polymer melt.

It is clear from Fig. 6-12 that neither the Newtonian or power law fluid accurately represents the real behavior of the polymer melt over the measured shear rate range but, in general, the power law is a much better general representation of the polymer melt at high shear rates. The flow curve can also be piecewise approximated by a series of power law sections and point wise by the first derivative (slope) of the flow curve.

Another aspect of the rheology of dies and feedblocks which will be important in understanding the design and performance of coextrusion equipment is the solutions obtained for the flow in channels with various cross-sections. Dies and feedblocks are comprised primarily of circular, rectangular and converging flow channels. In addition, die manifolds may have tear drop cross-section flow channels. Therefore, it will be important to understand the relationships between the polymer flow rate, the pressure drops and the die geometry. This is done by solving the flow problem for the fluid constitutive equation in the geometry describing the die or feedblock. This can be a very complicated calculation and can be done with advanced computer algorithms, a description of which is beyond the scope of this chapter. Instead, we will focus on the analytical solutions obtained from simpler constitutive equations, to gain an improved understanding of the factors relating to the geometry and the fluid characteristics and how they combine to determine the die design. This understanding will aid us in determining when it is possible to interchange two different polymers in a die and what outcome we might expect in terms of system pressure drop as well as layer distribution uniformity.

The primary goal of the feedblock and die designs is to stack and spread the melt layers and have a uniform product exit the die. This is done by designing for a uniform flow rate across the final exit plane of the die (Fig. 6-13). Because the flow is pressure driven, the flow rate is controlled by the pressure drop along all the flow paths from the die entrance to the die exit.

Therefore, understanding the model results for circular and rectangular flow channels will be important. Fig. 6-14 shows the flow problem for flow in a circular

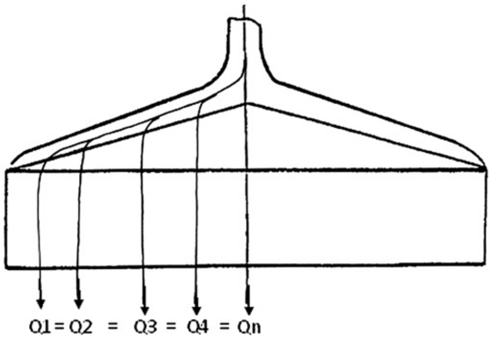

Fig. 6-13 Desired uniform volumetric flow rate (Q_i) across width of die.

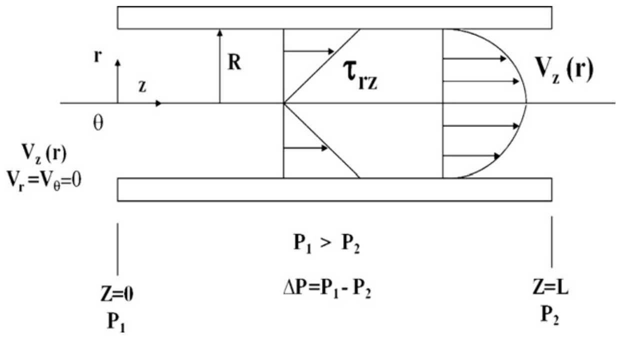

Fig. 6-14 Flow problem for circular pipe.

pipe and Fig. 6-15 shows the flow problem for flow in a rectangular slit.

Writing the differential equation for the flow in the pipe we find:

$$\frac{dP}{dz} = \frac{1}{r}\frac{d[r\tau_{rz}]}{dz} \tag{6.2}$$

Integrating from r = 0 to r = R yields,

$$\tau_{rz} = \frac{r}{2}\frac{dP}{dz} \tag{6.3}$$

Equation (6.3) shows that the shear stress varies linearly with position across the tube diameter from a value of zero at the center line to a maximum at the wall where r = R. It should be noted that this result is independent of the fluid type. The material constitutive behavior will be important in determining the velocity profile in the tube. The velocity profile (equation (6.4)) is determined by substituting the shear stress definition into equation (6.3), rearranging and solving for the velocity profile and, at this point, the fluid type, Newtonian, power law or other fluid type, will be important in determining the velocity profile shape.

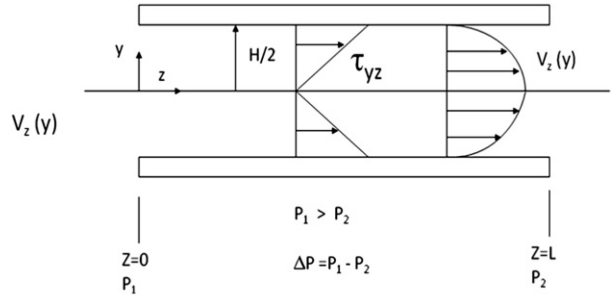

Fig. 6-15 Flow problem for parallel plates.

$$\begin{aligned}
\tau_{rz} &= \eta\dot{\gamma} \\
\eta\frac{dV_z}{dr} &= \frac{r}{2}\frac{dP}{dz} \\
V_z(r) &= \int_0^R \left(\frac{r}{2}\frac{dP/dz}{\eta(T,\dot{\gamma})}\right)dr
\end{aligned} \tag{6.4}$$

In order to relate the output, Q, of the tube to the pressure gradient driving the flow, it is necessary to integrate the velocity profile at the tube exit across the radius of the tube,

$$\mathrm{Q} = \int_0^R V_z\left(r\right)dr \tag{6.5}$$

Substituting in the definitions for a Newtonian and a power law fluid (equation (6.6)) into equation (6.4) and solving equation (6.5) gives equation (6.7) and equation (6.8) respectively;

$$\begin{aligned}
\eta &= \mu \text{ Newtonian fluid} \\
\eta &= \eta_0\left[\frac{\dot{\gamma}}{\dot{\gamma}_0}\right]^{n-1} \quad \text{Power law fluid}
\end{aligned} \tag{6.6}$$

For the case of the tube the results for a Newtonian fluid are:

$$\begin{aligned}
v_z &= v_0\left[1-\left(\frac{r}{R}\right)^2\right] \\
\mathrm{Q} &= -\frac{\pi R^4\Delta P}{8\mu L}
\end{aligned} \tag{6.7}$$

And for a power law fluid:

$$\begin{aligned}
V_z &= V_0\left[1-\left(\frac{r}{R}\right)^{(n-1)/n}\right] \\
\mathrm{Q} &= -\left(\frac{n\pi R^3\dot{\gamma}_0}{3n+1}\right)\left[\frac{R\Delta P}{2\eta_0\dot{\gamma}_0 L}\right]^{1/n}
\end{aligned} \tag{6.8}$$

And when n = 1 the power law results yields the Newtonian results.

Fig. 6-16 displays the velocity profiles in a tube for a Newtonian fluid and for various values of the power law index, n. For flow of the Newtonian fluid, the

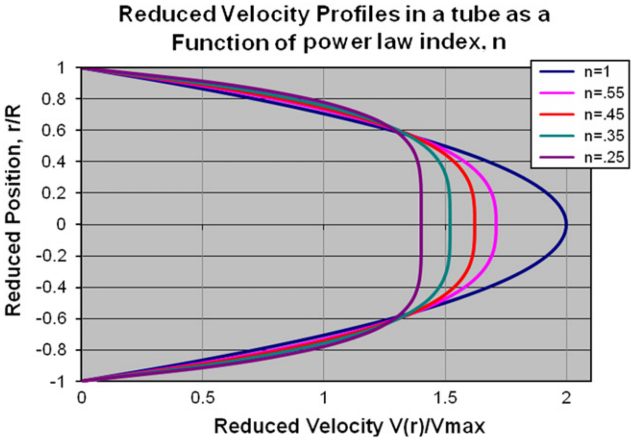

Fig. 6-16 Plot of reduced velocity profiles for flow in a tube as a function of the power law index, n showing the blunt flow (plug flow) front increasing as n decreases.

velocity profile is parabolic with a maximum melt velocity at the center line of the tube and a zero velocity at the wall. As the slope of the velocity profile represents the shear rate in the fluid, we find that the shear rate at the tube center line is zero and the shear rate at the wall is a maximum. For the power law fluid, the velocity profile is a blunt or plug-like flow with the plug-like nature of the velocity profile increasing with decreasing power law index.

Recalling the flow curve for a real polymer in Fig. 6-10, we understand from the shear rate dependence of the viscosity that the melt viscosity will not be uniform across the tube and will be at a maximum viscosity at the center and a minimum viscosity at the wall, even for a single polymer at a uniform temperature. This will be an important point to recall when understanding the need to maintain a decreasing viscosity across the flow of a coextruded structure and the driving force for flow rearrangement and encapsulation flow in feedblocks and die manifolds to be discussed later.

For flow in a thin, wide slit the differential equation describing the flow in Fig. 6-15 is:

$$\frac{dP}{dz} = \frac{d\tau_{zy}}{dy} \tag{6.9}$$

which on integration from -H/2 to H/2 yields

$$\tau_{zy} = \frac{dP}{dz}y \tag{6.10}$$

Again, the solution gives a linear dependence of stress with position in the slit with a zero shear stress at the center line and a maximum stress at the wall of the slit. Performing the same analysis for the slit as was done for the tube to determine the velocity profile in the slit and output from the slit for a Newtonian fluid yields:

$$\begin{aligned} v_z &= v_0\left[1-\left|\frac{2y}{H}\right|^2\right] \\ Q &= \frac{WH^3\Delta P}{12\mu L} \end{aligned} \tag{6.11}$$

And for a power law fluid:

$$\begin{aligned} v_z &= v_0\left[1-\left|\frac{2y}{H}\right|^{\frac{n+1}{n}}\right] \\ Q &= \frac{WH^2}{2\left(\frac{1+2n}{n}\right)}\left(\frac{H\Delta P}{2\eta L}\right)^{\frac{1}{n}} \end{aligned} \tag{6.12}$$

And when n = 1 is substituted into the power law results the Newtonian results are recovered.

Fig. 6-17 plots the velocity profiles for flow in a thin wide slit and, as was found for the tube, the velocity profiles are parabolic for the Newtonian fluid and plug-like for the power law fluid. Also the shear rate will be zero at the slit center line and a maximum at the slit walls with a maximum viscosity at the center and a minimum viscosity at the slit walls.

Feedblock designs

In general, the feedblock is designed to arrange the melt layers prior to entry into a die where the layer stack is spread to a much wider and thinner geometry than that in the feedblock. As we will see in the discussion on dies, the die manifold geometry into which the feedblock delivers the melt stack will have a profound impact on the final coextrusion quality.

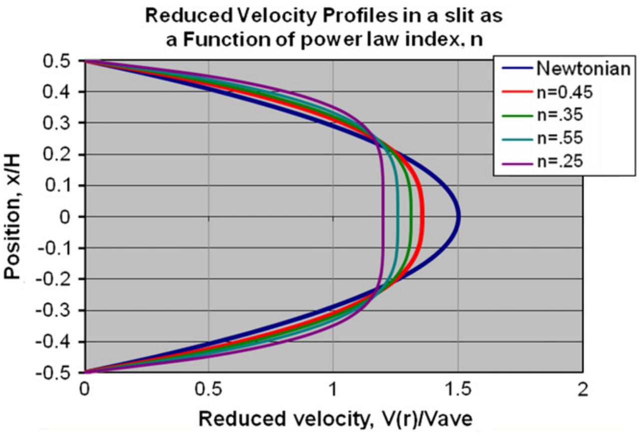

Fig. 6-17 Plot of reduced velocity profiles for flow in a slit as a function of the power law index, n showing the blunt flow (plug flow) front increasing as n decreases.

There are several feedblock designs generally available for use in coextrusion systems today. In general, the melt is combined in rather large cross-sections characterized by low shear rates. In general, the melt stack delivered to a die channel for subsequent spreading can have a round or rectangular cross-section. Rectangular flows will have an aspect ratio of width to thickness from 2 × 1 to 4 × 1 and the corners of the rectangle will be rounded to remove stagnation points and in the limit are oval in cross-section (Fig. 6-18) and are often times described as a racetrack entrance.

The first and still common feedblock design is the 'Dow' feedblock shown in Fig. 6-5. The primary parts to this feedblock are:

- the layer arrangement plate where the melt from each extruder is brought to the combination point
- the flow dividing section where each stream is divided into an equal volume
- the adapter section where the combined layers are combined and transported to the die manifold entrance.

There are many forms of the 'Dow' feedblock produced and used by many companies because they are simple in conception and manufacturing. In some instances, where rheological problems are encountered, the vanes are sometimes extended into the die adapter section. This is a difficult and expensive approach to implement but is at times effective.

In the 'Dow' feedblock, the primary design principle is that the velocity of the various layers in the combination should be the same when they are combined. This is accomplished by inserting flow dividing plates into the flow to divide the flow into perhaps 10 equal volumes. Because the geometry is uniform in cross-section of the plates, the velocity at the exit is uniform. A feature of this, and all feedblocks, is that if the layer uniformity exiting the die manifold is poor, then the plates can be replaced with vanes that are machined to various shapes such that more melt is placed in the regions which are found to be thin and less melt in regions found to be thick so that after spreading there is more material remaining at the thin point and less in the thick point and the average distribution is thereby improved. This is due to flow rearrangements called 'encapsulation' which will be explained below.

All feedblocks permit this melt profiling to improve layer distribution. In general, this profiling is used to overcome poor viscosity matching of the various layers. However, it might also have been possible to improve the layer uniformity with an existing feedblock by modification of the polymer viscosity level. However, profiling is a powerful means of overcoming some flow problems, especially when polymer replacement is not an option. If it is not possible to overcome the poor layer distribution by profiling or polymer selection then the feedblock/die combination should be replaced by a multimanifold die.

Another widely used feedblock designs are the WELEX designs where polymers are layered using a circular cross-section. This permits the easy adaptation to existing dies with circular entrances. Fig. 6-6 shows this feedblock concept. This feedblock is simple in conception and is easy to machine and they can be stacked in sequence to permit the addition of as many additional layers as space permits. Shaping of the melt layer is accomplished with removable inserts at each combination point. Fig. 6-19 shows another WELEX feedblock design where the flows are divided and stacked around a central torpedo. In this case, one stream is extruded against the flow and is then divided as it is swept down stream by the existing polymer flow. Then a central layer is injected at the downstream exit of the torpedo

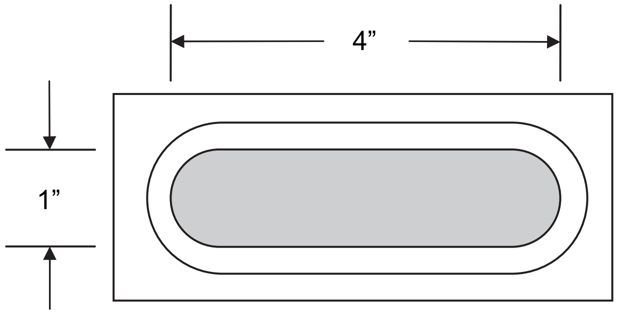

Fig. 6-18 Racetrack exit from feed block to match die entrance with rounded corners to prevent degradation.

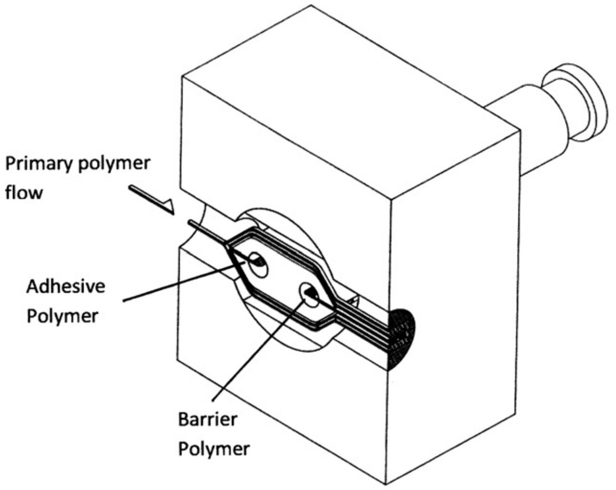

Fig. 6-19 WELEX center layer block for introducing an adhesive/barrier/adhesive structure in the center of a flow stream, creating five layers from three flows. Principal flow from left to right and adhesive exits counter the primary flow to encapsulate the barrier flow (Courtesy Frank Nissel).

producing a symmetrical ABA combination into the center of the flow. This could be used to add a central incompatible polymer surrounded by two adhesive polymer layers in to an existing single or multilayer extrusion system.

An adjustable feedblock was invented by the Cloeren Company (see Fig. 6-7) which permits the adjustment of the feedblock geometry while the coextrusion system is in operation. The principle behind this design is that the geometry of the combination point can be changed at constant output rate to change the average melt velocity and shear rate in the melt stream at the point of combination. This permits the modification of the melt viscosity in each layer at the combination point and can be used to eliminate coextrusion defects due to viscosity matching without the need to stop and rebuild the feedblock assembly. This feedblock technology has evolved over the years and been continuously improved with the addition of profiling pins as well as models where fixed but removable insets can be used in place of the adjusting vanes. The Cloeren feedblock systems have been very widely accepted in the coextrusion industry and are extremely versatile.

Extrusion Dies, Inc. also supplies an adjustable feed as well as fixed feedblock designs which are modular in design.

Die designs

Die designs for film and sheet have evolved over the years to improve the distribution of polymer melt across the width of the film or sheet being extruded. Initially, the dies were developed for single layer films and, initially, these designs were used for coextruded products. Since the beginning of coextrusion, further developments have resulted in die modifications specific to coextruded stacks delivered to the die from coextrusion feedblocks. Recent experimental studies have demonstrated the importance of these die changes to coextrusion flows and the maintenance of undisturbed coextruded layer structures [1].

Initial film dies were ‘crosshead’ slit dies which were fed from one end into a circular manifold and discharged melt through a narrow slit (land) (Fig. 6-20); these are sometimes called infinite cavity designs.

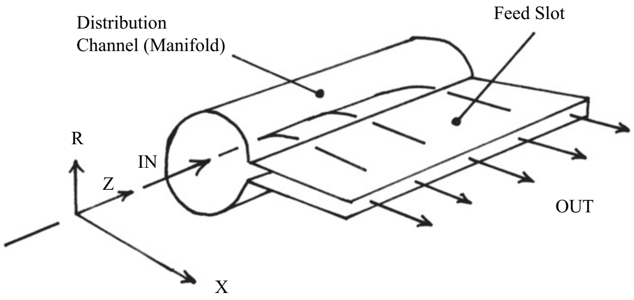

Fig. 6-20 Schematic diagram of end feed die showing flow into and through the manifold and die land.

End fed dies later evolved into center fed or ‘T-slot’ dies where the melt typically entered at the center of a circular manifold, spread in two directions and the melt discharged from a slit. It is to be noted that the T-slot die is symmetrical about the entrance port and the analysis of the manifold can be done as two end fed dies and, therefore, it is only necessary to evaluate the flow performance of one half of a center feed die. A die is, in essence, a pipe (or manifold) open at one end and closed at the other with a slit cut along its length through which the melt leaks. As the melt flows along the manifold, the internal manifold pressure changes due to viscous losses and changing fluid momentum. The viscous resistance will tend to cause the manifold pressure to drop while the momentum changes will tend to increase the manifold pressure and the driving force for flow will vary across the length of the manifold [4]. For a simple crosshead die with uniform manifold diameter and slot width and gap height, this will result in variable flow across the manifold width and a variable product thickness which is not desirable. What is desired is a film of uniform thickness across the die width.

The initial analysis of the crosshead die was performed by Carley [5] for isothermal, Newtonian and power law fluids defined as:

$$\begin{aligned} \dot{\gamma} &= \frac{dv}{dx} = f\left(\frac{\tau}{\tau_0}\right)^m \\ m &= \frac{1}{n} = \frac{d\ln\dot{\gamma}}{d\ln\tau} \end{aligned} \tag{6.13}$$

Where m, the flow index, varies from 1 to 6 for most polymer melts and is more commonly expressed today as 1/n where n is the power law index. Inertial effects were ignored in the analysis.

It is instructive to review the analysis for it highlights the basis for a good die design procedure and the results demonstrate the essential findings of flat die analysis. The analysis was focused on determining the uniformity of the flow from the die lips across the width of the die and defined a uniformity index (UI), which is the ratio of extrusion rate at the end of the manifold to the flow rate at the manifold entrance. The results were expressed in terms of the flow index (m), the width of the die manifold (W) and a die constant alpha (α) with dimensions of inch^{-1} for all values of m and which contains the die geometry dimensions of the manifold radius (R), the die gap height, (H) and the die land length, L.

$$UI = \left\{1 - \frac{[(1+0.05m)m\alpha W]^{(m+1/m)}}{(1+0.05m)(m+1)}\right\}^{m}$$
$$\alpha^{m+1} = \frac{\left(m+3\right)H^{m+2}}{2\pi m\left(m+2\right)L^{m}R^{m+3}} \tag{6.14}$$

The expression for UI is a function of the dimensionless group αW and is only dependent on the dimensions of the die and m, the flow index (or the power law index as m = 1/n) and not the fluid viscosity or the manifold pressure.

This result was compared to the exact solution obtained for the Newtonian uniformity index (equation (6.15)) and it was shown that for m = 1, UI resembles the first two terms of the expansion of the Newtonian result giving increased confidence in the result.

$$\begin{aligned} \mathrm{UI} &= 1 - \varepsilon = \sec h(\alpha W) \\ \text{for} \quad \mathrm{m} &= 1 \\ \mathrm{UI} &= 1 - \frac{(1.05\alpha \mathrm{W})^{2}}{2.10} \end{aligned} \tag{6.15}$$

The result of this flow uniformity analysis has all of the essential features of subsequent die design analyses. The Newtonian and power law results show that flow uniformity is independent of the fluid viscosity and the manifold pressure and dependent on the die geometry and the flow index.

Polymer viscosity is important in the analysis only through the flow index (m) and we can expect that, for a given die design, the extrusion of different polymers with the same value of m (m = 1/n) will yield similar flow distributions while the substitution of a polymer with a different power law index would be expected to give a different flow distribution and, therefore, thickness profile, across the die exit.

A key learning from this analysis is that, for any given film width, a center feed die will give better overall uniformity due to the decrease in manifold width as the results show that flow uniformity decreases with increasing manifold width, W. The results also demonstrate a decrease in uniformity with increasing die gap, H. Improvements to die flow uniformity may be achieved by increasing the manifold radius, R, or the die land length, L. These changes to R and L improve flow uniformity by minimizing the pressure drop differences across the width of the manifold and die land. However, a balance must be met as the increase in uniformity is offset by an increase in residence time in the die as the manifold radius increases and an increase in extrusion pressure, at constant output (or a decrease in output, at constant extrusion pressure), as the die land length L increases.

McKelvey and Ito [6] next proposed a die with a straight tapered circular manifold and a three gap die land where the three land lengths were a function of position across the die width (Fig. 6-21).

Again, the results of the analysis of this die's performance, the flow uniformity across the die width, showed a dependence only on the die geometry and the flow (power law) index m, as was found by Carley [5]. The analysis showed the flow variation across the width as a function of m the flow index for fixed die geometry where the die land gaps varied linearly across the die width. In principle, based upon this analysis, it should be possible to find a die land gap profile combined with a reducing diameter manifold, such that the flow deviations across the die width are reduced to zero.

In the design of flat film and sheet dies, what is critical to controlling uniform flow from the die across its entire width is a uniform pressure drop for all flow paths from the manifold entrance to the die lip exit (see Fig. 6-13). This is the primary goal of all die design procedures and, when combined with minimizing the polymer residence time by reducing the manifold volume across the die width and varying the die land length, results in the 'coat hanger' design (Fig. 6-22a). In the coat hanger die, the manifold is tapered as well as curved to permit the final land length of the die to vary in length to control the pressure drop. The coat hanger design is a natural outcome from the analysis of McKelvey and Ito [6].

When the coat hanger manifold concepts were first developed it was difficult and expensive to machine such dies and, therefore, a series of design compromises were developed to aid in the manufacturing and operating characteristics of the flat film die. Die manifolds were generally circular in cross-section with a streamlined flow from the manifold into the coat hanger gap (giving a tear drop shape manifold) and die land gaps generally decrease as the die exit is approached to accelerate the melt as it moves through the die to aid in preventing plate out from the melt onto die surfaces.

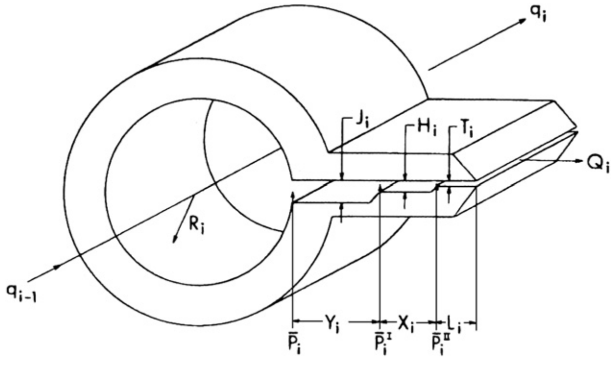

Fig. 6-21 Schematic diagram of die with a straight tapered circular manifold and a three gap die land where the three land lengths were a function of position across the die width (Redrawn from [6]).

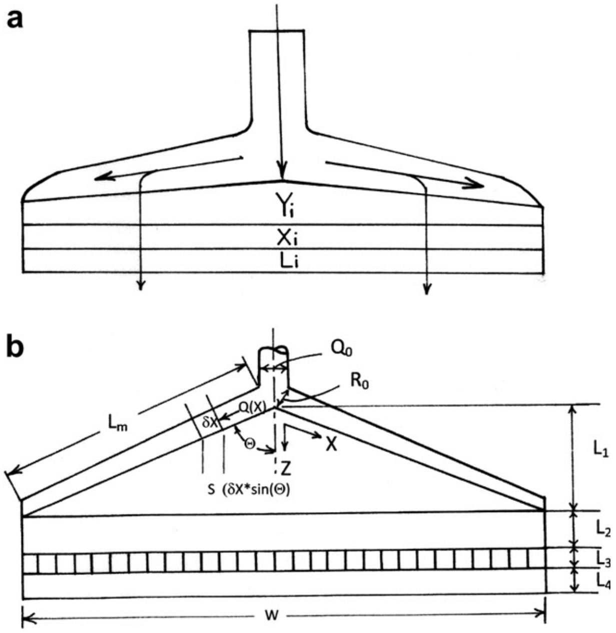

Fig. 6-22(a) Coat hanger die with three variable depth lands (Yi,Xi,Li) as in [6]; (b) coat hanger die of Chung and Lohkamp (redrawn from [8]).

A compromise coat hanger design is the ‘fish tail’ manifold configuration, where the manifold diameter and the die land height is reduced linearly across the die width. These dies have better flow uniformity than T-slot dies but, generally, do not give a uniform melt distribution across the die width [7] as does the true coat hanger.

Chung and Lohkamp [8] present a die and analysis aimed at improving the design of fixed angle coat hanger dies with circular cross-section manifolds (Fig. 6-22b) to give uniform flow rates across the width of the die. The analysis yields a variable manifold radius R(ξ) where the manifold radius is found to be a function of reduced manifold position (ξ) and the power law index (n).

$$\begin{aligned} \frac{R(\xi)}{R_0} &= (1+\xi)^{n/(3n+1)} \\ \xi &= \frac{x}{L_m} \\ L_m &= \frac{W}{2\sin\Theta} \end{aligned} \tag{6.16}$$

Here, again, we find that the power law index n is the most significant factor in determining flow uniformity from a film and sheet die.

Coat hanger die manifold designs, which are independent of operating point and material and which give uniform flow rate and uniform stress on the melt, may be designed [9] as well as coat hanger dies with uniform flow rate and residence times [10]. But these designs typically give a die with long coat hanger lengths and, as the width increases such that the dies becomes physically too long, are difficult to seal to prevent leakage.

The limitation in building dies with circular cross-section manifolds are twofold as discussed by Chung and Lohkamp [8] and Dooley [1]. First, in the transition from the manifold to the exit slit, the flow is not streamlined due to the abrupt transition from the manifold to the thin land area (see Fig. 6-21). Therefore, it was typical of die manufacturers to create a streamlined transition (Fig. 6-23).

Also, as described by Chung and Lohkamp [8], it is difficult and expensive to fabricate coat hanger dies with circular manifolds with varying radii from fixed radii cutting tools. Consequently, the back plane of the manifold was often cut with a flat back using rectangular cutters and the corners cut with a radius cutter to produce the familiar tear drop manifold often found for die manifolds. As will be explained later, the shape of the manifold has a profound effect on the flow of coextruded structures entering the die manifold from a feedblock. As disclosed by Cloeren [11] and later confirmed experimentally by Dooley [1], it has been shown experimentally that the rectangular feedblock is optimum for coextruded structures entering a die manifold from a multilayer feedblock and that the tear drop manifold creates layer non-uniformities.

These findings led to the invention of the ‘inverted preland’ die [12] for coextruded structures (Fig. 6-24) which combines the rectangular manifold with a constant length land of various gap heights, as found in McKelvey and Ito [6], with the exception that the initial land of the die is of a narrower gap than the second land and the

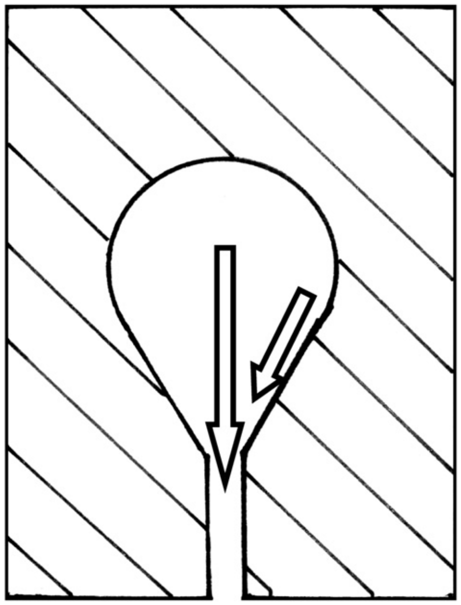

Fig. 6-23 Streamlined manifold design eliminating sharp transition from manifold to land as in Fig. 6-21

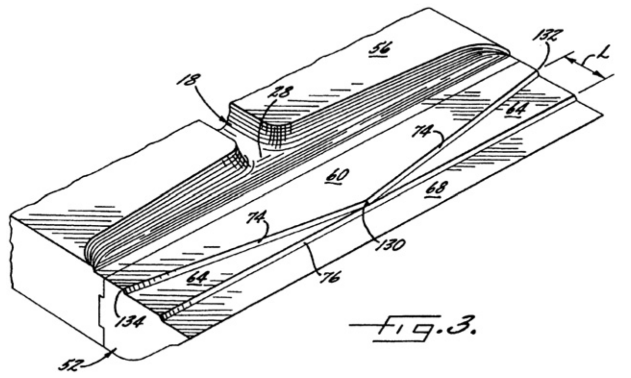

Fig. 6-24 Cloeren Inc. inverted preland die design (Figure 3 of US Patent 5,256,052) showing initial damming land (60) followed by deeper lands 64 and 68. The transition from 60 to 64 is a function of position across the die width and is dependent on the melt rheology.

shape of the transition between the first and second damming zones of the preland are rheology dependent.

From our earlier review of die design calculation models, it should be understood that the shape of the inverted preland transition will be dependent only on the power law index (n) of the polymer being extruded as was found by McKelvey and Ito [6].

Aside from the design for uniform flow across the exit, it has been established that there are several other important considerations for a die design which are polymer dependent, such as uniform residence time or a maximum residence time for temperature sensitive polymers, maintaining die cleanliness with a minimum melt velocity to prevent component or degraded polymer plate out on the die surfaces and lip, as well as to minimize internal die pressures to prevent die body distortion and to maintain stress levels below critical stress for melt disturbance etc. From all these considerations have come a series of die designs which are represented in the literature as the T-slot, the fishtail, various coat hanger and inverted preland dies.

All die designs require compromises in the fabrication due to limitations in machining capabilities. Early in the evolution of dies, these compromises were more significant in magnitude due to limitations from the manual set up of machining. Such design and fabrication compromises resulted in dies which were not optimum for the polymers available and had to be made mechanically adjustable to overcome the design and fabrication limitations. Such a mechanical compromise was the incorporation of an intermediate, adjustable flow restriction, called a choker bar, downstream of the manifold but before the final die land and the flex lip. The idea of a choker bar is to have an internal die gap which is adjustable across the die width so that any deficiencies in the manifold design, or machining, or changes in the polymer power law index, poor polymer temperature uniformity, significant output changes etc. might be accommodated by adjustment and a flat film profile obtained. Choker bars have been used for many years and can be difficult to adjust and create a potential source of polymer degradation in sensitive polymers or critical products. However, with multicavity coextrusion dies, it becomes very difficult to incorporate choker bars easily and inexpensively into the die construction as the number of die manifolds increases. Consequently, better die design procedures should be used to eliminate the need for a choker bar. It is my personal opinion that their use should be avoided whenever possible and the newer die designs and the improvement in fabrication capabilities of CNC machining permit the elimination of choker bars.

While the coat hanger die is the only manifold and land combination which, theoretically, may be designed to give uniform flow across the die width such that the manifold design is independent of the operating point [7], previous observations [13] of the performance of layer spreading with teardrop manifold dies in combination with feedblocks and recent experimental work in coextruded structures related to the secondary flows in these manifolds [14] indicate that they should be avoided when used in combination with the stacked multilayer melt streams exiting a feedblock.

Coextrusion systems for flat films and sheet

As described above, the choice of die design and its impact on spreading of melt stacks should be taken into consideration when feedblocks are combined with a die. However, the coextrusion of flat films and sheets can be successfully accomplished with multilayer feedblocks and single cavity dies, multicavity dies and combinations of feedblocks and multicavity dies. Which system is the best choice for any given application is dependent upon:

- the specifics of the application
- the polymers to be combined
- and the uniformity or quality requirements of the coextrusion which is to be produced.

Combinations of multicavity dies and feedblocks give the most flexible systems when multiple products are to be produced with a wide range of polymer types.

Originally, feedblocks with single cavity dies were the most cost effective form of coextrusion system as the use of multicavity dies was prohibitively expensive due to the difficulties associated with the machining of the relatively complex combination of body parts required for the multicavity dies. Today, with CNC machining capabilities, the machining of five (or more) cavity dies has been greatly improved and five cavity dies are readily available. Therefore, the choice of coextrusion system has been broadened and the coextrusion system choice becomes strategic in terms of current and future products and the ultimate flexibility required for the system. If a single coextruded product is to be run without modification, then the simplest system capable of supplying the desired product quality can be chosen relatively straightforwardly. The following examples will illustrate this.

For combinations of polymers with similar flow curves and viscosity levels, the use of a feedblock with a single cavity die can be an effective choice for the coextrusion. However, based upon the work of Dooley et al [1, 14], the use of teardrop manifolds should be avoided to minimize layer rearrangement and spreading problems due to secondary flows in the manifold. The amount of layer rearrangement seen in the manifold is related to the inherent elasticity of the material, with polystyrene being greater than polyethylene and polycarbonate showing little rearrangement in the study of Dooley et al [14].

If, however, the polymers in each layer have widely different viscosity levels and flow curves, then the layer spreading in the single cavity due to viscous effects alone will lead to poor layer uniformity and, perhaps, to other flow defects. In this case, the individual layers should be separated and individually spread to the final width and layer thickness in a single die cavity designed specifically for that polymer, prior to combining the layers.

Layer instabilities, causes and prevention

Coextrusion layer instability is often times called a ‘melt disturbance’ and there can be several sources, some of which are not directly related to the flow of the layers structure in the die, but rather to other processing problems. Therefore, it is important to eliminate all sources of poor melt quality which can be causing defects in the sheet or film, such as unmolten polymer, gels in the resin, large temperature gradients in the melt stream etc., before assuming that a rheological problem exists.

When you are trouble-shooting a ‘melt disturbance’, the first approach should be to determine ‘what has broken’ in the process, especially if the problem has recently arisen in an existing product or process. You should first determine that all temperature controllers are functioning properly and that there are no over temperature or burned out heaters causing large temperature gradients in the melt entering the die. Next, you should determine that the screw is still performing correctly and that there is no unmolten polymer in the melt stream and that the melt temperature and pressure entering the die or feedblock is uniform. Then, you should determine if there has been a change in the resin, either a resin grade change or an out of specification resin lot. Once this is done, it is possible to begin trouble-shooting the rheological problems causing the melt disturbance.

There are several coextrusion problems associated with the flow of layered polymer melts which are generally related to the relative viscosity of the various layers and their relationship to each other. This is easily illustrated by considering the flow of a single, polymer material with a homogeneous make up and temperature in a gap or pipe. Recalling the discussion above for flow in a gap or pipe, the velocity profile of the flow may be calculated and is displayed in Figs. 6-16 and 6-17. Because polymer melts are generally pseudoplastic or ‘shear thinning’, we can examine the viscosity of this single fluid across the flow profile. Recalling that the slope of the velocity profile is the shear rate, we find that the shear rate at the center of the flow is zero (0) and that the shear rate at the wall is a maximum. This will mean that, due to the shear rate dependence of the polymer, the viscosity of a single fluid at uniform temperature is not uniform across the flow channel and the flow will show a viscosity profile ($\eta(y)$) across the flow channel. In particular, we can see that the viscosity at the center line will be at the maximum or zero shear viscosity, η_o and the viscosity at the wall will be a minimum due to the increase in shear rate at the wall. This decreased viscosity at the wall is a self-lubricating effect in the flow as it will lower the pressure drop in the system and is therefore the lowest energy state for the flow.

Therefore, when we stack polymers in a layered coextrusion flow, we should ensure that the viscosity of the individual layers decreases as the flow channel wall is approached. If this is not done, the layers will attempt to rearrange themselves to place the lowest viscosity layer on the outside of the flow against the wall, at the region of highest shear rate, to lower the shear stress (pressure drop) in the system. This flow problem, where the viscosities are not properly stacked, leads to layer rearrangement or encapsulation.

Encapsulation has been reported and demonstrated experimentally in a tube and slot by several authors [15–17] by stacking high and low viscosity melts together. It has been found that the lower viscosity material will encapsulate the higher viscosity material given sufficient time. Han [17] has demonstrated a flow inversion in a tube by stacking a high and low viscosity melt together with the high viscosity melt against the tube wall and a low viscosity melt in the core of the flow. He demonstrated that, if the flow channel is long enough, the lowest viscosity material will migrate to the wall of the flow channel and completely surround (encapsulate) the higher viscosity components of the flow. This encapsulating effect is often seen in feedblock coextrusion and in die manifolds and die lands when the layer viscosities are not well matched or improperly

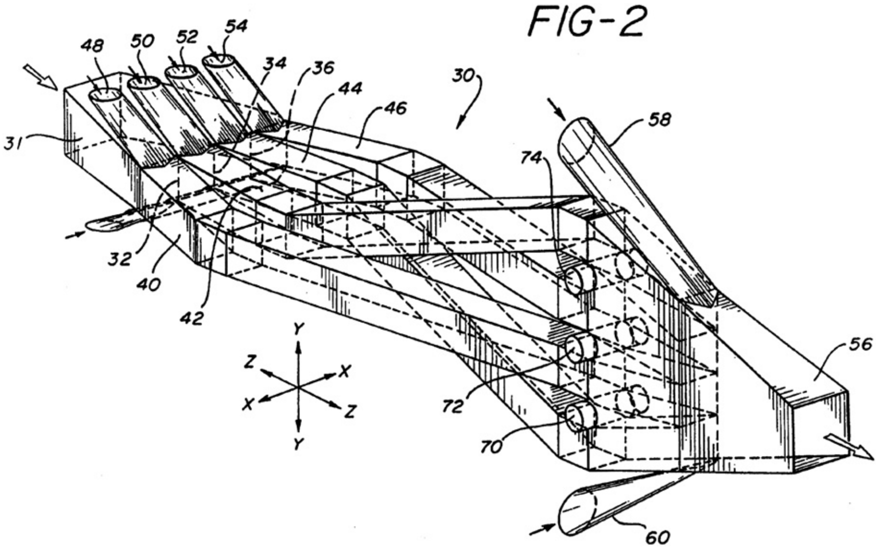

Fig. 6-25 Fig. 2 of US Patent 2,269,995 showing square cross-section flow channels used for flow dividing and stacking to produce multilayer flows.

positioned. This is the effect which feedblock profiling, described earlier, is attempting to accommodate.

Layer rearrangement in coextrusion flows in die manifolds and transfer conduits (piping) can also be due to viscoelastic effects as has been shown by Dooley et al [18, 19]. In these instances, circular transfer piping causes the least layer rearrangement due to balanced stresses resulting from melt elasticity forces. In rectangular melt transfer systems, as are sometimes used in multilayer combining adapters to give many layers from dividing and stacking simpler structures [20] (Fig. 6-25).

The layer rearrangements are driven by the secondary elastic flows and are quite spectacular giving multilobed, flower-like layer structures from circular feed streams in the rectangular flow channels (Fig. 6-26).

Of course, the extent of layer rearrangement will depend upon the length of the transfer conduit. This melt elasticity driven layer rearrangement is also a significant problem in tear drop shaped die manifolds [18]. Therefore, when producing layered sheets or films in single cavity dies being fed by multilayer feedblocks, it is desirable to have rectangular manifolds to minimize layer rearrangement due to the more balanced shear stresses at the polymer/metal surfaces of the die.

Layer instabilities or ‘melt disturbance’ which result in a deformation of the interface and perhaps the sheet or film dimensions, manifest themselves in many forms. At its onset, the sheet may still maintain good dimensional characteristics but the optical properties begin to deteriorate such that the clarity or ‘see through’ properties, of the film are impacted [21]. This instability exists primarily at the interface of the flowing polymers and is termed an ‘interfacial instability’ which is used

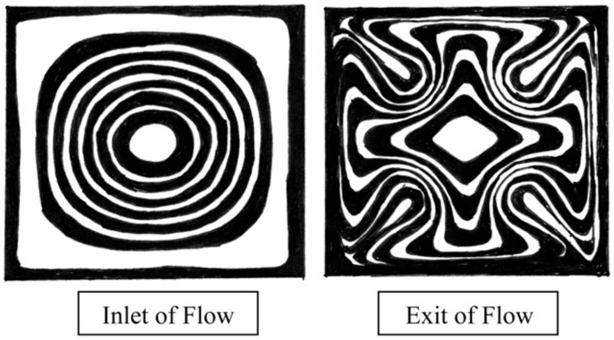

Fig. 6-26 Secondary flow impact on layer rearrangement in square melt pipe flow (redrawn Fig. 5-33, from Dooley PhD Thesis, University of Eindhoven, 2002).

Fig. 6-27 Melt disturbance of a three-layer sheet showing distortion of the sheet and the chevron appearance of the flow.

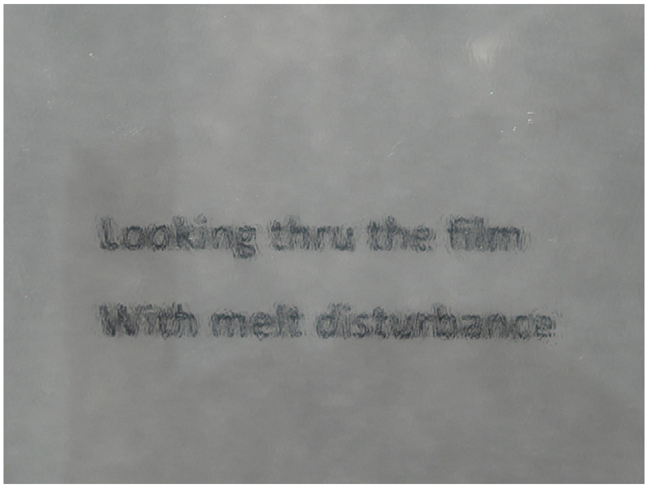

Fig. 6-28 Looking through a film containing melt disturbance and held approximately 8 inches in from of the lettering, showing the image distortion caused by the variable film thickness from the melt disturbance.

interchangeably with melt disturbance. This incipient interfacial instability manifests itself as a wavy or sinusoidal interface (Fig. 6-27) which results in light scattering of the image passing through the film giving a blurred image.

An example of the optical defect formed is shown in Fig. 6-28.

As the level of the instability increases, the interface can begin to form a pronounced wave which, on cross-section, appears to be breaking over itself (Fig. 6-29).

As the level of the instability increases, the interfacial instability can propagate to the surface deforming the sheet. This larger instability is known by several names such as ‘zig-zag’, ‘arrow heads’, ‘fish scales’ or ‘chevron’, depending on their severity. Looking through the film, this instability may appear as a wide parabolic wave front

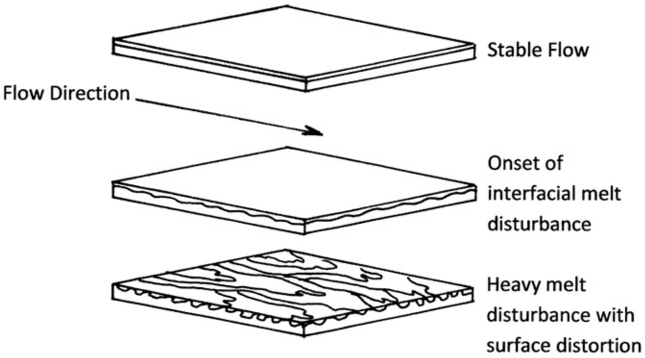

Fig. 6-30 Schematic diagram of two-layer flow showing the transition from stable to heavy melt disturbance with film distortion.

extending across the full width of the film (Fig. 6-30) and result in a pronounced thickness variation in the sheet.

Alternatively, the wave may be broken into several narrower bands of waves or into high frequency smaller waves which look like fish scales or arrow heads etc.

This defect has been isolated to the final die land and appears to be due to exceeding a critical shear stress for the coextruded polymer pair in the final die land, as was demonstrated experimentally [22] and is shown schematically in Fig. 6-31.

This defect is addressed by lowering the shear stress in the final land by several approaches including, lowering extrusion rate, increasing melt or die temperatures, opening the die gap and lowering the polymer viscosity with resin replacements.

Coextrusion instabilities and defects related to viscosity mismatching of layers is the most common form of coextrusion defect which I encounter. In general, the only acceptable level of interfacial flow defect is ‘none’ as a light and sporadic appearance of the defect will often times render the product unusable for both technical or a esthetic reasons depending on the application. For

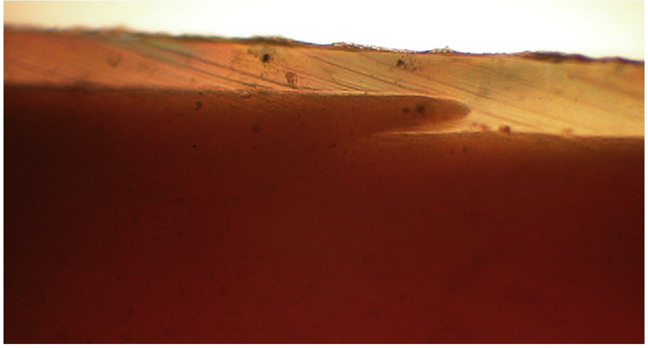

Fig. 6-29 Cross-section of wave-like melt disturbance of core layer entering the skin layer.

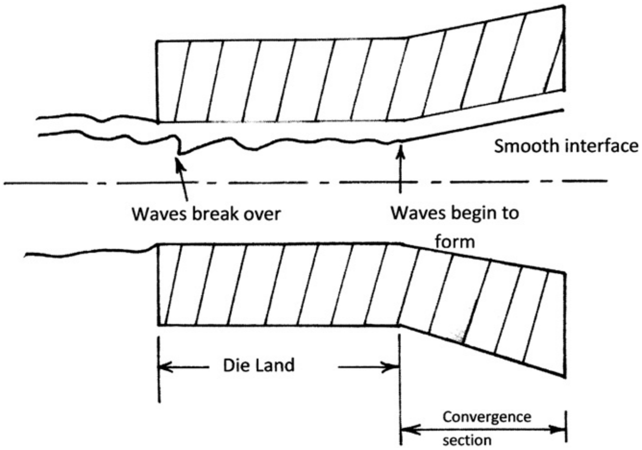

Fig. 6-31 Onset of ‘zig-zag’ type melt disturbance to stress level in the final land (Redrawn from [22]).

instance, an incipient interfacial defect appearing in a lane or sporadically across a film may not be readily visible in transmitted light in the clear film but, if the film is printed with a dark ink or metallized, the contrast between the film regions containing the defect and defect-free regions will enhance contrast between the defect and surrounding film which can make it very prominent.

In many commercial film and sheet products, coextrusion is used to modify the surface regions of a product by making use of thinner outer layers of special or modified polymers. Because the outer layers tend to be thin to minimize the use of the surface polymers, the interfaces of these thin layers are generally located near the flow surfaces where the shear rates are highest and changing rapidly as was shown in Figs. 6-16 and 6-17 and, in general, the interfacial instability will appear in a product as outputs are increased. This is because the die and interfacial shear stresses at the higher rates increase and due to changes in the average melt temperatures of the various layers as the extruder's screws are increased in speed as the overall layer output is increased. Usually, the increased extrusion rate will impact the thicker, interior layers more significantly than the outer layers as the extrusion rate is increased, resulting in an increase in melt temperature and a drop in melt viscosity of the thick interior layers, while the outer layers may change only a small amount.

With higher production rates, the thicker interior layers' viscosity tends to drop faster than the thinner outer layers for several reasons. First, the higher screw speeds and generally larger diameter extruders of the interior layers will heat the polymer melt more than with a smaller diameter extruder due to decreasing energy efficiencies of higher speed and larger diameter extruders [23]. Screw design and its impact on average melt temperature as a function of output level will therefore be an important consideration when increasing the extrusion rate of interior layers. Also, the interior layers may include reclaimed polymer, which is generally lower in viscosity due to the additional extrusion history used to make it. Therefore, the combined effects of higher melt temperature and lower component viscosity can result in a situation where the viscosity of the core layer becomes lower than that of the outer layers as overall output is increased.

Therefore, as productivity is increased, it becomes important to monitor the changes in rheological properties of the various layers' materials at the increased rates. If an interfacial instability appears, it must be addressed by process (extrusion temperatures, die temperatures, reclaim levels, line speeds etc), product design (layer thicknesses), material (reclaim quality, average viscosity changes) or equipment changes (screw design, die or feedblock) which result in a proper balance of layer viscosity and interfacial stresses.

Practical examples

Example 1

It is desired to produce coextruded films containing from three to five polymers. The film may contain layers of Nylon and/or ethylene vinyl alcohol polymer (EVOH) barrier layers, either separately or in combination, adhesive resins and various polyolefins. The films are to be 2000 mm (78 in) wide and range in thickness from 0.051 to 0.178 mm (2–7 mils). Structures are to include split barrier layers and both buried and surface nylon layers and symmetric and asymmetric structures such as:

- Nylon/tie/nylon/tie/LLDPE/LLDPE/m-LLDPE
- Nylon/tie/nylon/tie/PP/PP/EP copolymer
- Nylon/EVOH/nylon/tie/LLDPE/LLDPE/m-LLDPE
- LLDPE/tie/nylon/EVOH/nylon/tie/m-LLDPE
- PP/tie/nylon/EVOH/nylon/tie/EP copolymer
- LLDPE/tie/nylon/EVOH/nylon/tie/LLDPE
- PP/tie/nylon/EVOH/nylon/tie/PP
- LLDPE/tie/EVOH/tie/EVOH/tie/LLDPE.

There are several possible coextrusion equipment combinations which can be contemplated to produce these various film combinations and, while not all will be practical, several potential combinations are:

- a seven-cavity coextrusion die
- a five-cavity coextrusion die combined with a three-layer feedblock
- a three-cavity coextrusion die with two, two-layer and one three-layer feedblock
- a seven-layer feedblock and a single cavity die.

Choosing between the various combinations, the rheological compatibility, die mechanical complexity as well as the total equipment cost must be considered when selecting the coextrusion equipment. If we assume as a rough rule of thumb die cavities cost approximately \$1000/25.4 mm (\$1000/inch) and feedblocks approximately \$20 000/layer, then the approximate capital cost of each of the four ways to product the 2000 mm (78 inch) wide seven-layer films can be estimated and are approximately:

- 7 × \$78 000 = \$546 000 for a seven-cavity coextrusion die
- 5 × \$78 000 + 3 × \$20 000 = \$507 000 for a five-cavity coextrusion die combined with a three layer feedblock
- 3 × \$78 000 + 7 × \$20 000 = \$374 000 for a three-cavity coextrusion die with two, two-layer and one three-layer feedblock
- 1 × \$78 000 + 7 × \$20 000 = \$218 000 for a seven-layer feedblock and a single cavity die.

Therefore, the most cost effective way to produce this film would be with the fourth option, a seven-layer feedblock and a single cavity die and this is the option most often found in practice.

However, the third option, a three-cavity coextrusion die with two two-layer and one three-layer feedblock would likely be the most versatile combination because of the ability to combine various skin and tie resins with various core barrier combinations permitting independent control of layer distributions of the various combinations prior to the final combination to form the seven-layer combination. Three to five cavity dies are readily produced and the 2000 mm width is not a machining or mechanical constraint.

While there are many five-cavity and some seven-cavity dies being produced at this time, they are mechanically complex, large in physical dimensions and increased weight and the challenge of insuring the large area sealing surfaces between the multiple manifolds for a 2000 mm wide die would make manufacturing and the routine cleaning and reassembly of the die very difficult. In addition, it is generally more time consuming to heat the multicavity dies at start up. Also, as the number of cavities increases, there is a significant increase in the internal surface areas wet by polymer, which creates increased opportunities for polymer degradation, contamination and film defects. These reasons, as well as the lower cost, are why the seven-layer feedblock in combination with a single cavity die is the favored approach in applications of this type.

Example 2

It is desired to produce a 3 to 5 polymer, 5-layer oriented polypropylene film containing a continuous or cavitated PP core, clear or pigmented layers and various surface layer combinations where possible surface layers are PP, ethylene propylene (EP) copolymer, ethylene propylene butene (EPB) terpolymer, HDPE, LLDPE, EVOH, Nylon:

- EP copolymer/PP/PP/PP/EPB terpolymer
- EVOH/tie/PP/PP/EPB terpolymer [24, 25]
- EVOH/tie/cavitated PP/pigment PP/EPB terpolymer
- HDPE/PP/PP/PP/EPB terpolymer
- EP copolymer/PP/EP copolymer/LLDPE/ EP copolymer
- Nylon/tie/PP/PP/EPB terpolymer
- PP/PP/PP/PP/PP.

There are several possible coextrusion equipment combinations which can be contemplated to produce these various film combinations:

- a five-cavity coextrusion die
- a three-cavity coextrusion die combined with a three-layer feedblock
- a three-cavity coextrusion die combined with two, two-cavity feedblocks
- a five-layer feedblock and a single cavity die.

While the cost considerations are still important, these dies will generally be 40 inches or narrower in width (depending on the width of the orienting line) and, in the context of a PP orienting film line costing from $20 000 000 to $40 000 000, will be a relatively small cost. Therefore, in this particular instance, improved layer uniformity, resin change flexibility and layer rheological considerations generally outweigh coextrusion feedblock and die cost considerations.

Currently, the first and second options are widely used to produce these films. The last option would be a potential candidate if the desired film layer combinations were significantly limited to combinations of PP, EP copolymer, EPB terpolymer, HDPE only. Depending on its layer location, the addition of an LLDPE layer might be possible with minimal modifications to the feedblock or to the outer die cavity if it was to be a surface layer.

In my opinion, the second and third options are the most flexible approaches for this example because they permit the widest possible combination of materials with minimum die modifications. In the second case, the three-layer feedblock could be located on the central die cavity or one of the outer die cavities while, in the third case, the two-layer feedblocks could be located on both of the outer flow cavities or on an outer die cavity and the central die cavity.

When deciding on which feedblock/die cavity combination to choose, it is possible that by properly sizing the feedblock, several feedblocks could be purchased and all of the potential feedblock/die cavity combinations could be possible. This illustrates that a good deal of product design strategy needs to be taken into consideration when choosing the coextrusion equipment combination. To ensure the maximum flexibility in future product manufacturing, the feedblock/adapter combination should be sized such that the various potential feedblock/die cavity combinations can be substituted for each other without the need to modify or change extruder melt pipe connections to the adapter/feedblock combination. If this is not done initially, then changes between one feedblock/die cavity combinations to another may be economically difficult due to a need to replace all existing melt pipe connections between the extruders and the adapter/feedblock.

In the first three options, the full range of potential resins to be employed will likely require the use of more than one die if layer uniformity is to be optimized for all resins. This is because the die cavity designs for optimum layer uniformity are dependent on the shear thinning (power law index n) behavior of the various polymers as previously discussed. Fig. 6-10 displays the flow characteristics of various polymers contemplated for this example. What is easily seen on Fig. 6-10 is that the PP, EP copolymer, EPB terpolymer and HDPE resins show very similar shear thinning behavior (n values) while the EVOH and LLDPE show a significant difference (reduction or higher n values) in shear thinning. This means that if the EVOH or LLDPE resins are extruded through a die cavity designed for a PP based polymer (or a PP based polymer extruded through a die cavity designed for an EVOH or LLDPE based polymer), the layer distribution will not be optimum. Therefore, it may be necessary to have more than one die with various die cavities designed for a range of polymer products. Alternatively, depending on the polymer layer combinations, modifications to the feedblock combination geometry might be possible to profile the shape of the melt stack exiting the feedblock to permit improved layer distributions with existing die cavities. Which approach is best, acceptable or necessary, will be dependent on the permissible layer thickness variations permitted by the product end use application.

Example 3: Production of a three- to seven-layer sheet for thermoforming.

It is desired to produce coextruded thermoforming sheet containing from three to five polymers. The sheet may contain layers of Nylon, EVOH, polyvinylidene chloride (PVDC) or other barrier layers separately or in combination, adhesive resins and various polyolefins. The sheets are to be 1143 mm (45 in) wide and range in thickness from 12 to 45 mils. Structures are to include monolithic and split barrier layers and symmetric and asymmetric structures such as:

- LLDPE/tie/nylon/tie/nylon/tie/LLDPE
- PP/tie/nylon/tie/nylon/tie/EP copolymer
- LLDPE/tie/nylon/EVOH/nylon/tie/LLDPE
- LLDPE/tie/nylon/EVOH/nylon/tie/m-LLDPE
- PP/tie/nylon/EVOH/nylon/ ethylene vinyl acetate (EVA)/LDPE
- LLDPE/tie/EVOH/tie/EVOH/tie/LLDPE
- HDPE/tie/EVOH/tie/EVOH/tie/HDPE
- PS/scrap/tie/PVDC/Tie/scrap/PS
- PP/scrap/tie/EVOH/tie/scrap/PP
- Filled PP/Scrap/filled PP.

As with the film example, there are several possible coextrusion equipment combinations which can be contemplated to produce these various film combinations. However, because the layers are relatively thick, layer uniformity in layers other than the barrier layers are less critical. This permits the assumption that the coextrusion system will contain a combination of feedblocks and multicavity or single cavity dies:

- a three-cavity coextrusion die with two two-layer and one three-layer feedblock
- a three-cavity coextrusion die, with a five-layer feedblock
- a seven-layer feedblock and a single cavity die
- a five-cavity coextrusion die combined with a three-layer feedblock
- a two-cavity die with a five-layer and two-layer feedblock.

While no single system will be able to produce all possible layer combinations and thickness ranges, a wide range of products is possible with the three-cavity die and various multilayer feedblock combinations.

Summary

Multilayer coextrusion systems for flat film and sheet products are well developed and readily available in many configurations and from many suppliers. Care should be exercised in determining the physical configuration of the installation to minimize costs and physical constraints for future product configurations. Also, a great deal of thought should go into the specification for the system and accurate information should be supplied to the manufacturer (polymer type, viscosity curves, melt temperatures etc.) to insure the best outcome.

When choosing a coextrusion supplier, it is important to interview and judge them based upon the science and technology used for the design and manufacture of the system as well as the range of coextrusion technology which they employ. For instance, if a manufacturer is not interested in the polymer rheology, it is hard to imagine that they are truly designing the coextrusion system but rather just building it. If the supplier offers only limited possibilities, such as multicavity dies and no feedblocks, then they are likely not able to design coextrusion feedblocks successfully or cannot design the feedblock/die cavity combination.

Coextrusion is a powerful method to produce multilayer films and sheets for a wide range of applications. There are a wide range of approaches which can be used to produce these products and all are usually capable of producing a wide range of products within limitations. A thorough understanding of the coextrusion science and technology is required to achieve the best results.

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Chapter 7

7

Multilayer blown (tubular) film dies

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Introduction

Multilayer dies are used for coextrusion which started to become more popular among many processors in the late 1970s and early 1980s when original equipment manufacturers (OEMs) started to include these items in their product list. Prior to this, advanced processors developed their own coextrusion equipment and the technology was very closely guarded (and still is today). To understand how multilayer dies developed, it helps to divide tubular coextrusion into two categories: barrier and non-barrier.

Non-barrier coextrusion would contain coextrusion products made with different polyolefins combined for esthetics, strength, cost, etc. Barrier products are developed primarily for barrier functions, such as food or chemical packaging.

In the non-barrier category, almost all OEMs have provided successful two- and three-layer coextrusion dies since the early 1970s. However, barrier materials have more limited processing conditions and, therefore, present more difficult processing conditions.

Barrier resins, such as polyamide (PA), ethylene vinyl alcohol (EVOH) and polyvinylidene chloride (PVDC), have much smaller 'processing windows' than the polyolefins that most equipment manufacturers were used to. Barrier resins were also more prone to degradation making them less forgiving to poor die design as well as poor operating practice. As a result, successful coextruded barrier films require good die design, good screw design and good operating practices. It should also be mentioned that the continued increase in successful coextrusion parallels improvements in resin development. Over the years, resin companies continue to improve the processing behavior and thermal stability of barrier polymers.

There has also been a trend to increase the layers in a structure in order both to improve the film properties and reduce cost. For example, an excellent five-layer barrier structure could consist of PA/tie/EVOH/tie/ionomer.

However, a corresponding 10-layer structure could be PA/tie/LLDPE/Tie/PA/EVOH/PA/tie/EVA/ionomer.

It can be demonstrated that the 10-layer structure will provide improved barrier performance at equal amounts of barrier material as well as offer the possibility of reducing or replacing more expensive polymer with lower cost resins that provide adequate performance.

Conventional coextrusion dies

Probably, the most influential company initially to supply coextrusion equipment was Barmag, which is said to have provided more than 150 coextrusion dies by the mid to late 1980s. These dies were based on conventional cylindrical designs with rotating 'block' systems. The 'block' is a term used for the device that simply redirects the polymer from the horizontal direction (when it leaves the extruder) to the vertical direction (to enter the die).

Multilayer Flexible Packaging; ISBN: 9780815520214

In a single layer die, it can be a relatively simple 90° bend. However, for a multilayer die, the block can be much more complicated as it is required to uniformly divide the flow from each extruder and direct it evenly to the spiral distribution system for each layer. The block complexity can further increase when the die system is required to rotate or oscillate as a means of randomizing thickness variation.

Fig. 7-1 is a cross-section of a conventional style three-layer coextrusion die showing both a stationary (left) and a rotating/oscillating (right) block system produced by Brampton Engineering in the 1980s.

The rotating die systems (that were required for gauge randomization) posed a maintenance problem. Apart from the periodic maintenance (often resulting from failure) of the sealing system, the rotating blocks generally provided additional areas for polymer 'hang-up' and degradation. Combined with the additional flow length in the rotating block, this resulted in poor purge characteristics and long changeover times. In fact, many barrier film processors had a spare die that allowed them to continue production while another die was being cleaned or serviced. This also limited processors who developed coextruded products to those who had the financial strength to cover the intense development costs, production efforts and maintenance costs.

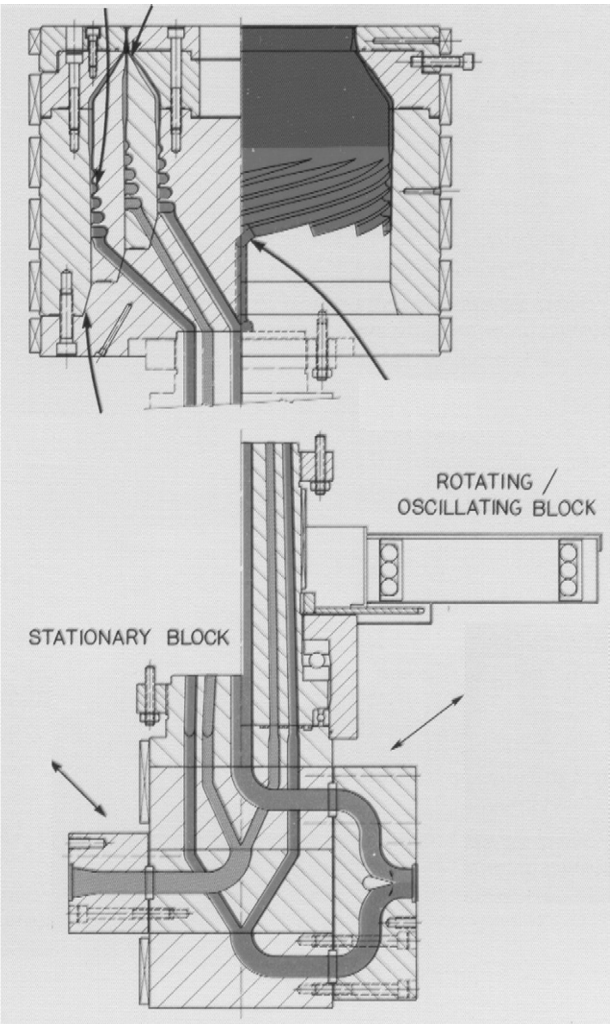

Fig. 7-1 Conventional spiral mandrel type coextrusion die with rotating block.

Despite the above-mentioned difficulties, the advantages offered by coextrusion encouraged R&D efforts by processors, material suppliers and equipment manufactures alike. The late 1980s and early 1990s were witness to many new materials, die designs and coextrusion products. One of the most important developments was the widespread introduction (due to patent expiration) of the oscillating haul off. While this device is downstream from the die system, it removed the gauge randomization requirement from the die, leading to great improvements in die passage streamlining. Without the need to rotate the die, manufacturers began paying more attention to channel design with regard to lower residence times. However, commercially available coextrusion dies were still essentially comprised of three or five single-layer dies (concentric cylinders) that were nested together (Fig. 7-2).

Each one of the cylinders could be considered as a conventional, single-layer spiral mandrel distribution system (Fig. 7-3).

The polymer melt would be distributed by the controlled material leakage out of the helical grooves (spirals). The subsequent layering effect also had benefits with respect to mixing and appearance. While these dies

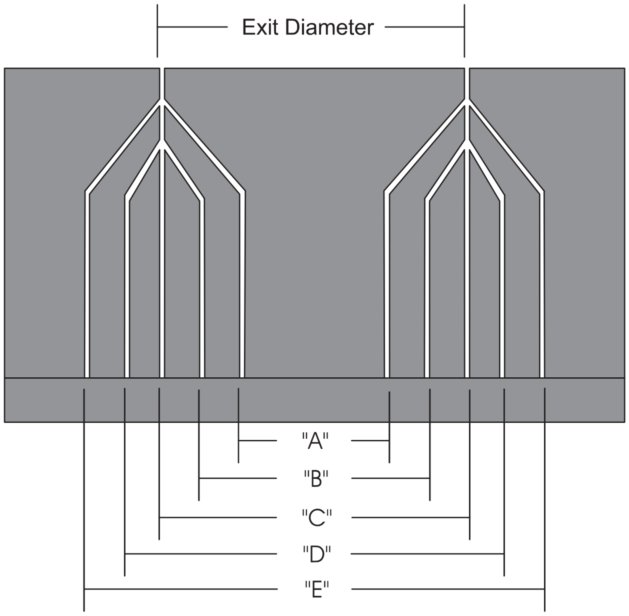

Fig. 7-2 Conventional coextrusion die consisting of five nested cylinders.

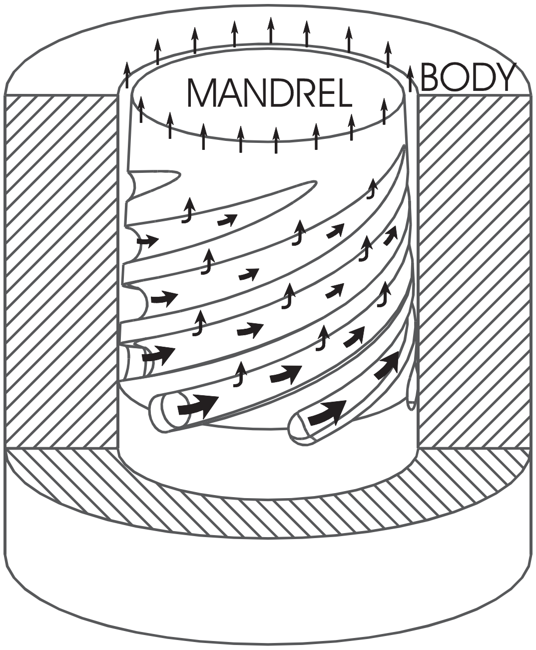

Fig. 7-3 Conventional cylindrical spiral mandrel distribution system.

have been successfully used for many years, the basic concentric cylinder design resulted in dramatically increased surface area as the layers increased [1]. This resulting larger surface to volume ratio has a higher degradation potential.

Stacked dies

In 1989, Brampton Engineering introduced a relatively new concept in coextrusion die design for conventional tubular (blown) film, which used a stacked layer distribution system. Unlike the conventional systems, the stacked dies arrange the layers vertically (Fig. 7-4).

It has been reported that some processors had developed similar systems for their own use, but it is believed that this was the first time that such technology was available commercially by an OEM for conventional blown film.

It should be pointed out that 'stacking' the layers is not a completely new concept. In fact, the 'stacked' configuration has been used with blow molding dies since the late 1950s and 1960s [2, 3]. However, these designs had some disadvantages which made them unattractive for blown film applications. In general, these designs used a simple side feed distribution system (Fig. 7-5).

The polymer is essentially split into two flow streams which are distributed around the die circumference and meet opposite to the entrance point. This would resemble a flat die distribution system that has been wrapped around so that the edges would connect. This distribution system, however, suffers from some drawbacks. First, where the streams merge, there is a stagnant flow region where the polymer could degrade. Second, the flow streams do not overlap as in a conventional spiral mandrel die. This means that the weld line orientation would be perpendicular to the die axis and was more likely to result in a weak point or a visual defect in the final product. In addition, the overlapping or layering provides some additional mixing. Having no overlapping makes the die more sensitive to any inhomogeneities in the melt stream from the extruder. For these reasons, it was desirable to incorporate

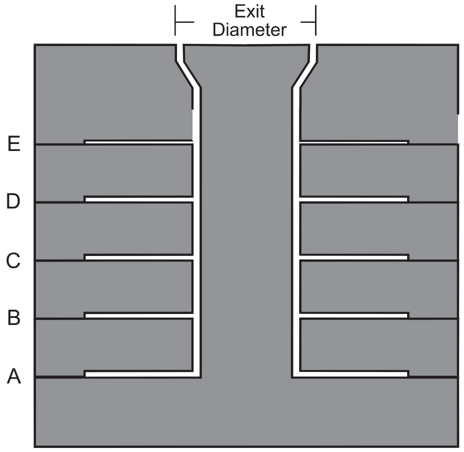

Fig. 7-4 Stacked type of coextrusion die.

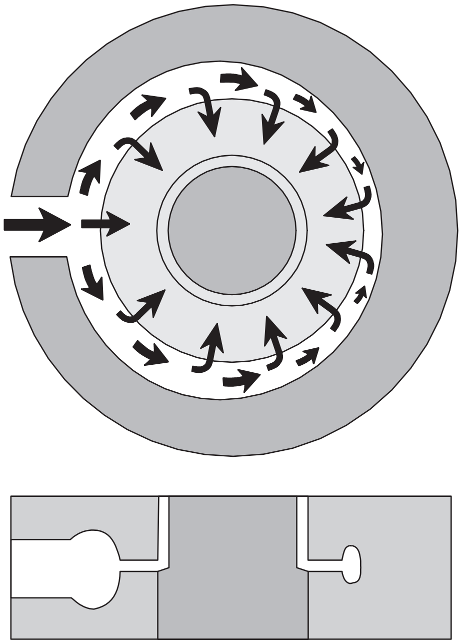

Fig. 7-5 A typical side-feed distribution system.

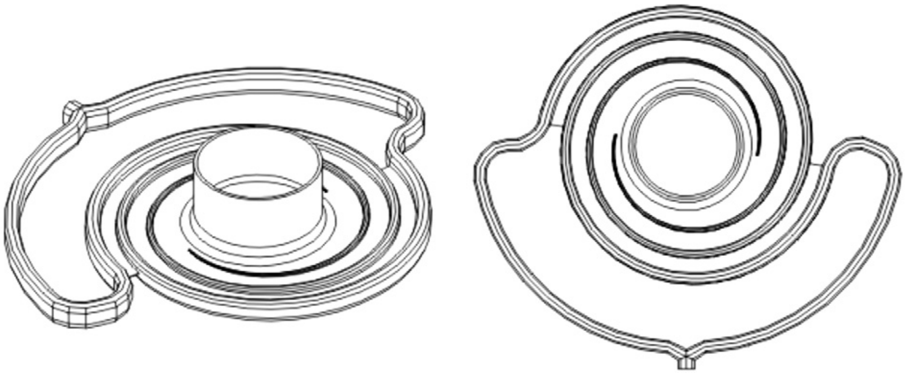

Fig. 7-6 A flat spiral distribution system with two spirals.

a spiral-type distribution system into this configuration. Fig. 7-6 shows a flat spiral distribution system used in a small, stacked die.

Fig. 7-7 is a drawing of a flat spiral distribution system with four spirals, each of which travels 360°.

In any spiral type die, it is highly desirable that the polymer entering the die be divided equally among the spirals. This is done with a binary distribution system prior to the spirals (Fig. 7-7 and 7-8). In the binary distribution system, the polymer entering the die is first divided into two identical flow streams. Then, each of these streams is also divided into two streams resulting in four streams of equal flow (see Fig. 7-7). This can be repeated again to get eight or 2^3 where '3' is the number of divisions or splits; hence the binary system. The flat spiral distribution system then distributes the flow in a similar manner, as would a conventional cylindrical spiral distribution system. The goal is to obtain a circumferentially uniform radial flow stream. This radial stream can then be redirected to flow in the die's axial direction and ultimately join with other layers prior to exiting the die. More details on this system can be found in a dissertation by Perdikoulias [4].

The primary advantage of the stacked die system was that it offered the potential to minimize each layer's wetted surface area, thereby minimizing the residence time and improving the system purge characteristics. Another advantage of the stacked die system was that it resulted in a modular die design, which had a few more potential advantages. First, it could, theoretically, allow a die to be more easily modified to conform to various structures by exchanging modules. The other potential advantage is that the individual flow modules could be operated at different temperatures so as not to expose thermally unstable materials to excessive temperatures for a prolonged period. These advantages have been successfully incorporated in tubular (blown) film dies of up to 10 discrete layers (Fig. 7-9) and possibly more.

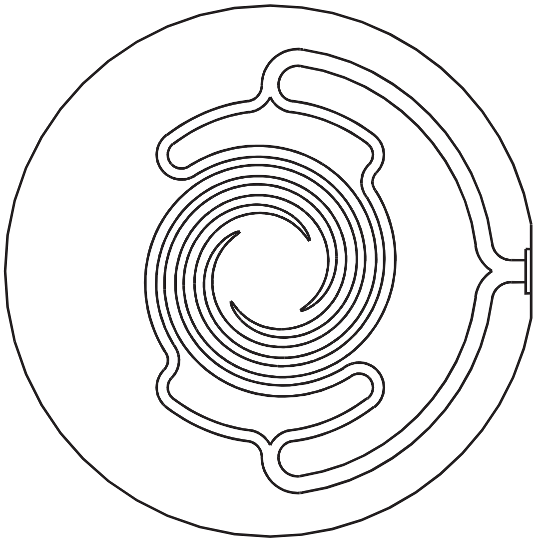

Fig. 7-7 A flat spiral type of distribution system with four spirals.

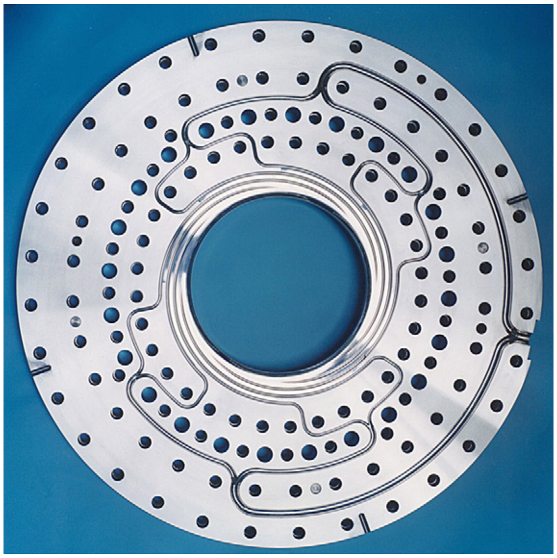

Fig. 7-8 A photo of a Brampton Engineering 'SCD' die distribution plate with eight spirals.

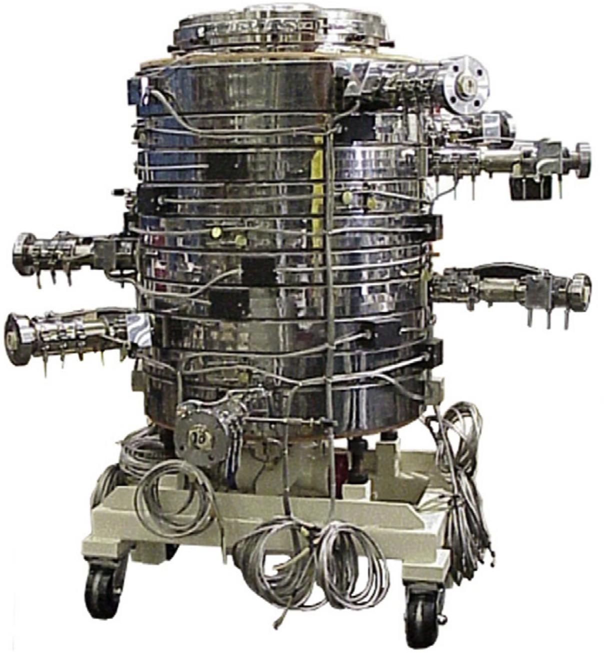

Fig. 7-9 Photo of Brampton Engineering 10-layer stacked die.

After the success of dies provided in the early 1990s, many manufactures followed suite and provided their own versions of stacked die systems [5, 6].

Interfacial instability

Along with the additional layers used in coextrusion, there can appear some additional and unique problems. The potential degradation problems and residence time distribution have been mentioned above. Another common problem is interfacial instability. When materials are coextruded, it is possible that the interface between the two materials does not always remain smooth and uniform. In fact, the phenomenon can be quite dramatic resulting in intermittent layer flow rendering the product useless.

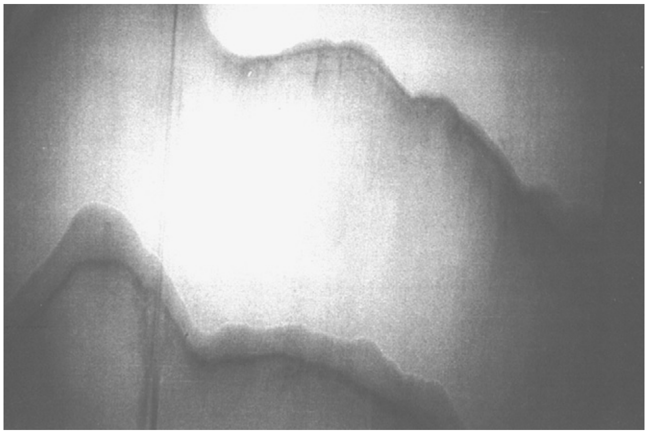

Fig. 7-10 Two-layer tubular film with interfacial instability.

Fig. 7-10 shows a two-layer film sample that exhibits strong interfacial instability. In one layer, carbon black at a low level has been added to assist visualization. If there were no instability, the film sample would have a uniform, gray appearance. Fig. 7-10 clearly shows that this is not the case. In fact, the dark ‘bands’ or ‘waves’ indicate that the carbon black layer has an erratic periodic flow behavior.

Instability phenomena in coextrusion have been the topic of many studies [4, 7–17]. However, it has only been relatively recently that the phenomenon was understood well enough for the development of die design criteria that could be used to correct or avoid the problem based on the material rheology and flow ratios [18–20]. There is now commercially available flow simulation software that can be used to predict the possibility of interfacial instability based on die geometry, material properties and processing conditions [21].

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Chapter 8

Process engineering

Eric Hatfield

MDO Engineering

Managerial summary

What process engineers do is one of the most misunderstood jobs of the engineering profession. Project engineers usually install equipment. Product engineers develop and enhance products for the customer. Maintenance engineers maintain and extend the life and reliability of manufacturing equipment. But what does a process engineer do?

The process engineer is the one who has the know how to take the raw materials that the product engineer feels the customer requires in his product and sets the operating conditions and runs it through the equipment the project engineer has installed. He/she has knowledge of materials and what process levers his equipment gives him to get the properties the customer desires.

A process engineer sees the manufacturing equipment and materials as one entity in a state of flux. To him/her the process is as if it is alive and he is the doctor who can adjust the conditions and inputs to get the desired healthy patient or product.

A process engineer usually (though far from always) reports to operations rather than engineering or R&D. His/her focus is on transforming raw materials to the finished product on the process in question. He/She does this in the most economic manner possible to get the highest quality product possible.

In short, a process engineer's job is to make more of a higher quality product for less money or cost.

Process engineering: What is it and why is it essential?

When your machine breaks down you call the maintenance engineer. When your customer wants to change a product you call your product engineer. When you cannot make the product correctly and are running scrap you call your process engineer.

The process engineer knows the strengths and limitations of the equipment and the product as it is being run on the equipment. The process engineer knows the age and wear on the extruder screws, nips, winders and other associated equipment and knows how long they can be pushed and what temperature and output adjustments need to be made as they wear.

Sometimes process engineering is confused with process control. With process control, a set point is maintained. However, a process engineer would select the set point.

Many (but by no means all) process engineers are educated as chemical engineers. Chemical reactions are in a state of flux, not static and this is how a process engineer must look at the process. It is in a state of flux with the raw materials reacting to the equipment and the conditions they are run at to get a film with the desired attributes.

Some tools of process engineers

There are a number of tools that a process engineer uses. Some of these are listed below.

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- *Engineering principles:* a process engineer applies engineering principles to what is happening to the raw materials as they go through the manufacturing equipment and are transformed into the finished product. He is not a big believer in making things as an 'art'. Everything has a scientific reason for why it happens. One just needs to figure it out.
- *Statistics:* a process engineer must deal with large quantities of often-conflicting data when troubleshooting a problem or getting a new product to run. Applying statistical techniques allows him to see 'the forest for the trees' and make scientific sense of the data.

  For example, using some simple data smoothing (e.g. moving average) for an extruder pressure fluctuation can reduce the noise in the data coming from the pressure transducer. Then, being able to determine more clearly the frequency and pressure fluctuations, the process engineer can go looking for other things in the process with similar frequencies and magnitudes.
- *Operator 'interrogation':* good operators often know what happened, but not always *why*. They are often taught and learn that if *that* happens do *this*. Many times this is the correct thing to do, however, they do not always know why they do *this* to fix *that*. A process engineer can take this knowledge and use it to learn the scientific reasons of why it works and also know when not to make the corrective action when it only appears to be the same problem.

  Operators and supervisors often see what is happening when a problem occurs. They will frequently draw their own conclusions as to what is making it happen. This can cloud the real cause and slow finding a solution for it. However, careful listening by the process engineer to what the operator has seen and done, along with the response, can quickly lead to the problem root cause. This requires tact, and careful questioning of the operator to get at the truth. Not unlike a detective questioning a witness.

  For example: suppose the film thickness is varying as much as 30% in the machine direction. The operator feels that this is because one extruder in the multilayer structure is surging. The process engineer checks the extruder in question and it is, indeed, surging, however, the layer is only 5% of the structure, the pressure surge was in the order of 15%. This is nowhere near enough to cause a 25% gauge change. Plus the frequency was repeating in a constant manner and the gauge variation frequency appeared to be random. Upon reviewing the other instruments, it was found that the first pull roll amps were surging a great deal. After tacking the roll speed it was found to be changing from 20 to 30%. Upon calling maintenance, it was discovered that the belt on the drive was loose and slipping. After getting this fixed and the line back into production, the process engineer can start investigating the cause of the extruder surging.
- *Data 'interrogation':* very similar to 'operator interrogation' as described above, a process engineer needs to be able to sort through a menagerie of data to find which things are important.
- *Past experience:* past experience is invaluable to the process engineer. A problem that one has seen in the past on a particular product or machine can rear its ugly head again.

  For example: the quality control (QC) laboratory technician tells the process engineer that the coex cereal liner film on one of the lines smells bad. This particular film has butylated hydroxytoluene (BHT) added to it for the customer. Past experience has shown when this happens the BHT had either exceeded its shelf-life or the extruder is running too hot. The process engineer checks the date on the BHT box and finds it is fine. He then looks at the melt temperature on the extruder and finds it too hot. After slowing the extruder down some and lowering some of the barrel temperatures, the foul odor is no longer in the film. Past experience permitted the process engineer to fix the problem quickly. If changing the extruder's temperature had not fixed the problem, then the process engineer would have had to dig deeper.
- *Knowledge of critical fitness for use (FFU) product demands:* knowledge of what properties are important to the film customer is important for the process engineer to understand. This knowledge allows him to know which problem to address first when confronted with multiple problems. It also tells him which properties to improve or make more robust when working continually to improve the film products.

  A process engineer is always running little experiments to see how the process responds and what happens to the final product. Most of these can be done while keeping the final product within its specification window. The results of these little experiments often permit the specification to be tightened to provide the film customer with a more uniform and consistent product.
- *An open, inquiring mind:* a process engineer needs to have most importantly an open and inquiring mind. In troubleshooting, he needs to listen to what is said by all and to review the data without prejudice and, when things seem to be running well, he continues to look for problems and interactions. Always studying the process and the multilayer film coming off the line.

Examples of how process engineers can save lots of time and money

- *Prioritize data or order of process changes:* when changes need to be made to the process, it is the process engineer who determines what changes to be made and in what order. This is only natural since he is the one who understands the process and its strengths and weaknesses the best.
- *Provide leadership and hands on training to operators and supervisors:* as the process engineer goes about his daily work of solving problems and running little experiments, he also teaches the front line supervisors and operators. This often just happens naturally since the process engineer is on the floor working next to the operator and having him make changes. Then the operator or supervisor is also there to see what the results are. This is in conjunction with the fact that often the process engineer is asked 'why' are we doing this? He then has a perfect opportunity to teach.
- *Take management goals to the bowels of the organization and explain them:* this is not commonly recognized and is normally not in a job description for a process engineer. In many cases, the process engineer is the best and often most efficient means of getting management information and strategy to the front line employees on the floor. This is because not only is the process engineer part of management and informed of upper management's plans and desires, he is also working side by side with the production operators. In many cases, they spend a great deal of time together troubleshooting and experimenting. This provides plenty of opportunity to talk and explain why management is doing certain things and what the company's plans and needs are.
- *Make R&D and new products work and aid in their commercialization:* in many cases, a new or enhanced product is first developed on a pilot line. When it comes to the manufacturing line, it is far from ready for day-to-day production. This is partly because the product development or R&D person has different priorities and perspective than those in manufacturing. (Remember the process engineer often reports through operations.)

  What is done making the product on the pilot line is just the beginning of turning it into a real product. The pilot line makes samples that are tested for the perceived attributes. It is then run on the customer's machine to see if it runs all right and the properties are indeed there. When it gets to the plant, it is in a rough form. Little or no thought has been given to operability, line speed, change over time, expected/possible yields, etc. In short, other than a raw material cost calculation versus selling price, little thought has gone into whether this product can be manufactured at a profit. This is where the process engineer goes to work.
  - Often different resin grades have been used. Sometimes this is necessary, but often it is not. A standard high density polyethylene (HDPE) grade can be used. This allows the plant to have fewer grades in the plant and allows purchasing to get lower prices by offering larger volumes.
  - The rate and yield at which a product can be produced must be determined and then pushed. Added to this, in many R&D pilot lines, or even trials on production machines, recycle is not put into the product. When the reclaim is added, the physical properties may change and the film may run differently on the customer's machine.
  - These are just a few of the areas that a process engineer must address to get the product to a commercial state that can be profitably produced.
- *Helps get new products accepted by plant:* many people are adverse to change and do not want to be bothered with trials for new products. Often the R&D guy is seen as an 'outsider' or 'from corporate'. It is the process engineer who acts as the go between and gets the new product into the plant's portfolio.
- *Bring new, or help implement technology onto the plant floor:* new technologies are brought to the plant in much the same way as new products are. The roll of the process engineer is much the same for new technologies as it is with new products.
- *Help QC and manufacturing address quality problems quickly and fix them:* QC technicians come to the process engineer first to fix a problem or the supervisor does after being informed of a possible quality problem.

Conclusion

The process engineer is the one that ties all the other engineering disciplines together to make the final product for the customer. He is the one that uses the equipment that is installed by the project engineer, to make the product out of the materials selected by the product engineer, to make the film for the final customer who, in turn, pays for it so the cycle can begin all over.

Chapter 9

9

Blown film, cast film and lamination processes

John R. Wagner, Jr.

Crescent Associates, Inc.

Blown film

Blown film is a major processing technique for producing a biaxial melt drawn film. This technique uses air pressure to produce a transverse direction (TD) draw and a higher speed haul off roll speed to provide a machine direction (MD) draw. Several billion pounds of polymer, mostly polyethylene, are processed annually by this technique [1]. Other polymers that can be processed by blown film extrusion are polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), ethylene vinyl acetate (EVA), ethylene vinyl alcohol (EVOH), polyamide (PA) and polyurethane (PU). Markets that blown film extrusion serves are:

- industrial films and bags
- agricultural and construction films
- barrier films
- stretch films
- PVC cling films
- laminating films
- can liners
- high barrier small tube systems.

Coextrusion to produce multilayer films is a major component of blown film production. Production line output goes from 100 pounds per hour (PPH) to 10 000 PPH. Coextrusion systems can have from two to nine extruders making two- to seventeen-layer films. If one has a four-extruder system, it is common to make a symmetrical seven-layer [ABCDCBA] structure from the four different polymers streams.

There are many manufacturers who produce excellent equipment for making multilayer blown films. Fig. 9-1 [2] is a simplified single-layer blown film line layout. Fig. 9-2 is a 3D overview of a seven-layer blown film line. Fig. 9-3 shows a nine-layer blown film die and bubble with three of the extruders. Fig. 9-4 shows a blown film tower and collapsed film going to the winder.

The components of a coextruded blown film line are:

- resin feed system
- extruders
- coextrusion die
- air ring

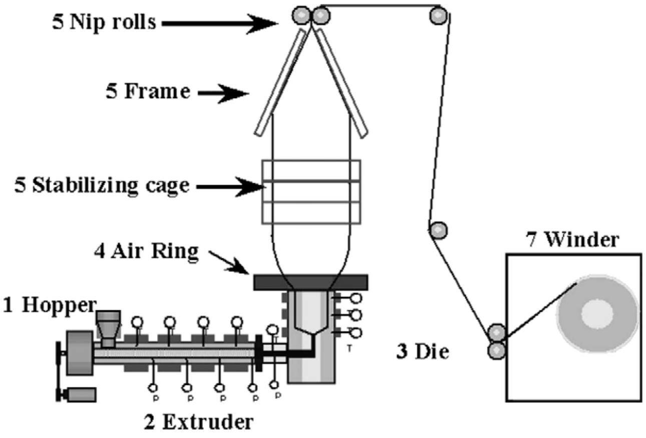

Fig. 9-1 Blown film process.

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Fig. 9-2 Seven-layer blown film 3D layout. Image provided by BE (Brampton Engineering) www.be-ca.com.

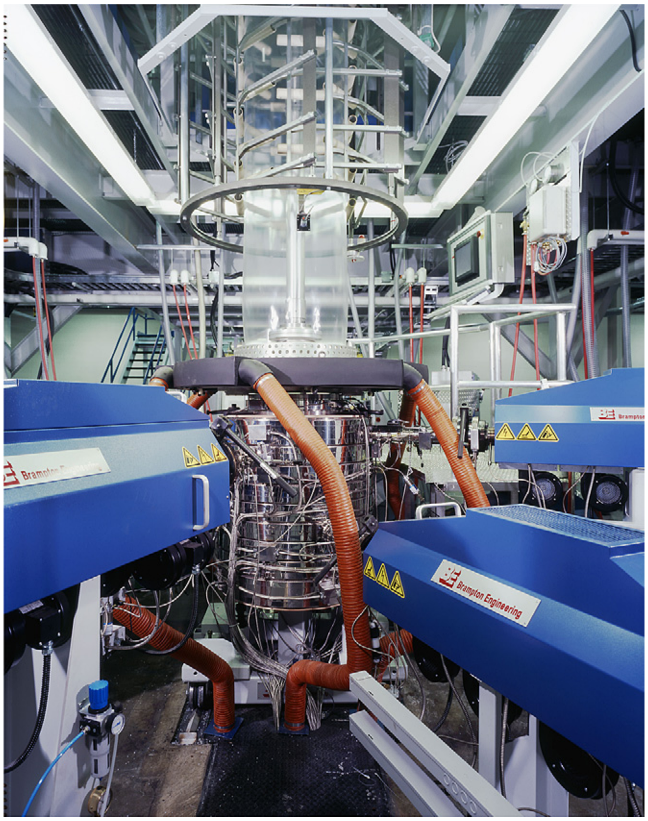


Fig. 9-3 Nine-layer blown film die and bubble. Image provided by BE (Brampton Engineering) www.be-ca.com.

Fig. 9-4 Blown film tower and collapsed film going to winder. Image provided by Davis-Standard http://www.davis-standard.com/.

- internal pressure control for adjusting bubble diameter
- collapsing frame
- take up or haul off roll which set the MD draw
- treatment system
- winder.

The design features that are important in producing quality film at a competitive price are:

- an efficient and properly sized resin handling and feed system
- an efficient screw design that gives quality melt with:
  - low and uniform temperature
  - stable pressure
  - at high rate
- an optimized die that provides good layer control and thickness uniformity. The die must also be designed for ease of maintenance and durability
- air rings that provide excellent cooling control and uniformity

- automated web handling systems for improved efficiency and reduced change over times
- modular design features for product changeovers
- integrated control systems that are intuitive, operator friendly and keep the process parameters on target.

For more detailed information, the reader can find many excellent works on the blown film process and operation. Guiles has a trouble shooting guide [3] and a blown film process description [4]. Butler et al [5] is an excellent reference. Vlachopoulos and Wagner [6] also have a chapter by Butler on the blown film process and troubleshooting. Calhoun in *SPE Plastics Technicians Toolbox Book 6* [7] has a chapter on blown film extrusion and Cantor in his book [1] includes a CD with a PE blown film simulation that is an excellent training aid.

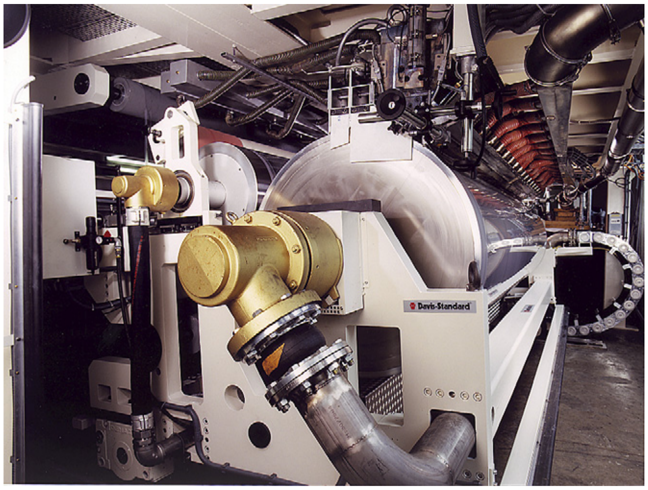


Fig. 9-6 Cast roll. Image provided by Davis-Standard http://www.davis-standard.com/.

Cast film

Compared to the blown film process, a cast film process quenches the molten extrudate on a chilled steel roller or rollers after it exits the die. Sheet can also be made by this process. However, with a sheet line, the line speeds are slower and there are multiple chill rolls to provide the required heat removal. The distinction between film and sheet usually is at 0.010" or ten mils (250 microns). Film is considered to be less than 0.010" and sheet greater than 0.010".

Fig. 9-5 [8] shows a schematic of the cast film process.

Different compatable resins can be combined with feedblock technology and/or in a multilayer die and extruded onto a chill roll where the film is solidified. There is usually a corona treatment station to enhance wettability and adhesion, plus a gauging system for measuring and controlling the gauge profile. A slitting section to remove the edge beads and then a combination slitter winder to make different width rolls. The trim is usually ground up and recycled back to one of the extruders.

Fig. 9-6 shows the die exit and first large chill roll and a second smaller chill roll. Fig. 9-7 shows the melt pipes that feed a multilayer die. In this case, there are four melt pipes for four different resins that can be combined in up to seven layers. Fig. 9-8 is a cast film winder that features in line slitting.

The reader is referred to references [3, 5, 6, 7] that provide more detailed information on the cast film process.

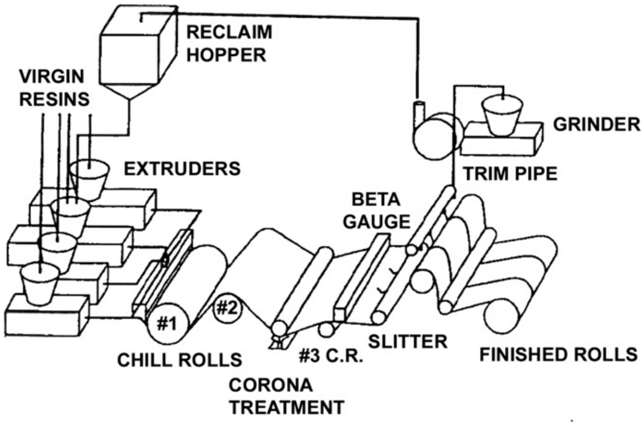


Fig. 9-5 Cast film process.

Fig. 9-7 Four melt pipes feeding multilayer die. Image provided by Davis-Standard http://www.davis-standard.com/.

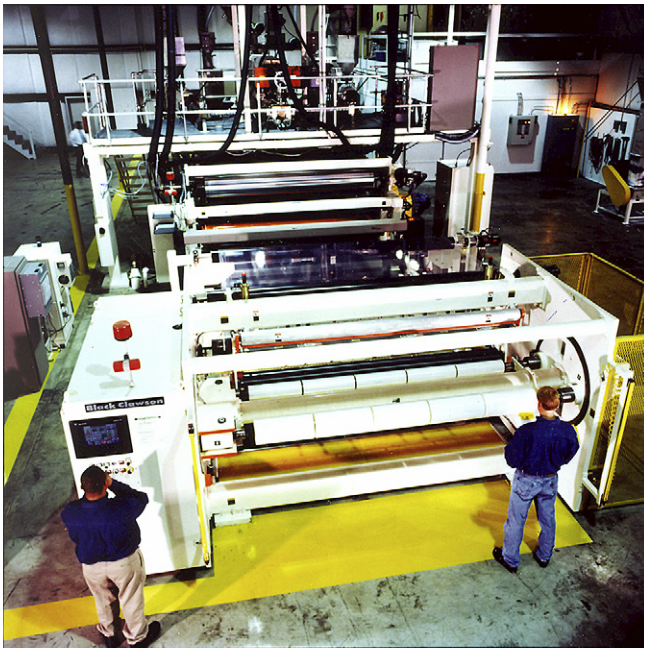


Fig. 9-8 Cast film winder. Image provided by Davis-Standard http://www.davis-standard.com/.

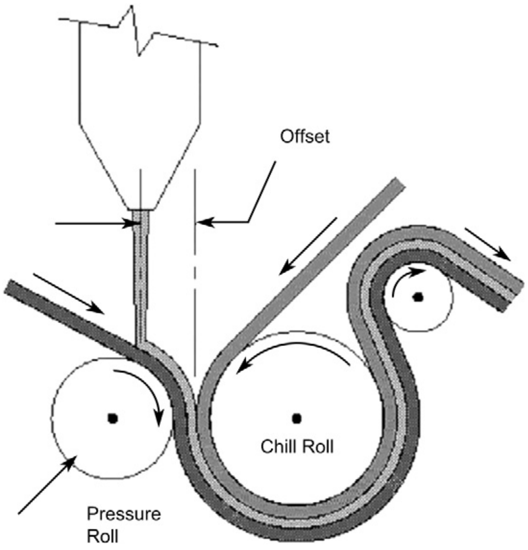
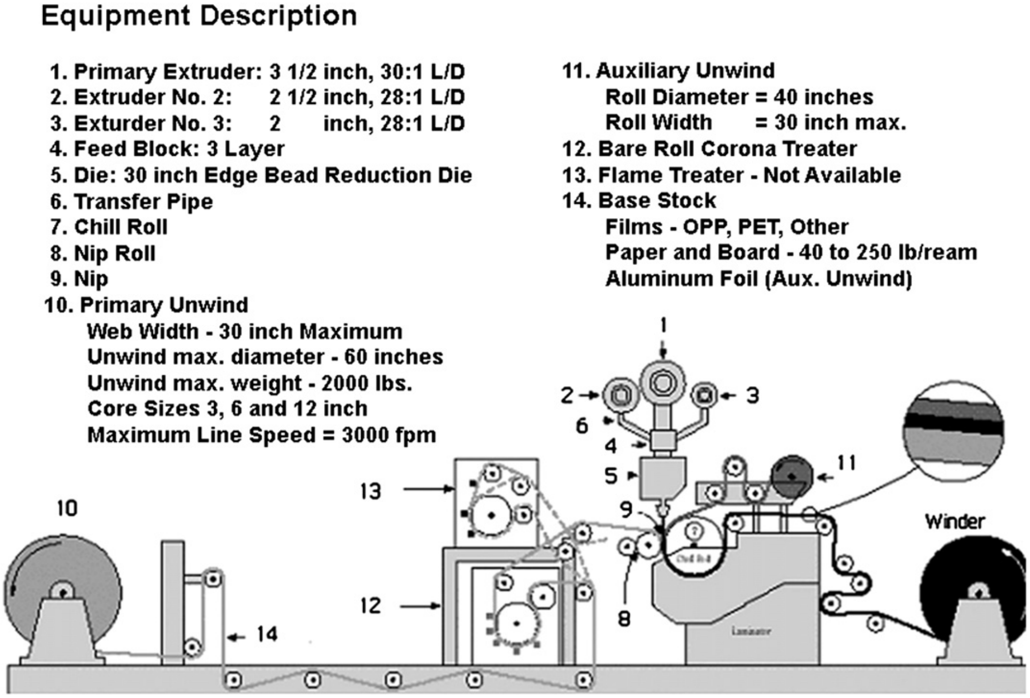


Fig. 9-9 Extrusion lamination detail.

Extrusion coating and lamination

The difference between extrusion coating and extrusion lamination is the presence of the second or auxiliary web that sandwiches the melt on the second side. For extrusion coating, only one substrate is used and the extrudate coats the surface and is quenched on a chill roll much like a cast film process. Fig. 9-9 [9] shows the detail for extrusion laminating where the auxiliary substrate is coming from the right side onto the chill roll and the extrudate is squeezed between the two substrates between the pressure roll and the chill roll.

Fig. 9-10 [9] shows a typical laboratory extrusion lamination line. This design has three extruders for



Equipment Description

1. Primary Extruder: 3 1/2 inch, 30:1 L/D
2. Extruder No. 2: 2 1/2 inch, 28:1 L/D
3. Exturder No. 3: 2 inch, 28:1 L/D
4. Feed Block: 3 Layer
5. Die: 30 inch Edge Bead Reduction Die
6. Transfer Pipe
7. Chill Roll
8. Nip Roll
9. Nip
10. Primary Unwind
    Web Width - 30 inch Maximum
    Unwind max. diameter - 60 inches
    Unwind max. weight - 2000 lbs.
    Core Sizes 3, 6 and 12 inch
    Maximum Line Speed = 3000 fpm
11. Auxiliary Unwind
    Roll Diameter = 40 inches
    Roll Width = 30 inch max.
12. Bare Roll Corona Treater
13. Flame Treater - Not Available
14. Base Stock
    Films - OPP, PET, Other
    Paper and Board - 40 to 250 lb/ream
    Aluminum Foil (Aux. Unwind)

Fig. 9-10 High speed laboratory extrusion lamination line.

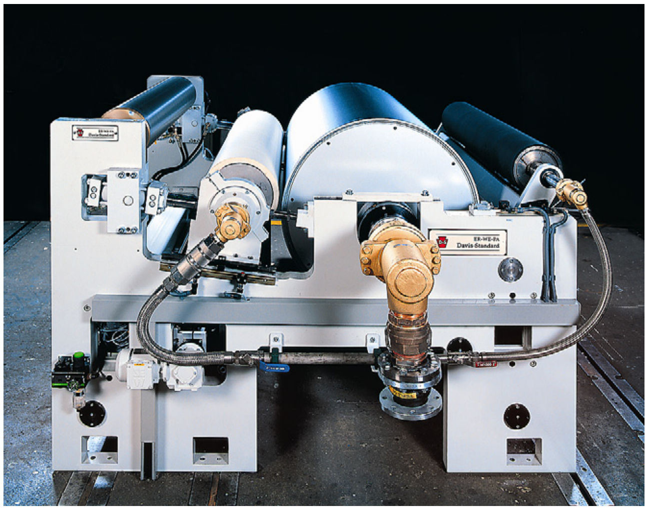


Fig. 9-11 Extrusion coating/laminating station. Image provided by Davis-Standard http://www.davis-standard.com/.

making multiple layers in the extrudate to facilitate the coated or laminated product properties.

Fig. 9-11 shows an extrusion coating/laminating station with a large cooling roll, incoming rubber backed cooled nip roller, cooled take off roll and idler tension measuring roll.

Fig. 9-12 shows a multilayer extrusion coating process in operation. You can see the main and two coextruders, combining block on the deckled single cavity die, chill roll and take off section.

Extrusion coating and laminating lines, like many processes, require:

- excellent melt quality
- proper configuration to fit products to be made
- good gauge control to promote high quality and economical resin usage
- automation to help maintain quality and repeatability
- flexible design to accommodate new products
- intuitive state of the art and updatable control systems to provide reliable process control.

Products typically made with extrusion coating and laminations are:

- lidding stock
- candy wrapper
- snack food bags
- medical packaging
- condiment packages
- soup sachets
- toothpaste tubes
- cable wrap.

The reader is referred to Cooper [9] and Giles [10] who provide further insight to this process.

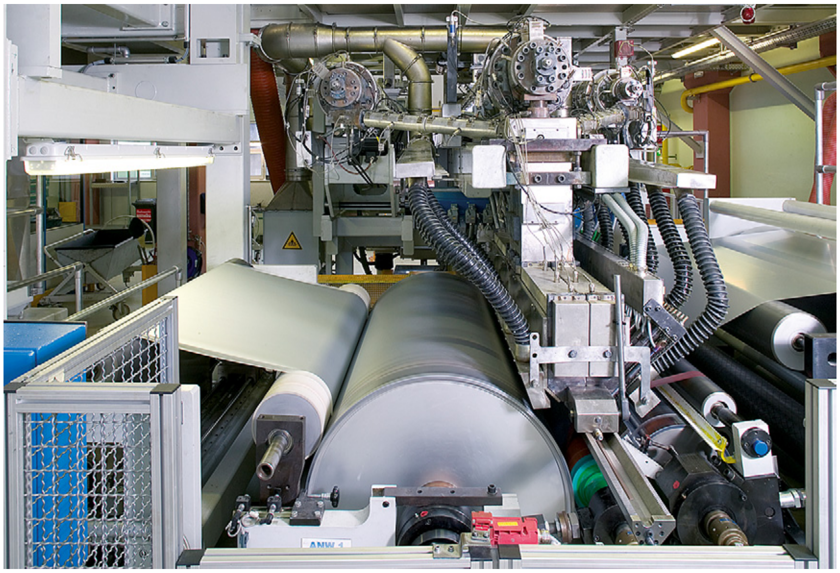


Fig. 9-12 Multilayer extrusion coating station in operation. Image provided by Davis-Standard http://www.davis-standard.com/.

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Chapter 10

Machine direction oriented film technology

Eric Hatfield

MDO Engineering

Managerial summary

Machine direction orientation (MDO) of films has been studied for decades. In the 1950s and 1960s, the academics studied property improvements when a film is stretched in the machine direction (MD). It has taken many years for industry to begin to commercialize the technology.

When a film is machine direction oriented, it is stretched in the machine direction only. In either simultaneous or sequential biaxial orientation, the film is stretched in both the machine direction and the transverse direction (TD).

An MDO machine is a stack of usually separately driven rolls mounted in side frames for support. The rolls are heated and/or cooled in separate temperature zones.

When a film is correctly machine direction oriented, many of its physical and barrier properties are greatly improved. For instance, the moisture barrier of high density polyethylene (HDPE) can be doubled. This can open the opportunity for down gauging or creating a film with much higher barrier at the same gauge.

Other film properties that can be improved are:

- optics: clarity, haze and gloss
- tensiles: increase in break and tear
- controlled shrink levels
- stiffness: secant modulus can increase from 2–3 times in both TD and MD directions.

The effect of this technology on multilayer flexible plastic films is to enhance their properties and increase the places where the advantages of multiple properties that you get from a single multilayer sheet can be utilized. Also some MDO products are best made as multilayer films.

Description of machine direction orientation hardware and technology

Machine direction orientation of film has been around for decades, but has been slow to gain prominence. This is due to the process subtleties that do not always appear to be straightforward. Despite this, there have been a number of unique (and profitable) products made using MDO.

Unlike the MDO *process*, the machine is relatively straightforward. The machine is basically a roll stack with separately driven rolls and multiple heat zones. A typical MDO will have 8–12 rolls.

The four sections in the MDO machine and process are

- *the preheat section:* these rolls heat the incoming film to the desired temperature for orientating the film.
- *the draw section:* in the draw section, the film is oriented, or drawn (stretched), between a set of rolls with, typically, a narrow gap between them. This gap

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is usually less than 3 mm and sometimes less than 1 mm. The rolls used in the draw section are usually smaller in diameter than the other rolls in the MDO. This is to get the tangent points closer together and thus reduce the distance over which the film is oriented.

- *the annealing section:* the annealing section heat sets or anneals the film to prevent it from shrinking back to its pre-oriented state.
- *the cooling section:* this section cools the film down from the annealing temperature to ambient and sends the film on downstream to the next process.

How a machine direction orientor works

There are four main steps or parts in an MDO (Fig. 10-1).

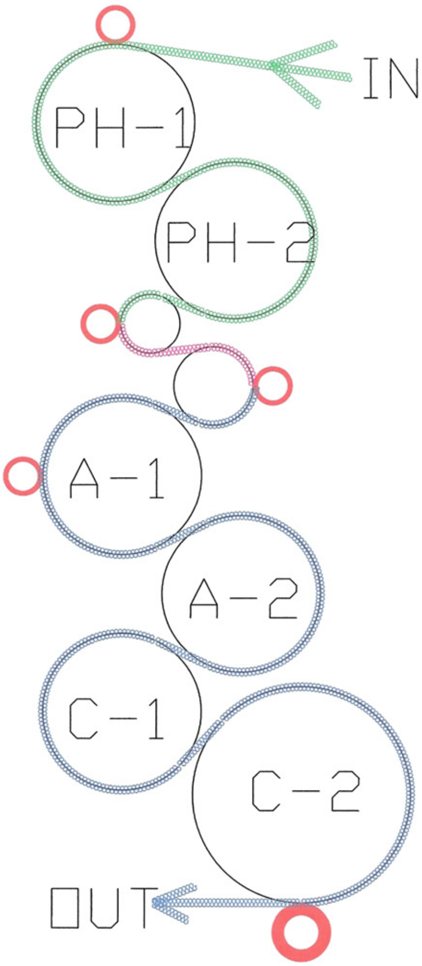

Fig. 10-1 MDO sketch.

Preheat

The preheat rolls are labeled PH-1 and PH-2. Their function is to raise the film temperature uniformly to orientation temperature without putting hard wrinkles into the film. The first preheat roll (PH-1) has a nip roll to control the incoming web tension.

Drawing

The draw rolls are the rolls between PH-2 and A-1. After the film is at the desired orienting temperature, it is stretched between the draw rolls. These are smaller diameter than the preheat rolls so that the distance between the tangent points is less. The gap between these rolls is adjustable for the gauge and desired film properties and appearance. The film can be stretched up to 10 times or more in this section. There are nip rolls on the slow roll and the fast roll for tension control.

Annealing

The annealing rolls are A-1 and A-2. This section heat sets the film and 'locks' the property changes from the orientation into the film. It also controls how much the film will shrink back when later exposed to heat. There is a nip roll on the first annealing roll for tension control.

Cooling

The last section (rolls C-1 and C-2) cools the film to near ambient temperature.

The process and its effect on the film

The film is heated to increase the polymer molecular mobility. This permits the film to be drawn at higher draw ratios. The film properties are a function of the orientation temperature.

There are various theories as to what happens on the molecular level when film is stretched. The one presented here has been used for HDPE and can be extrapolated to other polymers.

Before film is oriented via MDO, it has regions of ordered crystals (Fig. 10-2). These are tied together with molecules that go from one crystal, through the adjacent amorphous region, into another crystal. Around the crystals are amorphous regions where the molecules are arranged randomly. The crystals are plates where the molecules are tilted at an angle (34.4°) [1] to the film surface.

As the film is stretched in the machine direction, the random amorphous molecules begin to align themselves

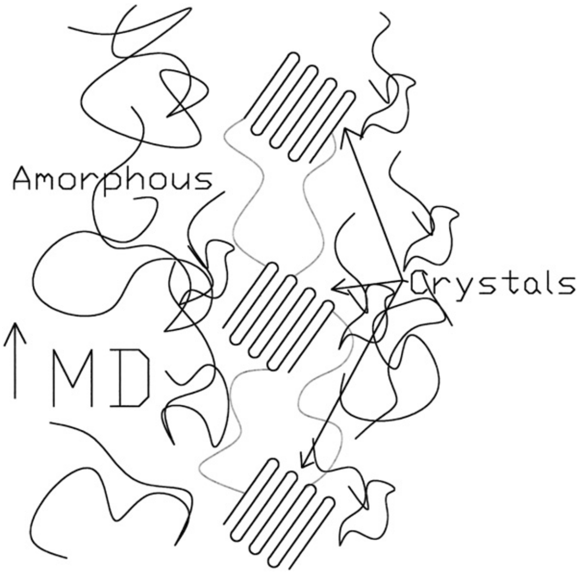

Fig. 10-2 Crystal and amorphous arrangement before orientation.

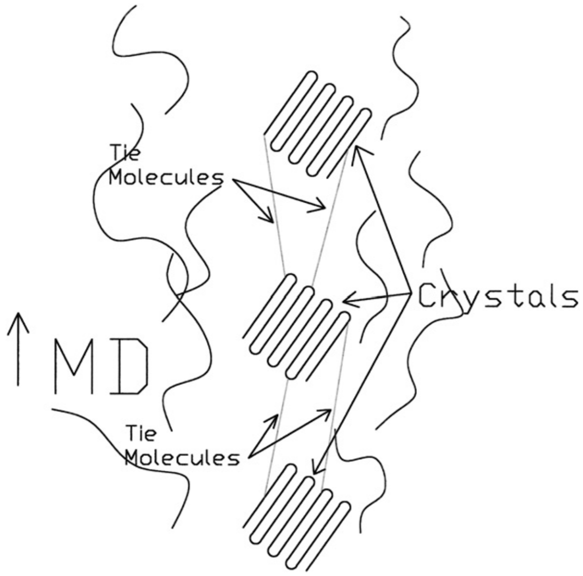

Fig. 10-4 Continued tie molecule orientation as the polymer is stretched further.

in the orientation direction (Fig. 10-3). This orientation continues until the molecules tying the crystals together are fully extended (Fig. 10-4).

In the next orientation phase, the angle or tilt of the molecules within the crystals changes such that they are aligned parallel to the film surface (Fig. 10-5).

In the third orientation phase, the crystals begin to unravel. This continues until the film breaks.

The above orientation phases take place at different draw ratios for different resins. This results in different properties. For a coextrusion, properties can be optimized at a given draw ratio using different resins in the individual layers.

Properties of machine direction oriented films

The following properties can be improved when a coextruded film is oriented in the machine direction:

- optics: clarity, haze and gloss
- tensiles: increase in break and tear

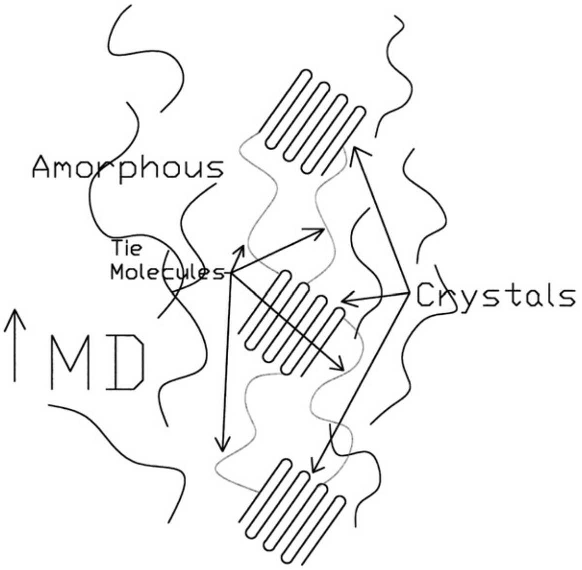

Fig. 10-3 Initial tie molecule orientation as the polymer starts to be stretched.

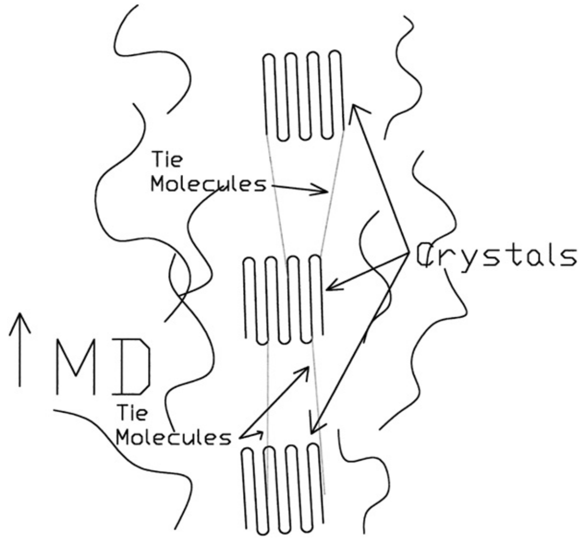

Fig. 10-5 Fully stretched tie molecules rotate crystals to bring them into alignment.

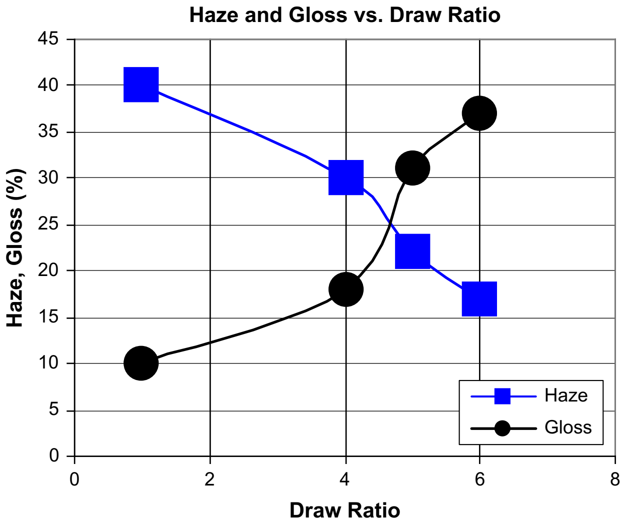

Fig. 10-6 Haze and gloss versus MDO draw ratio [2].

- controlled shrink levels
- stiffness: secant modulus can increase from 2 × to 3 × in both TD and MD directions inclusively
- barrier: both oxygen and water vapor
- dead fold
- film 'toughness' and ability to withstand puncture and heavy loads.

Detailed data for some of the properties follows.

Improved optics

In Fig. 10-6, one can see how the haze decreases and gloss increases as the draw ratio is increased to 6.

This improvement is demonstrated in the see through clarity which is shown in Fig. 10-7 (un-oriented film) and 10-8 (oriented film).

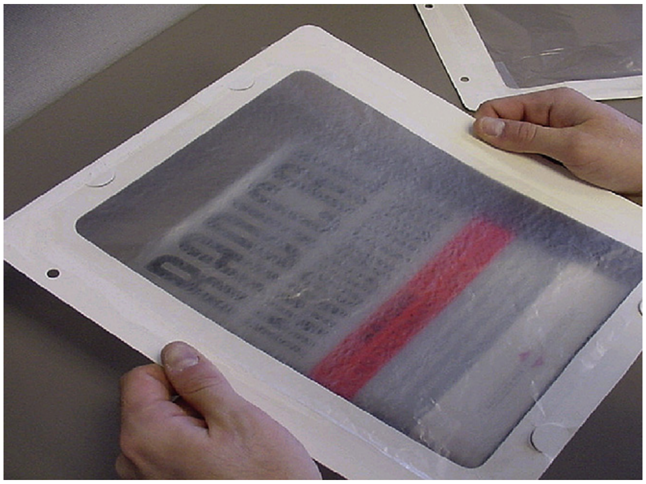

Fig. 10-7 Poor see through clarity of un-oriented film [2].

Fig. 10-8 Improved see through clarity of oriented film [2].

Increased tensiles

Fig. 10-9 shows the MDO tensile strength at break is greatly increased when linear low density polyethylene (LLDPE) is oriented in the machine direction. The TD tensile strength at break is only slightly reduced. Unlike HDPE, the TD elongation to break is still several hundred percent. When an item is packaged in an MDO film, such as the one in Fig. 10-9, the film must elongate in both the TD and MD directions. This permits the much higher MD tensile strength to come into play. This creates a much tougher package.

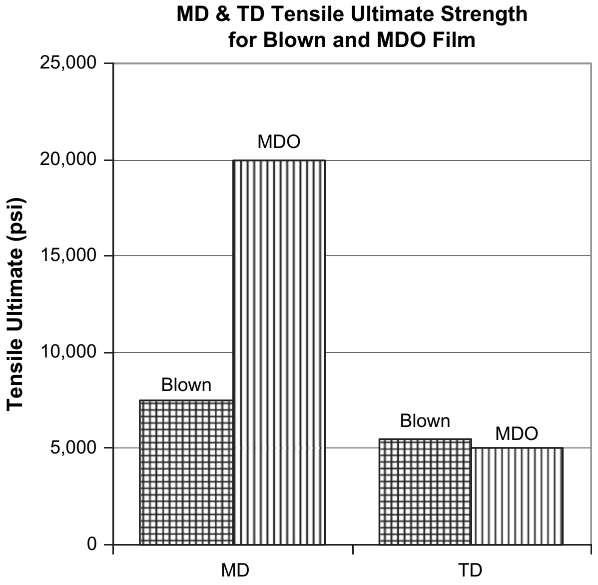

Fig. 10-9 MD and TD tensile ultimate strength for blown and MD oriented LLDPE [3].

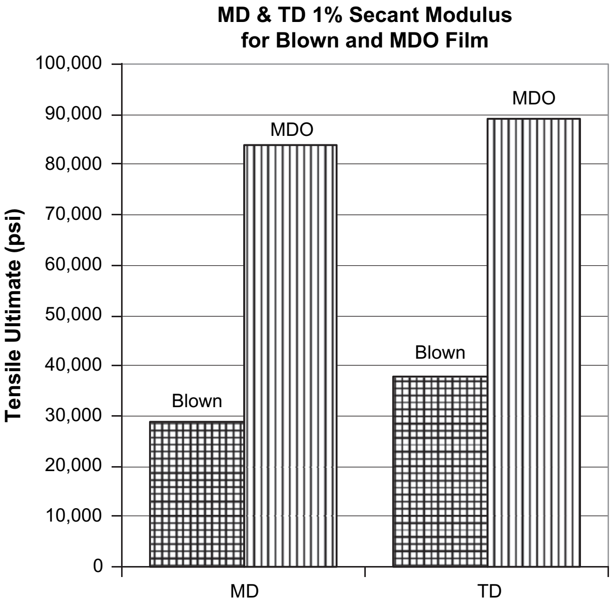

Fig. 10-10 MD and TD 1% secant modulus for blown and MD oriented LLDPE [3].

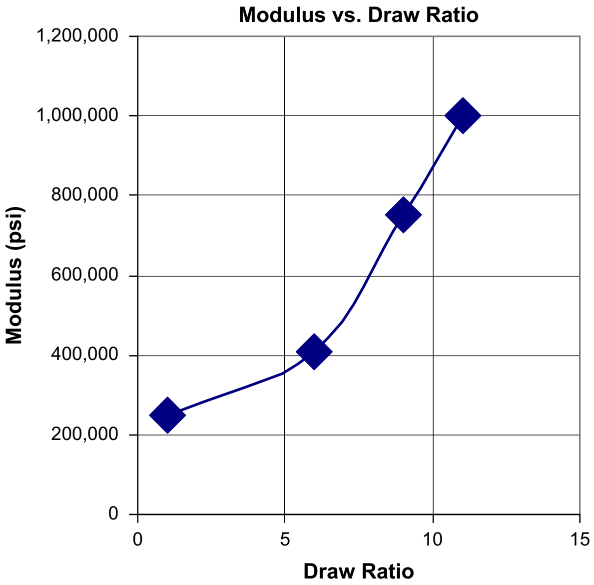

Fig. 10-11 MD modulus versus draw ratio for HMW HDPE [4].

Improved stiffness

The stiffness (as measured by secant modulus) is greatly increased for both LLDPE and HDPE. Fig. 10-10 presents secant modulus versus MD orientation for LLDPE and Fig. 10-11 shows MD modulus versus draw ratio for HDPE.

Improved barrier properties

When HDPE and LLDPE are MD oriented, their oxygen and water vapor barrier properties are increased two times or more. Table 10-1 shows the moisture barrier improvement for 2 mil LLDPE film after machine direction orientation and for 1.5 mil HDPE film at 6:1 draw ratio. Similar improvements are seen in oxygen transmission rates.

Table 10-1 Moisture barrier improvement for 2 mil LLDPE film after machine direction orientation and for 1.5 mil HDPE film at 6:1 draw ratio

	WVTR (gm/100 in^2 – 24 h/atm)	
	No MDO	**MDO**
LLDPE (2 mil)	0.95	0.56
HDPE (1.5 mil)	0.27	0.14

Summary

Putting films through the MDO process greatly enhances their properties. Barrier properties, both water and oxygen, can be doubled with the right orientation and annealing conditions. Film stiffness (measured by secant modulus) can be increased by two to three times and, in some cases, four times.

Optical properties (haze, gloss and clarity) can also be enhanced, as well as tensile properties. Films can also be made with controlled shrink levels and temperature.

The MDO machine is relatively simple in nature. However, the process conditions and materials selected can be far from straightforward.

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Chapter 11

Oriented film technology

Jürgen Breil

Introduction

Today, oriented plastic films are produced industrially in large quantities. As such, the majority are biaxially oriented, i.e. films are stretched in both directions, which is understandable when taking the improvement in characteristics into consideration [1]. The characteristics attained with biaxially oriented films ideally meet the demands on modern flexible packaging. As illustrated in Fig. 11-1, flexible packaging has to fulfil the protective function and product design in line with economic and, increasingly, environmental aspects. The required packaging product protection is attained by the excellent barrier properties against gases (water vapor, oxygen and others) as well as good quality seals. The product appearance is attained by high-gloss and transparent thin packaging film as well as by excellent printability. The requirements for sought-after economic packaging are met by good material utilization and the fulfilment of the demand for high-speed packaging lines. Environmental aspects, which play an ever increasing role, can be satisfied by utilizing environmentally-friendly materials (such as polyolefin), as well as the optimum raw material yield, thus ensuring maximum packaging effect with minimum material cost.

To what extent biaxial orientation improves properties is shown in Fig. 11-2 using biaxial oriented polypropylene as an example. Along with a significant increase in the mechanical properties (Young's modulus, tensile strength), a considerable improvement in the optical (haze, gloss) as well as the barrier properties can be seen. The overall improved barrier properties attained are due to the orientation of the molecule chains which, for a non-oriented polymer, are random, whereas in the stretching process, a clear molecule chain orientation occurs. As such, biaxial orientation of plastic films represents a refinement process which is applicable for almost all plastics. Semicrystalline plastics in particular, such as polypropylene (PP) and polyester, also augment the crystallinity by the stretching process, which considerably improves the mechanical values.

Fig. 11-3 shows the increase of the Young's-modulus in machine and transverse direction as a result of the biaxial orientation process for polypropylene and polyester. The exceptional mechanical properties in combination with the barrier and optical properties with comparably low raw material costs have led to the fact that biaxially oriented polypropylene (BOPP) and biaxially oriented polyethylene terephthalate (BOPET) films account for the largest and most significant share among stretched films.

Orienting technologies

In orienting technologies, one can, in general, differentiate between the orientation draw direction and the related stretching process. The stretching processes shown in Fig. 11-4 (longitudinal, transverse stretching, sequential-biaxial stretching, simultaneous-biaxial stretching) do not depict competitive, but rather supplementary features in order to attain specific film characteristics. As such, the required stretching equipment varies depending on the process. Stretching in machine direction is normally

Multilayer Flexible Packaging; ISBN: 9780815520214

Fig. 11-1 Flexible packaging requirements for protection, promotion, health/environment and economics.

done by means of a machine direction orienter (MDO) via rolls with increasing speed. Typical products are, for example, tear stripes or polypropylene adhesive tapes. For all transverse oriented films, the stretching process takes place by means of a transverse direction orienter (TDO), where the film is fixed on both ends and, upon passing through an oven at various temperatures, is stretched in a transverse direction. Typical examples of transverse stretched film types are shrink sleeves, where shrinkage merely occurs in the transverse direction. Biaxial orientation, in the machine and transverse direction, can be done either sequentially or simultaneously. In the sequential process, an MDO and a tenter frame are successively utilized [2, 3]. This process has the widest

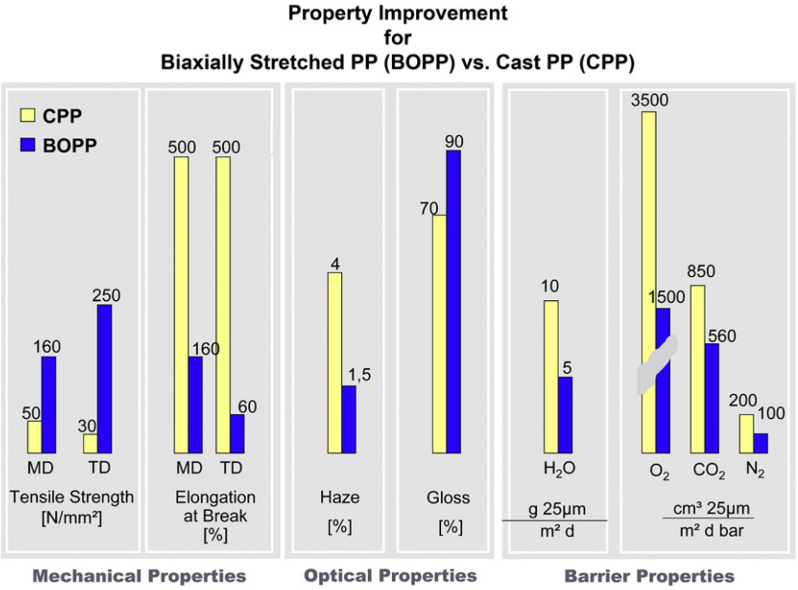


Fig. 11-2 Property improvement for biaxially stretched PP (BOPP) versus cast PP (CPP).

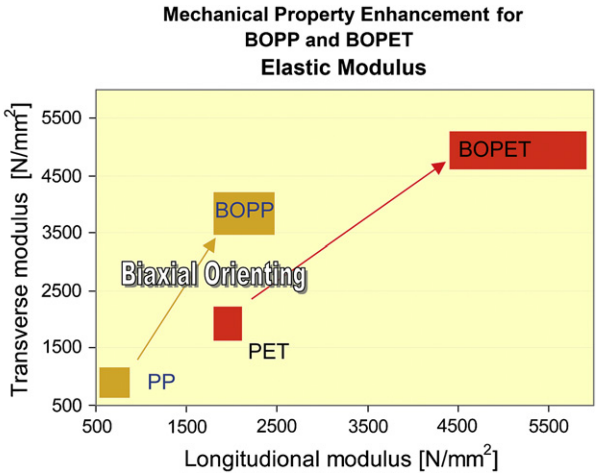


Fig. 11-3 Mechanical property enhancement for BOPP and BOPET.

prevalence for all stretched film types. All types of packaging films, tapes, labels and industrial films are manufactured with this process.

Simultaneous orientation, however, is possible with the tenter and the blown process (Fig. 11-5). The blown process is a so-called double bubble process where, initially, a tube is extruded, then rapidly cooled and then heated to the stretching temperature. A synchronous increase of the draw off speed and bubble expansion by internal pressure results in the required simultaneous orientation process.

Sequential stretching first in the machine direction and then in the transverse direction utilizing an MDO and TDO is the most prevalent process in use today. Fig. 11-6 is a cut away view of a three-layer coextruded BOPP line that shows the main extruder, two coextruders, die and casting station, MDO, TDO, gauging station, treatment and full width winder. Fig. 11-7 shows a typical BOPP process temperature profile. First, the PP resin is melted in the extruders, then quenched on the casting roll, transferred to the MDO where it is reheated and stretched in the machine direction. There is some annealing between the MDO and TDO. In the TDO, the web is reheated before transverse stretching, annealed and cooled down before winding. Fig. 11-8 shows a production line MDO and entrance to the TDO. Fig. 11-9 show a finished 10 meter mill roll after being removed from the winder.

Simultaneous orienting technology represents an alternative to the prevalent sequential orientation. Fig. 11-10 compares for BOPP the useable range for the stretch ratios between the sequential and simultaneous processes.

In sequential orientation, the stretching process occurs in two steps and a relatively small process window in terms of temperatures and stretching ratios is available. During simultaneous stretching, however, the usable stretching ratios are considerably larger. For instance, in machine and transverse direction, it is possible to set identical stretching ratios or even realize a higher stretching ratio in machine direction in order to achieve improved machine direction mechanical properties. A further advantage is the possibility to relax in simultaneous orientation by diminishing the clip spacing, not only in machine but also in transverse direction. Furthermore, it can be emphasized that, as a contact-free process, simultaneous orientation avoids the limitations of stretching via rolls. Such differences lead to several advantages in terms of the product characteristics as

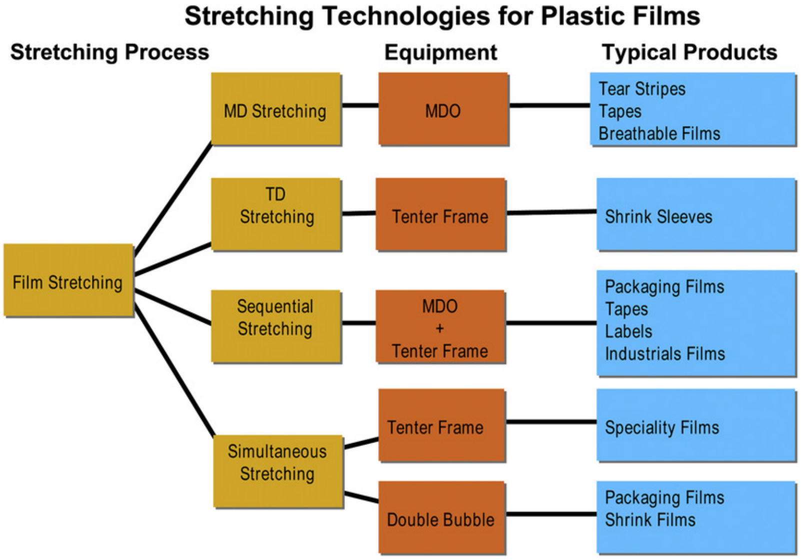


Fig. 11-4 Plastic film stretching.

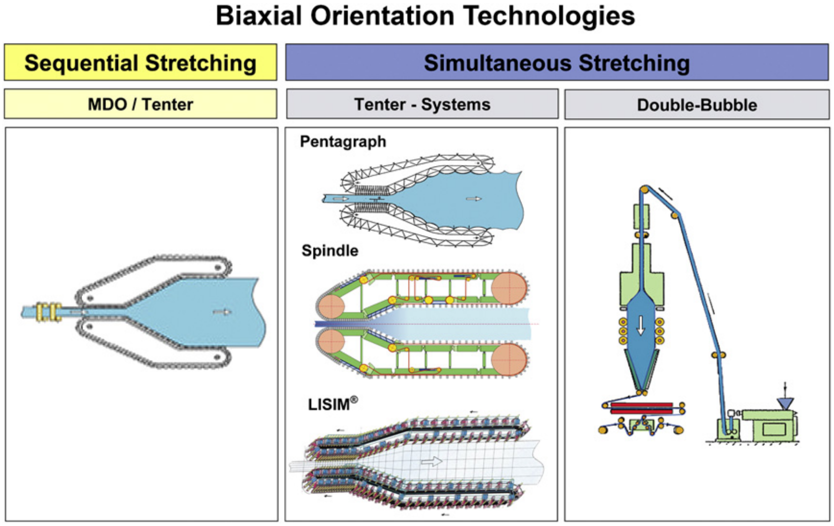


Fig. 11-5 Biaxial orientation.

shown in Fig. 11-11. In particular, a new developed system called LISIM® (linear motor simultaneous stretching system) offers the following advantages [4]:

- high productivity (speed, width)
- high flexibility (stretching ratios, relaxation rates) in MD and TD direction
- high reliability.

These features are achieved by individually driven clips with linear motor technology. The improved mechanical properties are due to higher stretching ratios. The shrink characteristics are controlled by the unrestricted relaxation and tensilizing stretching possibilities. Barrier properties can be improved upon considerably by using coextruded barrier materials, where the process is particularly advantageous for those materials which cannot be stretched sequentially due to the crystallinity created by the first MD stretching process. Improved sealing properties are made possible because low seal temperature copolymers can be applied. These low temperature heat sealing polymers are not processable in a standard MDO as they stick to the rolls during machine direction orientation. LISIM® technology has been scaled up from laboratory scale to production line dimension. Lines equipped with this technology for the production of polypropylene and polyester film have been running successfully and reliably for several years. The overall line layout is shown in Fig. 11-12. Apart from the orienter, the components of such a line are similar to those of a sequential line. In

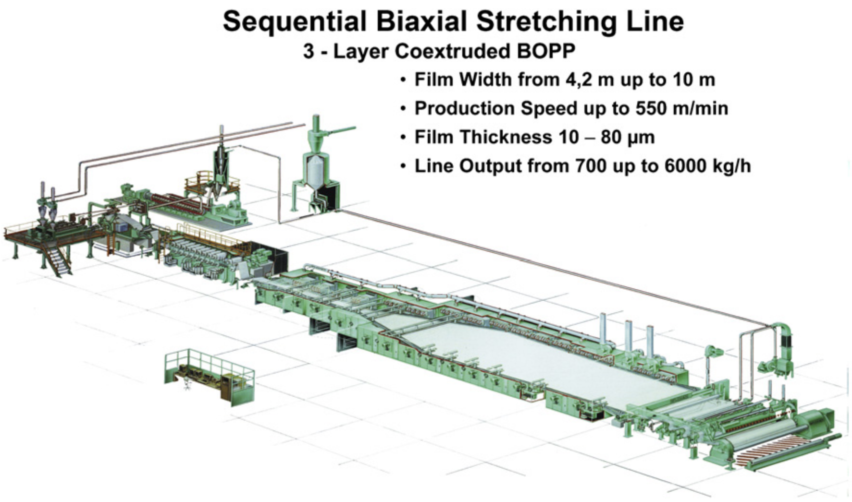


Fig. 11-6 A three-layer coextruded BOPP sequential stretching line.

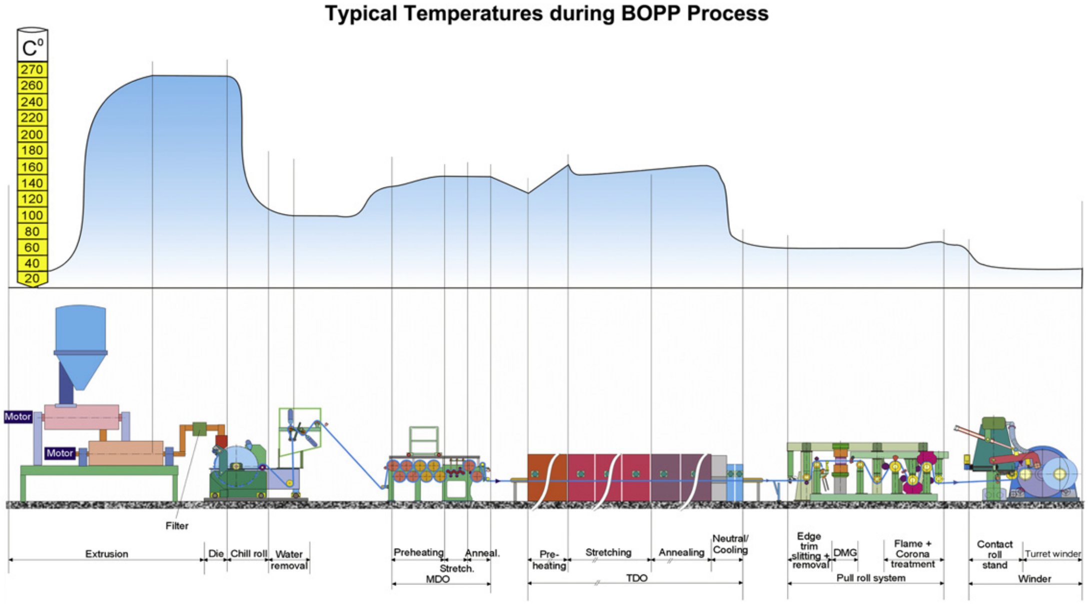


Fig. 11-7 Typical temperatures during the BOPP process.

Fig. 11-8 Machine direction orienter with entrance.

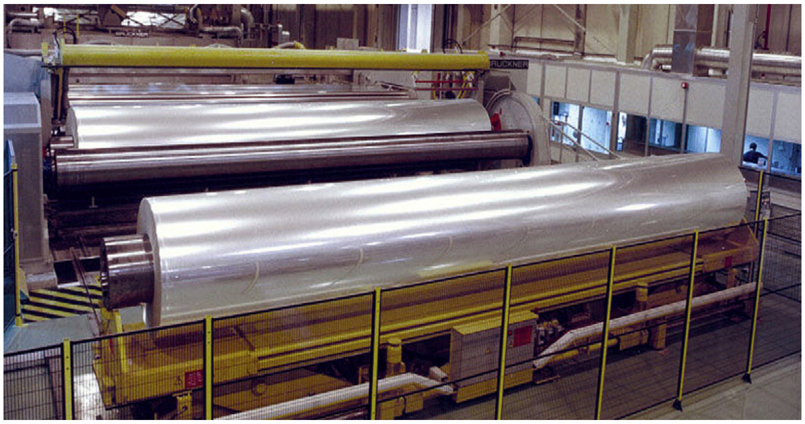


Fig. 11-9 Finished 10 meter BOPP mill.

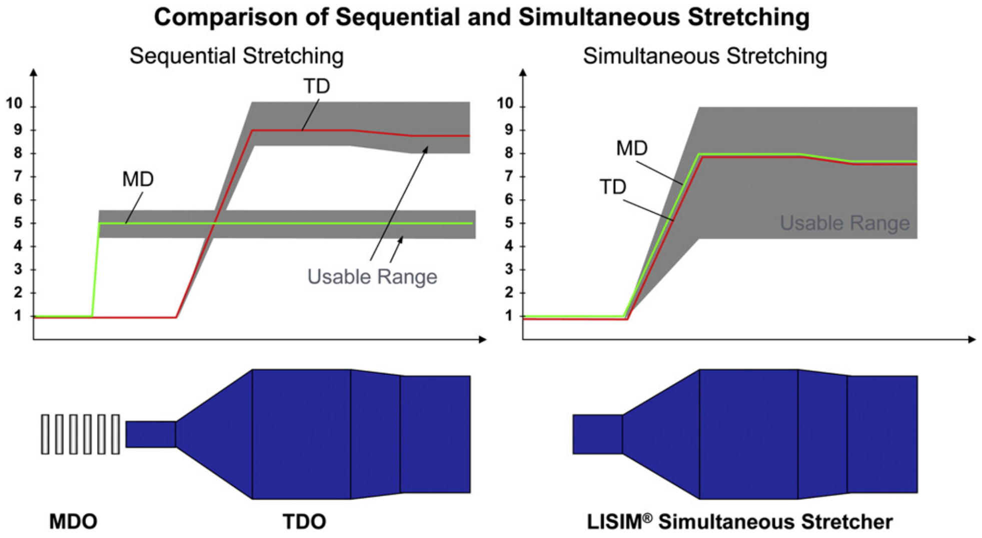


Fig. 11-10 Useable stretch ratios for sequential and simultaneous stretching.

particular, those components at the front end, i.e. raw material supply, extrusion and casting unit as well as those at the rear, i.e. pull roll and winder are, apart from minor details, identical. Only the orienter components are different. Instead of MDO and TDO, a simultaneous orienter is applied. Typical output figures for sequential and simultaneous stretching equipment, representing today's state of the art are shown in the list that follows. Basically, in terms of output data, it can be said that the efficiency of these high-speed lines is increasing, since the output capacity for certain film thicknesses is merely a matter of speed and working width. Over the past 40 years, ever since this technology was implemented on an industrial scale, constant efforts have been made not only to increase the working width but also the line speed. As such, new technological challenges are constantly arising with the aim to overcome the bottle necks in the line components. Today, the state of the art for BOPP lines features:

- working width 10 m
- speed 530 m/min
- output capacity 6000 kg/h

The trend for even higher output capacities will continue in the future. Nowadays, line concepts for even higher speeds and output capacities of 7 tons per hour and above are being designed.

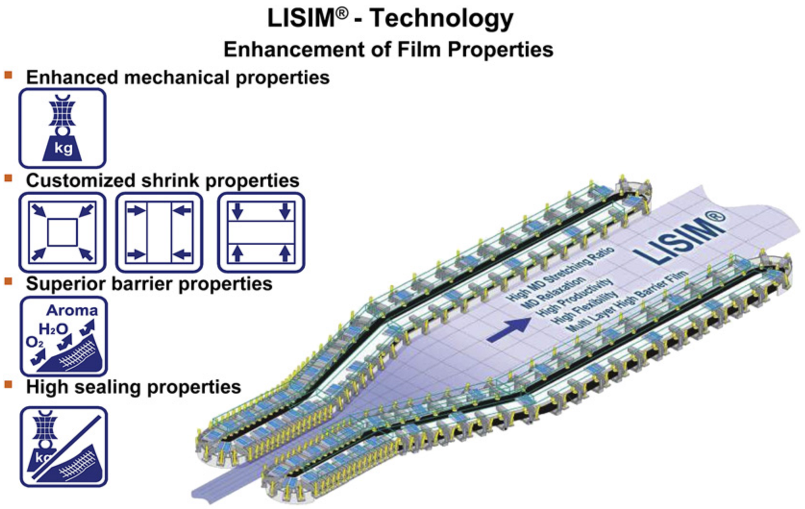


Fig. 11-11 Enhanced film property possibilities with LISIM®.

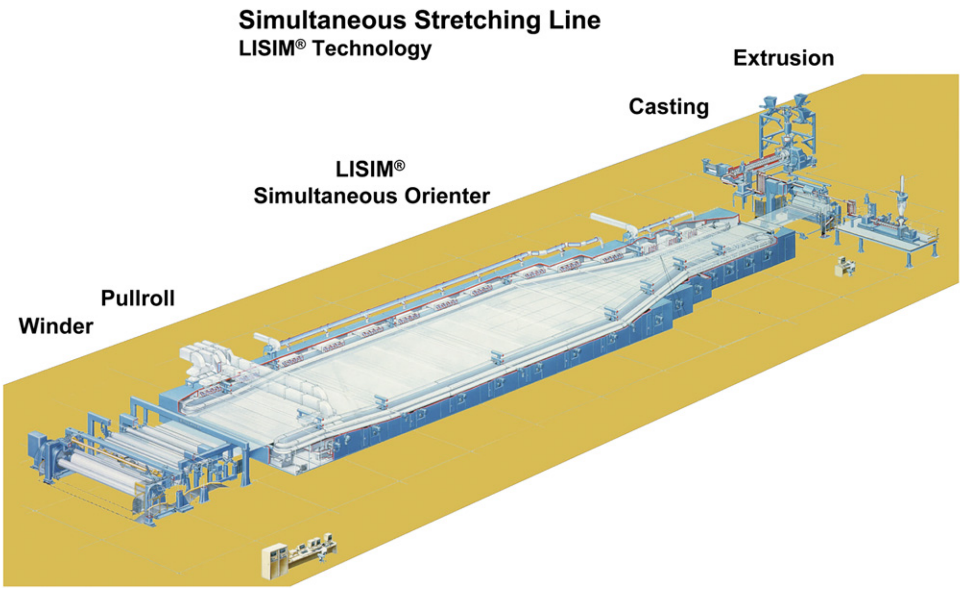


Fig. 11-12 Simultaneous stretching line.

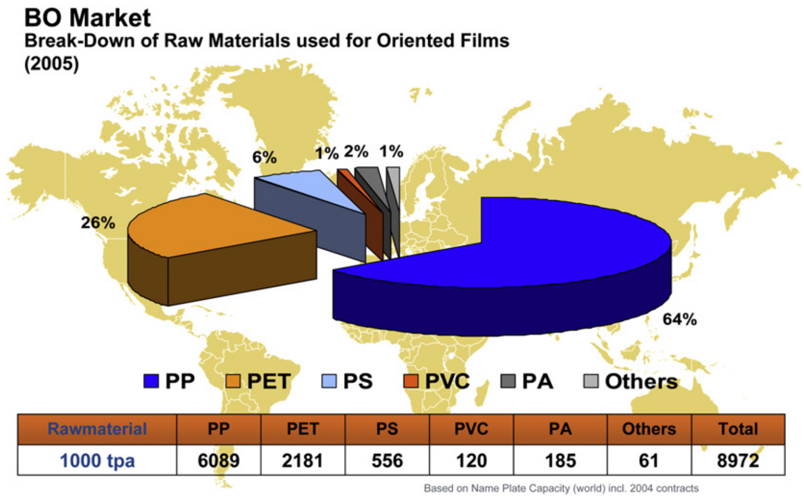
Oriented film types – applications

In addition to the orientation technology outlined previously, the film products and their applications will now be explained. In most cases, stretched films for packaging applications are further processed. The most significant converting processes are vacuum coating (metallizing, SiOx, AlOx), offline coating (acrylic, polyvinylidene chloride (PVDC), polyvinyl alcohol (PVOH) etc.), lamination with other stretched films, polyethylene (PE) sealing layers and printing (front printing, reverse printing). Such downstream processing will not be discussed in this chapter.

Considering the market for oriented films in general, the various raw materials used can be distinguished. Fig. 11-13 shows a breakdown of oriented films manufactured worldwide. Biaxially oriented PP film constitutes by far the largest share with over 6 million tons per annum. In view of the favorable relation between raw material prices and film properties, it can be assumed that the steady growth of 7% per annum will continue. Biaxially oriented PET film has the second largest share followed by polystyrene (PS), polyvinylchloride (PVC) and polyamide (PA).

Films oriented biaxially

Among oriented films, the biaxial orientation is the most preferred technology as it leads to improved properties in both (MD and TD) directions. This can be recognized by



Rawmaterial	PP	PET	PS	PVC	PA	Others	Total
1000 tpa	6089	2181	556	120	185	61	8972

Based on Name Plate Capacity (world) incl. 2004 contracts

Fig. 11-13 Biaxial oriented film.

Table 11-1 Film properties of common biaxially oriented films

Mechanical properties		**Unit**	**20 μm BOPP**	**12 μm BOPET**	**15 μm BOPA**
Tensile strength	MD	N/mm^2	140	230	250
	TD	N/mm^2	280	260	280
E-Modulus	MD	N/mm^2	2000	4400	3500
	TD	N/mm^2	3500	5200	3800
Elongation	MD	%	220	110	110
	TD	%	70	90	100
Impact strength		kg/cm	5	5	15
Tear propogation		g	3.5	3.5	7.5
Thermal shrinkage		%	5% at 135 °C	2% at 190 °C	2% at 160 °C
Density		g/cm^3	0.91	1.393	1.16
Yield		m^2/kg	55	59	58
OTR		cc/m^2 d	1600	90	40
WVTR		g/m^2 d	6.0	8.5	270–300
Surface tension		dyn	40	50–55	50–55

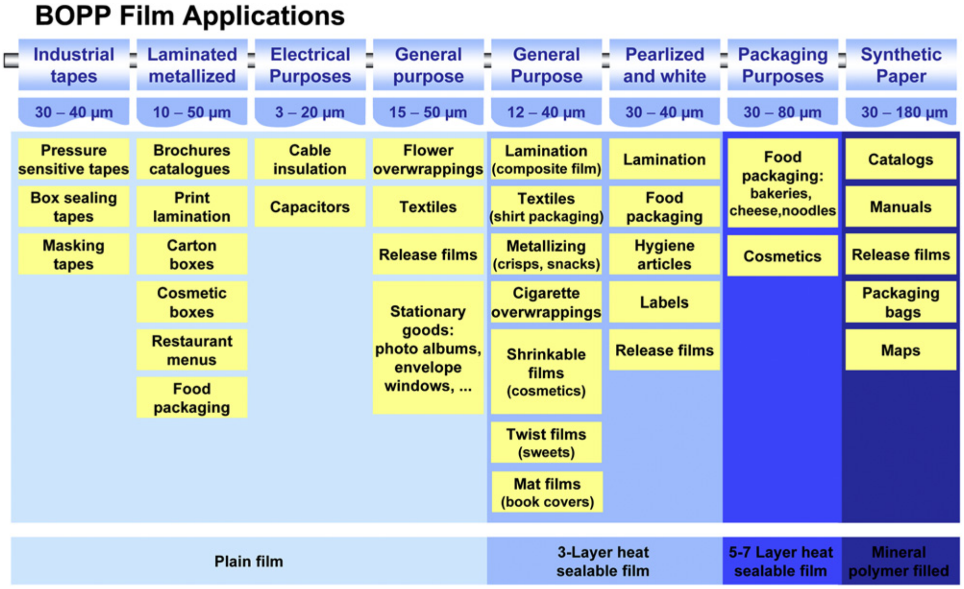
comparing the properties of the most common biaxially oriented film types, which are BOPP, BOPET and BOPA (Table 11-1).

The various film types mainly differ with regard to the mechanical, thermal and barrier characteristics and determine the particular application. Also, other properties, like thermal resistance or electrical properties, differentiate the film types and predestine them for specific applications.

BOPP films

With a worldwide consumption of over 6 million tons, BOPP films constitute by far the largest share in biaxially oriented film. The applications are very diverse and can basically be split into packaging applications, not only in the food but also in the non-food sector. Fig. 11-14 shows a few of these applications which play an important role in everyday life.

Fig. 11-14 BOPP film applications.



BOPP Film Applications

Industrial tapes	Laminated metallized	Electrical Purposes	General purpose	General Purpose	Pearlized and white	Packaging Purposes	Synthetic Paper
30 – 40 µm	10 – 50 µm	3 – 20 µm	15 – 50 µm	12 – 40 µm	30 – 40 µm	30 – 80 µm	30 – 180 µm
Pressure sensitive tapes	Brochures catalogues	Cable insulation	Flower overwrappings	Lamination (composite film)	Lamination	Food packaging: bakeries, cheese,noodles	Catalogs
Box sealing tapes	Print lamination	Capacitors	Textiles	Textiles (shirt packaging)	Food packaging		Manuals
Masking tapes	Carton boxes		Release films	Metallizing (crisps, snacks)	Hygiene articles	Cosmetics	Release films
	Cosmetic boxes		Stationary goods: photo albums, envelope windows, ...	Cigarette overwrappings	Labels		Packaging bags
	Restaurant menus			Shrinkable films (cosmetics)	Release films		Maps
	Food packaging			Twist films (sweets)			
				Mat films (book covers)			
Plain film				3-Layer heat sealable film		5-7 Layer heat sealable film	Mineral polymer filled

Fig. 11-15 BOPP film applications.

A further classification of such applications can be made in terms of the thickness range and the number of layers. The thinnest films are required for electrical applications, such as capacitor film, with a thickness of at least 3 µm. The thickest films are available within the synthetic paper sector up to 180 µm. As shown, films with a thickness range between 15 and 35 µm are widely applied for the varied packaging applications (Figs. 11-15 and 11-16).

One differentiates between one layer and multilayer, where three-layer coextruded film has the largest share. The core layer of PP homopolymer is coextruded with the outer PP copolymer layers. The outer layers have a lower melting point thus ensuring that the sealing process necessary for packaging applications can take place at temperatures that do not deform the main layer. In the last few years, there has been a strong trend towards five-layer and, in certain cases, also to seven-layer films [5]. The advantages of five-layer technology are, on the one hand, improved characteristics, such as better optical, gloss, transparent, opaque properties, as well as cost advantages, expensive additives are predominantly added in the thinner intermediate layers. In Chapter 16, Multilayer oriented films, the various structures and applications are further described. Biaxially oriented PP films are widespread, not only the transparent applications but also the white opaque film types which are mainly applied for packaging and labeling. Inorganic

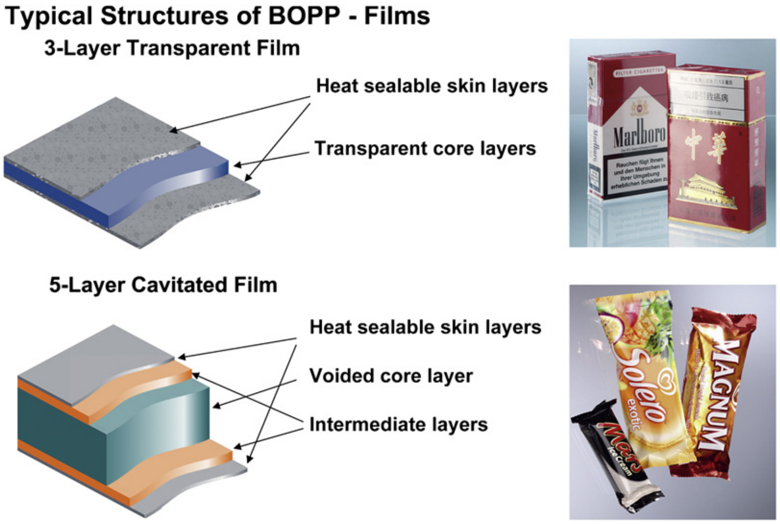


Fig. 11-16 Typical BOPP film structures.

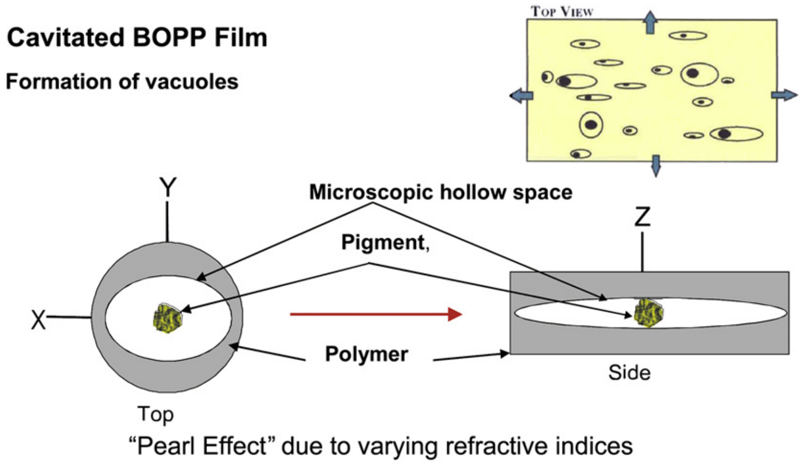


Fig. 11-17 Cavitated BOPP film mechanism.

additives (e.g. calcium carbonate) are implemented in the polymer matrix [6]. These particles lead to an initial flaking/separation from the polymer matrix during machine direction orientation, so that, during consequential transverse direction orientation, small cavities occur (Fig. 11-17).

In view of these so-called vacuoles, the light is refracted in varying ways such that the required pearl effect arises. At the same time, the density reduction gives rise to the fact that, with the use of the same raw material, compared to non-cavitated films, an enlarged thickness occurs. Both aspects are mainly used for confectionary, chocolate bars, ice-cream etc. Synthetic paper takes a special role among cavitated BOPP films. The effect of vacuole formation during orientation is also made use of, where a larger density range of 0.6–0.9 g/cm^3 can be produced. Applications for synthetic paper are extremely versatile and cover a large thickness range (Table 11-2). Three-layer and five-layer films are coextruded where the surface is optimized in order to attain good printability.

Fig. 11-18 shows a 100 µm synthetic paper cross-section showing the calcium carbonate particles, the cavities and the non-density-reduced skin layers. Synthetic paper is frequently coated in further processing in order to attain a better absorption and a quicker drying of the printing inks.

BOPET films

Biaxially oriented polyester films (BOPET), with approximately 2 million tons per year, are the second most common oriented film following BOPP. In the past, BOPP films dominated in packaging applications and BOPET films dominated in technical applications. Biaxially oriented polyester film, with its high rigid

Table 11-2 Thickness range for synthetic paper

Thickness (µm)	Recommended applications
50–180	Pressure sensitive, cut and stack and wrap-around labels; release liners, posters, ink jet printing base
75–100	Pressure sensitive, wrap-around and in-mold labels
75–200	Cut and stack and wrap-around labels, posters, maps, shopping bags, business cards, calendars, banners
75–250	Labels, books, posters, calendars
75–400	Maps, posters, tags, cards, charts, menus, phone cards, calendars, banners
130–700	Carriers, files, folders
250–1000	Cards, tags, book covers, folders, charts, maps

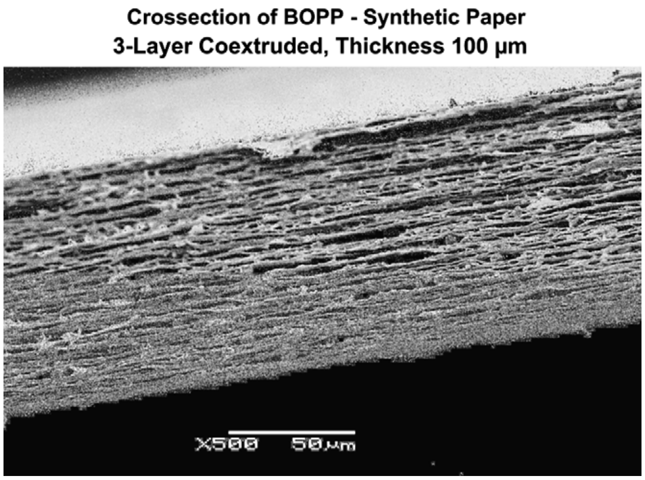


Fig. 11-18 Cross-section of 100 µm BOPP synthetic paper showing the calcium carbonate particles, cavities and uncavitated skin layers.

Fig. 11-19 BOPET film applications.

properties, was ideal as a carrier film for magnetic tapes, floppy disks and capacitors. Since this magnetic recording medium has been substituted by the optical data medium, this application has strongly declined over the last few years. At the same time, however, an increase in the prevalence of BOPET films in the packaging industry has taken place, resulting in a worldwide growth of 4–5%. Upon reviewing the breakdown chart for the various applications (Figs. 11-19 and 11-20), one can conclude that with approximately 40%, packaging applications represent the largest share.

The basic characteristics:

- high mechanical strength
- good temperature and chemical resistance
- dimensional stability over a broad temperature range
- adjustable friction coefficient
- excellent optical clarity
- good printability

reflect the specific beneficial features for the various applications accordingly (Fig. 11-21).

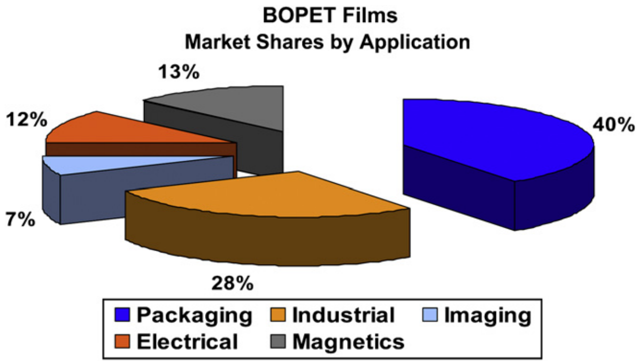
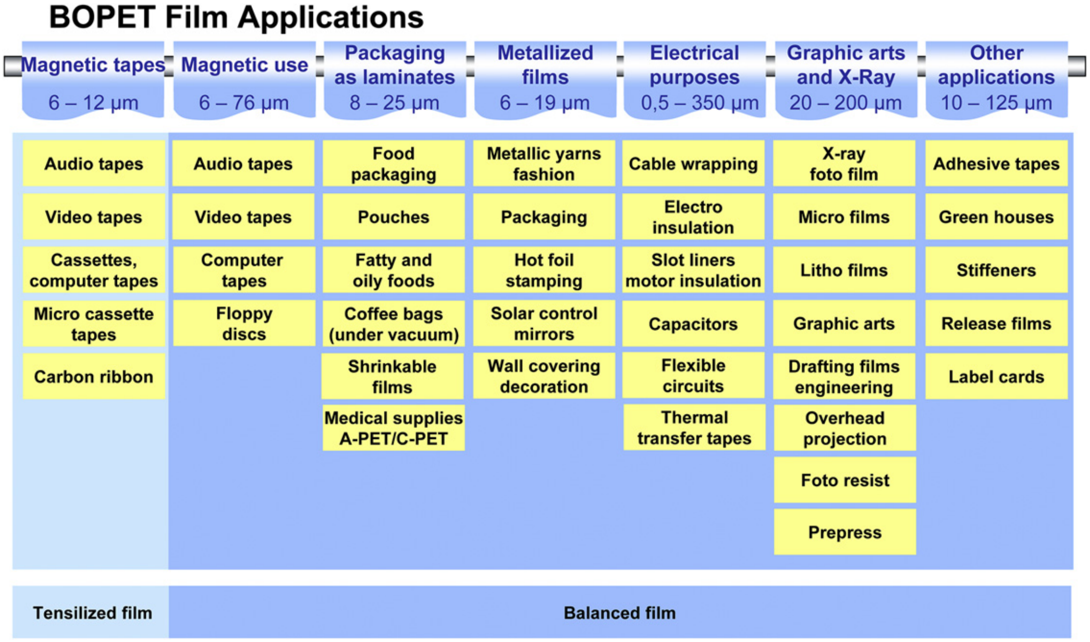


Fig. 11-20 BOPET films market share.

Variants ensue from the different stretching processes, recipes, coextrusion and coating processes. In the sequential stretching process, the longitudinal-transverse (MD/TD) process is dominant [7]. However, the transverse-longitudinal (TD/MD) process and the longitudinal-transverse-longitudinal (MD/TD/MD) processes are also applied. For the MD/TD/MD process, higher stiffness values in machine direction can be achieved. The simultaneous stretching process is applied for very thin films, e.g. for capacitor films, and the contact-free stretching technology allows for high-quality optical uses.

In view of the good stiffness values and sliding properties in the packaging sector, the benefits, such as excellent machinability plus good printability and optical appearance, are applied. With coextrusion, sealable or matte surfaces can be attained (Fig. 11-22).

Furthermore, a frequently applied advantage of coextrusion technology is the application of inorganic additives in the thin outer layers, in order to adjust the required friction coefficient without having a negative influence on the transparency. In-line coating processes are also widespread which ensure optimum printing ink adhesion. A common downstream processing phase of BOPET film is metallizing, which is mainly used to



BOPET Film Applications

Magnetic tapes 6 – 12 µm	Magnetic use 6 – 76 µm	Packaging as laminates 8 – 25 µm	Metallized films 6 – 19 µm	Electrical purposes 0,5 – 350 µm	Graphic arts and X-Ray 20 – 200 µm	Other applications 10 – 125 µm
Audio tapes	Audio tapes	Food packaging	Metallic yarns fashion	Cable wrapping	X-ray foto film	Adhesive tapes
Video tapes	Video tapes	Pouches	Packaging	Electro insulation	Micro films	Green houses
Cassettes, computer tapes	Computer tapes	Fatty and oily foods	Hot foil stamping	Slot liners motor insulation	Litho films	Stiffeners
Micro cassette tapes	Floppy discs	Coffee bags (under vacuum)	Solar control mirrors	Capacitors	Graphic arts	Release films
Carbon ribbon		Shrinkable films	Wall covering decoration	Flexible circuits	Drafting films engineering	Label cards
		Medical supplies A-PET/C-PET		Thermal transfer tapes	Overhead projection	
					Foto resist	
					Prepress	
Tensilized film	Balanced film					

Fig. 11-21 BOPET film applications.

improve the barrier properties, but also to attain an attractive visual appearance. For numerous food wrappings, the barrier properties, in terms of oxygen and aroma, are particularly vital criteria to ensure that the required minimum shelf-life is attained. With metallizing, an oxygen permeation value of $<1\ \mathrm{cm}^3/\mathrm{m}^2$ d bar can be reached (Fig. 11-23).

Biaxially oriented polyester packaging films are usually laminations, i.e. in a further process they are laminated with BOPP, PE film, aluminum foil or other packaging material. A typical laminate structure is shown in Fig. 11-24 as an example for coffee wrapping. The polyester film is reverse-side printed and laminated with aluminum foil as a barrier layer and polyethylene film as a sealing layer. Good transparency, high gloss and the print quality is thus reflected in the image appearance.

Apart from the packaging sector, there are numerous other industrial applications for BOPET films. For example, thermo-transfer films for bar code and ticket printers to name a few. The high temperature resistance is an excellent benefit. Biaxially oriented polyester is also widely used for capacitor and electrical insulating film, with thickness ranges from 0.5 µm to 350 µm.

In recent years, additional other applications for optical films have been gaining significance. In particular, LCD screens and flat screen TVs are undoubtedly ensuing good growth possibilities for high-quality BOPET films in the future.

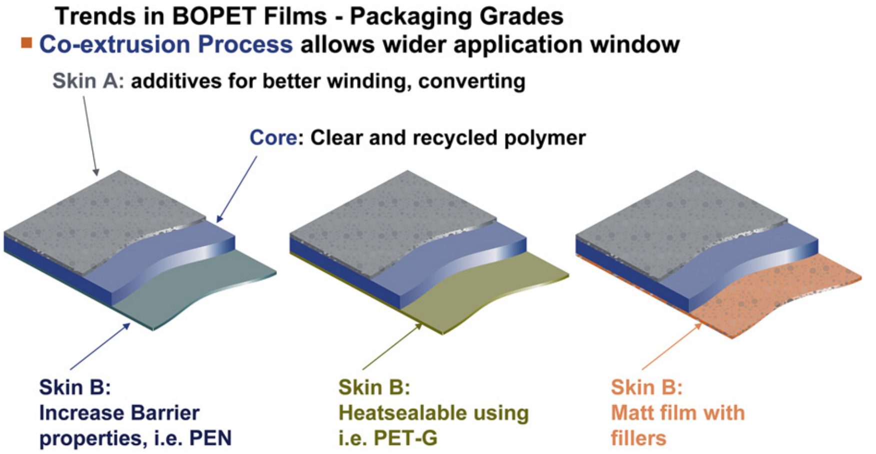


Fig. 11-22 Coextrusion trends in BOPET.

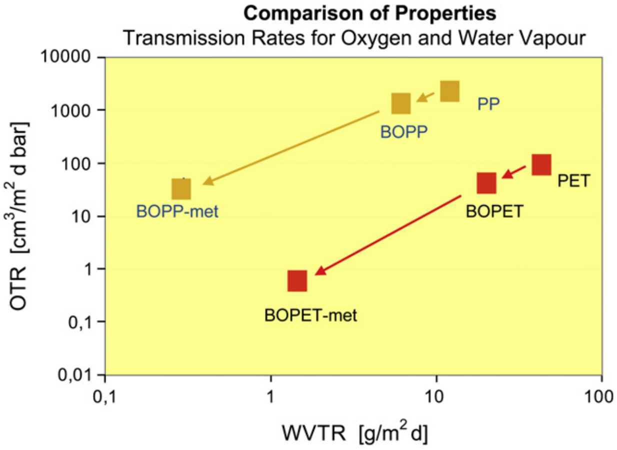


Fig. 11-23 Comparison of transmission rates for PP and PET.

BOPA films

With a worldwide volume of 250 thousand tons per annum, BOPA (polyamide or Nylon) films represent a small specialty segment, predominantly used in the packaging sector [8]. Particularly in view of the excellent puncture resistance along with good oxygen and aroma barriers, BOPA is primarily processed for flexible wrappings for sausages, cheese, fish and liquid contents (Fig. 11-25). Thickness is normally in the range of 12–25 μm. Special application, such as gas filled balloons is primarily made from metallized thin BOPA film (10–12 μm).

In principle, all above mentioned stretching processes are suitable for manufacturing BOPA films, i.e. not only sequential but also simultaneous and double bubble lines are used. Sequential stretching lines with longitudinal-transverse process and a working width of 4–5 meters are widely abundant. The stretching ratio is approximately 3 × 3, process temperatures are shown in Fig. 11-26.

For packaging applications, BOPA films are laminated with other films, mainly PE, in order to ensure the sealability for bag manufacture. Typical laminate structures are shown in Fig. 11-27.

BOPS films

The worldwide market demand for BOPS film (biaxially oriented polystyrene) amounts to approximately 600 thousand tons per annum and is basically split into two market segments [9]. Thinner 30–150 μm films are suited for applications such as envelope windows and separating film for photo albums, and thicker 150–800 μm films are mainly cover applications such as deep draw vacuum packaging film (Figs. 11-28 and 11-29). Thinner film types very often require a matte surface and deep draw applications require high transparency and luster. In addition, a good deep draw performance has to be ensured and can be adjusted via the stretching parameters.

Biaxially oriented polystyrene films are produced exclusively with the sequential process (longitudinal-transverse). In order to make the cast sheet, a roll stack is used to ensure that the thick film has optimum surface quality. The temperature is controlled to such an extent, thus ensuring that processing is performed at temperatures higher than the glass transition, as otherwise, polystyrene would be too brittle (Fig. 11-30).

Typical laminate for packaging with standard PET-film

Structure

Triplex-Laminate, i.e. for coffee, tea, peanuts, cosmetics

- **Coffee**
  - **PET12-alufoil- PE60**
- **Coffee bag**
  - **OPP30-reverse print-PET12met- PE60**
- **Peanuts**
  - **PET12-alufoil- PE60**
- **Cosmetics sachets**
  - PET12-alufoil- PE40

Fig. 11-24 Typical PET film.

Biaxially Oriented Polyamide Film

Typical Applications

- Frozen foods,
- Cooked foods
- Pickled vegetables
- Agricultural products
- Aquatic products
- Medical products
- Designer Balloons

Fig. 11-25 Typical applications of BOPA film.

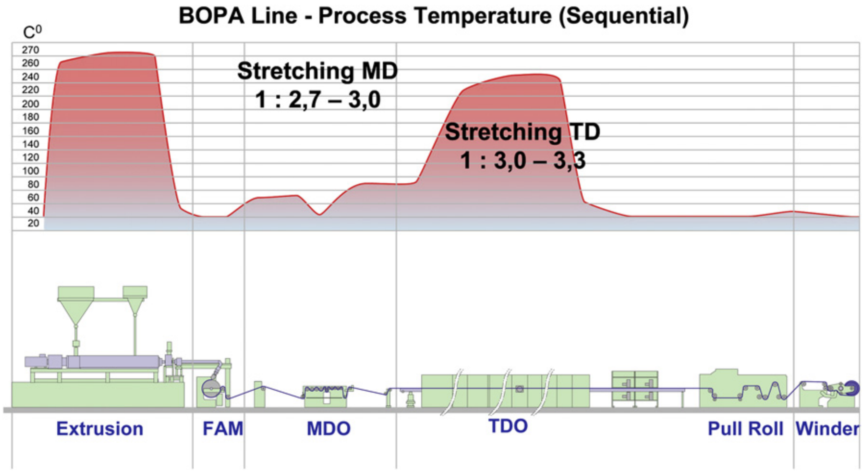
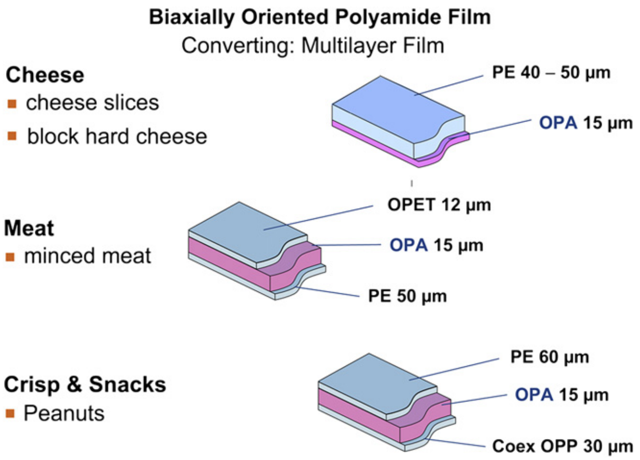


Fig. 11-26 Typical process conditions for MD/TD BOPA.



Biaxially Oriented Polyamide Film

Converting: Multilayer Film

Cheese
- cheese slices
- block hard cheese

PE 40 – 50 µm
OPA 15 µm

Meat
- minced meat

OPET 12 µm
OPA 15 µm
PE 50 µm

Crisp & Snacks
- Peanuts

PE 60 µm
OPA 15 µm
Coex OPP 30 µm

Fig. 11-27 Typical BOPA.

Other BO films

Besides the oriented films previously mentioned (BOPP, BOPET, BOPA, BOPS), various other specialty film types need to be mentioned.

Biaxially oriented polyethylene films (BOPE) are solely in use as shrink film applications, where there are many different products varying in layer structure, recipe and process parameters. In principle, each application has its own tailored shrink values, shrink forces, strengths and barriers. Barrier properties preferably are attained by coextrusion with ethylene vinyl alcohol (EVOH). For the production of BOPE shrink films, the double bubble process is almost solely used.

Oriented films from renewable resins represent another even more exotic film type on the market at present and are biodegradable. Polylactide (PLA) is the

Fig. 11-28 BOPS film applications.

major resin used since it has attractive properties and is already available in large quantities. The raw material is primarily based on corn. Similar to PS film, PLA film can be oriented and yields an attractive property spectrum (Fig. 11-31).

In particular, the excellent visual appearance has made it an interesting alternative for packaging. Furthermore, the deadfold characteristics should be noted which are a prerequisite for twist-wrap. Compared with other packaging films, the water vapor barrier, however, is considerably inferior, although this to some extent can be compensated by means of metallizing or SiOx coating. Further uses ensue in view of the permeability for water vapor and thus, such a characteristic is most suited for bread and vegetable packaging (Fig. 11-32).

Film oriented in machine direction

Films oriented solely in machine direction account for a small market share, since this stretching method is only interesting for certain special applications. As such, mono-axially oriented propylene films (MOPP) are used for decoration ribbons, banderoles and tear strips for

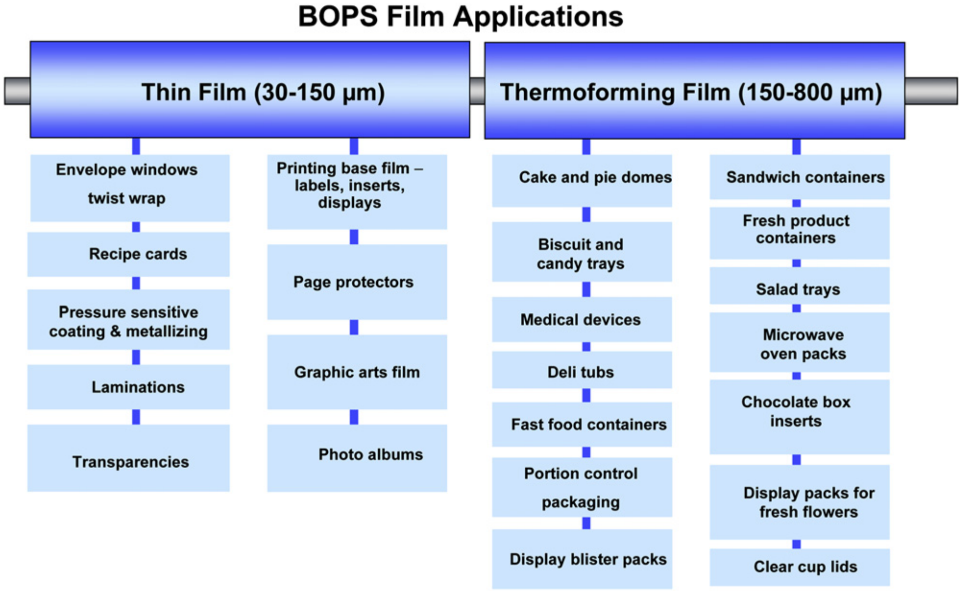


Fig. 11-29 BOPS film applications.

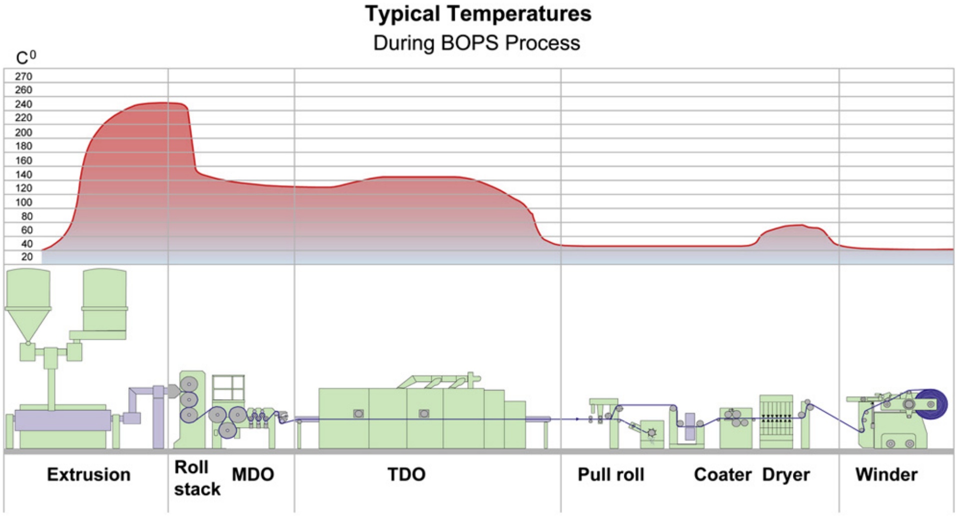


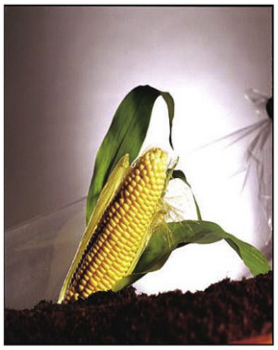
Fig. 11-30 Typical BOPS process temperatures.

cigarette packs, as they have a very high longitudinal strength. In addition, such films do have a distinct tendency to split, although this has no restriction on the above applications.

Breathable films made from highly-filled ($CaCO_3$) polyethylene are also oriented only in the machine direction. Defined hollow spaces up to the surface are thereby produced so that the required water vapor permeability is attained. Such film types are used in the hygiene sector as well as for the breathable layer in the building industry.

Also various special film types from longitudinally oriented polyamide (MOPA) are common. A three-layer structure PA/EVOH/PA is used to improve the barrier properties.

Packing from Biodegradeable Polymers - PLA
Product Features



Optical properties
- high transparency
- exceptional surface gloss

Converting features
- twistable with excellent deadfold
- both sides sealable
- low sealing temperature and high seal strength
- thermoformable
- printable
- adhesive or thermolaminatable to paper/board

Fig. 11-31 Product features for biodegradable polymers (PLA).

PLA Film Applications

- Bags for bread and other bakeries
- Packaging for fresh food – agricultural products (high WVTR works like anti-fog and can enhance shelf life, high stiffness suggest freshness)
- Packaging for cheese and butter (deadfold retention)
- Bags for cheese and salami (enables riping – longer shelf life)
- Shrink sleeve film and high modulus label films

Fig. 11-32 PLA film applications.

Fig. 11-33 Shrink film applications.

Film oriented in transverse direction

A relatively large and growing market segment is represented by films oriented in the transverse direction. These are applied solely as shrink films where the demands are such that the films only shrink in the transverse direction while machine direction shrink is not required. Such films are, to a large extent, used as sleeves and this anisotropic shrink behavior is required in order that the container-contours appear clearly and the desired print is attained (Fig. 11-33).

Shrink values of up to 80 % in the transverse direction can be attained, whereas full body sleeves can also be attained for containers with strong contours. Polyvinylchloride, PS, PET-G and PP materials are used where, in terms of shrinkage, the different characteristics of these materials become apparent (Fig. 11-34).

Trends for oriented films

Basically, oriented films are most suitable for meeting the trends in the packaging sector set by politics, society and the industry. The stipulations for example in Germany, namely packaging regulations, compel the industry to give consideration not only to the material and manufacturing costs but also to the disposal costs. This induces one to attain minimum packaging material and maximum protection with packaging. These goals can only be reached with high-strength materials to reduce thickness along with meeting the protection and barrier functions, plus operational properties that ensure high-speed packaging. With sophisticated orienting processes (e.g. simultaneous stretching technology), a significant increase of strength can be attained for all plastics. Furthermore, future potential in terms of

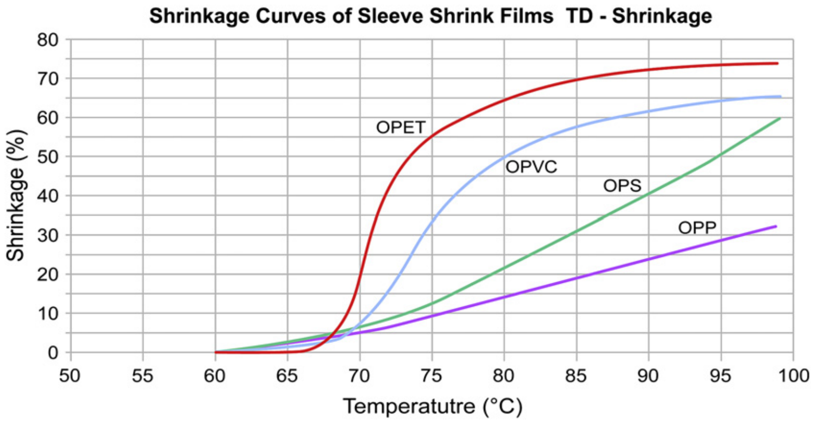


Fig. 11-34 TD shrinkage versus temperature for four shrink films.

packaging can be further developed, for example by the substitution of aluminium foil with transparent or metallized high-barrier stretched film. Another further large potential lies within the integration of many function layers in the production process of stretched films, so that complex processing steps can be waived [10]. For example, it was proven on a pilot line scale that all functions of a complex triplex laminate could be attained by a coextruded stretched film manufactured in one process step.

In view of the limited crude oil resources, coupled with ever increasing oil prices, plastics manufactured with crude oil bases are also subject to price increases. This, accordingly, gives a boost for alternative materials and thus the possibility of cost efficient production on an industrial scale. The production of suitable stretchable films for packaging applications from such alternative raw materials is evident in the PLA example. One can predict that much research and development will be performed within this sector in the near future.

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Chapter 12

Polymer blending for packaging applications

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Introduction

Blending of polymers is becoming increasingly important in packaging applications to enhance properties, improve processing or lower cost. Tailoring surface properties, such as coefficient of friction (COF), adding color, promoting adhesion, increasing output, improving stability and obtaining easy-opening features, are just a few of the attributes that can be achieved by blending.

The simplest blends can be made by mixing ingredients in the extruder used to convert the resin into a film or coating. For more complex blends, specialized screw designs or customized compounding equipment may be required to achieve the desired properties. These machines incorporate various mixing modes, such as flow rearrangement (distributive mixing) or high stress levels to break-up particles (dispersive mixing). Complex shear and elongational flow fields may also be used obtain optimum mixing.

The final blend properties will depend not only on the flow and stress history, which is process dependent, but also on the thermodynamics and the polymers' thermal and rheological properties. Most polymer blends are immiscible where the minor component forms a separate dispersed phase or domain within the major component. The major component forms a continuous phase or matrix. The phase size and shape is known as the blend morphology. Blend morphology has a profound effect on the final properties and is the subject of much study. Morphology is influenced by:

- interfacial tension (thermodynamics)
- dispersed to continuous phase viscosity ratio
- elasticity of each phase
- minor component concentration
- mixing and melting order
- and much more.

A basic understanding of these complex relationships between polymer properties and processing can aid in optimizing blends for a given application.

In this chapter, we will highlight some fundamentals of blending polymers for packaging applications. The literature is too broad for a detailed review of polymer blending and alloying. The goal is to familiarize the reader with those aspects of polymer blending that are important for in-line mixing of resins and other ingredients during film converting. Some blend requirements, however, are too demanding for in-line mixing and are best left to a resin manufacturer or compounder. Some of the technology that may used to design and produce such blends is also reviewed.

Why blend?

Even with the flexibility of controlling properties by introducing specific layers within the film, blending can still be critical for the package function. Blending may be needed to make the polymer stable enough to extrude or

Multilayer Flexible Packaging; ISBN: 9780815520214

have the right surface properties after extrusion. Blending may be a way to tailor specific properties into a layer, such as barrier or heat seal performance. The resin manufacturer often adds polymer additives, such as antioxidants, catalyst killers and various processing aids, to the polymer. But the film manufacturer may add these and other additives, such as slip, antiblock, antifog, antistatic agents or processing aids such as fluoroelastomers for reducing sharkskin. Typically, these additives comprise less than 1% of the final composition. They are usually in the form of a powder or liquid. Because of this, and their low concentrations, they are typically first made into a masterbatch, a highly concentrated blend of the additive with a carrier resin. Masterbatches are typically produced by outside compounders using specialized compounding equipment. The film manufacturer blends the masterbatch into the resin at the extruder feed hopper used to make the film or sheet.

Pigments such as titanium dioxide (TiO_2) and various colorants are typically added as a masterbatch. Since the additive or pigment is well dispersed in the masterbatch, blending can be done in a single-screw extruder without special screw designs or compounding equipment.

Blending may be used to reduce the resin cost. For example, a metallocene polyethylene plastomer (mPE) may be diluted with standard linear low density polyethylene (LLDPE) or low density polyethylene (LDPE) to lower cost. Recycle may be incorporated back into the film structure too. In-house scrap may be ground up and introduced into the extruder hopper as ‘regrind’.

Blending may also help improve resin processability. Two material grades with differing flow properties (such as melt index) may be blended together to achieve the proper flow for a given process. This is an example of a miscible blend described in more detail later. Low density polyethylene is typically blended into LLDPE to reduce extruder pressure and torque and increase output. Other examples where blending improves processing include blending amorphous nylon into nylon 6 to increase extruder output and adding amorphous nylon or ionomer to ethylene vinyl alcohol (EVOH) to improve thermoformability [1, 2].

A polymer deficient in one property is often blended with another one to enhance that property. Blending in cyclic polyolefins (COCs), for example, can enhance LLDPE stiffness [3]. Soft polymers are often blended into harder polymers to improve the toughness. Examples include blending ethylene vinyl acetate (EVA) into LLDPE, mPE into LLDPE and ethylene-propylene-diene rubber (EPDM) or mPE into polypropylene (PP) [4].

In the engineering polymer world, rubber is added to Nylon to improve low temperature toughness. Adding polyethylene terephthalate (PET) to polycarbonate (PC) lowers cost and improves chemical resistance and processability. Blends of PC and acrylonitrile-butadiene-styrene copolymer (ABS) have lower cost than PC and higher heat deflection temperature and toughness than ABS [5].

Barrier properties may be enhanced by blending. High density polyethylene (HDPE) is blended into LLDPE or LDPE to improve moisture barrier performance. Amorphous nylon, such as DuPont’s Selar® PA, is blended into Nylon 6 to improve the oxygen barrier at high relative humidity [6]. DuPont invented a laminar barrier technology where Nylon is blended into HDPE forming large platelets that impede the flow of species trying to migrate through. The laminar morphology is accomplished by choosing specific resins and processing conditions [7–10].

Adhesion may be promoted with several resins. Adding EMA or EVA to PE can improve adhesion to certain inks. Anhydride modified polyolefins are blended with PE or EVA to improve adhesion to Nylon or EVOH in coextrusion. An acid-based additive has been developed for enhancing the adhesion of LDPE to aluminum foil in extrusion coating [11].

Additives may also help control adhesion during the heat seal process. ‘Contaminates’ are often blended into sealant resins to achieve easy openability. Examples include blending polybutene-1 (PB) into LDPE, LLDPE, EVA or ionomers and EVA/ionomer blends [12–15]. The blend morphology and phase compatibility is important for these applications. For example, in the blends containing PB, the PB is the minor phase. It forms spherical particles that are stretched into fibers and ribbons during the film fabrication process. The poor compatibility between the PB and matrix resin results in failure along these fibers and ribbons near the sealant interface, lowering the seal strength.

Blending processes

Blending requires that the ingredients be brought together in the right proportions and then homogeneously mixed. In polymer blending, the former is important because there is little back-mixing in most continuous mixing devices used by the industry. This is particularly true of the single-screw extruder, which is the predominant device used by the film converting industry. For simple blends, such as those adding masterbatches, the pellets are pre-mixed together and fed into the extruder hopper. In more sophisticated compounding devices, such as twin-screw extruders, ingredients can be added at various stages along the extruder.

Once the polymer enters the extruder or other mixing device, it is melted and the mixing mechanism depends on the specific device employed. We will focus on mixing in single-screw extruders, introduce some more sophisticated devices and compare and contrast them to single-screw extruders. While specialty compounding devices, such as twin-screw extruders, kneaders and continuous mixers, have historically been used by the resin manufacturer or toll compounder and not by film converters, they are beginning to be used as in-line compounders for some large scale film operations [16].

Pellet pre-mixing

Pellet mixers fit into two general types, off-line batch mixers and in-line feeders/mixers. Batch mixers can be as simple as a cement mixer. The ingredients are weighed and poured into the mixer, blended and then transported to the extruder hopper. Batch mixers generally are less expensive and occupy less space than in-line mixers. They can be used to feed more than one extruder. Also, the ingredients' weight can be accurately measured, depending on the scale being used. On the other hand, they can be labor intensive, leave no automatic records and open up the chance for human weighing errors and the possibility for pellet segregation during transport. Human weighing errors can be eliminated with automatic weighing that use either gravimetric or volumetric feed systems, as described below.

In-line mixers generally are positioned above the extruder hopper. Each ingredient is fed by individual feeders. Fig. 12-1 shows a typical pellet blender. The ingredient feeders meter out a specific volume or mass over time, either by constant rpm of an augur (volumetric feeders) or by an augur whose rpm is controlled by the feed hopper loss in weight (gravimetric feeder). Volumetric feeders are less expensive but need to be manually calibrated for each ingredient since differences in density, bulk density and compressibility affect the feed rate. Gravimetric feeders have become the most commonly used feeders. Their calibration is usually much simpler than volumetric feeders. For example, the feeder may measure the weight loss in 30 seconds of operation at 10% of the maximum feeder speed to compute a feed factor that takes into account the variation due to bulk density, density, etc. The whole calibration process is usually done electronically and requires little operator interaction. Since the feed hopper weight is monitored by the computer control system, gravimetric feeders allow the individual feed rates to be recorded. Alarms can be set to ensure each ingredient is being fed to the extruder. Care must be taken when the feed hopper is refilled. Various control schemes, such as temporarily going into volumetric mode, are used to ensure feed continuity as the weigh cell is recalibrated. Understanding how the gravimetric feeder handles refilling is helpful in ensuring a trouble free operation.

Fig. 12-1 Pellet blender. Courtesy of Colortronic.

In-line mixers generally take up more space and are more expensive than batch mixers. They allow, however, for changing ingredient proportions during processing and can record the actual ingredient weights entering the extruder, which can be important for process control. They are also generally less labor intensive.

The ingredients in pre-mixed pellet blends may segregate if they differ in density, size or shape and are transported a long distance. Keeping the transport distance as short as possible and avoiding mixing powders with pellets can minimize segregation.

Using properly sized feeders and augers is important to ensure ingredients are controlled to the correct proportions. An oversized feeder will likely have less precision and accuracy. There are also practical limits to pellet blending. A 1% pellet blend corresponds to blending one pellet in every 100. When possible, it is best to strive for ingredients of 10% or higher for greater control and accuracy.

Care must be taken to clean thoroughly the feeders, mixers and transport lines when changing over products. One wrong pellet in a product can cause gel problems and other quality issues.

The film producer incurs extra risk when blending since the blend properties cannot be directly measured or controlled, especially if the blend is a thin layer in a multilayer film. Pre-made blends from a resin manufacture or compounder can be tested for properties to ensure they meet specifications. The error associated with pre-mixing is directly related to the precision and accuracy of the pellet pre-mixing system, how well it is maintained; and procedures that have been adopted to ensure the ingredients never run dry. Gravimetric pellet mixers typically have precisions ranging from about 0.1 to 1%, depending on hopper, feeder and auger size.

Melt blending

Once the ingredients have been fed in the correct proportions into the mixing device hopper, typically an extruder, the polymers and/or additives must be homogeneously blended together. This requires that the polymers be in the molten state. The mixing device melts the polymers, provides a means for mixing and generates pressure for subsequent operations such as making film when in-line mixing and pelletizing when compounding.

Mixing is described as either distributive or dispersive and is illustrated in Fig. 12-2. In distributive mixing, the polymer is rearranged by deformation. Separation and rearrangement of flow and kneading are two examples of distributive mixing. In dispersive mixing, particles are broken up and dispersed within the polymer matrix. Shear stress is important for overcoming the yield stress of the material. Dispersing pigment particles in a masterbatch is an example of dispersive mixing.

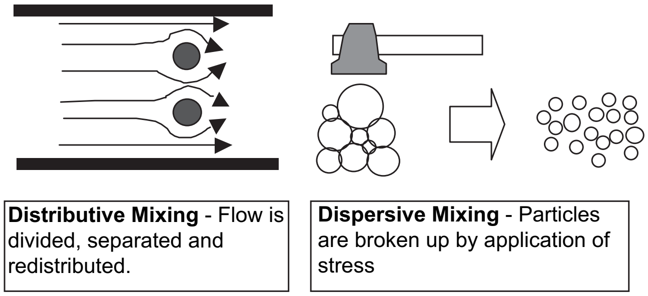
The single-screw extruder is the most commonly used device for film production. It efficiently melts the polymer and generates pressure for extruding the polymer through a flat or annular die. It is suitable for many blending applications but has its limitations, many of which can be overcome by optimizing the screw design. Single-screw extruders rely on the difference in friction between the solid polymer pellets and the barrel and screw surfaces to propel the pellets forward. Slippery ingredients may impede the pellet flow and cause surging and other unwanted effects. Single-screw extruders are typically flood fed, meaning the throughput is determined by the extruder screw speed, not how fast the ingredients are fed to the feed hopper. In more sophisticated compounding devices, such as twin-screw extruders, the throughput is decoupled from the screw speed. The output in these devices is determined by the feed rate and the screw speed can be increased or decreased to change the mixing intensity and energy input. Single-screw extruders are also generally not well equipped to handle powder (due to potential problems with segregation in the feed hopper and non-uniform melting) and liquid feeds.

The melting mechanism for pellet blends with different melt points in a single-screw extruder is not well understood. The standard melting model for uniformly melting pellets envisions a solid bed compressed against the trailing edge of the screw channel accompanied by an ever lengthening melt pool that results from the frictional heat near the barrel surface [17–19] (see Fig. 12-23). Disruptions in the solid bed can result in poor melt quality; unmelted particles may exit the extruder, plugging screen packs or appearing in the final film as ‘gel’ particles [20]. A disruption in the solid bed can cause surging. Phase inversions and other aspects of blending of polymers that have different melt temperatures may cause disruptions in the solid bed and are not well documented in the literature. The low melting polymer may also act as a lubricant, impeding the melting of the high melting component since viscous heat generation from the friction between the polymer and barrel wall is one of the primary avenues for polymer melting.

In a standard screw, the polymer melt is subject to non-uniform temperature and flow histories. There are circulatory flow patterns in the metering section of the screw (Fig. 12-3).

These patterns aid distributive mixing and, as they are non-uniform, they may lead to uneven mixing. The shear stress and flow rates vary across the flow channel (Fig. 12-4). As a consequence, the temperature varies across the flow channel. The temperature non-uniformity exiting the extruder can cause film thickness variability. Mixing elements incorporated into the screw design or at the extruder exit (such as static mixers) help homogenize the melt temperature for proper control of film thickness. These same mixing devices also help blend polymers. Mixing elements that have been utilized over the years include pins, restriction rings and more specialized designs such as the pineapple, Dulmage, Saxton and Maddock mixers [22].

Some mixing elements are characterized as distributive mixing elements – they achieve mixing by disrupting the flow. One of the easiest ways to do this is by inserting pins (Fig. 12-5), blisters or other elements that impede the flow. Pins can cause problems, however, as stagnant


Distributive Mixing - Flow is divided, separated and redistributed.

Dispersive Mixing - Particles are broken up by application of stress

Fig. 12-2 Distributive and dispersive mixing.

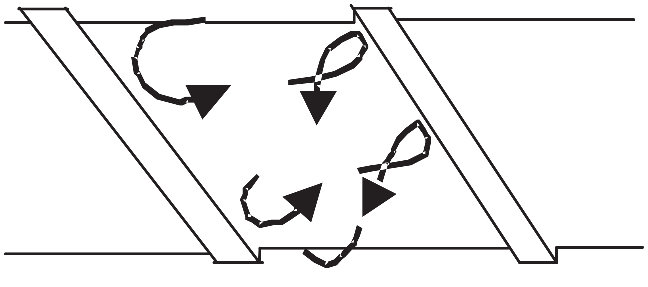


Fig. 12-3 Illustration of circulatory flow patterns in the metering section of a single-screw extruder. Adapted from Middleman [21].

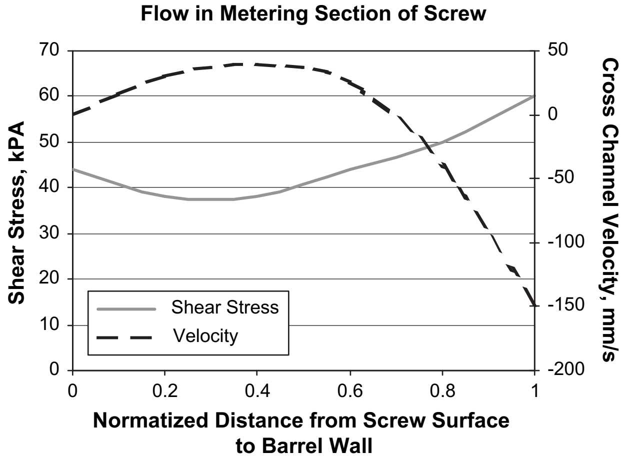


Fig. 12-4 Example of stress and velocity distribution of polyethylene in the cross channel direction of the metering section of a single-screw extruder. Calculations were done using commercial software from Polydynamics, Inc.

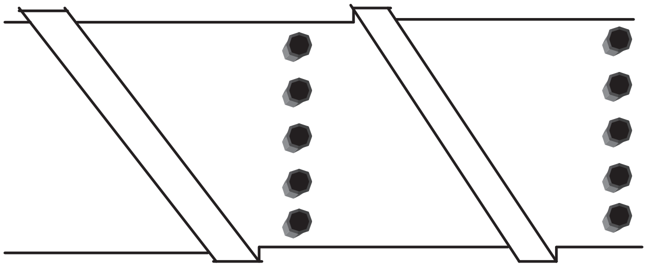


Fig. 12-5 Pin mixing section.

flow zones are created behind the pins, setting up the potential for gel formation with some thermally sensitive polymers. More sophisticated designs, such as the Saxton mixer [23] (Fig. 12-6), eliminate the dead zones while dividing up the flow. Other elements are dispersive in nature, such as the well-known Maddock mixer (Fig. 12-7). In this design, the polymer flows down a fluted section and over a small clearance between the screw and barrel, which introduces high shear stresses to break up agglomerates. Its actual effectiveness at dispersive mixing is suspect, particularly compared to specialized compounding devices, such as twin-screw extruders, but it is often used for multipurpose mixing.

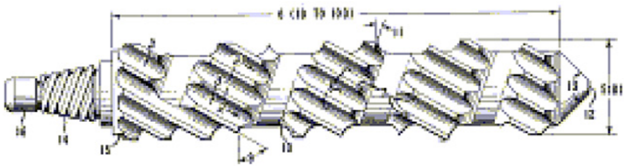


Fig. 12-6 Saxton [23] mixing section.

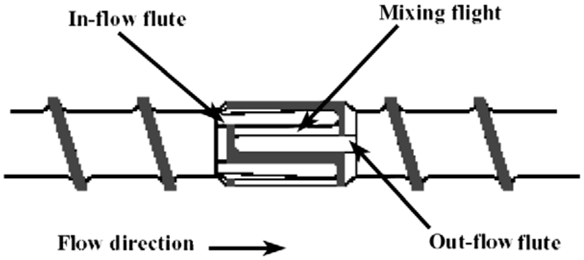


Fig. 12-7 Maddock screw element (adopted from Spalding and Hyun [20]). Courtesy of the Society of Plastics Engineers.

In recent years, several new high-performance screw designs have been developed that try to improve the mixing efficiency while increasing output. These screws generally work by having the polymer flow through a series of relatively tight clearances. The solid material is both entrapped and given time to melt or subject to high shear or elongational flow fields that aid in melting and mixing [22, 24]. The high performance section replaces the whole metering section of the screw. Some of the more commonly used high performance screws include the energy transfer [25], variable barrier energy transfer [26, 27], double wave [28, 29], stratablend [30], unimix [31] and CRD [32] screws. An example of a variable barrier energy transfer screw element is show in Fig. 12-8.

Although optimizing the screw design allows many polymer blends to be made on single-screw extruders, in some cases, specialty compounding devices may be necessary. This is especially true when intensive dispersive mixing, reaction or devolatilization is required. There are several compounder designs on the market. For general purpose compounding, co-rotating twin-screw extruders are often employed [33, 34]. Kneaders provide good distributive mixing, easily allow the introduction of liquid feeds and minimize temperature build-up, which is important for thermally sensitive polymers. Counter-rotating twin-screw extruders are often used for reactive extrusion and devolatilization since they can have long L/Ds (length to diameter ratios). The Farrel continuous mixer operates like a continuous Banbury mixer and is useful for making masterbatches with high filler loadings. Planetary mixers and other multiscrew devices are also available for specialty applications.

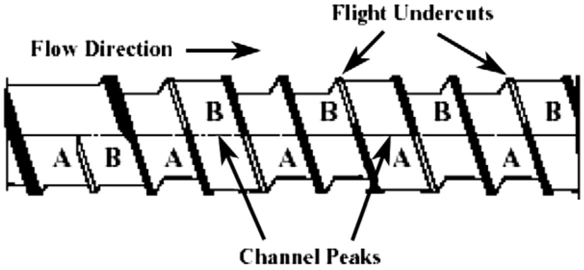


Fig. 12-8 Illustration of a variable barrier energy transfer screw. Adapted from Hogan et al [26]. Courtesy of the Society of Plastic Engineers.

Of the specialty compounding devices, the co-rotating twin-screw extruder is the most often used. Co-rotating twin-screw extruders offer considerable versatility in design and operation. As described earlier, feeding is independent of extruder rpm, which allows the mixing and energy intensity to be independently varied. Multiple feeding ports are common and screw designs can be changed from job to job to tailor the process. The screws are built from individual elements, which can be changed to suit the application. These elements come in several geometries with different mixing intensities. They provide good distributive and dispersive mixing and impart both shear and elongational flow fields. Fig. 12-9 shows some twin-screw modular elements. Some twin-screw extruders have screws that are self-wiping, which results in a narrow residence time distribution for better mixing control. One drawback is that they are poor melt pumps. Because of this, temperatures can be difficult to control at the extruder exit. Twin-screw extruders are not used alone for in-line compounding on a film line. They are adapted for better melt pumping by coupling the twin-screw extruder with a single-screw extruder or gear pump [16].

Twin-screw extruders and other specialty compounding devices are considerably more expensive than single-screw extruders.

Physics of blending

The properties of a polymer blend are influenced by specific interactions between the molecules (thermodynamics) and their response to deformation (rheology). The thermodynamics determine whether the blend forms a single phase (miscible) or multiple phases (immiscible). Miscible blends typically follow the rule of mixtures, namely the blend properties are directly proportional to the component ratio. There are a few commercially important miscible polymer blends on the market today. One is Sabic Noryl® which is a polyphenylene oxide (PPO) and high impact polystyrene (HIPS) blend.

How do we determine whether a blend is miscible? One method is to look at transparency, either by microscopy or light scattering. An immiscible blend forms separate domains within the polymer matrix that may diffract light if they are large enough. Another technique is to measure the glass transition temperature (Tg) using differential scanning calorimetry (DSC) or other thermal analyses. A miscible blend will have a single Tg, typically between that of the components. Both techniques use a fairly large sample or probe size, which can at times be misleading. Sometimes blends appear to be miscible because the probe size is too large. Other techniques with smaller probe sizes are x-ray and neutron scattering and various spectroscopy techniques, such as infrared (IR) and nuclear magnetic resonance (NMR).

Occasionally, we use the word ‘compatibility’ to describe the degree to which polymers interact. Miscibility is maximum compatibility. Compatibility is a subjective term and is not well defined. Miscibility has a specific definition – two polymers are miscible if they form a single phase over their entire composition range at a given temperature.

Immiscible blends, by definition, form multiple phases. In the simplest case, a two-component blend, the minor phase forms domains within a continuous major component matrix. The domain sizes, shapes and distribution are known as the morphology. Fig. 12-10 shows some immiscible blend morphologies. The morphology is influenced by the concentration, thermodynamics, component rheology and the flow and stress history during mixing and processing.

The morphology is critically important to the final blend properties, which often do not follow the rule of mixtures (Fig. 12-11). In many cases, blends are designed to create a specific morphology to achieve certain

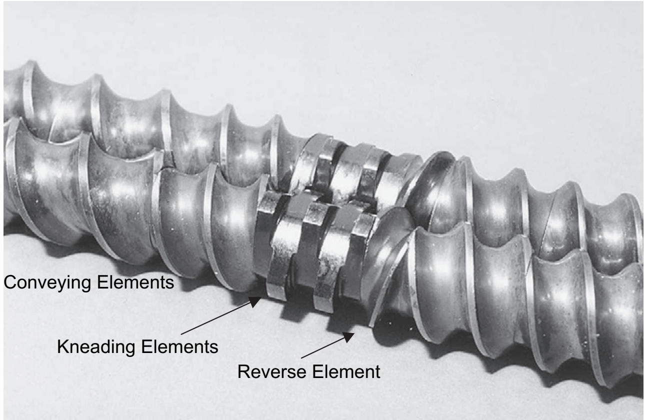


Fig. 12-9 Twin-screw extruder modular elements.

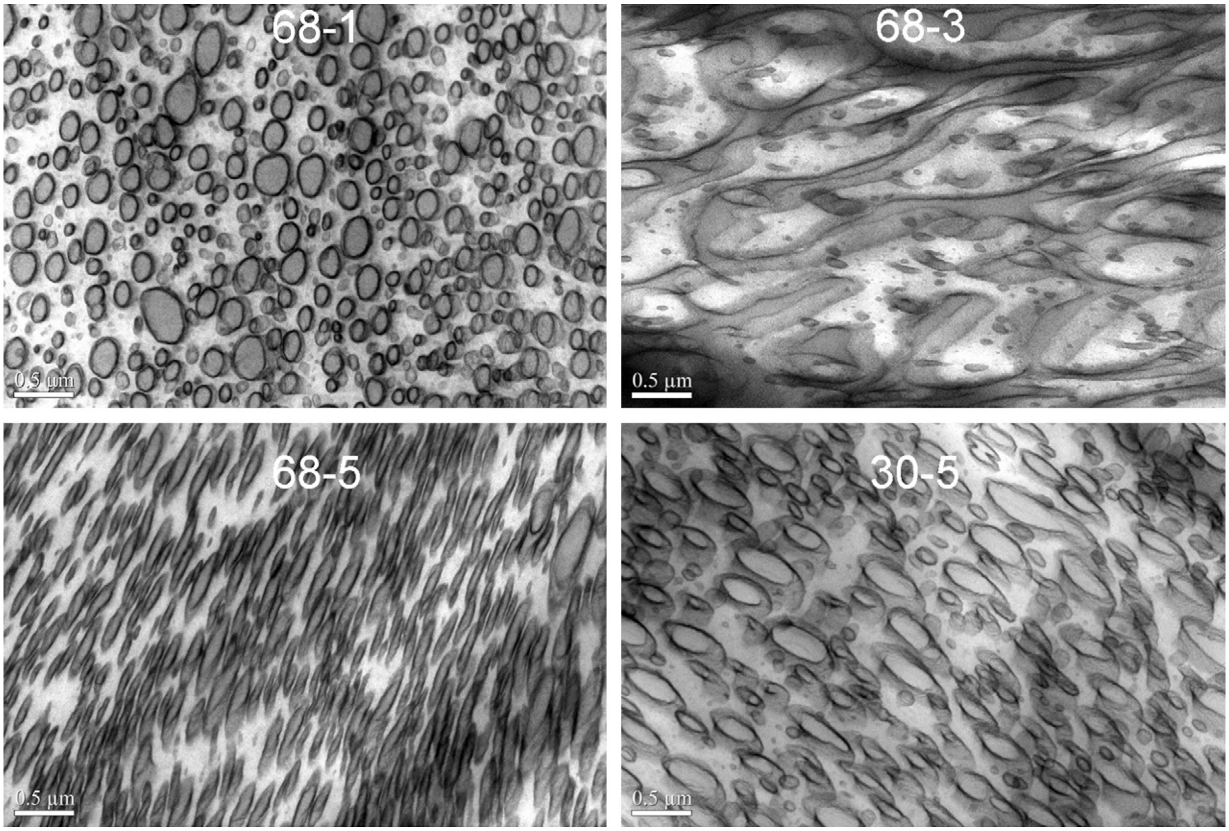


Fig. 12-10 Transmission electron micrographs (TEMs) of immiscible polyethylene – Styrene polymer blends of varying chemistries. Courtesy of Barbara Wood and I-Hwa Lee, DuPont. Further examples of TEMS of immiscible blends can be found in Wood [35, 36].

property gains. An example is super-tough nylon, which is a Nylon 66/rubber blend. The rubber must achieve a certain domain size in order to stop cracks from propagating during impact. Another example is Selar® RB laminar technology developed by DuPont. Here Nylon is dispersed in HDPE so that the Nylon phase forms platelets parallel to the surface. The platelets create a tortuous path for diffusion, resulting in improved barrier performance [7].

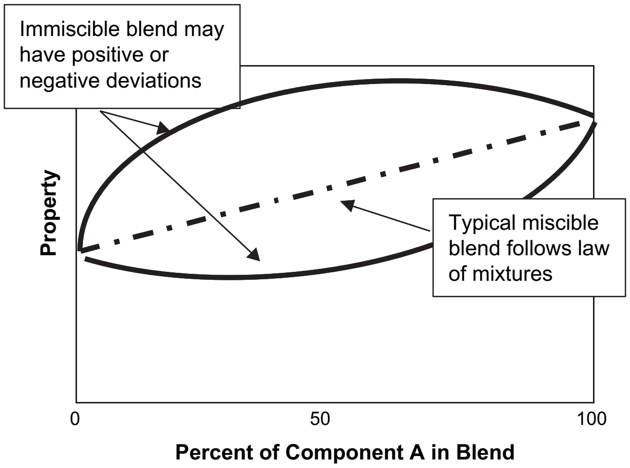


Fig. 12-11 Properties versus percent A in polymer blends.

Once a specific morphology has formed, it may change with further processing. The domains may coalesce or be stretched through orientation (see Fig. 12-10). Compatibilizers are frequently used to stabilize the blend morphology.

There is a third type of blend system, namely melt-miscible blends that are miscible in the melt state but phase separate in the solid state. An example is polyoxymethylene/polylactide (POM/PLA) [37]. This phenomenon may be important for ease of processing in order to obtain a fine dispersion of one component into another during melt blending.

Thermodynamics

When two materials are brought together, there must be a decrease in the free energy for them to transform into a single material or miscible blend. This can be expressed mathematically as:

$$\Delta G_m < 0 \text{ for miscibility} \qquad (12.1)$$

where:

ΔG_m	=	Gibbs free energy of mixing

The free energy includes enthalpic and entropic contributions:

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{12.2}$$

where:

ΔH_m	=	enthalpy of mixing
T	=	temperature
ΔS_m	=	entropy of mixing.

For most polymer blends, ΔH_m is positive and ΔS_m is nearly zero. Thus, it is rare that polymer blends are miscible.

Coleman et al [38] derived the following relationship for ΔG_m based on the work of Flory and Huggins:

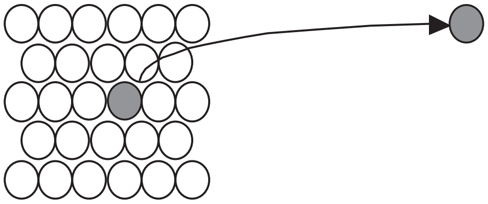
$$\frac{\Delta G_m}{RT} = \left[\frac{\Phi_A}{N_A}\ln\Phi_A + \frac{\Phi_B}{N_B}\ln\Phi_B\right] + \chi\Phi_A\Phi_B + \left(\frac{\Delta G_H}{RT}\right) \tag{12.3}$$

where:

ΔG_m	=	Gibbs free energy of mixing;
R	=	ideal gas constant;
T	=	temperature;
Φ_A	=	volume fraction of polymer A;
Φ_A	=	volume fraction of polymer B;
N_A	=	degree of polymerization of polymer A;
N_B	=	degree of polymerization of polymer B;
χ	=	interaction parameter;
ΔG_H	=	free energy of specific action between polymers, including hydrogen bonding.

The first term on the right side of equation (12.3) arises from combinatory entropy. Since N, which is related to molecular weight, is large for polymers, this term is nearly zero. The second term also arises from entropy and is always positive. The interaction parameter, χ, is defined by:

$$\chi = \frac{V_{ref}}{RT}[\delta_A - \delta_B]^2 \tag{12.4}$$



Cohesive energy density is the energy needed to remove a molecule away from its environment and is the square of the **solubilty parameter.**

Fig. 12-12 Illustration of cohesive energy density.

where:

V_{ref}	=	reference volume;
δ_A	=	solubility parameter for polymer A;
δ_B	=	solubility parameter for polymer B.

The final term, $\Delta G_H/RT$, is negative when specific interactions are present.

From equations (12.3) and (12.4), we see that we can improve compatibility by matching solubility parameters and achieve miscibility only when we incorporate specific interactions. Non-polar polymer blends, such as PP–PE blends, have no specific interactions beyond weak dispersive forces. As we shall see, even though their solubility parameters are nearly equal, they are not miscible.

In equation (12.4), we introduced the solubility parameter. We now discuss the origin of solubility parameters and how they can be helpful in understanding polymer blends. The energy per unit volume required to remove a molecule from a liquid or solid is known as the cohesive energy density. This is illustrated in Fig. 12-12. The cohesive energy density is a function of the forces that hold the material together. The solubility parameter is the square root of the cohesive energy density. It contains contributions from both non-polar (dispersive forces) and polar (dipole–dipole and hydrogen bonding) interactions.

Comparing solubility parameters is a way to quantify the 'like dissolves like' principle of chemistry. For two polymers to be miscible, the difference in solubility parameters should be between 0.1 and 3 Hildebrands, depending on their interaction strength. Coleman et al [38] defined a critical solubility parameter difference, $\Delta\delta_c$, below which the polymers may be miscible. As shown in Table 12-1, the value of $\Delta\delta_c$ depends on what interactive forces are present.

Table 12-2 lists solubility parameter values for some polymers used in packaging films. Returning to our PE–PP blend example, we see that the difference in their solubility parameters is less than 1 ($\Delta\delta<1$). However,

Table 12-1 Critical solubility parameter difference upper limit

Specific interactions involved	Polymer blend examples	$\Delta\delta_{critical}$ Hildebrands
Dispersive forces only	Polybutadiene–polyethylene (PBD–PE)	<0.1
Dipole–dipole	Polymethylmethacrylate–polyethylene oxide (PMMA–PEO)	0.5
Weak	Polyvinyl chloride–butadiene acrylonitrile copolymer (PVC–BAN)	1.0
Weak to moderate	Polystyrene acrylonitrile–polymethylmethacrylate (SAN–PMMA)	1.5
Moderate	Polycarbonate–polyesters	2.0
Moderate to strong	Nylon–polyethylene oxide (Nylon–PEO)	2.5
Strong	Polyvinyl phenol–polyvinyl acetate (PVPh–PVAc)	3.0
Very strong	Polymethacrylic acid–polyethylene oxide (PMMA–PEO)	>3.0

From Coleman et al [38]

since only non-polar dispersive forces are present, the critical solubility parameter difference ($\Delta\delta_c$) is less than 0.1. Thus, these polymers are not miscible.

It should be noted that there is some controversy around solubility parameters in the literature. They are exact for polymers with only physical interactions. There are errors associated with trying to extend the concept to polymer systems involving hydrogen bonding and other polar interactions and with the indirect methods used experimentally to measure them. These errors typically result in a range that is not very useful for predicting miscibility, hence matching solubility parameters is not a necessary and sufficient condition for the miscibility of polymers. They are useful guides for compatibility, however and, since most polymer blends are not miscible, this may be their greatest strength. The solubility parameter difference has been related to the inter-phase thickness between immiscible polymers. Immiscible polymers with a solubility parameter difference of about 0.5 Hildebrands or less may still build up enough strength at the interface for good mechanical properties [43].

Returning to our PP–PE blends example, PE is often used to modify the properties of PP. For example, ethylene–propylene rubber (EPR) is blended with PP to improve PP impact toughness. The EPR forms a phase with sufficient adhesion to the PP that the properties are enhanced, as would be predicted by their close solubility parameters.

LDPE–LLDPE blends are perhaps the most commercially important blends used in flexible packaging applications. A distinguishing difference between LDPE and LLDPE is long chain branching (LCB) in LDPE, which contributes to its relative processing ease. Typically, about 10–30% LDPE is added to LLDPE to improve melt strength, bubble stability and other film production in general. Hussein et al [44–47] found that LDPE and LLDPE are not miscible over their entire composition range. Miscibility is favored for LLDPE-rich blends. The miscibility range increases by lowering the LLDPE molecular weight (MW) and by increasing the short-chain branch length (replacing the butene comonomer with octene). At the same molecular weight and branch content, a Zeiger–Natta LLDPE is more miscible with LDPE than metallocene LLDPE (m-LLDPE), which has a narrow molecular weight and comonomer distribution. At the same molecular weight distribution (MWD) and molecular weight (MW), an m-LLDPE with higher branch content is more miscible with LDPE than an m-LLDPE with lower branch content. Comonomer type does not have an effect on miscibility of m-LLDPE with LDPE.

One can add specific interactions to promote miscibility. Coleman et al [38] have developed software that uses group contribution theory to predict solubility parameters of polymers that, in many, cases agrees well with experimental results. This is illustrated in Fig. 12-13. Here, vinyl acetate (VA) and styrene (St) contents are varied in an ethylene vinyl acetate copolymer–styrene vinyl phenol (EVA-StVPh) copolymer blend. Increasing the VA and the vinyl phenol content (VPh) promotes polar interactions (ΔG_H) that drive ΔG_m below zero (equation (12.3)). The experimental data are represented by the open and closed circles: the open circles represent miscible blends and the closed circles immiscible blends. The line demarking the region of miscibility comes from equation (12.3), using the software to predict the solubility parameters with specific interactions. The miscibility region depends on the comonomer percent in each polymer.

Table 12-2 Solubility parameters for some polymers used in packaging.

Polymer	Solubility parameter $cal^{1/2}/cm^{3/2}$ (Hildebrands)	Source
PE (polyethylene)	7.7–8.4	Van Krevelen [39]
PP (polypropylene)	8.2–9.2	Van Krevelen
PS (polystyrene)	8.5–9.3	Van Krevelen
PVC (polyvinyl chloride)	9.4–10.8	Van Krevelen
PVDC (polyvinylidene chloride)	9.9–12.2	Van Krevelen
PVOH (polyvinyl alcohol)	12.6–14.3	Van Krevelen
EVOH (44mol% ethylene)(ethylene vinyl alcohol)	17	Evalca literature [40]
EVOH (32mol% ethylene)	19	Evalca literature
Nylon 6	12.6	Evalca literature
EVA(9%VA) (ethylene vinyl acetate)	8.1	DuPont calculation [41]
EVA(25%VA)	8.2	DuPont calculation
EMA(20%MA) (ethylene methyl acrylate)	8.3	DuPont calculation
PET (polyethylene terephthalate)	10.3	Wu [42]

A practical note about compatibility and miscibility concerns masterbatches. The carrier resin in the masterbatch should be compatible and, ideally miscible, in the resin in which it is being blended. This way, the carrier resin will not harm the let down resin properties. Poor compatibility can lead to poor optical properties, reduced barrier performance and, for sealants, poor seal performance. Benkreira and Britton [48] found that better dispersion occurs when the carrier resin is lower in viscosity and has a lower melting point than the host polymer, for reasons that will be come clearer in the next section.

Solubility parameters may also prove useful for predicting miscibility of low molecular weight additives in polymers.

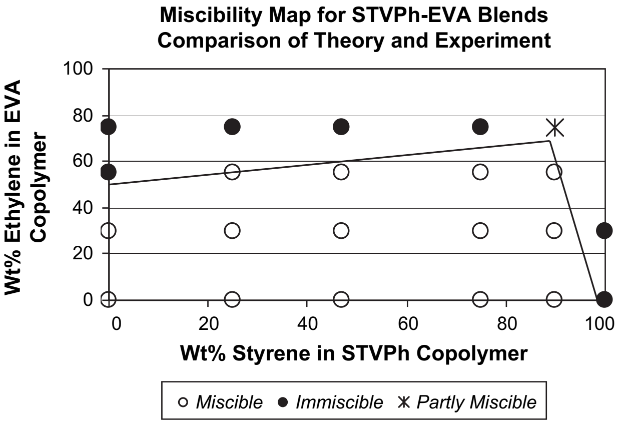


Fig. 12-13 Example of using specific interactions between molecules to achieve miscible blends. Taken from Coleman et al [38].

Morphology development in immiscible blends

To understand how morphology develops in a polymer blend, we will first look at how a single droplet suspended in a fluid is broken up during flow. The droplet is held together by interfacial tension, which arises from a non-uniform force distribution acting on the molecules at the interface (Fig. 12-14). Inside a material, a molecule is bound to its neighbors by attractive forces related to the cohesive energy density. At an interface, however, molecules are only partly surrounded by their own kind. The material across the interface may exert different attractive forces. The difference in these attractive forces gives rise to the interfacial tension. The more alike the materials are, the lower the interfacial tension and the smaller the driving force holding the droplet

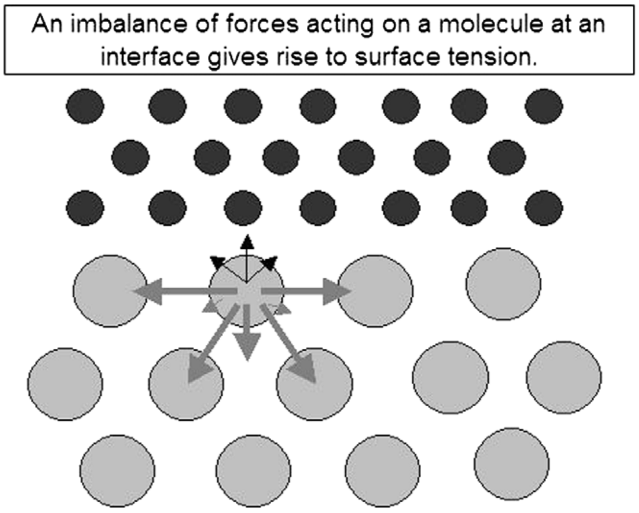


Fig. 12-14 Illustration of the origins of interfacial tension.

together. If the droplet has a radius a, then this holding force, $F_{interfacial}$, is proportional to Γ/a, where Γ is the interfacial tension.

We can relate interfacial tension to solubility parameters as introduced earlier. Wu [42] shows that the interfacial tension is related to the surface tensions of the two polymers:

$$\Gamma_{12} = \Gamma_1 + \Gamma_2 - 2\varphi\sqrt{\Gamma_1 \cdot \Gamma_2} \tag{12.5}$$

where:

Γ_{12}	=	interfacial tension between polymers 1 and 2;
Γ_1	=	surface tension of polymer 1;
Γ_2	=	surface tension of polymer 2;
φ	=	interaction parameter.

This is known as the Good and Girifalco equation. Wu tabulates the interaction parameter, φ, for several polymer combinations. They range from 0.79 to 0.98 for the polymers considered. The surface tension can be related to the solubility parameter:

$$\Gamma_1 = 0.2575 \cdot \frac{\delta_1}{\sqrt[3]{\rho_1}} \tag{12.6}$$

where:

Γ_1	=	surface tension (dynes/cm);
ρ_1	=	density of polymer 1 (g/ml);
δ_1	=	polymer 1solubility parameter $(\text{cal/ml})^{1/2}$.

Combining equations (12.5) and (12.6), recognizing polymer densities are around 1 g/ml and assuming $\varphi = 1$, we find that the interfacial tension is directly proportional to the square of the difference in solubility parameters:

$$\Gamma_{12} \cong 0.26 \cdot (\delta_1 - \delta_2)^2 \tag{12.7}$$

As shown in Fig. 12-15, the flow field exerts a drag force that acts to breakup the droplet. For shear flow, the drag force is equal to the viscosity of the continuous phase, η_c, times the shear rate, γ', acting over the area of the particle ($\approx a^2$):

$$F_{drag} \sim \eta_c \cdot \dot{\gamma} \cdot a^2$$

We define the dimensionless capillary number, Ca, as the ratio of the drag force to the interfacial force:

$$Ca = \frac{F_{drag}}{F_{\text{interfacial}}} = \frac{\eta_c \cdot \dot{\gamma} \cdot D_d}{2\Gamma_{12}} \tag{12.8}$$

where:

D_d	=	droplet diameter (= 2a)

When Ca exceeds a critical value, $Ca_{critical}$, the droplet breaks up because the drag force exceeds the force holding the droplet together. This hydrodynamic instability was first proposed by G. I. Taylor [49]. Taylor found that $Ca_{critical}$ for a Newtonian droplet imbedded in a Newtonian fluid is a function of the viscosity ratio (the ratio of the droplet viscosity to the continuous phase viscosity): η_d/η_c. This has since been confirmed by other investigators and is illustrated in Fig. 12-16. In a shear flow, $Ca_{critical}$ reaches a minimum when the viscosity ratio is 1. When the viscosity ratio exceeds about 3.5, the droplet cannot be broken up in a shear flow, as indicated by the rapid rise in $Ca_{critical}$. The bottom curve in Fig. 12-16 shows the relationship for $Ca_{critical}$ in elongational flow. Elongational

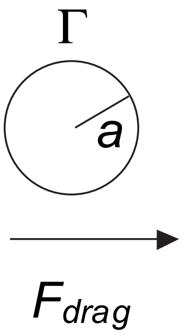
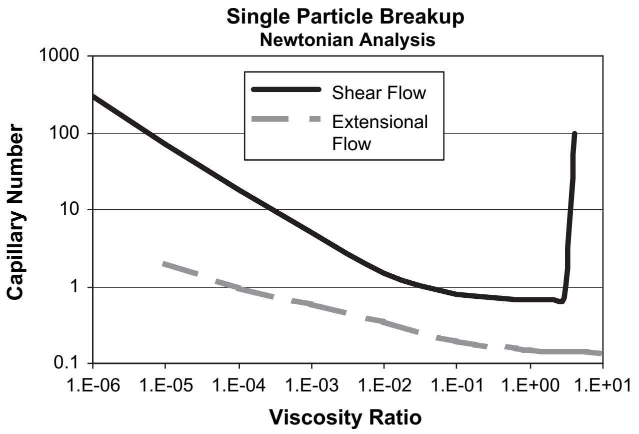


Fig. 12-15 Balance of drag and interfacial forces on a spherical droplet in shear flow.



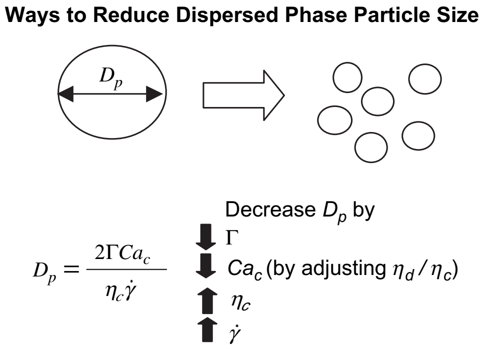


Fig. 12-17 Learnings from single droplet mechanics.

flow is more effective for breaking up droplets than shear flow; $Ca_{critical}$ is lower and droplets can be broken up even at high viscosity ratios.

For transient flow, a different mechanism for drop break-up has been proposed by Tomotika [51], based on Rayleigh's instability theory. Here, the droplet becomes an elongated ellipse or cylinder that, upon cessation of flow, breaks up into small droplets due to capillary disturbances, provided that the wavelength of these disturbances is greater than $2\pi a$ [52, 53].

The single droplet analysis gives us considerable insight into the dispersion of polymer blends (Fig. 12-17). Typically, we want the minor component domain size (D_d) of the blend to be small. For example, for good clarity, the dispersed phase should be less than the wavelength of light, about 0.3 μms. For toughening, small soft rubber domains help prevent cracks from propagating. Equation (12.8) shows we can decrease the droplet size by increasing the continuous phase viscosity, increasing the shear rate or by decreasing the interfacial tension. We can further reduce the droplet size by matching the polymer viscosities (a good guideline is to choose a viscosity ratio between 0.01 and 2) and using a mixing device that imparts elongational flow. The interfacial tension can be minimized by reducing the difference in solubility parameters (equation (12.7)) or by introducing specific interactions.

Compatibilizers are sometimes used to reduce the interfacial tension between polymers. Block or random copolymers often make good compatibilizers since they can be designed to contain two functionalities, each compatible with one of the polymers being blended. An example is using styrene–ethylene–butadiene–styrene copolymer (SEBS) to compatibilize high density polyethylene (HDPE) and polystyrene (PS) blends [54]. Another approach is to add functional groups to the compatibilizer that react with one of the polymers. An example is using an ionomer to compatibilize Nylon and PE blends. The acid groups in the ionomer react with the Nylon amine end groups and the ethylene backbone is compatible with PE.

While the break-up of a single Newtonian droplet in a Newtonian fluid is well understood, there are several difficulties in extending the analysis to polymer blends. The first is that polymer melts are typically non-Newtonian in their flow behavior (non-Newtonian fluids have viscosities that vary with shear rate and often exhibit elastic effects, such as normal stress differences and extrudate swell). Although several droplet break-up studies for non-Newtonian fluids have recently been published, this phenomenon is still not as well understood as the Newtonian case. Table 12-3 summarizes many of these studies. One aspect of non-Newtonian behavior is the polymer melt elasticity, characterized by the first and second normal stress differences. (Consult a rheology text such as Dealy and Wissbrun [55] for a broader discussion of melt elasticity.) Some investigators have used the dynamic storage modulus, G', obtained from dynamic mechanical analysis (DMA), as a way to characterize elasticity. G' is proportional to the first normal stress difference, but only at low shear rates. At higher shear rates typical of polymer processing, G' may underestimate the polymer elasticity. In general, it has been found that when the droplet is more elastic than the continuous phase, it is more difficult to disperse. An elastic force aids in holding the droplet together, resulting in larger $Ca_{critical}$ values and larger droplet sizes. Conversely, when the continuous phase is more elastic than the droplet, it is easier to break up the droplet because the matrix resin elasticity adds to the drag force on the droplet to break it up. Quantification and modeling of this behavior in flow regimes typical of polymer processing is still in its infancy.

Experimental studies with non-Newtonian fluids have also revealed different droplet break-up mechanisms. A Newtonian droplet immersed in a Newtonian fluid breaks up via Taylor [49] and Tomotika [51] instabilities (Fig. 12-18). Under some conditions, non-Newtonian fluids also break up in this manner, but other mechanisms have also been observed. In some cases, the droplet flattens in the flow direction and becomes elongated perpendicular to the flow [62, 71]. The ends of highly elongated particles find themselves in different planes with respect to flow and are torn apart by the velocity differences. At very high viscosity ratios, greater than the cut-off of 3.5 for Newtonian droplets, Mighri and Huneault [71] observed break-up via attrition at the droplet surface.

As the droplet concentration increase, the break-up mechanism becomes more complex. Utracki and Shi [53] and Macosko [76] found that when the polymer concentration exceeds 0.5–1%, the droplet size after shearing was much greater than that predicted by the single drop experiments. As the concentration increases, the probability that droplets will collide and coalesce increases. The coalescence kinetics are not well understood and are thought to be critically important to the final blend morphology. Utracki and Shi [53]

Table 12-3 Viscoelastic droplet deformation in a viscoelastic matrix under shear or elongational flow studies

Source	Expt or Theo	Droplet	Matrix	Flow	Result
Flumerflet [56]	Expt	Newtonian	Viscoelastic	Shear	Minimum droplet size and critical shear rate for break up increases with matrix elasticity
Tavgac [57]	Expt	Viscoelastic	Viscoelastic	Shear	Effect of elastic matrix depends on the viscosity ratio: when ratio is small, matrix elasticity stabilizes the droplet when ratio is high elasticity helps break up the droplets
Gauthier et al [58]	Expt	Viscoelastic	Newtonian	Shear	Small viscosity ratio: similar to Newtonian drop in Newtonian matrix. High viscosity ratio: $Ca_c > Ca_{c\text{-}Newtonian}$
Parabodh and Stroeve (in Utracki and Shi) [53]	Expt	Viscoelastic	Newtonian	Shear	For viscosity ratio <0.5, droplet viscoelasticity has a stabilizing effect For viscosity ratio >0.5 droplet viscoelasticity has a destabilizing effect
DeBruijn [59]	Expt	Viscoelastic	Newtonian	Shear	$Ca_{critical}$ for elastic droplet is slightly higher than for Newtonian droplet
Elmendorp and Maalcke [60]	Expt	Viscoelastic	Viscoelastic	Shear	Viscoelastic drop deformation in Newtonian matrix decreases with increasing drop elasticity Newtonian drop deformation in viscoelastic matrix increases with increasing matrix elasticity Problems with quantifying the behavior due to fluid shear thinning
Varanasi et al [61]	Expt	Viscoelastic	Newtonian	Shear	At any viscosity ratio $Ca_{critical}$ increases with increasing droplet elasticity
Levitt et al [62]	Expt	Viscoelastic	Viscoelastic	Shear	Studied PP droplets in PS matrix at different viscosity and elasticity ratios Shear flow at 1 s^{-1}. For high elastic matrix found that the droplet widened in the direction perpendicular to flow. The width of the flattened drops depended on the differences in second normal stress differences between the phases
Han and Funatsu [63]	Expt	Viscoelastic	Viscoelastic	Elong	Viscoelastic drops are more stable than Newtonian drops in both Newtonian and viscoelastic matrices
Milliken and Leal [64]	Expt	Viscoelastic	Newtonian	Elong	Viscoelastic drops with viscosity ratios less than 1 have smaller deformation and $Ca_{critical}$ than Newtonian drops. For viscosity ratio >1 the viscoelastic drop deformation behavior is similar to Newtonian drops
Delaby et al [65]	Expt	Viscoelastic	Viscoelastic	Elong	For negligible interfacial tension, viscoelastic drops deform less than the surrounding media when the viscosity ratio is less than 1 and more when the viscosity ratio is greater than 1
Miejer and Janssen [66]	Expt	Not disclosed	Not disclosed	Elong	At small viscosity ratios, the droplet deformation in planar elongational flow resembles that for the matrix
Chin and Han [67]	Expt	Viscoelastic	Viscoelastic	Elong	Higher droplet elasticity results in less deformation compared to the matrix
Shanker et al [68]	Expt	Viscoelastic	Viscoelastic	Elong	Higher droplet elasticity results in less deformation compared to the matrix
Mighri et al [69]	Expt	Viscoelastic	Viscoelastic	Elong	Used Boger fluids which have elasticity and non-shear thinning viscosity behavior For a given elastic matrix fluid, increasing the droplet elasticity decreased droplet deformation relative to the surrounding media. Droplet deformation increases with increasing matrix elasticity. Defined *k'* as first normal stress difference ratio divided by the viscosity ratio. When $k'<0.2$, the matrix elasticity has a greater effect on deformation than the drop elasticity. The opposite is true with $k'>0.2$. The study was conducted over a fairly narrow viscosity ratio range (0.5 to 1.1); shear rates were not disclosed

(*Continued*)

Table 12-3 Viscoelastic droplet deformation in a viscoelastic matrix under shear or elongational flow studies —*cont'd*

Source	Expt or Theo	Droplet	Matrix	Flow	Result
Mighri et al [70]	Expt	Viscoelastic	Viscoelastic	Shear	Used Boger fluids, which have elasticity and constant viscosity versus shear rate behavior Shear rates not disclosed; viscosity ratios ranged from 0.2 to 1.1. Defined k' as first normal stress difference ratio divided by the viscosity ratio For high matrix elasticity ($k'<0.37$), the elastic drop deformation in an elastic matrix was higher than for the Newtonian case with same viscosity ratio and interfacial tension. In some cases, droplet widening in the direction perpendicular to flow was observed. For $k'>0.37$, elastic drops deform less than the Newtonian case. The critical shear rate for droplet breakup increases with increasing k'. For $k'<4$, $\mathrm{Ca}_{\mathrm{critical}}$ increases rapidly with k'; for $k'>4$, $\mathrm{Ca}_{\mathrm{critical}}$ levels off at 1.75
Mighri and Huneault [71]	Expt	Viscoelastic	Viscoelastic	Shear	Studied model systems and PS/PE system with viscosity ratio between 5 and 20 under relatively high shear rate (1–20 s^{-1}) in shear flow. In PS/PE system, the PS drop widened in the direction perpendicular to flow which contributed to droplet break up (the ends of the highly elongated droplet are in different flow planes). At high shear, a second break-up mechanism different from the Newtonian case was observed: attrition from the surface. An EPR/PP system had similar break-up mechanisms as the PS/PE system despite a 10 × difference in interfacial tension
Van Oene [72]	Theo	Viscoelastic	Viscoelastic	Shear	Developed an expression for the dynamic interfacial energy to account for viscoelasticity: $\Gamma_{12} = \Gamma_{12}o + D_p/12^* [(N_{11}-N_{22})_d - (N_{11}-N_{22})_m]$ where: $\Gamma_{12}o$ = the interfacial tension in quiescent flow; $(N_{11}-N_{22})$ = the first normal stress difference Droplet elasticity greater than the matrix stabilizes the droplet; matrix elasticity greater than the droplet destabilizes the droplet.
Greco [73]	Theo	Viscoelastic	Viscoelastic	Shear and Elong	Assumed the materials are simple second-order fluids, which includes elastic effects for slow flows. Used a perturbation method to analyze the first normal stress difference effect on droplet shape for small drop deformations
Maffettone and Greco [74]	Theo	Viscoelastic	Viscoelastic	Shear and Elong	Developed a phenomenological model for the dynamics of a drop immersed in an immiscible fluid. Assumed the drop is ellipsoidal. Either or both fluids may have elasticity. Found that elastic drops deform less than Newtonian drops. Elastic drops in Newtonian matrix under shear are forbidden to break up at lower viscosity values than the Newtonian case. In elongational flow, the drop break up is easier when the matrix is elastic and more difficult when the droplet is elastic
Lerdwijit-jarud et al [75]	Expt	Viscoelastic	Newtonian	Shear	Studied deformation and break up of viscoelastic drops (Boger fluids) in a nearly Newtonian matrix. Viscosity ratio controlled to around 1.0. Shear rates up to 5 s^{-1} used The deformation decreases for isolated drops at constant Ca as the drop elasticity increases. They did not observe droplet widening in the transverse to flow direction and suggest widening is influenced by factors other than first normal stress difference (such as second normal stress difference, shear thinning or a shift of the critical condition to lower Ca when the matrix is elastic). $Ca_{critical}$ increases with increasing droplet elasticity. For a 10% blend, the steady state Ca is less than $Ca_{critical}$ for an isolated drop (they suggest this may be due to flow differences in concentrated suspensions). The steady state Ca was found to increase monotonically with the dispersed phase first normal stress difference

Expt: experimental; theo: theoretical

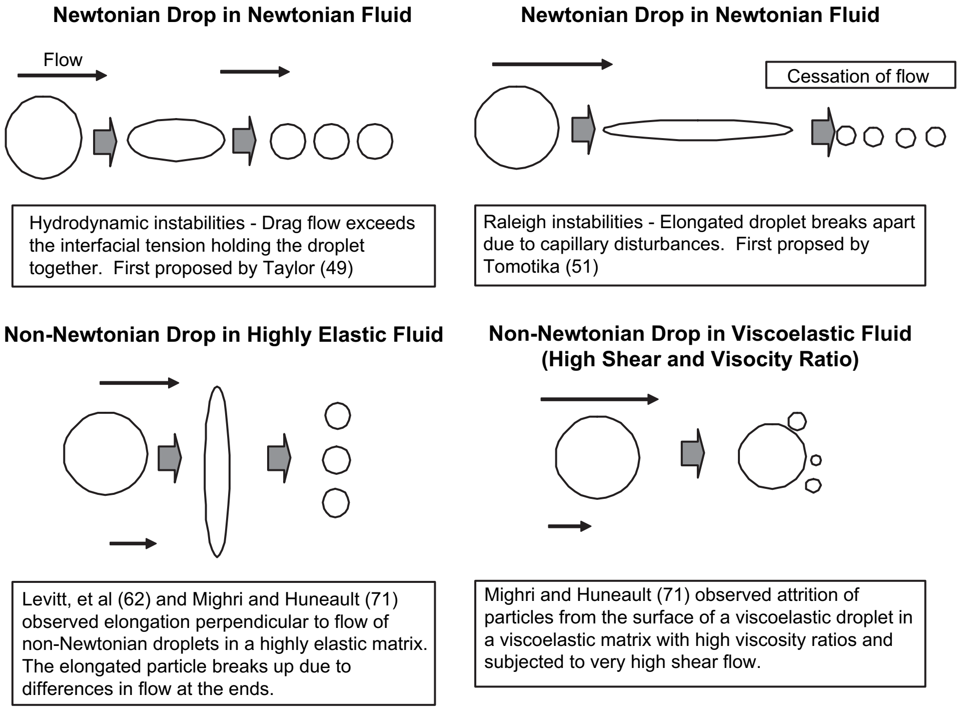


Fig. 12-18 Single droplet break-up mechanisms in shear flow.

observed that the same factors that enhance droplet break up, namely high shear rates and reduced droplet viscosity, favor coalescence. Recently, several investigators [76–78] have proposed that compatibilizers act to inhibit coalescence by providing a protective shell around the droplet (Fig. 12-19). The shell acts to repulse other droplets. Thus, dispersion stabilization may be more important to the droplet size than reducing interfacial tension. Indeed, Mighri and Huneault [71] found that an EPR–PP droplet–matrix system with very low interfacial tension broke up in a similar manner as a PS–PE system with an order of magnitude greater interfacial tension. They suggest that interfacial instabilities may not be required for non-Newtonian droplets to break apart.

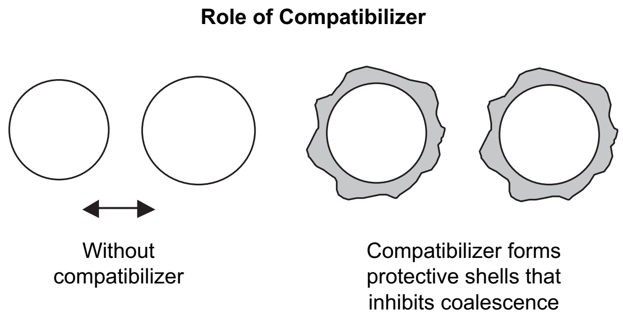


Fig. 12-19 Role of compatibilizers in reducing coalescence in polymer blends.

As the minor component concentration is increased, the morphology may change. At high enough concentrations, the minor component becomes the continuous phase. Fig. 12-20 shows the different morphologies possible for HDPE/PS blends studied by Bourry and Favis [54]. At low PS levels, the PS forms droplets in the HDPE matrix. As the PS concentration is increased, fibers are formed. At about 70% PS, the morphology becomes co-continuous – the HDPE and PS phases form an interpenetrating network structure where both phases

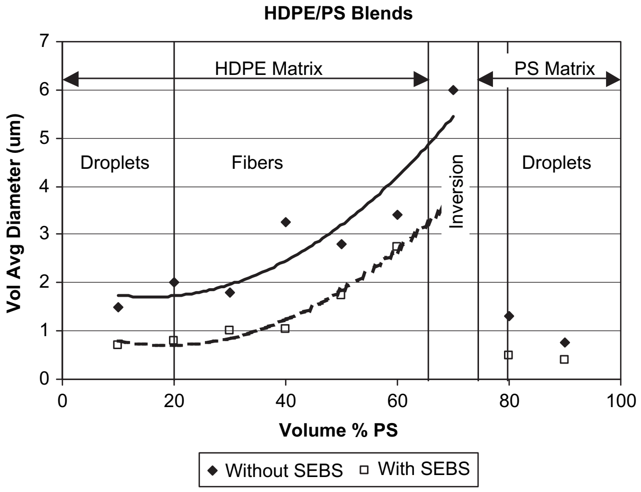
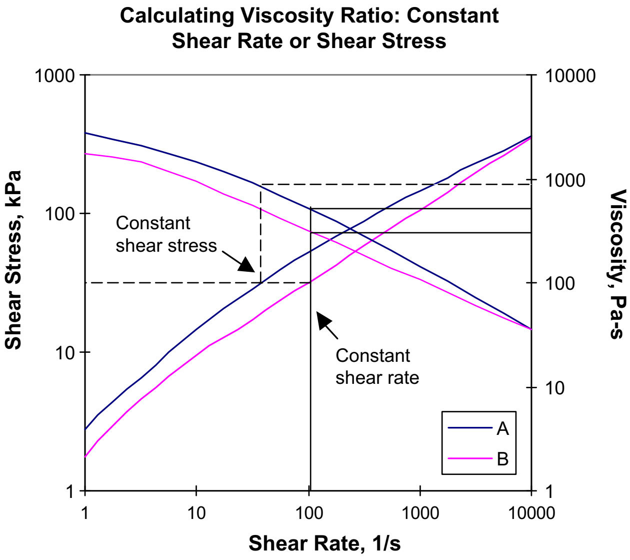


Fig. 12-20 Blend morphology as a function of concentration. PS-HDPE blends from Bourry and Favis [54].

are continuous. Higher PS levels results in HDPE droplets in a PS matrix. Note how the SEBS compatibilizer decreases the domain size.

Another concern in applying single droplet studies directly to polymer blends are uncertainties about the flow field in the mixing device and how to calculate the appropriate viscosity ratio. Polymer mixing devices, such as extruders, have complex flow fields involving both shear and elongational flow. The flow fields are typically nonuniform; the shear rate varies across the screw channel (see Fig. 12-4). Further complicating matters are temperature changes along the extruder. Given these complexities, Lyngaae-Jorgensen [79] proposes measuring the $Ca_{critical}$ versus viscosity ratio curve for the given device.

One must also consider the fact that the polymer melt viscosity varies with temperature and shear rate. Generally, there are two schools of thought on calculating the viscosity ratio. Some argue that the zero shear viscosities should be used. Others suggest using the viscosity at a representative shear rate for the process. However, it is stress, not shear rate that drives dispersion and droplet break up. Stress is determined by the flow field and is continuous across an interface, whereas the shear rate is discontinuous. A better method is to plot the viscosity as a function of stress (stress is equal to the viscosity times the shear rate) and compare the blend components at a representative stress for the process. This is illustrated in Fig. 12-21. Here, polymers A and B are the minor and major components, respectively. At a constant shear rate equal to 100 s^{-1}, the viscosity ratio is 1.6. But, at constant stress, the ratio is 2.6, very close to the 3.5 cut-off for shear flow.



	Viscosity,	Pa-s	Ratio
	A	B	A/B
Constant Shear Rate	520	320	1.6
Constant Shear Stress	840	320	2.6

Fig. 12-21 Calculating viscosity ratio.

The polymer temperature changes along the extruder as the polymer becomes molten and is conveyed to the exit. Huneault et al [80] showed that, for a PS/HDPE blend, the viscosity ratio varied by six orders of magnitude depending on the temperature (Fig. 12-22). Computing the viscosity ratio just at the final extrusion temperature may be misleading. They found that, for this blend, the mixing was much better than what they would have expected just by looking at the viscosity ratio at the final temperature (200 °C). Notice in Fig. 12-22 that the viscosity ratio is sometimes less than 1 and other times greater than 1. This indicates that, for the two polymers, the viscosity temperature dependence is not the same, another complication in computing the viscosity ratio.

So far, we have assumed that the polymers are both molten at the time they are mixed. This is generally not the case as mixing can begin during melting. Ghosh et al [81] studied the softening/mixing of two similar amorphous polymers and found that laminar sheets or striations form that subsequently break up into droplets. Lindt and Gosh [82] found that the striations come from the single-screw extruder melting process. A thin molten layer forms between the pellet solid bed and the barrel or screw surface caused by frictional heat and heat transferred from the barrel (see Fig. 12-23 for the solid bed melting model). The high stress and deformation rates in this region transform the molten polymer into laminar morphologies as the pellets melt. The domain size decreases from a few millimeters (pellets) to about 50 to 100 µm due to the melting process. They made measurements as well as calculations that confirmed

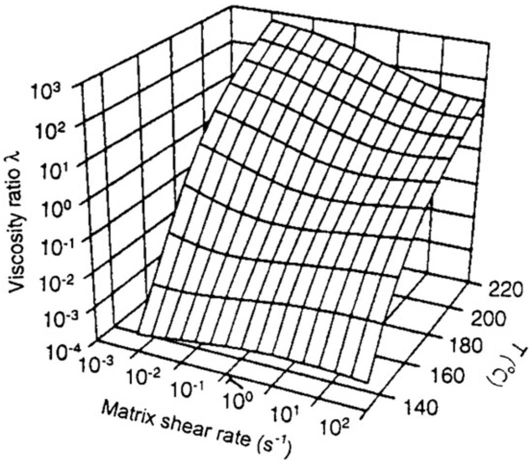


Fig. 12-22 HDPE-PS blend viscosity ratio variation as a function of shear rate and temperature. Taken from Huneault et al [80]. Courtesy of the Society of Plastics Engineers.

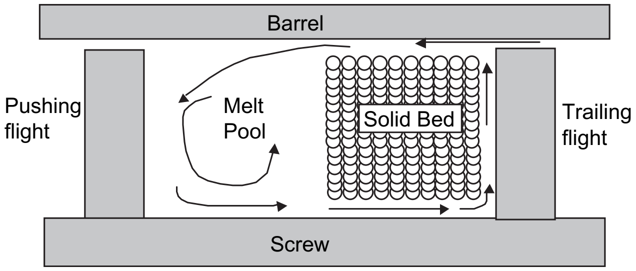


Fig. 12-23 Single-screw extrusion solid bed melting model. Melting above and below the solid bed causes the minor component to form thin layers or striations in a 2-component polymer blend (after Lindt and Gosh [82]).

these striations and abrupt domain thickness changes for blends of both rheologically similar and dissimilar resins.

Benkreira et al [83] found that, when mixing a masterbatch into a host polymer, most of the mixing occurred during melting and little thereafter. They proposed a laminar mixing model where the striation stretching during melting leads to a reduction in dimensions. Scott and Macosko [84] describe how component melting and softening in a batch mixer leads to the domain size reduction. They found sheets and ribbons are formed first, which become unstable due to flow and interfacial tension effects. Holes form, then a lace-like structure followed by irregular shaped particles and finally spheres (Fig. 12-24). Break up is driven by interfacial instabilities. Burch and Scott [85] found similar behaviour for miscible polymers during the initial mixing stages and proposed instabilities due to dynamic interfacial tension as the cause. Willemse et al [86] found that sheets or striations formed during single-screw extrusion and that the final droplet size depended on the striation dimensions at the start of break up rather than the capillary number. The sheet to droplet break up during shear is very effective at dispersing the minor phase, more so than the elongated droplet to sub-droplet mechanism found in single drop experiments.

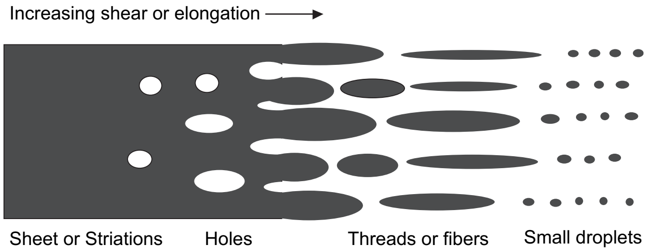


Fig. 12-24 Morphology development during melting and subsequent shear in an extruder. Striations or sheets form during melting. Shear and stress cause holes to form, followed by threads and particle break-up. This process leads to large changes in the minor phase morphology.

In a single-screw extruder, Tyagi and Ghosh [87] followed a PP–EVA blend as it developed its morphology using freeze experiments pioneered by Maddock [17]. In these experiments, after the extruder has reached steady-state, the screw is stopped and the polymer is quickly quenched. The screw is pulled and samples from the screw channels are analyzed. Tyagi and Gosh found that striations formed in the feed zone. The dimensions quickly diminished along the channel length. In the compression zone, the shear and elongation increases, causing the striations to break up. The droplets that form are an order of magnitude smaller in size than the striations thickness prior to break up. The break up into droplets requires a step-up in shear and stretching. They conclude that, for an extruder to be an effective mixer, periodic flow reorientations should occur. This concept is used in high performance screw designs where the polymers flows through tight clearances.

Li et al [88] found that the minor phase melts faster during mixing when a compatibilizer is present. They attribute this to faster heat transfer between the phases due to their intimate contact. Faster melting can affect the final blend morphology.

Shih et al [89] studied the solid–melt transition for many polymer blends in a batch mixer equipped with a glass window. They found that blends go through four stages from solid to melt:

- elastic solid pellets: below the glass transition temperature (Tg) or melting point (Tm) the solid pellets were observed sliding in the mixer. Torque was low
- deformed solid pellets: as the temperature increased, some components began to soften and deform. The torque started to rise
- transition material: which took on several different forms including
  - ○ a fluid with suspended solid particles
  - ○ fractured or semi-fluid material
  - ○ and a dough-like material
- This was the transition zone between solid and liquid. Different blends took on different transition phases. The temperature increased sharply and then remained constant near the polymer melt temperature (T_m) if it was crystalline. Torque rose sharply
- viscoelastic material: the typical liquid appearance was observed. Temperature rose to about 20–50 °C above the matrix resin T_m or T_g and the torque decreased.

During the transition phase they observed several phase transitions that aided in the mixing process. Shih [90] and others [91, 92] found that phase inversions are to be expected when the minor component melts first. The molten minor component surrounds the still solid major component. As the major component melts, it becomes the continuous phase. This inversion is accompanied by a spike in the mixer torque and dramatically reduces the minor component phase size. They also describe how phase inversion can explain some unique morphology, such as major component regions imbedded within the minor component domains.

The phase inversion onset is a function of the volume fraction ratio and viscosity ratio. A simple expression is given by: [54, 93]

$$\frac{\eta_1}{\eta_2} \sim \frac{\Phi_1}{\Phi_2} \tag{12.9}$$

where:

Φ = volume fraction.

Two polymers with the same viscosity will undergo a phase inversion when the minor component reaches about 50% of the blend composition. If the minor component viscosity is substantially less than the major component, the minor component can become the continuous phase. This is the case when the minor component melts first. As the major component melts and its viscosity decreases, then conditions no longer favor the minor component as the continuous phase and the phase inversion occurs.

Morphology development in blown film

Several morphologies have been described for immiscible blends in blown film, including elongated particles, such as fibrils and ribbons. Forming elongated morphologies is a two-step process:

- sphere-like dispersed domains are formed during extrusion (in the absence of blowing or drawing). Shear flow fields in the extruder and die dominate the morphology. The domain size is a function of:
  - the dispersed phase concentration
  - viscosity ratio
  - interfacial tension
  - continuous phase viscosity
  - shear stress
- stretching and orienting the spherical particles in the elongational flow fields at the extruder exit (blowing and drawing) form elongated structures. The morphology is influenced by:
  - initial domain size
  - polymer elasticity
  - minor component percentage
  - draw ratio.

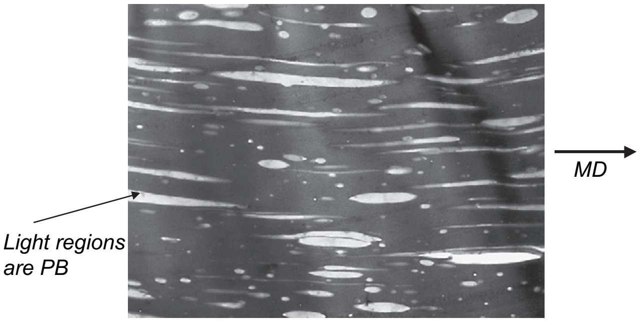


Fig. 12-25 Elongated second phase (PB-1 in a polyolefin matrix) found in blown film. Photograph courtesy of DuPont.

Fig. 12-25 shows the elongated morphology in a blown film. Here polybutene-1 (PB) has been added to a polyolefin to create a peelable sealant. Pirtle et al [13] suggest that too much PB phase orientation in a peel-seal blend can produce unwanted stringy seals. Thus, morphology control is important for packaging applications. We will now examine some factors that influence the morphology in more detail.

Viscosity ratio

A viscosity ratio near 1 typically gives the smallest particle domains. These are difficult to elongate; the smaller the particle size the harder it is to deform the particle. David et al [94–96] found that the dispersed phase viscosity has to be less than the matrix to obtain elongated morphologies. For viscosity ratios greater than 1, the dispersed phase cannot be deformed enough to create the elongated morphologies.

Interfacial tension

As described by equation (12.8), the lower the interfacial tension, the smaller the particle diameter (in the extruder and die). Smaller particles are more difficult to elongate. Adding compatibilizers to the blend tends to reduce the particle size and make elongated morphologies (such as laminar structures) more difficult to obtain [97, 98].

Minor phase concentration in blend

Increasing the dispersed phase volume fraction (ϕ_d) generally gives larger particle sizes, resulting in more fibril or laminar structures. The larger particle sizes may be due to coalescence, which becomes more significant as the concentration increases. David et al [94] found co-continuous fibrils formed as ϕ_d increased. This was determined experimentally by extracting films with a solvent that selectively dissolves the minor component. As the volume fraction was increased, more minor phase was extracted, suggesting co-continuous morphologies were forming.

David et al [94, 96] found that the onset of co-continuous fibril morphology occurred at a lower volume fraction than predicted by equation (12.9). They attribute this to elongational effects.

Polymer elasticity (non-newtonian behavior)

Getlichermann and David [96] found that a viscosity ratio less than 1 was not sufficient to create elongated morphologies. If the dispersed phase was Newtonian in behavior, elongated morphologies were not observed after blowing and drawing. The polymers non-Newtonian (elastic) behavior helps to stabilize the 'threads' that forms during elongation, allowing more elongation without the threads breaking up into small particles.

They suggested that dispersed phase tension thickening is one attribute that should help stabilize the thread and help create elongated morphologies. Tension thickening refers to elongational viscosity measurements, which are difficult to conduct. Linear polymers, such as LLDPE, have transient elongational viscosity that decreases with time (tension thinning), whereas polymers with long chain branching (such as LDPE) tend to increase with time (tension thickening).

Extruder RPM

Equation (12.8) predicts that, as extruder speed is increased, the increased shear rate should reduce the droplet size. As discussed previously, smaller particles formed in the extruder and die are more difficult to elongate after they exit the die. Lee and Kim [98] found just the opposite for a LDPE–EVOH blend. They attributed this to the shorter extruder residence time at higher rpm. The EVOH, which melts at temperatures 50 °C higher than the LDPE, has less time to melt fully and be dispersed. This gives rise to a larger particle size at the extruder exit and a greater tendency toward elongated laminar morphology.

Extruder temperature

The extruder and die temperatures affect the morphology through their impact on the viscosity of both components. As the temperature is increased, η_c decreases. As described by equation (12.8), this allows less stress to be applied to breaking up the droplets, giving larger particle sizes. Also, the polymers' viscosity temperature dependence may differ, altering the viscosity ratio.

Shear stress in extruder, adaptor and die

During pressure driven flow in an extruder, adapter tubes and die, there is a shear stress distribution across the flow channel. The highest shear stresses occur at the wall. The wall also experiences the longest residence times since the flow rate at the wall is low. Thus, there may be a morphology distribution as a result of the stress differences. This was found to be true by Lee and Kim [98] in LDPE–EVOH blends and it has also been documented for blends involving PB-1 and LDPE [99].

Screw design

For laminar morphologies, the literature teaches not to over-mix the blend [7]. Careful screw design may be needed to accomplish this.

Draw ratio

Before drawing (or blowing) (see Fig. 12-26 for blown film process description), the minor component morphology is typically spherical as it exits the extruder [94–98]. It is the elongational flow fields imposed by the drawing and blowing process that give rise to the highly elongated structures. The degree of elongation depends on the process. David [94] found the convergence/divergence in a capillary geometry only gave rise to elongated ellipsoids. A flat die gave rise to fibrils in the machine direction (MD) and a blown film die gave fibrils and ribbons with two-dimensional orientation in the machine and transverse direction (TD) as well as co-continuous fibrils.

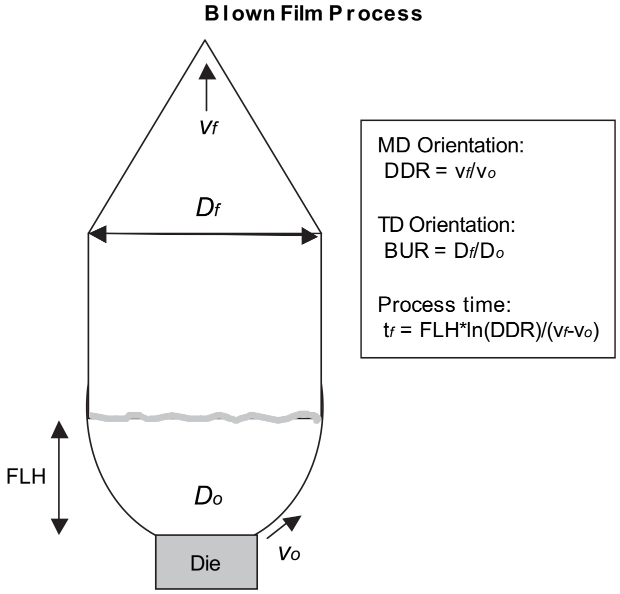


Fig. 12-26 Blown film process.

The draw ratio in the MD is characterized by the draw down ratio (DDR), which is defined as the haul-off speed divided by the polymer melt velocity as it exits the die. The blow-up ratio (BUR) characterizes the draw ratio in the TD or hoop dimension. BUR is defined as the final bubble diameter divided by the die diameter. The draw down ratio is inversely proportional to BUR times the final film thickness divided by the die gap (Equation 12.10):

$$DDR = \frac{V_f}{V_o} \approx \frac{\text{Die Gap}}{\text{BUR x Film Thickness}} \tag{12.10}$$

where:

V_f	=	haul-off speed;
V_o	=	velocity of polymer at die exit.

Thus, DDR decreases with increasing BUR and film thickness and decreasing die gap. (In Equation (12.10), we have ignored the density change between solid and melt.)

David [94] found that the fibril diameter is not a straightforward function of draw ratio. Without any drawing, the particles were spherical with a diameter of 0.5 µm. At a DDR of 5 and 20, the fibril diameters were 0.1 and 0.2 µm, respectively.

Frost line height and process time

Process time in the blown film process is defined as the time it takes the polymer to begin to freeze once it has exited the die. It is proportional to the frost line height and inversely related to the haul-off speed (Equation (12.11)):

$$t_f = \frac{FLH}{V_f - V_o} \ln\left(\frac{V_f}{V_o}\right) \tag{12.11}$$

where:

t_f	=	process time;
FLH	=	frost line height;
V_f	=	haul-off speed;
V_o	=	velocity of polymer at die exit.

The effect of process time on the blend morphology has not been addressed in the literature. It is only within the last few years that this parameter has been accepted as an important scale-up parameter for blown film. It encompasses important aspects of the film blowing process, including the cooling and crystallization time. More important for this discussion is that the process time is inversely proportional to the elongation rate. Stress is related to the draw ratio and to the draw or elongation rate. Therefore, process time is inversely related to the stress imposed on the process [100].

Dispersion of rigid particles and nanocomposites

Dispersing inorganic and other particles in polymers is not well studied. As White [33] explains, this may be because breaking up agglomerates is hard to quantify, particularly since most fillers have a particle size distribution. Generally, it is thought that high stresses are needed to achieve dispersive mixing. Such stresses are typically not found in a single-screw extruder. Hence, most mineral-filled polymers are manufactured in specialized compounding equipment as described earlier. In packaging applications, blending fillers is generally limited to letting down masterbatches. Here, the filler, pigment or additive has been pre-dispersed and simple distributive mixing is all that is required.

One noteworthy aspect of dispersing rigid particles into polymers is particle attrition. Fillers, such as glass fibers, mica and clay, may have long aspect ratios that are important for the blend properties. Too much dispersive mixing can reduce their aspect ratio, degrading performance. Filler abrading the mixing device surfaces can also cause excessive wear. Adding mineral filler in a downstream stage where the polymer is molten rather than to the first stage with the solid pellets can significantly reduce abrasion and attrition.

A key question when dealing with pigments is how do you know if good mixing has been achieved? One commonly used method is to compare a sample against a visual standard. Spectroscopic techniques have also been used, as well as microscopic image analyses [83]. Various indices, such as striation thickness, variance in minor component concentration and segregation scales, have been used, as discussed by McKelvy [101]. More recently, computer image analysis (red-green-blue correlations) has been used. Translating such color analysis to a quantitative distributive mixing index has been difficult. Recently, Alemaskin et al [102, 103] have made progress in developing such an index by employing Shannon entropy. They have used both computer simulation and experiments to verify the method. They simulated mixing two ABS colors in a conventional single-screw extruder metering section using a numerical particle tracer analysis. The results were compared with extrusion experiments under similar conditions. Here, the extruder was stopped, rapidly quenched and the screw pulled to obtain samples along the extruder length. The color homogeneity evolution was measured

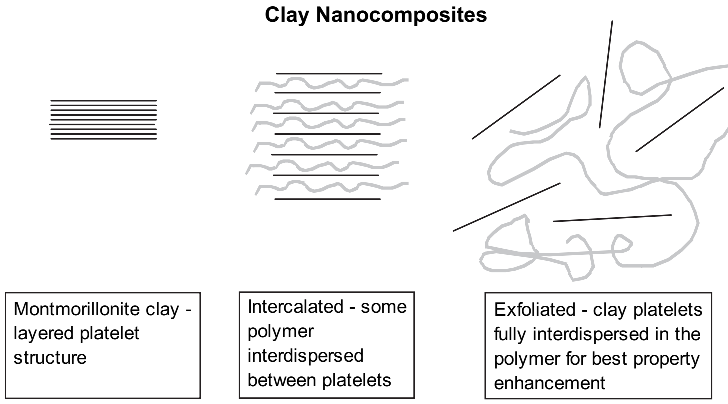


Fig. 12-27 Illustration of states of clay nanocomposites.

using digital computer imaging. Color homogeneity indices based on entropic considerations were computed for both the simulations and digital images and they qualitatively agreed. Such an approach can potentially be used for scale-up, control and process design optimization.

A polymer filled with nanocomposites is a special case. These blends are typically with inorganic particles that have nanometer dimensions. They have been found to be effective in improving:

- stiffness
- mechanical strength
- barrier
- electrical conductivity and
- flame retardance

at levels between 3 and 5wt%. Still in its infancy, two nano-fillers have received the most attention, carbon nanotubes and clay. Carbon nanotubes have been found to impart good electrical properties for shielding and other potential applications. Except for some specialty electronics applications, carbon nanotube composites are not suited for packaging applications.

Of greater interest are clay nanocomposites [104–110]. Most work to date has been done with montmorillonite clay, initially at Toyota. In its natural state, each montmorillonite particle is an agglomeration of many layers of nano-sized platelets. The platelet length and width range from a few tenths of a micron to about 1.5 μms. Their thickness is only about 1 nm and is the reason they are considered nano-materials. Their high aspect ratios give them their unique properties.

The platelets are hydrophilic and are held together at a distance of about 3.5 Å by attractive forces. Clay suppliers add surfactants to the clay to promote inter-platelet expansion to about 20 Å. To obtain the best properties, the platelets must be completely separated from each other. This complete dispersion into the polymer matrix is known as exfoliation and is illustrated in Fig. 12-27. There are two typical ways to accomplish this. One is to introduce the clay during the polymerization process. The monomer is absorbed into the spaces between platelets. As the monomer polymerizes the platelets separate. This process is only amenable to certain polymers where the clay can be introduced during polymerization. Most often it has been applied to nylon.

The second is to compound the clay particle with an already polymerized polymer and rely on the stress generated during mixing to separate the platelets. The surfactant selection is critically important; it must help turn the hydrophilic environment between the platelets into one that is compatible with the monomer or polymer. In some cases, compatibilizers are used to aid in the exfoliation. For example, in PP–montmorillonite nanocomposites, maleic anhydride grafted PP is often added as a compatibilizer. Nevertheless, so far it has proven difficult fully to exfoliate montmorillonite in a compounding process and is the focus of continued R&D. The first approach of polymerizing in the presence of the clay has been more successful.

Adding nano-sized particles to the polymer restrains the molecule's movement, more so than in conventional fillers because of the extremely high surface area that is generated. The restrained motion enhances stiffness and heat deflection temperature. Because the individual platelets are small, toughness and optical properties do not suffer. Of particular importance for packaging applications is the potential for increased barrier performance, especially oxygen barrier. The orientation of the platelets is flexible and their longer dimensions line up in the extrusion and orientation direction. The resulting platelet network structure creates a more tortuous path for gas molecules to diffuse through. Reductions in gas permeability of 60–80% for nylon or EVOH nanocomposites have been reported [104, 109].

Rheology of polymer blends

Utracki [111] provides a good review of the rheology of polymer–polymer blends. Miscible blends are easier to characterize than immiscible ones. Often a log-mean rule is used to estimate the miscible blend viscosity, although there may be some positive deviation (equation (12.12)):

$$\log(\eta_{blend}) = X_A \log(\eta_A) + X_B \log(\eta_B) \tag{12.12}$$

where:

X_A	=	weight fraction of polymer A in the blend;
X_B	=	weight fraction of polymer B in the blend.

Equation (12.12) is useful for estimating the viscosity or melt flow index (MI) for two grades of the same polymer. For example, a 70–30wt%, LDPE1–LDPE2 blend where the LDPE1 MI is 4 and LDPE2 MI is 12 g/10 min, yields:

$$\begin{aligned} \log(MI_{blend}) &= 0.7\log(4) + 0.3\log(12) \\ MI_{blend} &= 5.6\,\frac{g}{10\text{ min.}} \end{aligned}$$

For immiscible blends, Lyngaae-Jorgensen [79] points out that steady state data, such as capillary rheometry data, look superficially like homogeneous polymers. Unless they have been compatibilized [111], however, their behavior may be complex. They typically do not follow time–temperature superposition and mixing rules since the individual phases may behave differently. Their transient behavior and die swell may also be complicated. The immiscible blend morphology is the driving force for this complex behavior.

Reactive polymer blends are a special case. Typically, the reactive blend viscosity increases due to the formation of cross-links that effectively increase the polymer molecular weight. An example is blending maleic anhydride modified PE with nylon. The nylon viscosity can increase by an order of magnitude.

Some additives can cause gels and other problems when blended with a polymer. For example, the acid groups in acid copolymers and ionomers can react with a coupling agent used in some TiO_2 grades, causing gel and other problems. Adding wax, tackifiers and other low molecular weight additives to polymers will reduce their viscosity.

How rigid fillers effect viscosity can also be complex. For very dilute solutions of rigid spheres in a Newtonian fluid, Albert Einstein derived the following result (equation (12.13)):

$$\eta = \eta_f(1 + 2.5\phi) \tag{12.13}$$

where:

η	=	viscosity of the suspension;
η_f	=	viscosity of the suspending fluid;
ϕ	=	volume fraction of the rigid spheres.

The assumptions for this equation break down quickly for filled polymers: the filler loading is not typically dilute, the filler is not spherical and the polymer matrix is non-Newtonian. Dealy and Wissburn [55] describe the following complexities:

- non-Newtonian effects caused by particle concentration and aspect ratio
- buoyancy effects
- particle migration and agglomeration.

A number of equations have been proposed, including the following by Maron and Pierce [112] (equation (12.14)):

$$\eta = \frac{\eta_f}{[1 - (\phi/A)]^2} \tag{12.14}$$

Here, A is a constant that is a function of the filler. Dealy and Wissbrun propose that it can be thought of as the maximum filler packing fraction. For example, the value for A for spheres is 0.68, close to 0.637 which is the theoretical maximum packing fraction. The value for A decreases with the increasing filler aspect ratio (0.44 and 0.16 for L/Ds equal to 8 and 30 respectively). The value of A for a particle size distribution is greater than that for a uniform particle size. A non-uniform filler size distribution, therefore, can reduce the concentrated suspension viscosity.

There are other complications. One is the viscosity to choose when dealing with polymers, since η_f varies with shear rate. Dealy and Wissbrun point out that plotting the viscosity versus shear stress rather than shear rate, as noted earlier for polymer–polymer blends, gives the best results. At low shear rates, the filled polymer may exhibit a yield stress, below which the material behaves like a solid (and does not flow). The yield stress increases with filler concentration.

Conclusion

Blending is an important aspect of polymer/property design for many packaging applications.Achieving a consistent quality blend with the desired properties requires proper attention to both process and product design. The polymer blend properties are a complex function of the stress history imposed by the process and the rheological and thermodynamic properties of the components. Based on experience and science, we can propose several guidelines for reducing these complexities to practice:

- careful control of the blend components fed to the mixing device feed hopper is important since most continuous mixers, such as extruders, do not have very good back mixing
- all things being equal, target 10% or more for the minor component for better accuracy and control
- single-screw extruders can be used for many blending applications where only simple distributive mixing is required. For more demanding applications, high performance screws or ultimately specialty compounding devices, such as twin-screw extruders, may be required
- when using a masterbatch concentrate, make sure the masterbatch carrier resin is compatible with the resin it is being blended into
- very few polymer blends are miscible. For miscible blends, the viscosity can be approximated using the log mean rule (equation (12.12))
- the immiscible blend morphology influences the properties, which generally deviate from the mixing rule. Some examples include using small domains of a soft resin to improve toughness without detracting from optical clarity and laminar morphologies to help improve barrier performance
- the immiscible blend morphology is influenced by:
  - the component concentrations
  - stress history imposed by the compounding device
  - the viscosity and mutual attractiveness (thermodynamics) of the components
- the minor component domain size of an immiscible blend can be reduced by:
  - increasing the stress (by increasing the viscosity of the matrix phase and the shear rate or rate of elongation during mixing)
  - matching phase viscosities (a 0.01–2 viscosity ratio is preferred, particularly for shear flow)
  - lowering the interfacial tension by matching solubility parameters
  - minimizing coalescence
- compatibilizers reduce interfacial stress and coalescence thus reducing domain size. They also reduce the minor phase melt time, which can affect domain size
- elongational flow is generally more efficient than shear flow for dispersing the minor component of an immiscible blend. The flow in single-screw extruders is typically dominated by shear flows unless special mixing elements are used. Both shear and elongational flow can be found in twin screw extruders
- most mixing in a single-screw extruder occurs as the polymers melt, forming sheets or striations that break up into holes and droplets as the shear and elongation are increased along the extruder. Increased shear and stretching in the compression zone or high performance metering zones (such as energy transfer screws) promote sheet break up
- for immiscible blends, orientation during the blown film process often elongates the minor component domains within the matrix resin
- dispersive mixing may be required to break up agglomerates when blending mineral fillers or pigments with polymers. For this reason, these blends are often made as masterbatches using specialized compounding equipment and let down using a single-screw extruder by the film manufacturer.

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Chapter 13

Water- and solvent-based coating technology

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Introduction

The coating process is an essential technology in the successful development and commercialization of flexible packaging films. Many available packaging substrates by themselves are not able to meet the specific requirements for a functional packaging film. Additional functional layers are often coated on the substrate to meet the requirements for the desired oxygen and moisture barrier, for adhesion, for preventing static-caused defects and for printability, aesthetics and durability. Multiple layers can be applied to both substrate sides. Recent advances in coating technology have resulted in the ability simultaneously to coat 12 or more layers. With slot die coating, two or three layers can be simultaneously applied with readily available commercial hardware. The hardware gets more involved and complicated with additional layers. For simultaneously coating more – many more – than two or three layers, slide coating (or precision curtain coating, which in many ways is similar) is the preferred method. Applying multiple layers simultaneously is much more efficient than multiple single layer coatings and also allows very thin individual layers to be coated. Slide coating is not used for single layers as it is more expensive and more technically complex than slot die coating and, at relatively high speeds, slot die coaters can coat thinner individual layers.

This chapter discusses several aspects of the coating process and aims to provide a broad understanding of the many different coating applicators that are used. In addition, the major web coating process elements are discussed. The aim is to familiarize the reader with the many different coating processes available, so that coating technology can be applied successfully when developing products.

Coating uniformity

Coating uniformity can be described by several methods and it is often given as a range, such as a ± 10% uniformity. This specifies that all the data are expected to lie within 10% of the mean value. However, the range is not a precise value and depends on how many data points are involved. As more data accumulate, one would expect occasional points to lie further from the mean. To be more precise statistical definitions should be used. If many data points are involved (an 'infinite' number), we may ask what range will include 99% of the data, or 95%, or 99.7% – as is done in statistical process control. We believe that the commonly used range would include about 99% of the data and, thus, is approximately the same as the 99% confidence limits. The coating uniformity we give in later sections is thus the approximate 99% confidence limits and, in statistical terms, would be ± 2.58 true standard deviations from the mean. When the standard deviation is estimated from a data sample, the number would be higher than 2.58 depending on how many samples are used to estimate the standard deviation and one would have to use the two-sided *t*-distribution to get this number.

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Coating structures

A typical coated structure is a flexible substrate with functional layers coated on either side or on both sides. The substrate can be a single polymer, such as polyethylene (PE), biaxially oriented polypropylene (BOPP), polyethylene terephthalate (PET) or polyvinyl chloride (PVC). There can be a single coated layer or multiple layers depending on the product requirements. The layers may function as oxygen, light or moisture barriers, or may be release layers to which adhesives will not stick. In addition, adhesives are often coated to form laminated structures. Also, conductive antistatic layers may be coated to prevent charge buildup.

The specific coating solution composition depends on the coating's function. However, all coatings have the following general ingredients:

- a binder, which is the non-volatile solid in the dried coating that binds the functional ingredients, such as pigments, clay or other additives, together to form a film. The binder is usually composed of one or more polymers. The polymer may be dissolved in the coating solution or dispersed as a latex
- a solvent to dissolve the binder and some of the ingredients and to suspend and disperse all the insoluble components
- dispersed functional particles, such as pigments for color and opacity, silver halides for photographic activity or iron and chromium oxides for magnetic activity
- additives, such as surfactants or dispersants added as coating aids, plasticizers for flexibility, protective colloids (usually the binder), UV absorbers, biocides to prevent bacterial growth, cross-linking or hardening agents for toughness and insolubility and conductive materials such as cuprous chloride or some carbon blacks to prevent static buildup
- particles on the coating surface, such as silica or hard latex spheres, to control reflectivity and to give surface roughness to prevent 'blocking' or adhesion between adjacent layers, such as occurs between glass microscope slides.

The final solution properties, most importantly the viscosity, may affect the coating process, as we will explain later.

Web coating machine hardware and functions

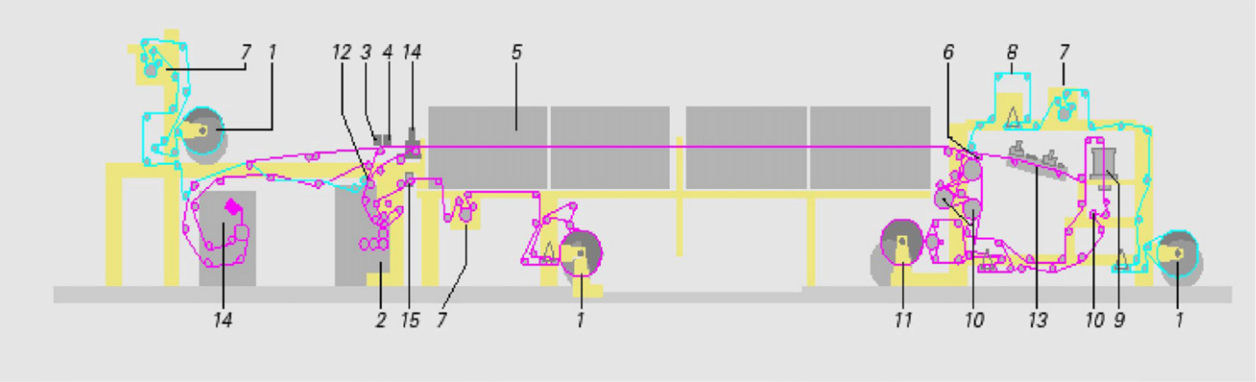
The coating machine used to produce the coated product is complex and has many separate elements that must function well while interacting with each other. The machines are typically quite versatile. They can continuously produce different product structures at high productivity and low cost. They can produce the more common continuous coatings such as barrier layers, release layers, adhesives or antistatic layers. They may also produce intermittent coatings, such as in the printing process and in coating anodes and cathodes for thin film batteries

In general, there is an ideal coater arrangement for any given product. However, most coating machines produce many different products with different coating thicknesses and, therefore, the machine usually is a compromise made for the several applications. The coating machine has several process elements that are required continuously to produce the coated product.

The first element, while essential, is not part of the coating machine itself. It is the kettles and mixing equipment used to mix the fluids that are to be applied to the substrate. The final coating solution contains solvents, binders, pigments, colorants, cross-linkers, surfactants, etc., which need to be dissolved, dispersed and mixed and treated to prepare a uniform homogeneous solution or dispersion. Usually, this is done in temperature-controlled kettles with high or low shear mixers. Scales and filtration equipment are part of this system. High shear mixers are needed to disperse particles and to obtain the desired particle size. After the solutions are mixed, they are filtered to remove larger particles and then either sent to storage or transferred to the solution feed equipment, which is a part of the main coating machine. The solution preparation equipment is not integrated into the coating machine; it is a separate batch operation.

Coating itself is a continuous process and the individual elements must be integrated and function at the same speed. While all coating machines have the same common elements, the exact component design depends on the specific product and productivity needs. Each unit is essentially a semi-custom unit. Coating machine line speeds can range from about 0.01 m/s (2 fpm) for some medical test strips up to 15 m/s (3000 fpm) or even faster for clay coatings on paper, depending on the exact design. Coating widths can vary from about 10 cm (4 inches) to 3.7 m (12 ft) or even wider, depending on need. Fig. 13-1 shows the components of a typical coating machine.

The web transport system conveys the uncoated substrate from the unwind stand through the coating station and the dryer to the rewind stand, while maintaining the appropriate speed and tension control. It has several components. The unwind stand holds the uncoated substrate roll and feeds it into the coating applicator and then onto the dryer. Drive rolls, which may be pinch rolls or S-wrap rolls, other pull rolls with large wrap angles to avoid slippage or vacuum rolls or tables, pull the substrate through the coater at the desired speed and tension. At the rewind stand, the coated product is wound into rolls. There are dancer rolls or force



1. *Unwinder*
2. *Coating unit*
3. *Infrared lamp (short wave)*
4. *Infrared lamp (medium wave)*
5. *Air floatation dryer*
6. *Dry laminating station*
7. *Corona station*
8. *Edge guide unit*
9. *Remoisturising station*
10. *Cooling station*
11. *Rewinder*
12. *Wet laminating station*
13. *Ultra-Violet curing station (UV)*
14. *Curtain coater*
15. *Web cleaning station*

Fig. 13-1 Coating machine with three unwinds and two laminating stations. Courtesy Polytype Converting SA.

transducers to measure and provide feedback to control the tension in the substrate and edge guide systems to keep the substrate running straight in the coating machine.

The feed system maintains the coating solution at the proper temperature and pumps it at the desired rate to the coating applicator through filters to remove unwanted solid particles and through a de-bubbling system.

The coating solution is applied to the moving web with a coating applicator. There are many different applicators and configurations that can be used for this purpose and these details will be discussed later. The coating station holds the coating applicator in a fixed position and permits the operator to set precisely and accurately the coating parameters such as gaps, roll speeds, etc. These settings must be maintained during the coating run. The coating station should not induce chatter in the coating.

The dryer dries the wet coating by supplying heat to evaporate the solvent and circulating air to remove the solvent. Most web dryers are impingement devices that blow hot air against the wet coating. In flotation dryers, hot air also blows against the back, uncoated side. This not only supplies additional heat but also supports the moving substrate. Additional heat may be supplied by infrared heaters. Infrared heaters are frequently used to increase the dryer capacity without increasing the dryer length.

The coating line may also contain a section between the unwind and the coating applicator to surface treat the substrate before it is coated. Flame treatment, corona treatment and gas plasma treatment may be used to improve the substrate wettability. This improves the coating quality and increases adhesion to the substrate by increasing the substrate surface energy and by removing or cross-linking a weak boundary layer on the surface. Web cleaners and static control devices may also be included in this section.

After the dryer and before the rewind there may be a post-treatment section where coatings may be cross-linked with ultraviolet light or an electron beam, moisture may be added by passing the coated substrate through a steam chamber or another sheet may be laminated to the coated substrate.

In addition to production coating machines, laboratory pilot coater machines are also available. These pilot coaters contain the same basic components as the manufacturing lines, however, they are narrower, often 15–60 cm (6–24 inch) wide, and run at relatively low speeds, 0.05–0.25 m/s (10–50 ft/min). They can produce commercial quality coatings and can be used for research and development, scale-up, product development and small volume production. All of the components – unwind, coater, web transport, dryer, rewind – and all of the control systems are contained in a steel and glass enclosure (Fig. 13-2).

There are two laboratory coater designs that are used to develop product – batch sheet coaters and continuous coaters. Sheet coaters are used to develop new products where many different solutions need to be coated and only small samples are available. These methods use devices, such as draw-down blades, dies or wire-wound rods (Mayer rods), to spread a uniform solution layer across a substrate. Most applicators can provide wet coating thicknesses from 5 to 1300 μm (0.2–50 mil). Spray coaters may also be used to coat sheets. The coated substrates or sheets may be dried by ambient air or in a laboratory oven.

Laboratory automated sheet coaters are available. In these coaters, the sheet coating is mechanically controlled. The coated sheets may be fed directly into a dryer, with the temperature and residence time controlled. Compared to hand coaters, these give better

Fig. 13-2 Yasui Seiki CAD laboratory coater. Reprinted with permission of Yasui Seiki Co.

Fig. 13-3 Laboratory sheet coater. Courtesy Werner Mathis USA.

reproducibility with much higher productivity and lower overall costs. A typical laboratory sheet coater is shown in Fig. 13-3.

Coating applicators

Classification of applicators

There are many coating methods that are routinely used to coat various products. The methods range from the Mayer rod (wire wound rod) coater, which has been in use for over 100 years, to relatively new methods, such as the multilayer precision curtain coater and the multilayer slot die coater. Table 13-1 lists the major methods that are in current use. Each method has several configurations for the web path in the coating applicator, application point, blade design or doctoring devices and the number and size of rolls used. As a result there are about 1000 specific configurations that are in routine use.

Table 13-1 Major coating methods

Forward roll	Reverse roll
Reverse roll hot melt	Reverse roll precision
Forward gravure	Reverse gravure
Offset gravure	Mayer rod
Dip	Dip and scrape
Dip and squeeze	Floating knife
Kiss	Slide, multilayer
Meniscus	Slot die
Knife/metering bar	Knife over roll
Knife over blanket	Extrusion hot melt
Doctor blade	Air knife, metering mode
Air knife, squeegee mode	Curtain
Saturator	Spray
Rotary screen	Trailing blade
Coextrusion	Flexographic
Comma direct/indirect	Microgravure

It is convenient to classify these methods according the mechanism that is used to control the wet coating weight or thickness. These four basic classes are:

- self-metered
- doctored
- pre-metered
- hybrid.

In the *self-metered methods*, the coating bead conditions control the final coating weight. In this classification, there are two separate modes that are in operation, the free meniscus and free meniscus plus film splitting. In the free meniscus mode, the conditions in the meniscus, or coating bead, control the solution volume that is applied to the substrate. The principal variables are viscosity and line speed. Increases in these will increase the coating weight. Examples are:

- dip coating
- meniscus or bead roll coating
- forward roll coating.

In the free meniscus plus film splitting mode, the coating is applied by the free meniscus mode and then additional roll(s) are added to create a nip or coating solution bead. The film is split in this nip and part of the coating remains on the substrate and part is returned to the coating pan. A reverse roll coater is an example of this method. This is a very popular method and, with precision bearings, can give high quality coatings with excellent uniformity (± 2%).

In the *doctored coating methods*, a two-part applicator is used. The continuous liquid film is applied by any suitable method, such as with an applicator roll, as in the previous methods. A doctoring device is then used to remove excess coating and thus control the final coating weight. This method can give good coating quality and stability with a many different coatings. The disadvantage is that the coating solution that recirculates back to the original feed system can lead to dirt, bubbles and aging problems. Examples are air knife coaters, blade and knife coaters, wire-wound or Mayer rod coaters, and dip and scrape coaters.

In the *pre-metered methods*, all of the coating solution fed to the coating die is applied to the substrate. Assuming a good coating is obtained, the coating thickness is just the flow rate per unit width divided by the substrate speed. Examples are slide coaters, slot die coaters, extrusion coaters and precision curtain coaters. The advantages of these methods are:

- ease of controlling coverage
- excellent coating uniformity (±2%, except in extrusion coaters) and excellent coating quality
- no recirculation
- multilayer coating capability. Over 12 layers for slide and curtain coating and up to three layers for slot die coating. Five or more layers can be made in an extrusion die, but normally a single layer die is used preceded by a combining adapter
- coverage is not dependent on viscosity.

The *hybrid methods* combine features of more than one method to control coverage. Gravure coating is the most significant hybrid method. In gravure coating, the cells or indentations on the gravure roll surface are filled in the coating pan and then a doctor blade is used to remove the excess coating solution that is then recirculated. The majority of the solution in the cells transfers to the substrate. The coverage is controlled by the cell volume and the fraction that transfers. Thus, it is at least partially pre-metered. However, the doctor blade and the force applied to press the gravure cylinder against the substrate on the impression role also play very important roles.

The coating methods can also be classified according to the number of layers that can be simultaneously applied. However, this limits the understanding of how the methods function and most methods apply one layer at a time. Only the slide, precision curtain, extrusion and slot die coaters can apply multiple layers simultaneously.

Role of substrate

The substrate used in the coating process is a key element for a successful web coating process. The substrate carries the coated layers. The effect of the substrate on the coating process needs to be understood, optimized and controlled to insure high quality and minimum cost. *Web* and *support* are other terms that also refer to the substrate.

The major areas of technical importance for the substrate are:

- substrate structure
- surface properties, treatment, and coatability
- mechanical properties
- defects arising from the substrate
- substrate flatness
- substrate specifications
- substrate manufacturing
- substrate roll unwinding and winding
- substrate web handling in the coating machine
- storage.

The substrate structure is critical because there are many substrates that are used in the coating process. They all have different properties that may require different operating conditions for all of the other elements in the coating process. In addition, there are many new substrates that are being introduced and often they require operating conditions that are not attainable with existing process hardware.

Several major properties categorize and describe substrates. The first is porosity. The structure may be open (porous) or closed. An open porous structure has many cells penetrating into the substrate. On coating, the coated solution partially or fully fills the pores and the balance, if any, remains on the surface. This causes the coated layer to vary in thickness from top to bottom. In order to get a uniform thickness, a filler or sealer layer is coated which fills or covers the pores. A doctoring coating process is used to give a flat surface. Examples of the open structure are:

- paper
- fabric
- sintered metals, which may be porous or closed.

In the second porosity class with closed structures, there are no pores and the surface is uniform and flat, unless it has been deliberately embossed. Examples of these substrates are:

- PET, polyethylene terephthalate. Trade names include Mylar® and Cronar®
- PEN, polyethylene naphthalate
- PE, polyethylene
- PP, polypropylene
- PS, polystyrene
- PVC, polyvinyl chloride
- PVF, polyvinyl fluoride. A trade name is Tedlar®

- PVDF, polyvinylidene fluoride
- PI, polyimide. Kapton® is an example
- cellophane.

Foamed plastics may be open or closed. Open foamed structures may be used as filters in air handling equipment or as absorbent sheets. Closed foam sheets may be used as insulating layers in clothing or blankets or as a packing material. An extreme example is bubble wrap.

The coating applicator selected depends on the surface nature. A slot die applicator will give excellent results with a closed, flat surface because the coating will not penetrate and will be flat and uniform. The same applicator with an open surface will not give a flat coating, because some will penetrate into the pores. For an open structure, a knife or blade coater is normally preferred because the blade is a fixed distance above the substrate and should give a flat top coating while insuring that the pores are filled.

The substrate porosity influences the way the coating dries. For an open structure, the coated thickness that must be dried varies from the deepest penetration into the pores to the surface (this may be the substrate thickness). This long diffusion path may greatly increase the drying time. A variation in pore size from roll to roll can lead to a wide variation in drying time. With a closed flat substrate, the coating thickness is uniform and the drying time is shorter than with an open structure at the same coverage. Thus, the coating will dry faster and be more uniform. The tendency of the solvent to wet the substrate (or conversely, the ease that the substrate releases the solvent on it) also affects the drying rate in open structures.

With embossed plastic substrates, the embossed depth is usually much less than the pore depth which, in open structures, may be the substrate thickness. Thus, the coating thickness variations tend to be less than with an open structure, even when coated with a doctoring applicator. With embossed structures, the increase in drying time compared to a flat surface is often too small to be noticed.

A second important substrate characteristic is its thickness and stiffness. Stiffness varies with substrate thickness cubed and with the modulus of elasticity. Therefore, different substrates at the same thickness can have different stiffness. Thus, polyester films are much stiffer than polyethylene films at the same thickness. Substrates can be grouped into three basic categories depending on stiffness:

- very stiff and difficult to bend. These substrates are usually metals that are thicker than foils, such as aluminum for lithographic printing plates, steel and tin plate for a variety of uses, and copper for electronic circuit boards, and also thick plastic webs
- average stiffness. These are the majority of the plastic and paper webs that are used in the web coating process. They normally range in thickness from about 25 to 250 μm (1–10 mil)
- low stiffness. Composed of thin substrates under about 15 μm (0.5 mil), depending on the specific plastic and aluminum and copper foils. These distort and wrinkle very easily in the coating machine. Thin substrates are used in applications like thin film batteries to give more battery power in a given volume. There is also an economic incentive to use a thinner substrate and save on raw materials costs.

Web stiffness is an important property during coating application, transport, drying and winding. Thicker substrates do not bend as easily and therefore require larger diameter rolls when there is a significant wrap angle. Thicker substrates require higher tension levels and, therefore, more power to transport through the coater from the unwind to the rewind.

On the other hand, thin substrates deform and wrinkle easily. Also, they require low tension levels. Although they can wrap around rolls easily, the low tensions they require may not be enough to drive idler rolls without scratching. In addition, in flotation drying, the substrate can contact the opposing nozzles. This effect is sometimes called parachuting because of the substrate appearance.

A coating line is usually designed and optimized for a particular substrate and it may not have the capability to run widely differing products without modification.

A third major substrate property is its wettability and the coating adhesion to the substrate surface. The coating solution must wet the substrate surface and spread uniformly in order to get good coating uniformity. To get good wetting, the substrate surface tension should be a little greater, perhaps by 5 dyne/cm, then that of the substrate. The coating surface tension can be measured using a Wilhelmy slide or the du Noüy ring balance [1]. The substrate surface tension or surface energy (these terms are equal, as 1 dyne per cm equals 1 erg per square cm) can be estimated with ‘dyne pens’. These are felt-tip pens filled with known surface tension liquids. The substrate ‘dyne level’ equals the highest surface tension liquid that will still spread on the substrate. This is the highest surface tension that the coating fluid can have and still spread. If this condition is not met, then the coating solution surface tension must be adjusted down with surfactants. Surfactants are rarely needed for organic solvents that inherently have low surface tensions and almost always are needed in aqueous systems. In addition, the substrate surface tension or energy can be increased by flame treatment, electrical discharge (corona discharge) or plasma treatment. Fig. 13-4 gives more details of the wetting requirements.

For good adhesion, the coating fluid must wet the surface and also adhere to it. A weak ‘boundary layer’ on the substrate surface is the usual cause of poor adhesion. Surface treatments such as flame, corona or plasma treatment not only increase the surface tension or energy,

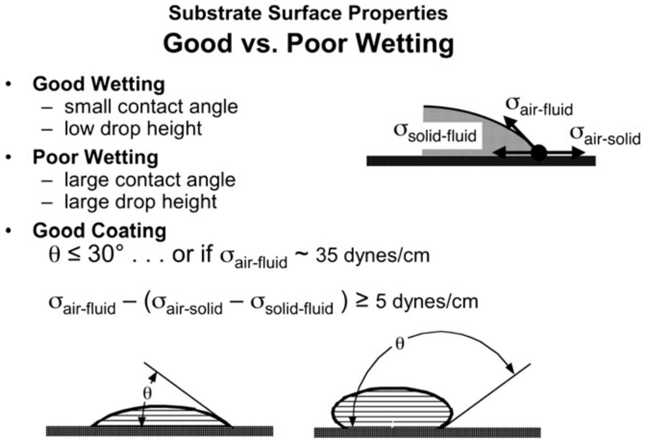


Fig. 13-4 Wetting requirements. The upper sketch shows that, for the fluid to spread, the force to the right (the surface tension of the solid) should exceed the sum of forces to the left, the solid–liquid interfacial tension plus the liquid surface tension times the cosine of the contact angle. When the fluid spreads, the contact angle tends towards zero and the cosine tends towards unity.

they also greatly improve adhesion by either removing the weak boundary layer or cross-linking [2]. In addition, special pre-coat layers may be coated on the substrate to improve adhesion. These are sometimes called *subbing* layers.

Coatabilty limits

In all coating methods, when one tries to coat too fast, air gets entrained under the coating and the coating quality suffers greatly. This is the coatability high speed limit. Air also tends to be entrained when one tries to coat too thin a layer. The low coverage and the high speed coatability limits are very similar. There is also a low speed, or high coverage, coatability limit. When one tries to coat too slowly or to apply too thick a coating, the fluid may run back and some of it may not be carried off.

Different coating methods may have other limitations. Thus, in forward roll coating, the ribbing defect appears when a dimensionless group, called the capillary number (equal to the viscosity times the coating speed divided by the surface tension), exceeds a critical value that varies with the coating gap to the roll diameter ratio. In reverse roll coating, quality coatings can be made free of ribbing and another defect called *cascade*, even at very high capillary numbers, in a region determined by the gap and the metering roll to the applicator roll speed ratio.

Other limitations may be present. For example, in curtain coating, a certain minimum flow rate per unit width is needed to maintain the curtain integrity, independent of coating speed, but dependent on the fluid properties. The minimum thickness that can be curtain coated at any speed is then equal to the minimum flow rate per unit width required for the curtain integrity, divided by the coating speed. As a result, for reasonably thin coatings, fairly high speeds are needed. Thus, curtain coating is inherently a high speed coating process.

In slot die coating, there appears to be a low speed limit below which coatings can be made but only with certain coating defects.

Description of coating methods

Self-metered methods

Dip coaters

Dip coating, along with brush coating and wire wound rod coating, is one of the oldest coating methods. The web passes under an applicator roll that is partially submerged in a pan of the coating fluid (Fig. 13-5). The web is actually dipped into the coating solution. The wet thickness is determined by:

- fluid properties
- coating speed
- withdrawal angle.

The thickness increases with viscosity and coating speed. Dip coating has a wide operating range, is easy to run and the hardware is inexpensive.

Operating parameters for dip coating are:

- viscosity 20–2000 cP or mPa-s
- wet thickness 10–200 µm (0.4–8 mil)
- line speed 0.5–7.5 m/s (100–1500 ft/min)
- coverage uniformity ±10%.

Dip coating is very commonly used for coating continuous objects that are not flat, such as fibers, and also for

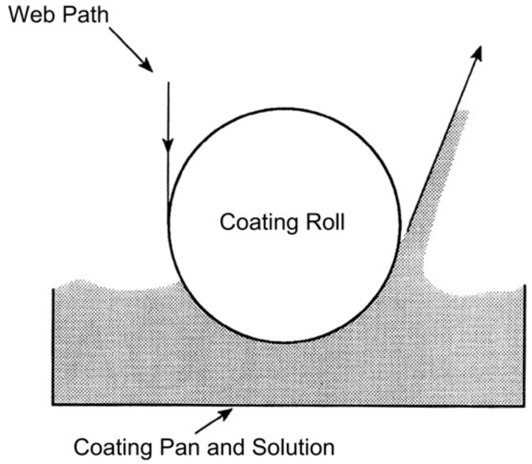


Fig. 13-5 Dip coater. From Modern Coating and Drying Technology, (Cohen, E.D., Gutoff, E.B., eds), Copyright © 1992 Wiley-VCH. Reprinted with permission of John Wiley & Sons, Inc.

irregularly shaped discrete objects. Drops of coating at the bottom of dip-coated articles may be removed by applying electrostatic forces while the article is moved along a conveyor.

Meniscus or bead-roll coaters

In the meniscus or bead-roll coater, the web passes under a back-up roll that is just above the liquid level in a pan. The pan is raised until the solution touches the web and then is lowered just a little so that the solution still maintains contact with the moving web but only due to surface tension. The coverage is determined by:

- viscosity
- solution surface tension
- coating speed.

Different configurations are available, including a two-roll design, where an applicator roll dipping into the solution picks up the fluid and transfers a portion of it onto the web on a back-up roll with a gap just slightly greater than the thickness of the approaching fluid. Only surface tension keeps the substrate in contact with the fluid. Meniscus coating is limited in that the coating speed is very low, only about 0.1–0.2 m/s (20–40 ft/min) and a low viscosity solution is needed. However, high quality optical coatings may be produced. In the past, these coaters have also been used for adhesives and for photographic coatings.

Kiss coaters

In kiss coating, there is no back-up roll. The coating solution is applied to the unsupported substrate by a rotating applicator roll, called a kiss roll. There are many kiss coater designs. While the kiss roll can turn with or against (reverse) the web direction, it usually operates in the web direction. Kiss coaters are tension sensitive and are often used to apply excess coating prior to a metering device. Operating parameters for a kiss coater are:

- viscosity 50–1000 cP or mPa-s
- wet thickness 5–75 μm (0.2–3 mil)
- line speed 0.5–5.5 m/s (100–1100 ft/min)
- coverage uniformity ±10%.

Forward roll coaters

In forward roll coaters, the substrate passes between an applicator roll and the backing roll, both of which are rotating in the same direction as the substrate. The applicator roll drags fluid into the nip (Fig. 13-6). The fluid exiting the nip splits into two directions, with some adhering to the substrate and the rest remaining on the applicator roll, to be returned to the coating pan.

In pan-fed forward roll coaters, the applicator roll dips into the coating pan where it picks up the coating fluid. In fountain fed coaters, an upward pointing slot die coater sends a fountain of fluid across a wide gap against the bottom of the applicator roll. In nip-fed coaters, fluid is fed directly into the nip and kept from flowing out by edge dams.

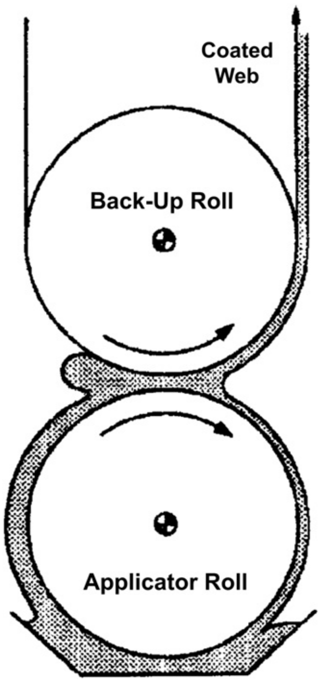


Fig. 13-6 Two-roll, pan fed forward roll coater. From Modern Coating and Drying Technology, (Cohen, E.D., Gutoff, E.B., eds), Copyright © 1992 Wiley-VCH. Reprinted with permission of John Wiley & Sons, Inc.

The forward roll coater is not widely used, especially compared with the popular reverse roll coater, because it gives a relatively poor quality coating and has less viscosity latitude and lower line speeds. It is also very susceptible to a defect called ribbing, where the coating thickness varies sinusoidally across the substrate. It appears as though a giant comb or rake were dragged down the wet coating in the machine direction. Ribbing occurs when the capillary number, the dimensionless ratio of viscous to surface forces, exceeds a certain value that depends on the gap-to-diameter ratio. The capillary number is:

$$C_a = \frac{\eta \cdot U}{\sigma}$$

where:

η = coating fluid viscosity;
U = average surface speed of the two rolls;
σ = surface tension.

It is very difficult to avoid ribbing in forward roll coating. When the fluid is not self-leveling, a smoothing bar is often used to smooth out the ribs. It has been found that a fine wire or thread stretched across the gap exit and touching the liquid eliminates ribbing [3].

The range of operating parameters for forward roll coating is:

- viscosity 20–2000 cP or mPa-s
- wet thickness 10–200 μm (0.4–8 mil)
- line speed 0.5–7.5 m/s (100–1500 ft/min)
- coverage uniformity ±10%.

Reverse roll coaters

In reverse roll coaters, the applicator roll is rotating in the direction opposite to the substrate that is carried on a backing roll and a reverse-turning metering roll removes excess fluid from the applicator roll and returns it to the coating pan. The coating fluid is applied to the applicator roll by any of a number of techniques, such as having it rotate in the coating pan (pan fed), or by applying the fluid by a fountain from a slot die (fountain fed). The important action takes place in the gap between the applicator roll and the metering roll. The fluid remaining on the applicator roll after metering is completely transferred to the substrate traveling in the reverse direction on the backing roll. There are many possible configurations, one of which is shown in Fig. 13-7. The metered coating thickness on the applicator roll is a function of:

- the metering and applicator roll gap
- the metering roll to applicator roll speed ratio
- the applicator roll speed capillary number.

The reverse roll coater is one of the most widely used coating methods. It is an extremely versatile coating method and gives a very uniform defect-free coverage over a very wide coating speed range. It can coat low to extremely high viscosity fluids. The principal advantage is that reverse roll coating can be adjusted to give a stable, defect-free coating at high coating speeds. Using precision bearings, reverse roll coaters can give a coverage uniformity of ±2%.

Operating parameters for reverse roll coating are:

- viscosity 200–50 000 cP or mPa-s
- wet thickness 14–450 μm (0.6–18 mil)
- line speed 0.1–8.5 m/s (20–1700 ft/min)
- coverage uniformity ± 2–10%.

A defect called cascade or seashore, which is caused by air entrapment, can appear under certain conditions in the metered flow on the applicator roll. Both ribbing and cascade can be avoided by adjusting the capillary number based on the applicator roll speed, the metering roll to applicator roll speed ratio and the metering/applicator roll gap.

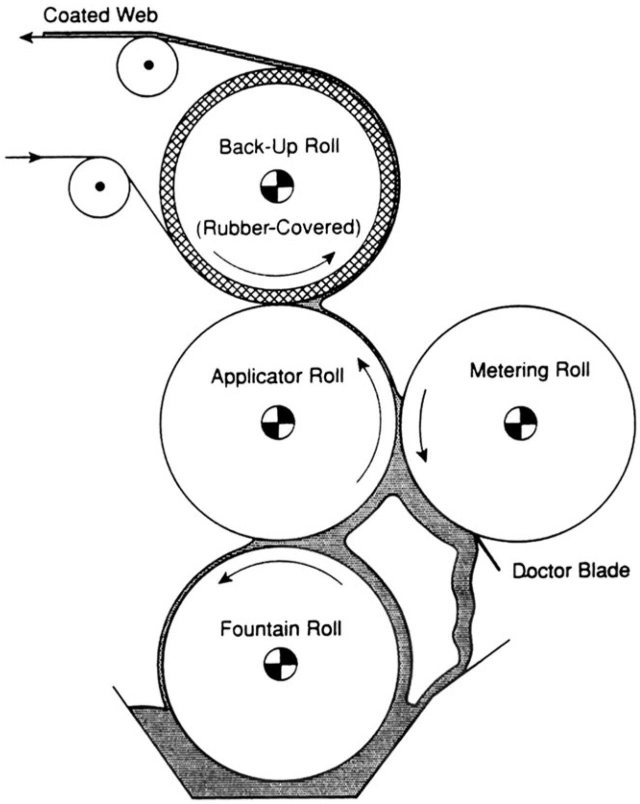


Fig. 13-7 Four-roll pan-fed reverse roll coater. From Modern Coating and Drying Technology, (Cohen, E.D., Gutoff, E.B., eds), Copyright © 1992 Wiley-VCH. Reprinted with permission of John Wiley & Sons, Inc.

Doctored methods

Mayer rod or wire-wound rod coaters

The Mayer rod coater has been in use for about 100 years and is still one of the most widely used methods. In it, a wire wound rod (Fig. 13-8) is used to doctor off excess fluid from the moving substrate. For increased life, the rod

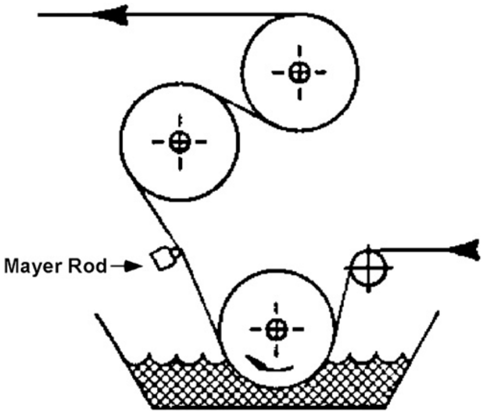


Fig. 13-8 Mayer rod or wire-wound rod coater. From Modern Coating and Drying Technology, (Cohen, E.D., Gutoff, E.B., eds), Copyright © 1992 Wiley-VCH. Reprinted with permission of John Wiley & Sons, Inc.

is slowly rotated. This evens the wear and prevents particles from getting caught under the rod and causing streaks. Normal rotation is in the reverse direction to the substrate travel. The wire-wound rod can be held against an unsupported substrate (Fig. 13-8), or against the substrate on a backing roll. When used against an unsupported substrate the web tension affects the coverage.

The coverage is mainly controlled by the wire diameter wound onto the rod. If the wet coating occupies the area between the wire and the substrate, then it is relatively easy to show that the coated thickness should be 10.7% of the wire diameter. It is always less then this, sometimes as low as one half. The actual coating thickness as a percentage of the wire diameter depends on:

- the fluid rheology
- the substrate speed
- the web tension when coating against unsupported substrate
- the rotation direction.

Different rod designs give different coating weights. Now, rods machined to have the same profile as the wire wound rods are also available. Mayer rod coating is very popular. The coating rods are compact and simple, but they wear rapidly when used with abrasive fluids. However, they are inexpensive and can be rapidly removed and replaced.

Because the wire wound around the central rod has an undulating surface, one would expect the coating to have a similar undulating surface. However, the down-web lines that one frequently sees are usually spaced at other than the wire diameter and are due to ribbing. If the solution is not self-leveling, a smoothing rod may be used to smooth out the surface.

Rod coaters are commonly used for low solids, low viscosity coatings such as used to coat adhesives, optical coatings for windows, barrier layers on polyvinylidene chloride, carbon paper and silicone release papers. Dry coating weights range from 1.5 to 10 g/m^2 and speeds are as high as 5 m/s (1000 ft/min). Operating parameters for wire-wound rod coating are:

- viscosity 50–1000 cP or mPa-s
- wet thickness 4–80 μm (0.2–3 mil)
- line speed 0.05–5 m/s (10–1000 ft/min)
- coverage uniformity ±7–10%.

Air knife coaters

The air knife coater is a versatile coating process that is used for many products. However, the air blower power consumption is high and newer pre-metered coaters can give higher qualities. Therefore, air knife coating is used less these days. Fig. 13-9 shows the major components of an air knife coating process. They are:

- a coating pan and back-up roll to apply the coating solution to the moving substrate
- an air knife positioned after the pan regulates the final wet coating weight by doctoring the coating with a focused air jet.

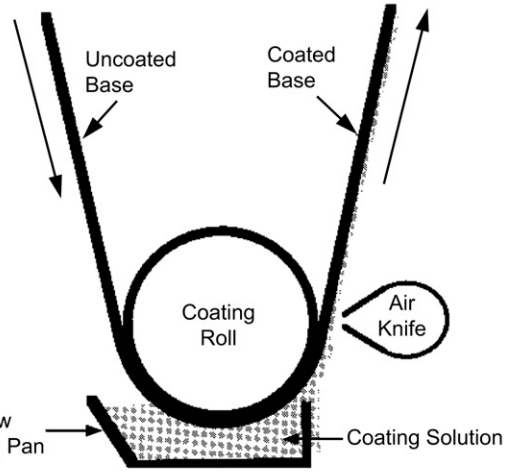


Fig. 13-9 Air knife coater. From Modern Coating and Drying Technology, (Cohen, E.D., Gutoff, E.B., eds), Copyright © 1992 Wiley-VCH. Reprinted with permission of John Wiley & Sons, Inc.

The excess solution is collected in an overflow pan and is either recirculated and re-used or scrapped. The coating weight is determined by:

- the coating line speed
- the coating solution viscosity
- the air knife characteristics.

The air knife characteristics are the volume, velocity and air jet geometry impinging on the coated layer, including the air knife angle of incidence relative to the substrate. Increasing fluid viscosity and line speed increase the thickness and increased air knife pressure reduces the thickness.

The air knife can function in the precision or the squeegee mode. These give a very different coating and performance characteristics, although the same name is used for both processes. In the precision mode, the air knife uses lower pressures and doctors off some of the coating to control the coating weight and to level the surface to give a reasonable quality uniform coating. Good coating quality is usually obtained, although the method is susceptible to streaks and chatter.

The operating parameters for air knife precision coating are:

- viscosity 1–50 cP or mPa-s
- wet thickness 1–200 μm (0.04–8 mil)
- line speed 0.2–2 m/s (40–400 ft/min)
- coverage uniformity ±5%.

In the squeegee mode, the air knife operates at much higher pressures and coating speeds than in the precision mode and effectively blows off the majority of the coating. This process is used for porous supports, such as paper, where the coating is absorbed into the voids. After the air knife, which effectively functions as a leveling device, the coating solids remain in the voids and in a thin surface layer.

The operating parameters for the air knife in the squeegee mode are:

- viscosity 5–500 cP or mPa-s
- wet thickness depends on pore depth
- line speed 0.6–10 m/s (125–2000 ft/min)
- coverage uniformity ±5%.

The advantage of the air-knife processes are:

- the low initial cost
- versatility for coating a variety of substrates and solutions
- ease of changing and maintaining the coating
- and good coating quality.

The disadvantages are:

- the noise
- contamination problems created by the air stream
- the resulting spray
- solution viscosity limitations
- a somewhat restricted coating weight range
- and the high air blower operating cost.

This method tends to give a uniform coating coverage and the coating profile will follow the support profile. This is a precision method and can give good uniform coatings and has been widely used for both photographic and paper coatings.

Knife coaters

The knife coater is a two-part applicator where the coating fluid is applied by any of several methods and then a stationary, rigid knife doctors off the excess coating. Knife coating, either against a backing roll or on unsupported substrate, is a simple, inexpensive and effective coating method. These are simple devices, easy to operate and need little maintenance.

Knives are usually held perpendicular to the substrate and are thick and rigid to prevent them from deforming due to the moving coating layer pressure. There are several possible knife configurations and shapes. The knife-over roll coater (Fig. 13-10) is probably the most common knife coater. It is simple and compact. The driven back-up roll may be precision made and chrome-plated with a controlled gap between the substrate and the knife, or it may be rubber-covered with the knife pressing against the substrate. Here, the pressure against the knife determines the coating weight, with higher pressures giving lower coating weights. Sometimes, the knife is pressed against an unsupported substrate that is held taut by the substrate tension. Coating against a backing roll is more accurate than coating against an unsupported substrate, as it is independent of substrate tension. A full width endless belt may be used to support a weak substrate and pull it through the knife area without tearing, to overcome the knife drag.

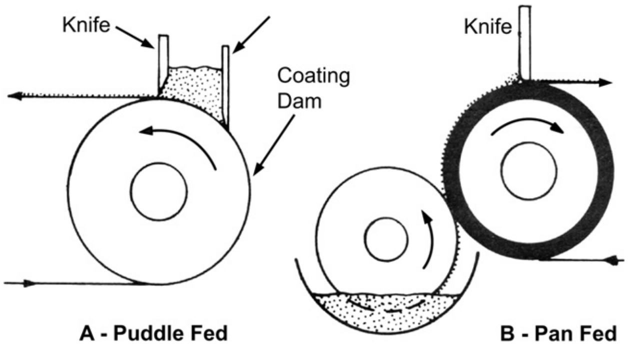


Fig. 13-10 Knife-over-roll coater. From H. Weiss, Coating and Laminating Machines, Converting Technology Co., Milwaukee, 1977, with permission of Mrs Sheila Weiss.

The knife ends can be square, beveled or rounded. The wet coverage is exactly one-half the gap when the end is square and parallel to the substrate, the upstream face is perpendicular to the substrate and there is a fixed gap between the knife end and the substrate. In this case, there is no pressure-driven flow and the flow is due only to the substrate dragging the fluid through the gap. The coated thickness will be greater than half the gap when there is converging flow up to the gap, especially when the converging angle is relatively low and the gap is tight. In this case, strong hydrodynamic forces build up and tend to lift the knife. They also cause pressure-driven flow in addition to the drag flow, so more fluid flows under the knife and the coated thickness is greater than half the gap.

Diverging flow on the downstream side of the knife should be avoided as this very frequently causes ribbing. Thus, instead of using a round rod as a knife, one uses a bull nose knife, where the downstream quadrant of the knife has been machined away.

In knife coating, any depressions in the support are filled in to give a smooth, flat surface. Knife coating tends to level rough surfaces rather than give a uniform coverage, a characteristic that can be desirable or not depending on the finished coating requirements. Streaks and scratches are hard to avoid, especially with high viscosity liquids.

The operating parameters for knife coaters are:

- viscosity 50–40 000 cP or mPa-s
- wet thickness 10–750 μm (0.4–30 mil)
- line speed 1.7–25 m/s (350–5000 ft/min)
- coverage uniformity ±10%.

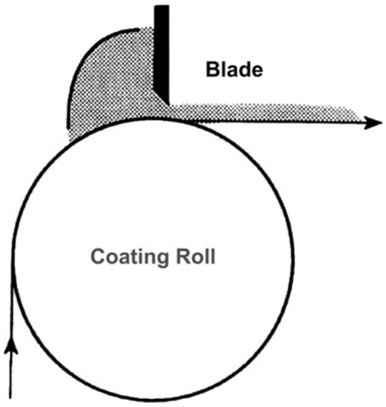


Fig. 13-11 Rigid blade coater. From Modern Coating and Drying Technology, (Cohen, E.D., Gutoff, E.B., eds), Copyright © 1992 Wiley-VCH. Reprinted with permission of John Wiley & Sons, Inc.

Blade coaters

Blade and knife coaters are very similar in their configurations, operation and variables. While knives are thick and rigid, coating blades are thin, only 0.2–0.5 mm (8–20 mil) thick, and can be rigid or flexible spring steel. As in knife coating, blade coating gives a smooth surface and fills in surface depressions.

Flexible blade coaters can be used with a horizontally moving substrate (Fig. 13-11), with a downward moving substrate or with an upward moving substrate (Fig. 13-12). As with knife and many other coaters the fluid may be pan fed, fountain fed or nip fed.

Blades, being thinner than knives, wear faster and have to be changed relatively often, perhaps 2–4 times a day. Blades are always pressed against the substrate, which is supported by a chrome-plated steel roll or a rubber covered backing roll.

Blade coaters are commonly used on pigmented coatings. They have the unique feature of troweling in the low areas in a paper substrate, thus producing a coated surface that has excellent smoothness and printing qualities. The backing roll is usually covered with resilient material and is driven at the same speed as the web to stabilize the web and draw it past the blade. A replaceable blade is rigidly clamped at one end and the unsupported end is pressed against the substrate. The wet coverage is adjusted by varying blade thickness, the blade angle and the force pushing the blade against the substrate. The force on the blade can be obtained by an inflatable rubber tube between the blade and a rigid member or by rotating the blade holder to apply a greater or lesser force at the tip while keeping the angle the tip makes with the substrate approximately constant.

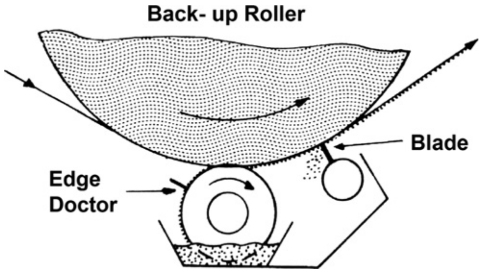


Fig. 13-12 A blade coater against upwards moving web. From H. Weiss, Coating and Laminating Machines, Converting Technology Co., Milwaukee, 1977, with permission of Mrs Sheila Weiss.

The wet coverage decreases rapidly as the force on the blade increases, since the force is concentrated at the blade tip. In knife coaters and in rigid blade coaters, the metal does not deflect. However, with flexible blades, further increases in force bend the blade more and a larger blade area presses the liquid against the substrate. With increasing loading, a point is reached after which the blade tip lifts up and the coverage then begins to increase.

The beveled blade coater uses a rigid blade held at an angle of 40–55° to the substrate. The end is parallel to the substrate and pressed against it. If, initially, the end is not parallel to the substrate, it will soon become parallel due to abrasion by the pigmented fluid. When the loading on the blade increases, the wet coverage decreases. With the same force, but using a thicker blade, the pressure, or force per unit area, on the coating fluid between the blade and the substrate is less and the coverage then is more.

Both sides of a substrate can be coated simultaneously by using two flexible blade coaters on opposite sides of the substrate, pressing against each other and also the substrate between them. The substrate usually travels vertically upward. The coating solution can be different on each side. The blades tend to be thinner and more flexible than the standard blades and the angle to the substrate is lower. The substrate has to have sufficient tensile strength to be pulled through the nip. Another configuration for two-sided coating is to use one flexible blade against the substrate on the roll, where the substrate moves vertically downward. On one side, the coating fluid is nip fed between the substrate and the blade and, on the other side, the fluid is nip fed between the substrate and the roll. Edge dams between the substrate and the blade and between the substrate and the roll keep the coating fluids contained.

The operating parameters for blade coaters are:

- viscosity 50–40 000 cP or mPa-s
- wet thickness 10–750 μm (0.4–30 mil)
- line speed 1.7–25 m/s (350–5000 ft/min)
- coverage uniformity ±10%.

Pre-metered methods

Slot die coaters

In the slot die coater, the coating solution exits the slot between the die lips that are positioned very close to the substrate, forming a gap of 100–500 μm (4–20 mil). The fluid that exits the slot, wets the die lips and forms a coating bead between the lips and the substrate. The coating fluid pumped to the die is deposited on the substrate. Fig. 13-13 shows a two-layer slot coating die. Although mainly used for coating single layers, slot coating can be used for two or even three simultaneous layers. A pump or a pressurized vessel feeds the fluid through a flow meter and control valve to the coating die. The die can operate at room or higher temperatures, if needed. The die may be maintained at the desired temperature by water flowing through internal channels in the die.

A slight vacuum (up to 1000 Pa or 4 in of water) stabilizes the coating bead by having the atmosphere press it against the substrate so that thinner coatings may be made. The maximum coating speed is increased slightly. A vacuum pump or a steam eductor provides the vacuum. Higher vacuums may be needed for higher viscosity liquids. There should be rubbing contact to seal the sides or ends of the rotating backing roll against air leaking into the vacuum box. The coating bead itself provides the seal where the coated substrate leaves the system. Where the substrate on the backing roll enters the vacuum box, the gap must be as small as possible without the substrate surface touching anything stationary, to avoid scratching the substrate. The air in the vacuum chamber can and does resonate as in a musical instrument, such as in a giant tuba. These are just pressure fluctuations that, if large enough, can cause chatter marks at wide gaps. It is very difficult to eliminate this resonance, but one can reduce the amplitude of the pressure fluctuations by keeping the inward-leaking air flow as small as possible.

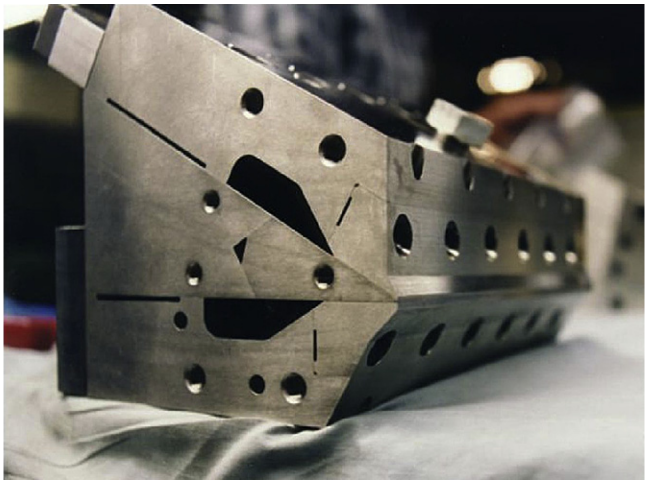


Fig. 13-13 Two-layer slot coating die. Reprinted with permission of Cloeren, Inc.

In pre-metered coating, when a uniform coating is made, the necessary flow rate per unit width is just the desired wet coating thickness times the substrate speed. The viscosity does not enter into the calculation. Of course, if the viscosity varies from place to place in the die (due, perhaps, to temperature variations), then the flow rate per unit width and the coverage will also vary. In pre-metered coating, coverage control is simple and straightforward and, in all the pre-metered methods using fixed or non-adjustable dies, a uniformity of ±2%, even for very wide coatings, is obtained relatively easily.

The coating quality and the coating weight uniformity in the slot die are a function of die design and die geometry. Recent advances in understanding the fluid mechanics in the slot die have resulted in computer programs that help us design the die internals and lips to meet the specified requirements. Since the coating fluid rheology is either known or can be measured, the die can be designed to give uniform flow across the width with no adjustments. Because the viscosity is relatively low, the pressures within the die are also relatively low and the die can be much less massive than an extrusion die that works with very high viscosity fluids and still withstand the spreading forces.

Typically, the substrate is supported by the backing roll in slot die coating. However, for very thin coatings, under about 15 μm (0.6 mil) wet thickness, the gap between the coating lips and the substrate becomes very tight, under about 100 μm (4 mil), and the system becomes difficult to control and operate. The bearing's run-out can become a significant fraction of the gap and this can cause chatter marks as the beads fills and partially empties. Dirt can hang up in the gap to cause streaks. If the substrate contacts the coating die, the substrate can tear, causing a shutdown. Coating against unsupported or tensioned substrate should be used for very thin coatings. In this case, web tension becomes an important variable.

The operating parameters for a slot die coater are:

- viscosity 15–20 000 cP or mPa-s
- wet thickness 10–250 μm (0.4–10 mil)
- line speed 0.02–8.5 m/s (5–1700 ft/min)
- coverage uniformity ±2%.

Extrusion coaters

The terms extrusion coater and slot die coater have no generally accepted definitions and are often used interchangeably. However, we consider them two different processes. In an extrusion coater, a high viscosity material (usually >50 000 cP), such as a molten polymer at elevated temperatures, is extruded from a coating die and onto a substrate where it is cooled and solidified. In the extrusion process, the fluid exiting the slot does not wet the die lips. It forms a ribbon that is laid down onto the substrate. In slot die coating, in contrast, the low viscosity fluid wets the die lips and fills the gap between the die and the substrate by forming a coating bead. In extrusion coating, there usually is a relatively wide gap between the die lips and the substrate.

In coextruding multiple layers, in contrast to slot die coating that uses a die with multiple feed ports, multiple distribution channels and multiple exit slots as in Fig. 13-13, normally only a single layer extrusion die is used with one feed port. Attached to the feed port is a combining adapter [4] or feedblock with one rectangular chamber into which all the feed ports lead. The die feed port is now rectangular to match the combining adapter, unlike its usual round shape. This process works because different high viscosity layers do not mix and remain separate throughout the coating process.

As high pressures are required to push the high viscosity fluid through the die, the die and support equipment are rigid and massive to prevent distortion from the high forces generated. The support equipment needed includes the extruder to melt and pressurize the thermoplastic polymer so it will flow through the extrusion die. The die is heated by electric heaters or by a heat transfer fluid circulating through channels in the die, permitting temperature control of the die. The die also contains adjusting bolts every 3–15 cm or so across the width that control the lip openings and other bolts to control internal choker bars, to obtain uniform cross-web coverage. With manual die bolts, it is very difficult to get a completely flat profile. The preferred system is an on-line thickness gauge that measures cross-web profile and feeds a computer-controlled system to adjust the bolts. In this system, the bolts themselves are electrically heated to cause them to expand or contract and the computer controls the bolt temperatures. This is used to control the internal gap or the lip opening. A sophisticated computer program is used, as increasing the flow under one bolt decreases the flow under neighboring bolts.

An extrusion coating line is like a standard coating line. It has an unwind, a rewind, a web transport system and a coating applicator – the extrusion die. Often, there is a laminating station. There is no dryer because there is no solvent to remove. In its place there is equipment, often a chill roll, to cool the coated web down from the high coating temperature of perhaps 150–200 °C (300–400 °F). The driven chill roll is often chromium or nickel plated with a mirror or matte finish or with an embossed surface. The extruded film takes on the chill roll finish. The chill roll may be 60–90 cm (24–36 inches) in diameter with perhaps a 120 ° wrap angle and utilizes chilled water or water–ethylene glycol mixtures. It reduces the coated film temperature to about 65 °C before it is stripped off the roll. Impingement air nozzles can be used to cool the web further. These only cool the web as there is no solvent to remove.

Extrusion coating is often used in food packaging where vapor and oxygen barriers are required and good heat sealability is desired. Necessary adhesives can be applied using extrusion coating. The expanding food packaging industry is the direct result of packaging improvements that can be attained by improving the surface and physical characteristics of a flexible web, by extrusion coating and by coextruding multilayered films. Operating parameters for extrusion coaters are:

- viscosity 50 000–300 000 cP or mPa-s and higher
- wet thickness 13–525 μm (0.5–21 mil)
- line speed 0.6–9 m/s (120–1800 ft/min)
- coverage uniformity ±5%.

Slide coaters

The slide coater is a specialty coater that is only used to coat simultaneously multiple layers. We know that as many as 17 layers have been applied simultaneously, although often no more than 12 are needed. The slide coater is primarily used to coat color and black and white photographic films and papers. In color films and papers, at least nine layers, three for each of the three primary colors, are coated simultaneously. The slide coater hardware was originally fabricated by the photographic product manufacturers and thus was not widely used. Recently, commercial sources for the hardware have become available.

A slide coater is shown in Fig. 13-14. It consists of rectangular plates with flow distribution channels machined into the plate with an individual coating solution feed port in each plate, except the top or cover plate. The plates are stacked to form a slide or inclined plane and are then bolted together along the sides and back. The fluid is

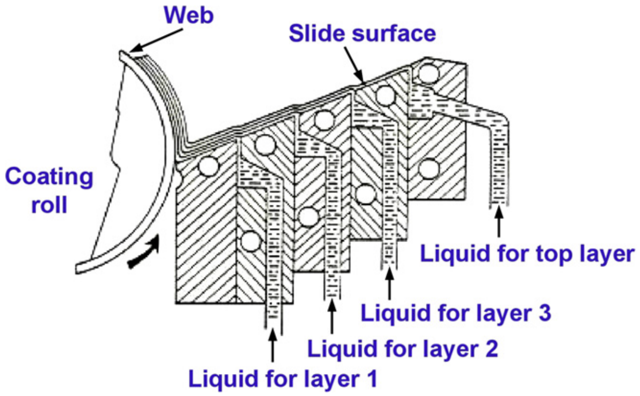


Fig. 13-14 Slide coater. From Mercier, J.A., Torpey, W.A., Russell, T.A., US Pat. 2,761,419, Sept. 4, 1950.

pumped to the plate, is distributed along the channel width and then exits through the slots and onto the slide and flows down the inclined plane in laminar flow without mixing. At the bottom of the slide, the layers flow across the gap onto the upward moving substrate. In the gap, the fluid layers form a coating bead. As with the slot die, a slight vacuum may be applied to stabilize the coating bead and permit a considerably thinner wet coating and also to increase the maximum coating speed by perhaps 25% and reduce some coating defects.

As with all of the pre-metered methods, the coating thickness is equal to the flow rate per unit width divided by the coating speed. With a good die design and flow control system, a very accurate coating coverage of ± 2% can be obtained and the coating quality is excellent.

Coating defects that look like waves can result from interfacial instabilities in the fluid flowing down the slide. To avoid these interfacial waves, the physical properties of all the layers should be close to each other so that the system resembles a single layer. The important properties are density and viscosity. The densities are usually close to each other and rarely differ by even 10% and often are not subject to adjustment. The individual layer viscosities should be reasonably close to each other and can often be adjusted by adding thickeners. Kobayashi [5] has suggested that, to avoid interfacial waves, in any set of adjacent layers the ratio of the upper layer viscosity to the lower layer viscosity should be no more than about 1.5 or 2 (a ratio greater than 10 is also good) or less than 0.7. These critical ratios must be only approximate, as the layer thickness is also important. It is known that interfacial waves are less likely to form on the slide with thicker layers and the layers will be thicker on the slide when one coats faster and thus requires a higher flow rate. Thus, interfacial waves are less likely to form on the slide in production coaters than in pilot coaters at their much lower coating speeds.

The bottom layer should have the lowest viscosity to reduce drag forces and allow higher coating speeds. There is even one patent [6] that suggests using plain water as a desirable bottom or carrier layer to increase the coatability window. In one case with a viscosity of 50 cP for the second layer, the viscosity ratio is about 60, well over the 10 that Kobayashi [5] suggests, as noted in the previous paragraph.

In order for the layers to spread on the slide, the top layer surface tension should be lower than that for all the other layers. It does not matter what the other surface tensions are, as long the top layer has the lowest value. When surfactant is needed to get good wetting, as in aqueous coating, surfactant does not have to be present in the bottom layer as long as it is present elsewhere, as diffusion in these thin layers is so rapid that surfactant will be present in the bottom layer when needed.

The operating parameters for the slide coater are:

- viscosity 1–500 cP or mPa-s
- wet thickness 25–250 μm (1–10 mil)
- line speed 0.1–5 m/s (20–1000 ft/min)
- coverage uniformity ±2%.

Curtain coaters

In a curtain coater, the coating applicator forms a falling sheet or curtain of the coating solution that falls onto the substrate passing under the curtain. There are two variations of this method that have very different properties, the standard curtain coater and the precision curtain coater.

Standard curtain coaters

In the standard curtain coater, the curtain can be formed by fluid overflowing a weir or by a downward pointing die. The curtain is normally wider than the substrate and a catch basin is used to collect the overflow and return it to the feed system. This is not strictly a pre-metered system as all of the coating does not go onto the substrate. This technique has been in use since 1903 and is still widely used to coat adhesives, paints, food products, paperboard, plywood, irregular shapes, chocolate, thick coatings and electronic coatings. Both continuous substrates and discrete sheets can be coated with this method.

It is a simple, inexpensive method of applying a coating with a moderate coating quality. One disadvantage is that a high flow rate of about 0.5–1.5 $\mathrm{cm}^3/(\mathrm{s}\cdot\mathrm{cm}$ width) is needed to maintain an intact, stable curtain. About double this minimum is desirable for a reliable coating process. Because of the high flow rate needed for a stable curtain, curtain coating is inherently a high speed process. Water is the preferred solvent because of the environmental issues created by evaporation from the curtain. Wire edge guides or thin rods are used to prevent the edges from necking in due to surface tension.

When a weir is used to form the curtain, the weir usually is formed of many adjacent small Vs. The coating is delivered to the open weir uniformly across its width by a pipe having diffuser jet openings. The coating fluid flow rate controls the falling curtain thickness.

As with any recirculating system, air bubbles can be a problem.

The operating parameters for the standard curtain coater are:

- viscosity 150–2000 cP or mPa-s
- wet thickness 25–250 μm (1–10 mil)
- line speed 1.5–6.5 m/s (300–1300 ft/min)
- coverage uniformity ±5%.

Precision curtain coaters

The precision curtain coater was developed to coat multilayer photographic films. A slide is used to generate the multilayer structure that then flows over an added die lip to form a curtain. Sophisticated wire edge guides or rods are used to prevent the curtain from necking in due to surface tension. For precision coating, the curtain has to be completely uniform across the width. The curtain is narrower than the substrate, so there is no overflow and thus it is a true pre-metered coater.

The die's vertical distance above the substrate can be adjusted and the falling curtain is protected from stray air movements by transparent enclosure sheets. This method is used only with continuous substrates. Similar to the standard curtain coater, this method has a high minimum flow rate to create a stable curtain and this, in turn, necessitates a relatively high coating speed. There is a minimum speed set by the minimum flow rate per unit width for a stable curtain divided by the desired coating thickness. Below this speed, the system will not function properly.

The precision coater is now used for applications other than coating photographic films. The method patents have expired and reasonably priced hardware is available. A good application of this method is coating single layer pressure sensitive adhesives. Speeds up to 165 m/s (3300 ft/min) can be obtained with low defect levels.

The advantages of precision curtain coating are a high maximum coating speed, multilayer capability and excellent coating quality. There is a very wide coating gap, easily allowing splices to pass, unlike the tight gaps in the other coating methods that usually require applicator withdrawal in order to allow splices to pass, and thus result in a yield loss. The wide gap also prevents the gap from catching dirt carried in by the substrate that leads to streaks and spots.

The operating parameters for the precision curtain coater are:

- viscosity 5–500 cP or mPa-s
- wet thickness 5–500 μm (0.2–20 mil)
- line speed 1.5–15 m/s (300–3000 ft/min)
- coverage uniformity ±2%.

Hybrid methods

Gravure coaters

Gravure coating uses low viscosity (10–5000 mPa·s or cP) liquids to coat thin layers (1–25 μm wet coverage). It is used for long runs and it is used as a precision method to give thin coatings that other techniques cannot do. In gravure coating, a chrome-plated cylinder, the gravure cylinder, is patterned with small depressions (cells) or reservoirs and normally picks up the coating fluid from a coating pan or reservoir. The excess fluid picked up is then doctored off, leaving fluid in the depressions. This fluid is then transferred to the substrate carried by the impression roll. The coating liquid can be applied to the gravure roll by methods other than the pan-fed system. Also, ceramic gravure cylinders are increasing in use. While they are more expensive than the conventional cylinders, they give an order of magnitude increase in cylinder life.

There are several process configurations used. Most use a back-up or impression roll to create a nip and coating bead. In *direct gravure*, the coating solution transfers directly from the gravure roll to the substrate on the impression roll.

In *forward gravure*, the gravure cylinder or the offset roll, if used, and the impression roll all run in the same direction. In *reverse gravure*, the gravure cylinder or the offset roll, if used, and the substrate on the impression roll run in the opposite direction. The sliding motion between the substrate and the reverse gravure cylinder requires that the gravure cylinder or offset roll force against the substrate on the impression roll must be relatively light. In *differential gravure*, the gravure cylinder and the back-up roll run at different speeds. This is one way to control the coating coverage. In one gravure configuration, there is no impression roll and the substrate is unsupported, similar to kiss coating. Here, the web tension control is very important.

The fluid transferred from the gravure cylinder to the substrate or the offset cylinder depends on the fluid quantity in the engraved depressions, the cell pattern and the fluid fraction that is transferred to the substrate on the impression roll. In forward gravure, a high force is needed on the gravure cylinder against either the substrate on the impression roll or the rubber-covered offset roll to get a higher cell fluid fraction to transfer. The usual force is about 2000–20 000 N/m (12–120 1b/inch). A different engraved cylinder is needed for each different coating weight. The fluid viscosity cannot be above about 5000 mPa-s and should also have a low surface tension. The coated fluid will tend to have the engraved roll pattern and so we would like it to tend to level. Reverse gravure and differential gravure with its sliding motion can improve leveling, or a smoothing bar may be used to remove the pattern.

There are three common cell patterns for gravure cylinders that are in routine use (Fig. 13-15). The pyramidal and quadrangular cells are similar, except that the quadrangular has a flat, not a pointed, bottom in order to empty more easily. The trihelical pattern consists of continuous grooves spiraling around the roll, usually at a 45° angle. The volume factor is the term used to represent the total cell volume per unit area and therefore has the units of height. It typically ranges from 4 to 300 μm. The cell volume fraction that transfers varies greatly depending on the system. The cell pitch controls the substrate pickup stability. With high impression roll pressures, one can expect about 58–75% cell volume transfer. The cell pitch or count is the number of cells per

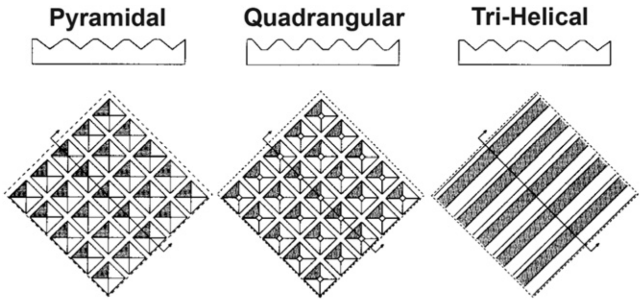


Fig. 13-15 Gravure cell patterns. From Modern Coating and Drying Technology, (Cohen, E.D., Gutoff, E.B., eds), Copyright © 1992 Wiley-VCH. Reprinted with permission of John Wiley & Sons, Inc.

centimeter measured perpendicular to the pattern and usually ranges from 4 to 160 per cm (10–400 per inch). The cell pattern may be made by mechanical engraving, chemical etching, electromechanical engraving or laser etching.

Excess solution is doctored off the gravure cylinder, usually using a 0.1–0.4 mm (4–16 mil) spring steel blade making a 55–70° angle with the incoming gravure roll surface. The blade is slowly oscillated about 6–50 mm (1/4–2 inch) to give even wear and to dislodge dirt that could cause streaks. Or one can use a reverse-angle doctor blade that makes an angle of 65–90° with the exiting surface. This blade does not have to be loaded against the cylinder face as now the fluid presses the blade against the surface, and so the reverse blade can be made of softer materials, such as bronze or plastic.

Using the standard doctor blade, a relatively soft blade, or one having a lower loading against an almost smooth cylinder with a shallow pattern, allows excess liquid to pass through, similar to the flexible-blade coater. A stiff, highly loaded blade against a cylinder having a large volume factor (cell volume per unit area) wipes the surface clean. In place of separate doctor blades to remove the excess coating solution, closed feed chambers with two doctor blades, one to seal the bottom and the other to doctor the top, may be used both to supply the fluid and doctor off the excess. These chambers are fairly small and are fed by what looks like a slot die. Air may be removed from the chamber on start-up by a suction pump.

Leveling the coating can be a problem. A large spacing between cells often results in printing the cell pattern rather than a uniform coating.

The operating parameters for gravure coaters are:

Chamber

- viscosity 10–200 cP or mPa-s
- wet thickness 1–75 μm
- line speed 0.1–12 m/s (25–2300 ft/min)
- coverage uniformity ±2%

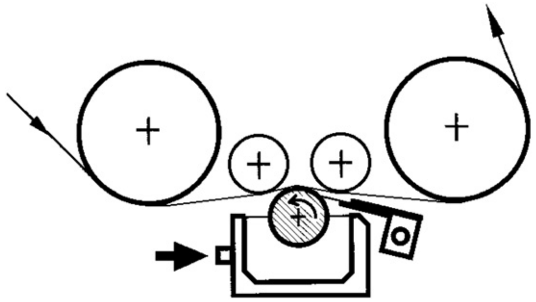


Fig. 13-16 Microgravure™ coater. Reprinted with permission of Yasui-Seiki Co.

Direct

- viscosity 1–500 cP or mPa-s
- wet thickness 3–65 μm
- line speed 0.1–12 m/s (25–2300 ft/min)
- coverage uniformity ±2%

Offset

- viscosity 50–1300 cP or mPa-s
- wet thickness 3–210 μm
- line speed 0.05–5 m/s (10–1000 ft/min)
- coverage uniformity ±2%.

Microgravure™ Coaters

The Microgravure™ coater is a very useful gravure coating technique for applying a low coating weight on a thin gauge substrate. The method gives a uniform and smooth coated layer that is widely used for imaging, electronics, packaging, coated batteries and other specialty applications.

The method is a reverse kiss gravure coater. A typical configuration is shown in Fig. 13-16. The gravure rotates in the opposite direction to the substrate and, as it is a kiss coater, there is no back-up roll. The method is unique in that it uses small diameter rolls, 20–50 mm (1–2 inch) versus 150–300 mm (6–12 inch) for conventional gravure and, in using the kiss principle, so that there is no back-up roll. This results in a small stable bead that, combined with the reverse application, gives a very good quality and a low coating weight.

The operating parameters for the Microgravure™ coater are:

- viscosity 1–4000 cP or mPa-s
- wet thickness 8–80 μm (0.3–3 mil)
- line speed 0.005–1.7 m/s (1–330 ft/min)
- coverage uniformity ±2%.

Effect of solvent

There are many different solvents that are used in the coating process. The two principal categories are organic and aqueous. A solvent's primary function is to dissolve and disperse the formulation ingredients and maintain a stable solution or dispersion both during storage before coating and also during coating. Most often the coating solution contains insoluble particulates in addition to the soluble ingredients and these must be dispersed and kept stable. Therefore, the primary criterion in selecting a solvent or solvent system is that it dissolves or disperses all of the formulation ingredients.

The other requirements for the solvent system involve:

- safety
- health
- environmental
- economic considerations.

The solvent and its vapors should be non-toxic to the coating machine operators. Emissions and waste disposal must meet local and federal guidelines. Water as a solvent has several advantages. It is readily available, its vapors are not an explosion hazard, it is safe to use and it is inexpensive. However, it may not dissolve the organic compounds in the formulation. Also, its high heat of vaporization requires more drying capacity. To increase aqueous solubility, co-solvents and surfactants may be used in the formulation. In addition, the polymeric binders can be synthesized using an emulsion polymerization process to give emulsions that are already in an aqueous formulation. Although pure water is environmentally benign, the final formulation may present disposal problems.

Organic solvents have excellent dissolving power and require less drying capacity than aqueous systems. However, they or their vapors can be hazardous to the operators' health, they may be expensive and their vapors are not 'green' as they are volatile organic compounds. Also, most organic vapors are explosive in certain concentration ranges. We are mainly interested in the lower explosive limit or LEL. This is the minimum vapor or gas concentration in air, measured as volume percent, below which flame propagation (an explosion) cannot occur on contact with an ignition source. Below the LEL there is too little combustible fuel to sustain a flammable mixture. To avoid explosions, some companies operate with a nitrogen blanket in the dryer. Then all solvent concentrations are safe. However, the unwanted oxygen in the dryer has to be rigorously maintained below a safe level, normally 5%. Nitrogen is typically supplied as a cryogenic liquid and the cold liquid nitrogen is used to condense out solvent from the dryer exhaust. The cleaned-up nitrogen is recycled to the dryer, along with make-up nitrogen that has been vaporized in the condenser while condensing solvent.

If there are safety and health hazards, the coating process can be designed to minimize these hazards. However, this requires additional ventilation and may require special procedures and equipment. Toxic fumes usually need to be separated out, collected and treated before disposal and disposal may have to be in a hazardous waste site or by combustion.

For the coating applicator, the coating quality and operability are not a function of the solvent system. The formulation coatability in a coating applicator only depends on:

- solution or dispersion rheological properties
- quality level required
- desired coverage
- uniformity
- line speed.

If the coating solution properties are the same for an aqueous and a solvent-based formulation, the product coated will be the same, although the product quality may greatly differ.

However, when selecting a coating method, the solvent evaporation rate, the vapor level in the coater air, the solvent emitted by the dryer and explosion hazards need to be considered. Some coating methods are better suited to solvent coating because they emit less solvent. A slot die coater has only a small bead exposed to the coating room atmosphere and will emit less solvent than roll coaters that have large rotating wet surfaces and therefore higher evaporation rates. With curtain coating, the falling curtain also has a large surface for evaporation that will give high ambient solvent concentrations. Thus, it is more suited to aqueous coating then to solvent coating.

It should be mentioned that in drying, due to water's relatively high diffusion rate, its small molecular size and the high heat of vaporization, most aqueous system drying takes place in what is known as the constant rate period while, for solvents, most drying occurs in the falling rate period. This has no effect on the coating process and is mainly of interest in calculating drying.

Hot melt coaters

Some formulations can be coated without using solvents. Among these are formulations with thermoplastic polymers and adhesives that have been heated and melted. Temperatures up to 200 °C (392 °F) are used to reduce the viscosity (Fig. 13-17). At the high temperature, the hot melt viscosities can range from 9000 to 100 000 mPa.s or cP. Formulations with these viscosities can be coated using reverse roll and slot die techniques and extrusion dies may also be used. The applicators require heat sources to maintain the temperatures needed to keep the polymers fluid. Additives can be incorporated into

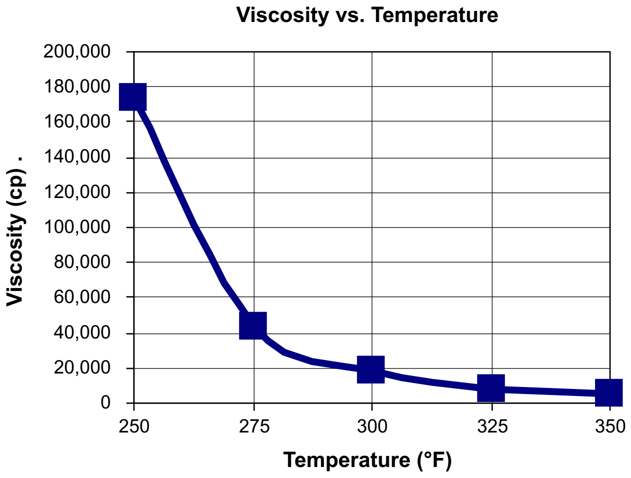


Fig. 13-17 Viscosity–temperature relationship for a hot melt coater.

the binder using high temperature mixing equipment or extruders that can heat the binder and mix it with additives.

This method completely eliminates solvents and their safety, health and environmental concerns. The coating machine can be simpler because solvent dryers are not needed. The dryers are replaced with cooling rolls or short air impingement cooling sections.

Selecting a coating method

A major requirement for the successful manufacturing of a coated product is that a defect-free high quality product be produced with high productivity. This will insure a competitive product and competitive costs. To meet these requirements, the appropriate coating method must be used in the scale-up and manufacturing process. This selection can be complex because there are many factors that go into choosing the best method.

All coating methods can coat a product at some conditions. However, those conditions may not ensure a high yield, defect-free product. Coating with a non-optimal coater and coating conditions will produce a product with some defects causing a resulting high yield loss. Both time and money are wasted by trying to make the product by a process that is not appropriate. Often a non-optimal method is used because it is available at the site and must be used. Forcing a product into available facilities can, in the long run, be very expensive. It may be a better choice to modify the existing coating machine to use a new coating method while retaining the existing dryer and web handling equipment. Under other conditions, it is appropriate to install a completely new machine. One should mention that a coating process that works well at low speeds in the laboratory may not be appropriate for a manufacturing plant coating at high speeds. Conversely, a high speed coating process may not be appropriate for laboratory trials.

Selecting a new coating method, or a new machine, may be needed when new products are being developed, when increased capacity is needed and when quality and productivity improvements are needed. A study may also be carried out to see whether the current coating method is the best. It may be necessary that the best method be used to meet the requirements for the product. The procedure that should be used for this analysis consists of the following steps:

- establish the product requirements and the basic data
- evaluate the different coating methods' capabilities
- match the coating requirements with the coater capabilities
- select the best method
- use the best method.

The first step is to establish the product requirements and to prepare a basic data document that quantifies the product requirements. There are two basic data categories. The independent parameters are those that are fixed and must be met, for they are the basic process needs. The second category is the dependent parameters that are controlled by and arise from the independent variables. The required product volume to be manufactured over 3–5 years is an independent variable. The coating speed and width are dependent variables that arise from the volume that needs to be coated in a given time.

In preparing the basic data, the best available quantitative data should be used. If there is some uncertainty about a particular parameter, then the best estimate should be included and changed as more data become available. At this stage, information should not be too narrow. Consider possible future needs. It is easier and cheaper to delete information as selection proceeds than to add an important factor later. The independent variables that need to be specified are as follows:

- dry coating weight
- coating weight uniformity
- number of layers
- quality level needed
- substrate: type, thickness and surface treatments
- minimum coated width needed
- volume per unit time for the next 5 years
- drying and curing needs
- maximum mill cost needed
- solution application efficiency desired
- timing to market.

The dependent parameters that need to be specified are as follows:

- wet layer thickness
- coating width (this is normally wider than the minimum coated width)
- web width
- line speed
- solvent system to dissolve ingredients
- solution rheology
- available hardware
- safety and environmental issues.

The second step is to evaluate the different coating methods' capability. There are several sources that can be used for these data. There are published data in the literature, such as Cohen and Gutoff [7, 8], Gutoff and Cohen [9], Scriven [10]. Companies that manufacture coating applicators are happy to share these data. Contract coating companies also make these data available and discussions with coating personnel can produce useable data.

The third step is to compare the basic product requirement data, Step 1, with the capabilities of the methods, Step 2, and then select the method that meets the criteria. There will be differences in the coating methods capabilities to meet all of the requirements. Therefore, the selected methods need to be analyzed to choose the best ones. A good way to do this analysis is to prepare a spreadsheet that has the coating methods being considered on the vertical axis and the requirements on the horizontal axis (Fig. 13-18). Each method is then rated for its ability to meet the specific requirements. A simple three level rating system will work, where a 1 definitely meets a requirement, a 0 has the potential to meet a requirement and a −1 does not meet a requirement. The values for all the requirements are then summed and the methods ranked. The top two or three are the methods that should be pursued. A wagon wheel chart can also be used. The spokes of the wheel are the requirements and they are quantified with the range of each requirement. One chart is used for the requirements and the operating range is colored in blue and a second chart is used for the capabilities of the method and is colored in yellow. They are then overlaid and the method with the widest operating ranges where needs and requirements are in green can be determined (see Parodi [11]).

The fourth step is to select the best method to be used in scale-up and production. To do this, the best two or three methods from Step 3 are evaluated in pilot plant experiments. Statistical designs should be used to determine the product response to key coater variables and to evaluate product quality and performance. In addition, the operability window for the methods should be determined. A few experiments will be required to select the best methods and to check reproducibility. If the best coating methods are not available locally, then tests should be run using facilities at contract coaters or coater manufacturers.

Applicator Methods	**Overall Rank**	**Can Batch Coat?**	**Ctg. Wt. mg/cm^2**	**Quality**	**Coverage Uniformity**	**Width (Inches)**	**Solvent**	**Volume ft^2/day**	**Availability**	**Experience**	**Capital Needed**
GOAL		**Yes**	**0.3-1.5**	**Mod.**	**1-10%**	**.5-15**	**All**	**20-1100**	**Yes**	**Yes**	**>200 K**
Spray	**9**	1	1	1	1	1	1	1	1	1	0
Gravure	**8**	1	1	0	1	1	1	1	1	1	0
Hirano, comma	**4**	1	1	1	1	1	1	1	-1	-1	-1
USP 5 360,629	**4**	1	1	1	1	1	1	1	-1	-1	-1
Slot die	**3**	-1	1	0	0	0	1	1	1	1	-1
Extrusion coater	**2**	-1	1	0	0	1	1	1	-1	1	-1
Slide	**2**	-1	-1	1	1	1	0	1	0	1	-1
Curtain, precision	**2**	-1	-1	1	1	1	0	1	0	1	-1
Wire-wound rod	**1**	-1	-1	-1	-1	1	1	1	1	1	0
Printing, flexo, gravure	**0**	1	0	0	0	1	0	1	-1	-1	-1
Curtain, std.	**0**	-1	-1	1	1	1	0	1	0	-1	-1
Knife-over-roll	**0**	-1	0	-1	-1	1	1	1	1	0	-1
Reverse roll	**-1**	-1	-1	0	0	1	1	1	-1	-1	0
Forward roll	**-1**	-1	-1	0	0	1	1	1	-1	-1	0
Choinski patent	**-1**	1	1	0	0	0	0	0	-1	-1	-1
Air knife	**-2**	-1	-1	-1	-1	1	0	1	-1	1	0
Blade	**-3**	-1	-1	-1	-1	1	-1	1	-1	1	0
Porous roll	**-6**	-1	0	-1	-1	1	-1	-1	-1	-1	0
Screen	**-5**	1	-1	-1	-1	-1	-1	-1	-1	1	0
Rotary screen	**-6**	1	0	-1	-1	-1	-1	-1	-1	-1	0

USE CRITERIA: *1* = Meets Goal; *0* = Potential to Meet Goal; *-1* = Does Not Meet Goal

Fig. 13-18 Coating methods comparison using a spreadsheet.

The fifth and final step is to use the best method in scale-up and production. Using contract coaters should be considered to scale-up the product and to confirm the pilot plant findings on the operability window and on the effects of key variables. Contract coaters should also be considered for initial manufacture during construction of the production facilities. If, during these tests, the first method does not meet expectations, then the second method should be tried.

Drying and solidification

The web coating dryer removes the solvent used in the coating process without adversely affecting the coating quality and the product performance parameters. The dryer transfers heat into the liquid coating, thereby evaporating and removing the coating solvents. The dryer can also cross-link or harden the binder, vaporize chemicals other than the solvent and equilibrate the dried coating with ambient air.

Most systems impinge hot air on the coating surface and, in flotation drying, on the back side too. Along with providing heat, the air also removes the solvent from the coating surface. Also, the heat transfer rate and, thus, the drying rate, can be increased by increasing the air velocity impinging onto the coating surface and on the back side.

There are many different hot air convection nozzle configurations for delivering air to the film surface with many nozzle and jet designs. The two general configurations are single-sided dryers and two-sided or flotation dryers. In single-sided dryers, the air impinges on the coated side from nozzles, jets, slots or orifices and rolls are used to support the web in the dryer. In two-sided dryers, the air impinges on both sides and also serves to float and support the web and aid in its transport through the dryer. Two-sided drying almost doubles the heat transfer rate compared with single-sided drying. (In two-sided drying, the heat transfer coefficient is effectively doubled but, because the web and coating temperature are increased somewhat, the temperature driving force, that is, the air temperature minus the coating temperature, is decreased slightly. Thus, the heat transfer rate is less than doubled.) In addition, as the drying air supports the web, there are no rolls contacting the web. Thus, scratches caused by the web sliding on a roll and repeat marks and contamination caused by roll contact with the moving web are eliminated.

Typically, these dryers often have separate sections or zones where the air temperature, velocity and solvent level can be controlled independently. The zoning improves quality by allowing mild treatment in the start of the drying process where the coating is very liquid and easily disturbed, and more severe conditions in the later zones where the coating is drier and is more resistant to deformation.

Drying air temperatures need to be controlled for several reasons. Higher drying temperatures result in more rapid drying. However, there are temperature limitations both for the substrate and for the coating. When plastic films are heated they can distort and stretch under the machine tension required to transport the film. Each plastic has its own temperature limit. The wet coating must not be heated above its boiling point or blisters will form on the surface. The as-coated coating boiling point may be near the solvent boiling point. However, as the coating solvent concentration decreases, the boiling point rapidly rises and, thus, the allowable temperature also rises. In addition, the coatings themselves may have a maximum temperature above which the coating degrades. Many photographic coatings, for example, should not be heated above about 45 °C to prevent degradation.

In addition to supplying heat by convection using air impingement dryers, conduction heat transfer by running the coated web over a heated roll and radiation heat transfer using infrared or microwave radiation are also used. In conduction drying, the hot roll is usually heated by steam. Air still has to be supplied to carry away the solvent vapors. Chilled rolls or drums are also used rapidly to cool hot extruded films. As the temperature falls, the plastic viscosity rapidly increases and the film solidifies. Chilled rolls can also be used at the end of a dryer to cool coated webs down to ambient conditions. Heat transfer by conduction is very efficient, but the large diameter, double-walled rolls are very expensive and have large inertias. This technique is used mainly at low speeds and is not often used in newer systems.

When infrared and microwave radiation are used to supply heat, air must still be used to carry away the solvent. Radiation provides a high heat input over short distances. Infrared dryers are often used in conjunction with convection dryers. They are frequently positioned at the start of drying to bring the coating rapidly up to the desired temperature and evaporation rate. The higher initial evaporation rate gives a more rapid increase in viscosity than with an impingement dryer alone, thus allowing a more rapid increase in the impinging air velocity without damaging the wet coatings. Infrared heaters can also be placed between the air nozzles. This increases the drying rate and thus the production rate without increasing the dryer length and without requiring additional air handling systems.

Microwave radiation is used only for aqueous coatings, since the heat is created by rapidly oscillating water molecules that are strong dipoles. Most other molecules have very low sensitivity to microwave radiation. This radiation is not often used as it is more expensive than the other heating methods.

Constant rate and falling rate drying

The drying process is divided into the constant rate period and the falling rate period. The requirement for constant rate drying is that the coating behaves as if it were a solvent pool and, as there is always enough solvent on the surface, the drying rate is then determined by the heat transfer rate to the surface and the mass transfer rate from the surface. These are determined by what takes place in the air and not by diffusion in the coating. In the constant rate period, the drying rate is constant only at equilibrium, not throughout the whole constant rate period. Because the heat transfer rate is determined by the temperature driving force from the air to the coating (and by the heat transfer coefficient), the coating has to remain below the drying air temperature for there to be a temperature driving force. In fact, in single-sided impingement drying of aqueous coatings, the equilibrium coating temperature in the constant rate period is the so-called wet bulb air temperature.

However, at the start of the dryer, the equilibrium conditions have not yet been reached, but it is still in the constant rate period. There are cases where equilibration is never reached in the constant rate period and the drying rate continuously changes, yet it is still in the constant rate period. (One example is a photopolymer coating on 0.5 mm aluminum sheeting. The heat capacity of the 'thick' metal is so great that the temperature can be accurately and easily calculated by just assuming that uncoated aluminum is being heated up in the dryer. And the drying rate is always changing in this constant rate period.)

After the constant rate period is over, the coating no longer resembles a solvent pool. The surface appears dull and dry. Now, the drying rate is determined by how fast solvent can diffuse to the surface and not by the conditions in the air. The diffusion rate to the surface is determined by the diffusivity and by the concentration driving force (dc/dx) in the coating surface. The diffusivity is a function of the coating temperature and of the solvent concentration in the coating. As the coating dries and the solvent concentration decreases, the diffusivity drops rapidly, the evaporation rate and the evaporative cooling decreases and the temperature rises to approach the drying air temperature. At higher temperatures, the diffusivity is higher. The drying rate continuously decreases in the falling rate period because the effect of the lower concentration on reducing the diffusivity is much greater than the effect of the increasing temperature on increasing the diffusivity.

Pollution considerations in drying

An important consideration in drying is that the solvent vaporized during drying is frequently a pollutant and must be removed from the exhaust air before it is discharged into the atmosphere, to insure that government standards are met. To do this, the exhaust air is passed through a treatment facility where the solvent vapors and other pollutants are separated from the air by condensation, by adsorption onto activated carbon or other adsorbent, or by absorption into a circulating aqueous solution. The solvent can be recovered and reused or, if it is flammable, it can be burned. There are several commercially available systems to perform both functions. If the solvent is a pollutant, then the amount used should be reduced and consideration should be given to using a non-polluting solvent if possible.

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Chapter 14

14

Vacuum metallizing for flexible packaging

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Introduction

There is a long history of roll-to-roll vacuum deposited coatings with evidence that the earliest use, around 70 years ago, was for food packaging [1]. Since then, this industry has grown enormously. Metallizing is still the most dominant process with packaging, with over 65% of metallized film as the most dominant application. Of this 65% portion, approximately 56% is oriented polypropylene (OPP) and 37% polyethylene terephthalate (PET) [2]. What has changed over the last 70 years is the variety of substrate materials and the functionality of the deposited coatings. Broadly speaking, there are four main areas of use: decorative or aesthetic, barrier, functional and security. It is possible that some coatings provide more than one of these functions.

Decorative coatings

Decorative coatings for packaging began with the simple metallization of polymer films and papers, which gave the web a bright metallic appearance. This bright metallic web enabled products to be wrapped, boxed or labeled using a material that stood out from their competitors. As with all competitive products, once one company produced a brighter package or label, there was a rush by others to follow suit. As more products incorporated metallic effects to their packaging designs, there was a desire to differentiate products and so variants were produced. Instead of bright metallic silver reflecting material, colored metallic coatings were produced, either by using a dyed substrate material or by over coating the metallic coating with a transparent colored lacquer. Since then, the most significant development was the introduction of embossed holographic substrate materials that can also be produced in silver or colored metallic versions.

Consumers scanning a shelf of products will generally have their attention drawn to packages that have some brightness to the design. Initially, this was simply a very white surface area. Tests were carried out with packages with no white areas to almost all white designs and people walking past and scanning the products always had their attention drawn to those products with a high white content. This changed with the introduction of the metallized webs. The products, with even a small metallized component included in the design, had a brighter appearance than the white packages and as such they stood out more and attracted the consumer's attention. Similarly, with the introduction of metallized holographic substrates, these gave an even brighter appearance than the plain metallized webs [3]. In fact, holographic designs were assessed as being 3.5 times brighter than white [4]. As there are so many competing products, it is regarded as essential to attract the consumer's eye quickly, since it has been shown that there is a higher chance of a purchase for those products that have been seen first. It has been demonstrated, particularly with the introduction of

Multilayer Flexible Packaging; ISBN: 9780815520214

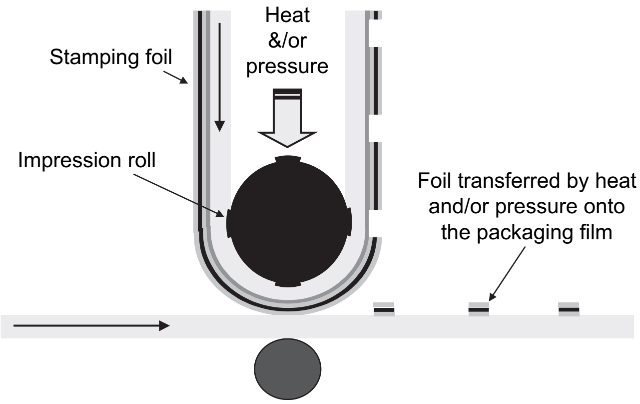

Fig. 14-1 Schematic of hot or cold stamping foil: transfer process.

holographic designs, that there can be a considerable increase in market share following the introduction of holographic packaging [5–7].

There are a variety of different methods for getting the metallic look onto packages. The most commonly used method is to metallize the whole substrate, such as paper or polymer, and to then print or laminate with the printing selectively over the metal to complete the desired design. Where most of the metallic coating is over printed and hidden and only a small patch exposed, it is required to metallize the whole surface, which can be an expensive solution. An alternative approach, to achieve the same end result, is to use either a hot or cold stamping foil. In this process, the metallization is onto a polymer substrate that has been pre-coated with a release coating. Following metallization, an adhesive is applied to the metal surface. When this material is pressed onto a surface, the adhesive sticks to that surface and the metal coating is transferred from one surface to the other. The metal separates from the original substrate because of a failure within the release coating or between the metal and the release coating. This process can be done either before or after the printing and on the same machine. Depending on the system used, this can either be a hot or cold process (Fig. 14-1 and 14-2). If done cold, there tends to be a higher pressure required to transfer the metal. Hot transfer may be an easier process but, in some cases, the elevated temperature is a problem. An example of this would be in the hot stamping of a holographic foil where the temperature can degrade the embossing, reducing the height of the embossing by polymer relaxation, which can be seen as a lowering of the hologram brightness.

The quality of the metallized film is largely dependent upon the substrate material quality. Metallized paper may appear dull unless the surface has been deliberately coated and smoothed to increase the specular reflectance. Polymer films that contain a high filler level may also have a rough surface and so scatter much of the light giving a highly diffuse reflectance and lower specular reflectance (Fig. 14-3). This has led to coextruded films that have an unfilled surface which gives a very smooth surface and, consequently, a very highly reflecting coating.

Holographic embossing can be done either before or after metallization.

A final method of adding a metallic coating to packaging film, that also starts life as a metallized film, is by printing using metallized ink [8]. The quality of the metal pigment used to make the ink metallic can affect the reflectivity. The metallic pigments used to be made from ball milled aluminum particles that were known as ‘cornflakes’

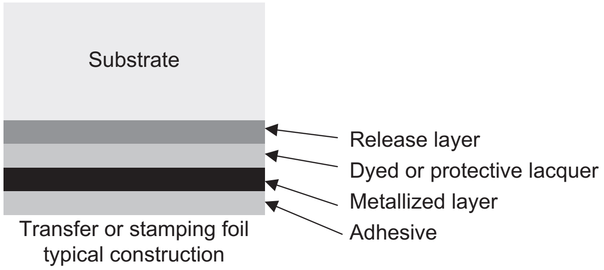

Fig. 14-2 Schematic of hot or cold stamping foil: foil construction.

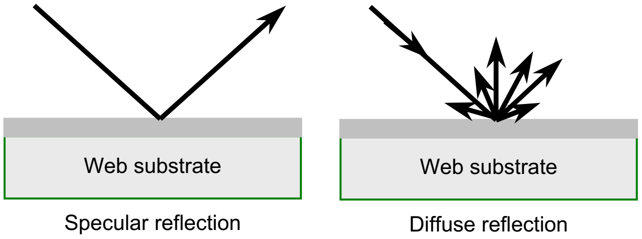

Fig. 14-3 A schematic diagram showing the difference between specular and diffuse reflective coatings.

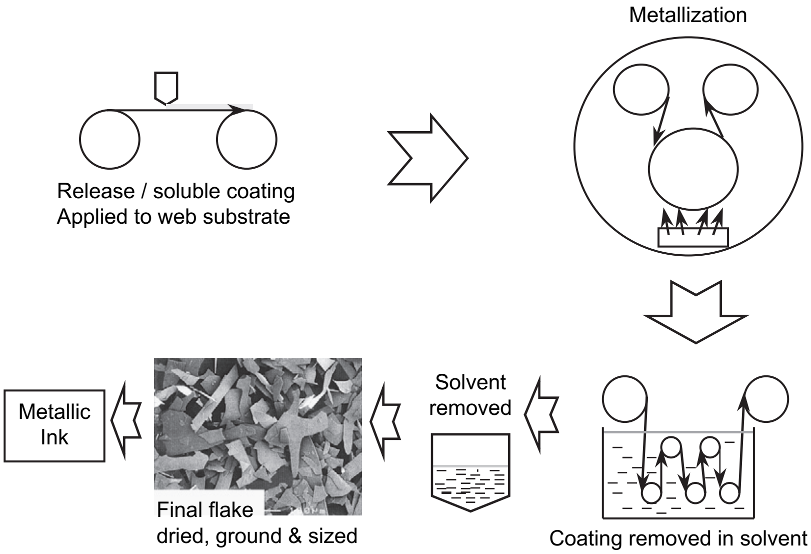

Fig. 14-4 A schematic of the flake metallic pigment production process.

because of their crinkled shape [9]. This uneven surfaced pigment produced ink with a highly diffuse reflectivity. This pigment has been considerably improved with the change to using vacuum metallized pigment. This process is shown schematically in Fig. 14-4.

A roll of polymer with a very high quality, smooth, flat surface is coated with a release layer and then metallized. After removal from the metallizer, the film is passed through a stripping bath where a solvent interacts with the release coating and allows the metallic layer to be lifted off the surface. This metallic layer is fragile enough to break up into flakes. This slurry is filtered and the solvent exchanged to a suitable carrier for the manufacture of ink. When the ink is printed, these flat flakes of metal align parallel to the substrate surface. Each flake has a very high specular reflectance and so, although not all flakes are perfectly aligned, they are closely enough aligned that the specular reflectivity remains high.

Barrier coatings

'Barrier coatings' is very broad category and includes coatings that reduce light, oxygen, water vapor or other gas transmittance [10]. We shall look at each of these properties in turn.

Light barrier

Many foods are degraded by the photocatalytic reactions of light that can lead to the degradation of color, fats, flavors or vitamins within the food. This can shorten the food shelf-life, as well as making the food unattractive, off flavor and, thus, harder to sell.

Oxygen barrier

Oxygen can turn fats rancid as well as oxidizing vitamins, such as vitamin C, reducing their potency. It is not only foods that require barrier packaging. Some of the newer high technical specification devices also need to have protection against oxidation. Examples of this would be the organic light emitting devices (OLEDs) and copper indium gallium di-selenide (CIGS) solar cells.

Water vapor barrier

Water may be absorbed or lost by foods and turn them 'stale' causing a texture change, thereby losing much of their appeal. An example of this would be potato crisps or chips that are expected to be brittle and crispy but, if they absorb excess moisture, they lose this feature, which would lead to customer complaints.

Foods that are already moist, rather than absorb moisture, may actually lose moisture and the food dries out. Examples of this would be cheese, moist cookies or dried fruits. This moisture loss changes the food from what is expected and shortens the life time of the product.

As with oxygen, OLEDs and solar cells can be adversely affected by moisture and so require a suitable moisture barrier.

Gas barrier

There are instances where it is advantageous to exchange normal atmospheric gas with an alternative (called gas flushing) that can maintain some property of the food better than air. In these cases, the aim is to provide a barrier to the gas being flushed into the package, as well as a barrier to keep out the air and water vapor in the environment. The materials used in gas flush operations are known as modified atmosphere packaging (MAP) films.

Barrier coatings are aimed at providing a structure that resists the diffusion of gases or liquids through the material. Nature drives all systems towards a state of thermal and concentration equilibrium so, if a food has been packaged in a modified gas atmosphere, rich in specific gases, this gas will be diffusing out and the surrounding atmosphere will diffuse in, until an equal concentration with the surrounding atmosphere is reached within the package.

Polymers have a limited gas, moisture and chemical barrier performance, with some polymers performing better than others. Simplistically, it was observed that both glass and metal foil had a good barrier performance and it was thought that producing thin layers of glass and metal onto a polymer would produce an ideal barrier material. The metal or glass could be thinned down with the polymer acting as a support material. What does become clear is that the barrier performance is never as good as predicted [11]. The glass or metal coating should be a perfect barrier, but it is not.

Glass is a brittle material and can easily be cracked and so can be quite fragile. Some of this is overcome by using very thin and more flexible coatings. Metal coatings are somewhat more flexible than glass or ceramic coatings, but they also do not achieve their predicted performance. In regards to the gas barrier properties, the main problem for these films is pinholes [12–14]. Pinholes are formed when dust or debris that is on the polymer surface during metallization is moved after metallization leaving behind an uncoated small area known as a pinhole or pinwindow. There may also be other methods of producing pinholes such as pick-off, where high winding forces and high spots on the films unmetallized surface coupled to poor adhesion of the metal layer can lead to the transfer of some of the coating from the metallized surface to the unmetallized surface. Anywhere there is a pinhole there is effectively no barrier.

Handling the film following vacuum coating can also introduce more defects, not just because any dust can be moved, but also by any additional film slipping that can cause scratching as well as any folds or stretching that occur to the film, as part of the packaging process, that can cause cracking and other stress-related defects.

Barrier coatings can be divided into two main groups, opaque and transparent barrier coatings. Opaque barrier materials are primarily aluminum metallized coated polymer films. The barrier requirements may be a mixture of gas and moisture barrier as well as the opacity for light barrier. The coating thickness will determine the opacity and may also affect the gas and moisture barrier.

Transparent barrier coatings, although they have been available for around 20 years, are in many respects still in their infancy compared to the aluminum metallized films. These transparent barrier coatings provide the same oxygen and moisture barrier but have no opacity. This allows consumers to see the products they are buying and so may have some selling advantages. Also, during high-speed manufacture and packaging, it makes scanning the products for metal contamination much easier than when using metallized films. The transparent barrier coatings are, in general, two to three times more expensive than aluminum metallized films. Years of development work that has gone into reducing the cost of these coatings [15–18]. This has resulted in several different techniques and materials all aimed at producing transparent barrier materials.

There are a number of competing processes that most use to deposit transparent barrier coatings. One of the earliest was a series of induction heated, thermal evaporation sources that were used to deposit silica coatings [19]. Probably the simplest and most cost effective process that has been developed used a standard aluminum metallizer and introduced oxygen into the process just after the aluminum was deposited, relying on the very high aluminum reactivity to oxidize the growing coating [18]. The most flexible deposition process uses an electron beam deposition source that can deposit almost any material and so has the flexibility to deposit a transparent barrier material on one roll of substrate and then deposit an optically opaque barrier material onto the next roll. However, this is a much higher capital cost system than the simple aluminum metallizers and the coating costs are correspondingly higher [17].

The final process that is expected eventually to deliver lower cost transparent coatings is plasma enhanced chemical vapor deposition (PECVD). In PECVD, a source gas is introduced into the vacuum system and, using plasma technology, the gas is broken down into the required chemical components to deposit a silica coating. Although this process started out as a quite a simple design, it has increased in complexity as the speed and barrier performance has increased. The current process [16] requires a system that costs almost as much as an electron beam deposition system. One continued advantage is that the precursor liquid is inexpensive and so the material costs are lower than most other transparent barrier materials. Ultimately, the cost of transparent barrier coatings is controlled by the raw material costs as opposed to the processing costs.

Functional coatings

In one sense, this group is something of a catch-all as it contains coatings as different as microwave susceptors, antistatic coatings for semiconductor packaging, some of

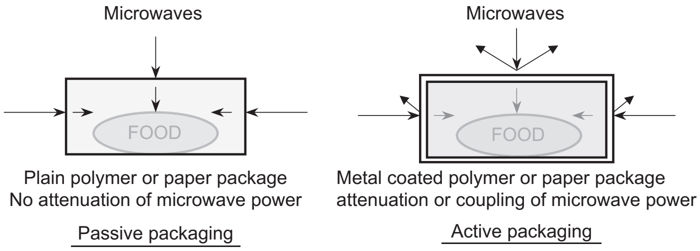

Fig. 14-5 A schematic comparing active and passive microwave packaging.

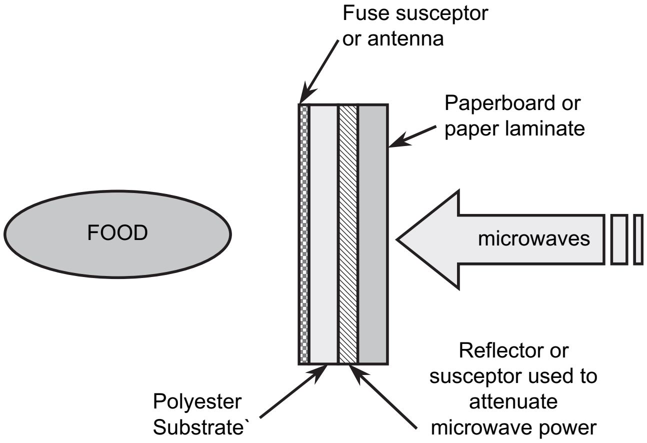

Fig. 14-6 A simple packaging structure.

the electromagnetic shielding coatings and some radiofrequency identification devices that can also fall under heading of security coatings.

Microwave radiation can be used to heat foods directly, where the microwave energy is coupled into the water molecules of the food (Fig. 14-5) vibrating them, generating heat in the food. Fig. 14-6 shows a typical microwave structure. However, different foods contain different amounts of water and so will heat at different rates. Thus, in instant meals that may contain a variety of foods that all need to be heated at the same time, it is useful to control how the microwave power is coupled into different areas to allow all the food to arrive at the preferred cooked state at the same time. This can mean using complex patterns, some of which are shown in Fig. 14-7.

For microwave cooking, there are several different types of coatings that can be used. A continuous thin metal layer can act as a microwave energy absorber, a patterned coating can act as an antenna and can focus the power into the food to provide extra heating. Finally, a continuous thick metal coating can act as a reflector blocking out some of the microwave energy to portions of the container. By using combinations of these different coatings, complete meals can be cooked selectively.

A second application for microwave cooking is where a surface is required to be heated to a temperature high enough to crisp or brown the food in contact with the surface. One of the difficulties is to limit the device temperature to prevent charring of the food. The microwaves are absorbed within the thin conducting metal coating and this absorbed power causes the metallized surface to heat up. Use is made of the different thermal expansion coefficient between the substrate and metal coating to control the ultimate surface temperature. As the polymer expands faster than the metal it puts the metal coating into tension. Then, if the differential expansion is large enough, the metal coating cracks. As it cracks, it loses conductivity and this limits the microwave heating as the microwaves are no longer as effectively absorbed by the coating.

One of the problems seen in the early packages relying on this feature was that the cracking could be variable and so there would be some uncracked areas, that overheated, and other areas that failed early and underheated the food giving incomplete cooking. To correct for this problem, a pattern of de-metallized areas was incorporated into the metallized surface design [21, 22]. These patterns concentrated the stress so that the stress

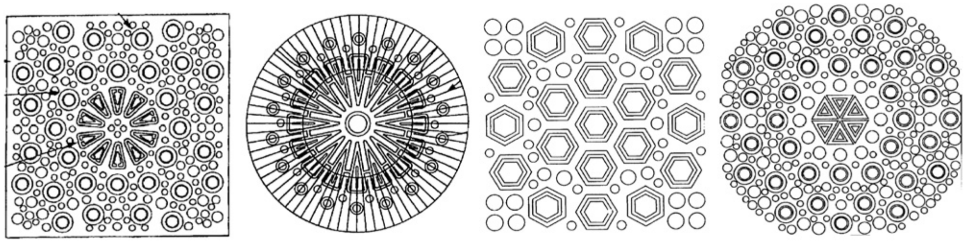

Fig. 14-7 A variety of patterns produced for microwave heating of foods [20].

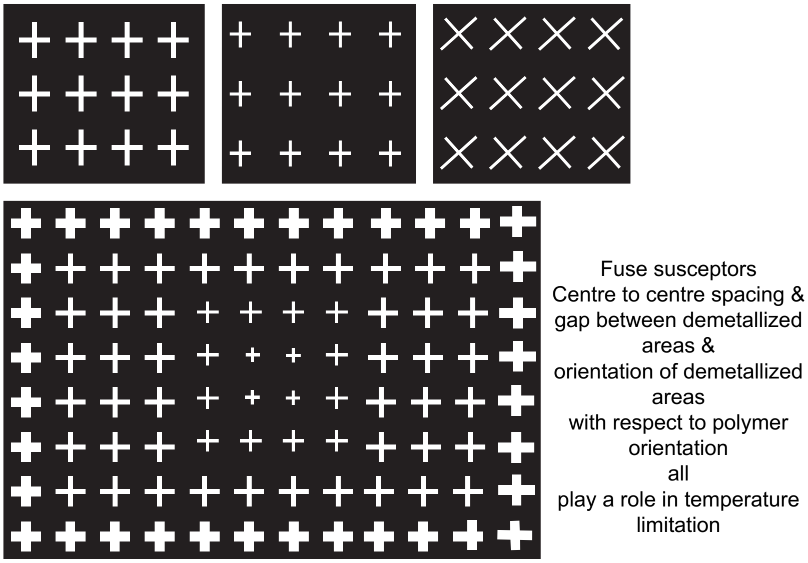

Fig. 14-8 Various fused susceptor designs. The white areas are demetallized.

concentrators would act as a fuse (Fig. 14-8). In this way, the metal would crack across these stress concentrators in a very uniform manner and the film would reproducibly reach a specific temperature and then the fuses would crack the temperature limiting.

Antistatic or electromagnetic screening applications are applications where the applied coating may be part of the same total structure or may be for separate applications. Packaging materials for electronic components, such as semiconductor chips, can be quite complex structures (Fig. 14-9). There may be a problem of using polymer films for packaging, as polymers in contact with other materials can build up a significant triboelectric (static) charge. This static charge can reach several thousand volts and, if this high voltage is discharged across the semiconductor or electronic device, it can damage the electronics. As polymers are insulators, once the charge has been generated, it is very slow to dissipate. Thus, there may be a conductive coating applied to the polymer film that is capable of leaking any charge away. As charge can build up on both the inside of the package as well as on the outside of the package, this conductive coating may need to be applied to both surfaces.

Furthermore, the antistatic bags may be subject to an electrostatic discharge from outside and so it can also help to have a coating that is sufficiently conducting to protect the packaged products against a static discharge. A metal coating can provide a 97% shielding for a 1000 V static pulse. Coupled to all of this, it is preferable for the coatings to be transparent, so that the bar code on the packaged goods can be read or the product visually identified, without having to open the package and expose the products to potential contamination or damage. Fig. 14-10 shows several basic structures for antistatic packaging materials.

Having several combinations of antistatic films, coatings and metallized layers in the product designs gives the option of using the material as either metal-in or metal-out to form the bags. This is largely self-explanatory with the metal coatings either facing the inside or outside of the bag. The metal-out structure needs to be protected

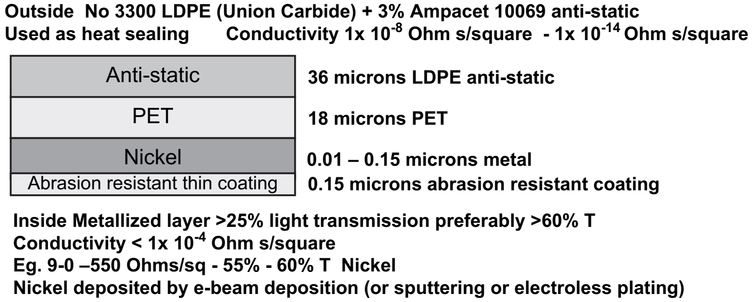

Fig. 14-9 A typical antistatic coating as per US Patent 4,151,344.

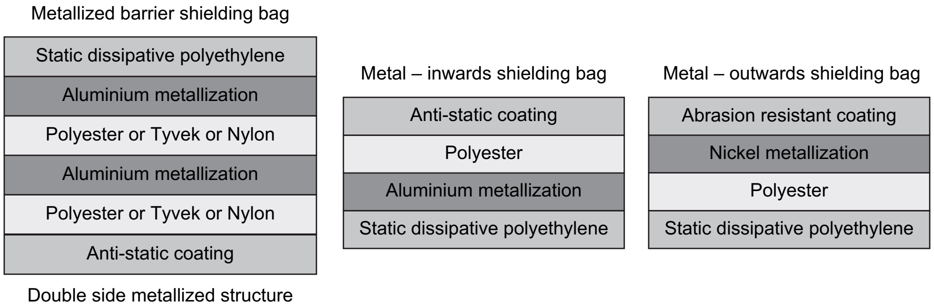

Fig. 14-10 Some of the basic metallized antistatic structures.

from damage to the thin metal coatings by over coating or lamination. The metal-in bags can be slower to dissipate charge than metal-out bags where the metal coating is closer to the surface than for metal-in bags.

There is a class of higher specification bags with metal coatings on both sides of the film allowing an even higher static protection. The classification of the products to be packaged, as well as the materials suitable for packaging them, has to meet various standards that are periodically revised [23].

Other variations are where the material is required to have a high moisture barrier performance as well as a high corrosion resistance for long shelf-life products. Generally, this requires much thicker metal coatings that are no longer transparent. Also, as semiconductors are being developed to work at lower power levels, they tend to have a lower damage threshold and so the static protection has to be improved. This also includes protection against induced currents, due to electromagnetic interference (EMI) or radiofrequency interference (RFI) and this can also require thicker metal coatings. These metallized structures still have a greatly reduced quantity of metal than that of foil packaging and so are regarded as having a lower environmental impact.

Security applications

The security packaging application that most people think of is the holographic security labels, as these are one of the most visible and well-publicized security applications. They are by no means the only vacuum deposited security devices available. There are tamper evident coatings that fracture if lifted, a whole range of radiofrequency identification labels (RFID), holographic tear tapes, customs and tax stamps and a variety of color shifting or optical variable devices [24].

With estimates suggesting that 5–7% of world trade is made up of pirated or counterfeit products, it is no surprise that companies have had to develop ways to enable legitimate products to be verified. High margin products are prime targets and often have the newest defensive devices included in the packaging design. The spread of counterfeit protection can mean that, when the high security protection technology becomes compromised or easy to defeat, it becomes cheaper. Then, it is typically applied to lower value products where the required protection is much lower. This is what has happened to holographic security devices.

Holograms were once very difficult and expensive to produce, commanded a high price and had limited sources. Now, almost anybody can produce holograms and, as the consumers find it difficult to discriminate between good ones and bad ones, it means that their value as a single security device is limited. The levels of complexity that can be included in a hologram means that they can still be used as forensic security devices. This allows a ‘wallpaper’ background hologram to be used as part of the general packaging esthetics but, within the overall design at one or more specific locations, various high level security features can be added to the design. In this way, extra security is added, as simple counterfeiting would not be able to replicate the entire design. Simple holographic labels can also have other security features, such as optical variable or interference coatings added, so that the combined design becomes much more difficult to reproduce. This increases the level of difficulty to counterfeit and therefore increased security.

The basic design process is the same for security holograms as for decorative holograms. A holographic pattern (an origination) is designed and produced. This pattern is then ‘written’ or exposed onto a light sensitive film with a photopolymeric coating. The film is then ‘developed’, which produces a plate with a surface structure or topography due to the removal of unreacted photopolymer from cross-linked and insoluble photopolymer. This surface structure is metallized to make it conductive and a thick metal plate grown by electroplating the metallized surface. This electrodeposited plate is known as a shim and from this shim replicas are produced that are pressed into a suitable surface, to reproduce the origination surface structure. This origination structure, when suitably illuminated, will

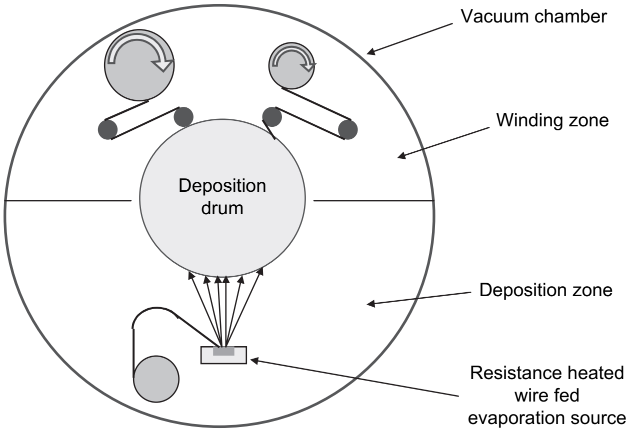

Fig. 14-11 Basic aluminum vacuum metallizer system.

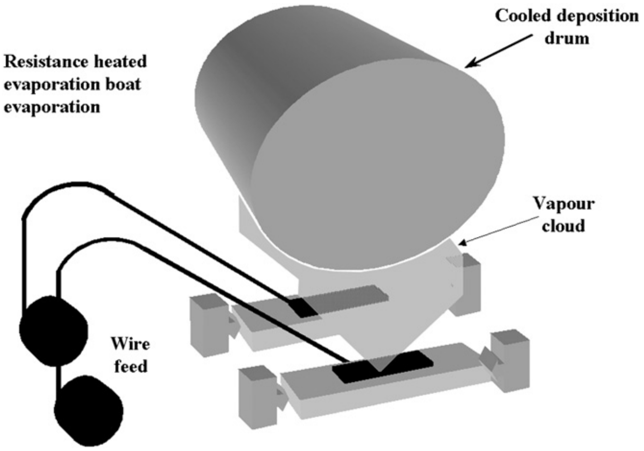

Fig. 14-12 Resistance heated boats in an aluminum vacuum metallizer system.

reproduce the original image or artwork. This embossed surface is then aluminized. This material can then be laminated and printed to make a complete packaging material with the hologram as an integral part of the packaging material. Details of a variety of optical security designs and devices are given in the book edited by Rudolf van Renesse [25].

Another vacuum coating security coating that finds its way onto packaging is labeling materials for tamper evidence. Tamper evident labels are designed to indicate if the package has been opened. Unfortunately, the criminals who tamper with products rarely use the correct method of entering the package to adulterate the products and so often the tamper evident labels are only of limited use. The vacuum deposited labels usually include several vacuum deposited layers, one layer of which is fragile, such that it will be relatively easily broken [26]. The total design of the optical layers can produce a particular color to the label but, when the frangible layer is broken, there becomes an additional air layer, which disrupts the optical design and the color is lost indicating the label has been used or tampered with.

A large growth area is radiofrequency identification tagging (RFID) for products.Vacuum metallized coatings can be used for the antenna part of these devices. This does require the vacuum coating to be patterned to form a suitable shape to form the antenna. The conductivity required depends on the device and the range that the tag is to be interrogated from. The greater the distance, the better the coating layer conductivity has to be. What this means is, that for many of the applications, a conducting printing ink has sufficient conductivity to work well. Therefore, there is little or no justification for using the more expensive vacuum deposition production process.

Basics of metallization

The basic metallization process comprises a large vacuum coater that contains the substrate to be coated, the deposition sources and the feed system to supply material to the deposition sources (Fig. 14-11 and 14-12).

The aluminum is supplied as wire on reels and each reel is controlled to feed the wire onto a resistance heated intermetallic boat. As the wire touches the boat, it melts and forms a molten pool where it evaporates. The vacuum level is such that there is no gas to cause any collisions. Therefore, the vapor cloud arrives uninterrupted at the cooled deposition drum. The vapor condenses on the film as it passes through the deposition zone around the deposition drum [27].

Many of the transparent barrier coatings are deposited by different deposition processes, such as induction-heated evaporation, electron beam evaporation or plasma enhanced chemical vapor deposition. Induction heated evaporation sources (Fig. 14-13) use induction heating instead of resistance heating to evaporate the silica source material to produce silica coatings. The induction heated source based machines are similar in cost to standard resistance heated source aluminum evaporators.

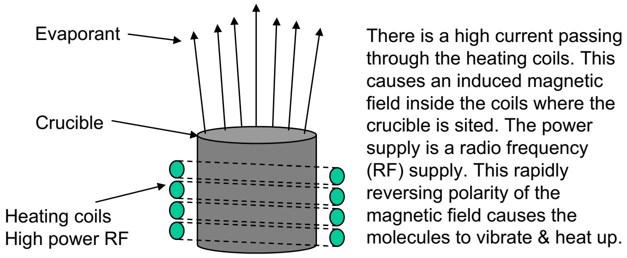

Fig. 14-13 A schematic of an induction heated evaporation source.

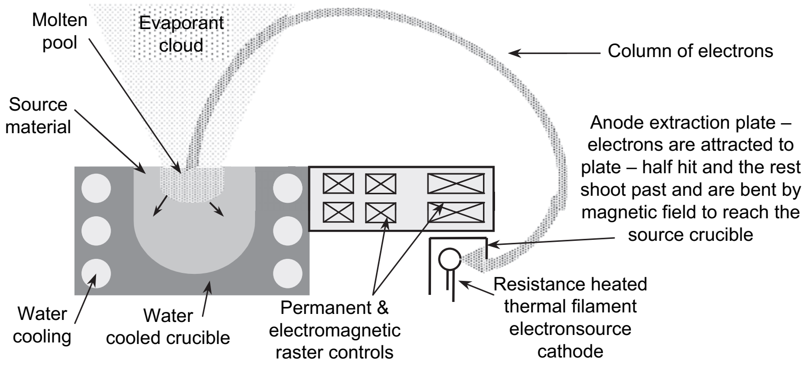

Fig. 14-14 A schematic of a small electron beam gun.

Electron beam evaporation is much more versatile as it can be used to evaporate many different materials. In this process, a hot filament is used to provide electrons that can be accelerated, bent and focused onto a crucible where the electron beam energy is used to heat the source material. This evaporates the material, which condenses onto the substrate. The electron beam source (Fig. 14-14) can be a very large source which can coat approximately up to 1.25 m width of material per gun by sweeping the beam across the coating width. Alternatively, a series of smaller electron guns can be used across the film width, in exactly the same way as the resistance heated sources (Fig. 14-15). The larger, sweeping e-beam source based systems are anywhere from double to triple the cost of an equivalent resistance heated source machine. This means that electron beam heating is preferable for depositing materials that are not as easily done using resistance heated sources, such as silica, as a transparent barrier material.

The other major deposition process, specifically developed for the deposition of transparent barrier coatings, is plasma enhanced chemical vapor deposition (PECVD). In this process, a gas or liquid precursor chemical is fed into the vacuum chamber where a plasma is produced, which decomposes the precursor chemical and one or more of the by-products are condensed onto the web to make the coating (Fig. 14-16).

The transparent barrier coatings use a precursor that can be decomposed to provide a source of silicon or a sub-oxide of silica that can be combined with oxygen to produce the desired silica coating. The normally diffuse plasma is densified using magnetic confinement and this can help speed up the deposition rate. This process has the advantage that the cost of the precursor is low compared to some of the e-beam and induction heated precursor materials. The deposition rate tends to be slower than by electron beam deposition. Thus, there is competition between the two processes to produce the most cost effective (cheapest) silica barrier coating. The system cost for the electron beam deposition process is higher than for the PECVD process but the deposition rate is higher. It is possible to increase the deposition rate of the PECVD process by having multiple deposition sources, but this adds to the system complexity and cost.

The precursor material for the PECVD that is most widely used is hexamethyldisiloxane (HMDSO). The decomposition of this material also produces carbon and some of this carbon can be advantageously included in the coating to improve the barrier performance further.

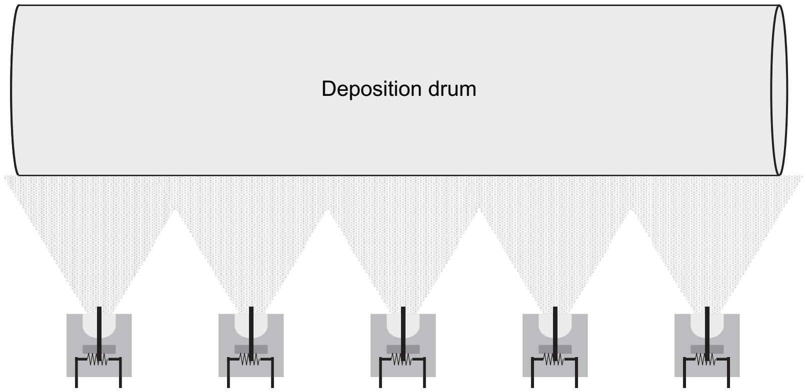

Fig. 14-15 A schematic of a series of electron beam deposition sources showing them arranged for overlapping deposition.

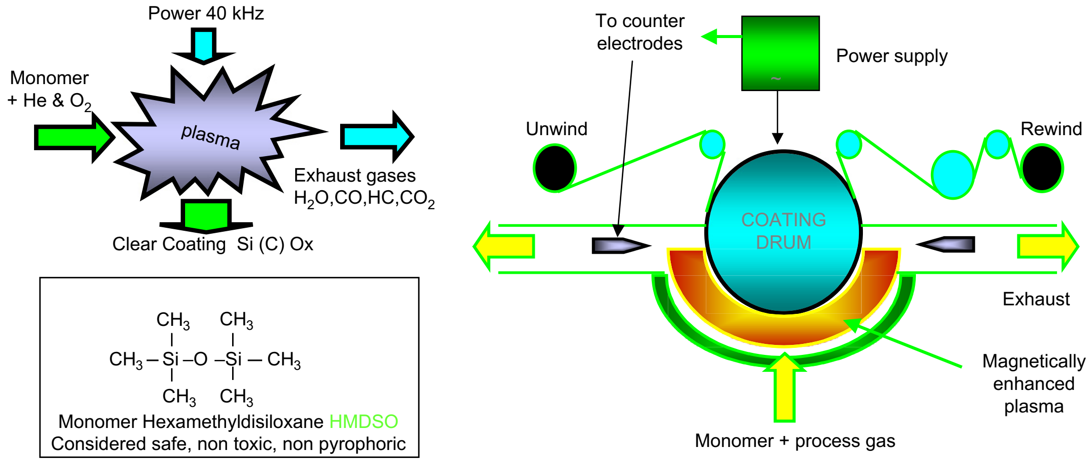

Fig. 14-16 A schematic of the PECVD process using hexamethyldisiloxane (HMDSO) as the precursor.

Common to all deposition processes is that the incoming web substrate quality and any surface pre-treatment affects the final coating quality. There are many factors that affect the deposition process quality, starting with the incoming substrate material quality. Most adhesion problems observed in vacuum coated products can be attributed to problems with the incoming material. This can include fillers or additives as well as residual products from the polymerization process that can be present on polymer film surfaces.

These surface contaminants will usually form a weak boundary layer, cause the substrate surface energy to be low and any layer deposited on the surface will have poor adhesion due to the weak layer between the coating and the substrate surface.

It is always good policy for the substrates to undergo surface treatment. This can be by flame, corona, atmospheric plasma or vacuum plasma treatment [28]. It is important for any surface treatment to be done correctly, as it is possible to make the adhesion worse if it is done incorrectly. Surface treatments ideally increase the presence of oxygen at the surface to improve the metal bonding [29]. Also, surface treatment can be used to remove low molecular weight material or other contaminants, as well. The atmospheric surface treatments have a common problem that, after they have been used to increase the polymer film surface energy, the film is then rewound and may be stored for some time. Once the film is rewound, the treated surface comes into contact with the untreated opposite (back side) surface that will still be contaminated. Once in contact with the untreated surface in the roll, any low molecular weight material may transfer from the untreated surface onto the higher energy treated surface, contaminating the treated surface. This gives vacuum plasma treatment a distinct advantage.

If the surface treatment power (or residence time) is plotted against surface energy, it can be seen that the surface energy (dyne level) will increase. This increasing surface energy will eventually reach a plateau. However, if the adhesion is plotted against treatment power, there is no plateau. Instead, the adhesion increases through a maximum adhesion level and then it immediately begins to decrease. If the treatment power is increased past the peak adhesion level, it can sometimes fall below the original low surface energy. Therefore, it is important for any surface treatment to be optimized so that the adhesion is close to, or preferably at its maximum. This is best done by plotting adhesion versus Watt density of the treatment process.

It is important to optimize the surface treatment for each film, in part because each polymer reacts differently to treatment and also due to the different formulations obtained from different suppliers. Different manufacturers, of what is nominally the same film, will have different proprietary coatings or additive packages with different chemical compositions. Therefore, what may be an optimized process for one film is likely not an optimum for others.

Treatment levels that cause a decline in a desired property, such as adhesion, are said to be ‘over treated’. What happens is that the over treatment damages the polymer surface by continuing to break polymer backbone bonds. This results in lower molecular weight (decreased chain length) surfaces with the result that the surface becomes carbonized and eventually powdery. The chemical composition of the over treated surface may not change much and so the surface energy remains at the high level. However, the increasing number of short chain molecules, due to the continued chain scission, creates a new weak boundary layer between the polymer and any subsequent operations, such as metallization or printing, that will reduce its adhesion to the substrate.

Many coatings applied by vapor deposition are expected to be barrier coatings and there are many factors that can affect the barrier performance. In Fig. 14-17, the schematic shows how the theory predicts

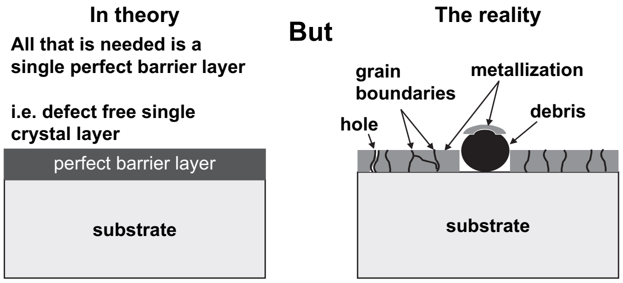

Fig. 14-17 A schematic comparing a theoretical and a real barrier coating.

a perfect barrier for a coating with no defects. The reality is shown on the right where some potential barrier problems are displayed. If you consider that the coating may only be 10–50 nanometers, the depiction of the debris is inaccurate in that the particle is shown as very small relative to the coating thickness. Typically, the debris would be microns in diameter and much bigger than the coating thickness. This is why it is relatively easy to move the debris after the metallization and leave a pinhole and possibly scratch the surface as well.

The other defects shown in Fig. 14-17, such as grain boundaries and channels in the metal layer, generally relate to the substrate polymer, surface treatment and deposition process. If the substrate has a low surface energy, the depositing metal will not easily wet the surface and the deposit may be poorly formed. If the substrate has been surface treated to increase the surface energy, the metal will wet the surface better and allow a better nucleation and crystal growth. This improved wetting gives some advantages to the coating quality and can often appear as a higher optical density at constant deposition rate.

The improved surface wetting leads to a more continuous coating at a lower coating thickness. It also reduces the number of holes in the coating. These holes are formed where several growing crystals impinge against each other as they grow on the surface. If you imagine pushing three balls together there will always be a gap in the centre. This happens on the surface when several growing crystals impinge but, with continued deposition, these holes are progressively filled in by continued crystal growth. The smaller and fewer holes remaining at the end of the deposition will result in an improvement in the barrier performance.

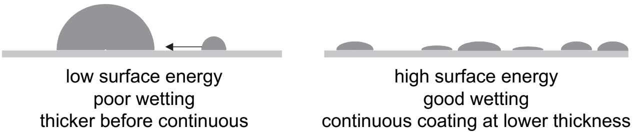

Fig. 14-18 A schematic diagram showing how surface energy can affect the wetting and hence coating quality.

Fig. 14-18 shows the impact of substrate surface energy level on the nucleation and growth due to improved wetting. Improved wetting will improve not just the adhesion, but also reduce the number of holes in the coating and improve the barrier performance. The nucleation and growth process is not perfect and there will still be some defects as well as some grain boundaries, which also are an easy diffusion path through the coating.

Fig. 14-19 shows how the growth of the coating would progress if it were to be continued to a few microns thick [30, 31]. The material that deposits on the substrate surface can start to nucleate and grow with any crystal orientation and the spacing of different crystal planes will be different. This means that the planes with the greatest separation grow more quickly and these will eventually shadow slower growing crystals. The result of the shadowing is the columnar growth as shown in Fig. 14-19. Most metallized coatings are very thin and so this gross columnar coating is never observed. However, what are seen are the roots of this columnar growth. This can have grain boundaries which directly connect the atmosphere to the substrate and so present a very direct diffusion path through the coating.

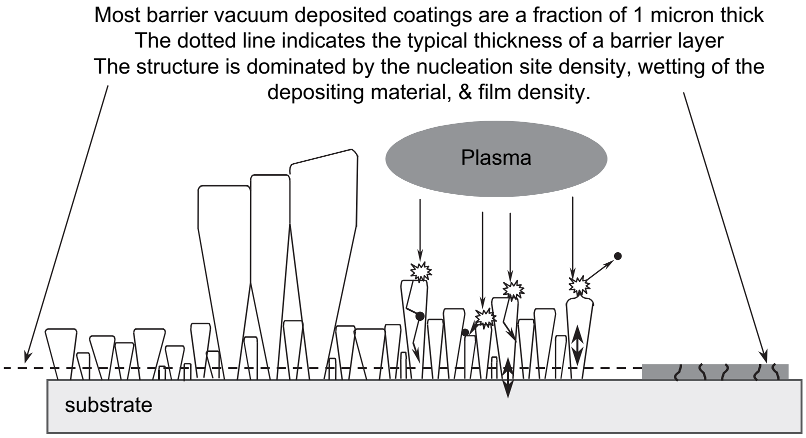

Fig. 14-19 A schematic of the nucleation and growth of a thin film coating.

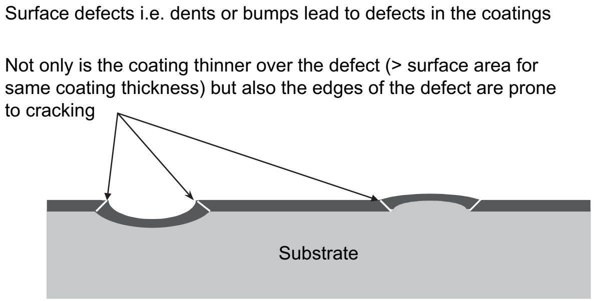

Fig. 14-20 A schematic of how bumps and dents lead to stress raisers and subsequent cracking of the coating.

The transparent barrier coatings are sometimes improved by the deposition process, as some of the coatings experience or are subjected to, a plasma bombardment during the growth of the coating [32]. This ionic bombardment from the plasma has the effect of compacting the coating as well as removing any poorly bonded material from the surface. This results in an adhesion improvement, as well as an improvement in the coating density, which can minimize the number and size of grain boundaries. Fewer and smaller grain boundaries give fewer defects through the coating, reducing this component of the diffusion. This may not be without side effects, as increasing the coating density can also increase the stress in the film, which can lead to substrate curl and handling difficulties.

The substrate surface cleanliness and quality become much more important in the formation of ultrabarrier coatings used for packaging the OLEDs or solar cells. In this case, any bumps or dents in the surface can lead to subsequent coating cracking (Fig. 14-20).

If we look at all these potential defects, we can rank them. Pinholes are the most detrimental and, to make significant barrier improvements, efforts need to be made to minimize surface debris on the substrate surface before coating. Next would be getting the surface energy high enough to increase wetting, improve the adhesion and minimize the holes between impinging crystals. After this, densifying the coating will improve the barrier further. Finally, it may also be worth considering looking at the substrate surface material to see if there are any others that give better barrier performance.

Pinholes can be reduced by reducing the surface debris. This can be achieved by substrate surface cleaning. Plasma treatments do little to remove large debris and only clean the surface at the molecular level. Care must be taken to use a physical cleaning method that does not damage the surface during the process. Two surface cleaning methods that work well are:

- a tack roll in contact with the web surface and which the debris sticks to and so can be removed [12]
- ultrasonically pulsed gas, electrostatic neutralization and then a vacuum extraction of the particles. The ultrasonic pulsing flutters the web, which shakes off the dust, with the vacuum extraction removing the debris as it leaves the surface. The electrostatic neutralization helps prevent the dust being attracted back onto the surface.

For the ultra barriers, which have to have a much higher coating perfection than typical barrier coatings for food packaging, not only does the substrate need cleaning but any remaining very small debris as well as any inherent bumps or dents are covered by the deposition of a polymer coating inside the vacuum system immediately before the regular deposition process [33, 34].

This polymer deposition process (Fig. 14-21) has to deposit a coating thick enough to cover all the defects. Also, the deposited polymer needs to have sufficient

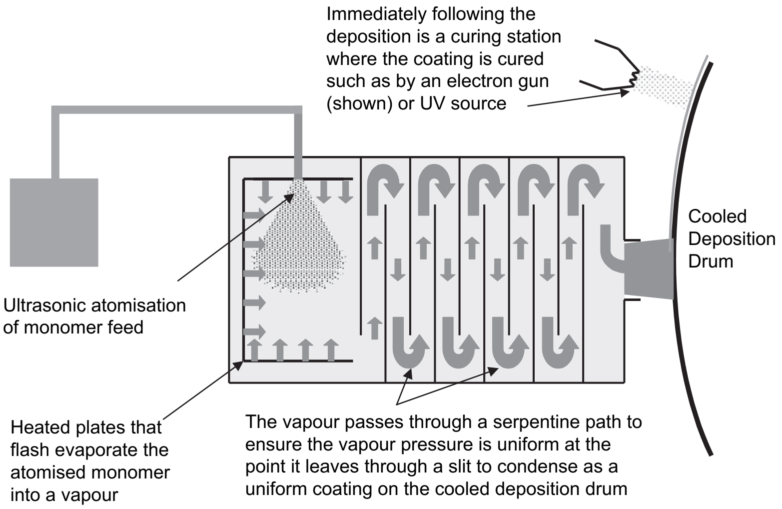

Fig. 14-21 A schematic of in-vacuum polymer deposition.

time in the liquid state to allow the coating to level out on the surface before it is cured. In this way, the new surface is expected to be the cleanest, flattest and smoothest and most defect free surface possible. This surface may still require a plasma treatment to increase the wetting of the subsequent coating. Despite this high quality surface preparation, the barrier performance of the coatings is still not as good as required for the high-tech applications. To improve the barrier further, a second polymer coating is sometimes added, after the metal or transparent ceramic barrier layer, to protect the barrier layer from subsequent damage that would reduce the barrier performance. It has been suggested that the polymer fills any holes by capillary action reducing the diffusion rate (Fig. 14-22).

Even with these additional pre- and post-deposition layers, this still does not produce the necessary barrier performance for the highest specification barriers. To achieve this higher specification, additional alternating layers of polymer and inorganic material are added. Even these multiple coating layers do not eliminate all defects, but what they do is significantly increase the tortuous path length that any gas or liquid has to follow to pass from one side of the barrier coating to the other (Fig. 14-23).

The idea of the tortuous path has been utilized for many years for packaging films. It was recognized that pinhole defects were a big problem that was expensive and impossible to eliminate totally. At best, pinholes can only be reduced, which still leaves a significant barrier problem. The low cost solution was to metallize both sides of the substrate. The fact that pinholes are randomly distributed means that, although there are pinholes on both sides, statistically the pinholes will rarely be directly aligned. The effect of this is that the diffusion path becomes tortuous and, thus, the diffusion rate is significantly reduced.

Another significant packaging material is paper and this too can be metallized. Approximately 66% of the paper is used for labeling [35, 36]. Metallization of paper allows gold and silver effects to be included in the label design. Paper is a very different substrate than the polymer films, particularly with regard to the water content. Paper can contain as much as 20% water if stored for a prolonged period in conditions of high humidity. This moisture content adds a huge vapor load to the pumping system. Vacuum systems that are designed to metallize paper usually have additional cryopumping included specifically to pump the water. This increased capacity of the cryopumps can reduce the water content of the paper to below 5%.

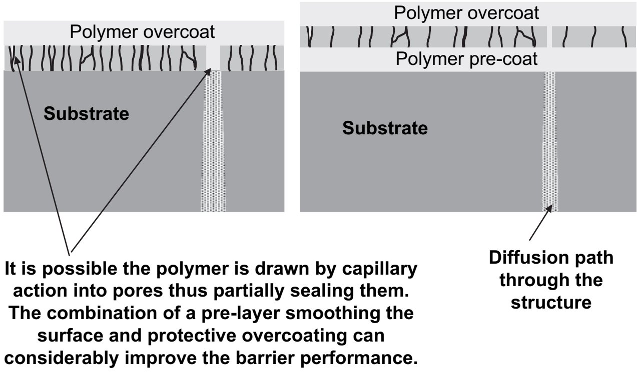

Fig. 14-22 A schematic showing the benefits of minimizing surface defects.

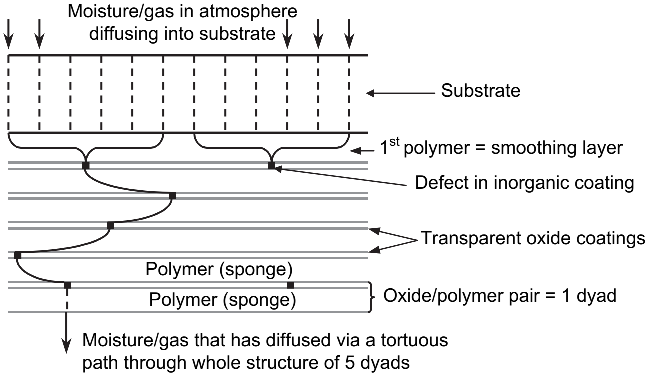

Fig. 14-23 A schematic showing how a tortuous path improves barrier performance.

Care must be taken that the moisture level does not fall too much, as the paper can become brittle and very fragile resulting in tears or web breaks becoming a significant problem. Similarly, after metallization, it is often required that the paper be rewound so that it can become re-hydrated on exposure to the atmosphere. If this rewinding is not done, the paper can re-hydrate on the roll and the resultant swelling of the hydrating paper can damage the roll.

The paper surface quality is also important to the metal reflectivity. Therefore, it is common for the paper to have one or more polymer coatings to prepare the metallization surface by both sealing and smoothing the surface. The surface may also be calendared before coating. The calendaring process both smoothes and compresses the paper fibers and is a surface polishing process. Metallized paper has a high demand in products where it is perceived that polymers can add an odor or taint that papers do not have. One of the biggest users for metallized paper is the tobacco industry.

Pattern metallization

Pattern metallization is the title given to the process where the aluminum deposition is masked in some way so that only part of the polymer web surface is metallized. There are several ways that this can be achieved.

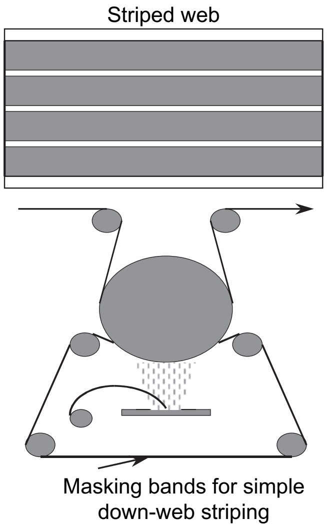

Fig. 14-24 A schematic showing the process of using a masking band that produces simple stripes.

Either the polymer surface can be printed with a pattern before it is put into the vacuum coater or the aluminum is printed after it is deposited with a resist and then the exposed aluminum removed by etching.

In the first case, the printed pattern is a soluble material so that after the whole surface is metallized, the roll is removed from the vacuum system and rewound through a solvent. In the solvent, the printed pattern will dissolve away taking with it the metal deposited onto the printed pattern [37].

In the second process, the substrate is metallized. It is then printed with a protective pattern (resist), covering the metal in the areas where the metal is to remain and then the roll passes through a sodium hydroxide solution, which will remove, or etch, the aluminum in the areas not protected.

There has always been a desire to reduce the process steps by bringing the patterning process into the vacuum system where the patterning and metallization are done at the same time. This is done for simple striping by rotating a metal mask that comes into contact with the polymer (Fig. 14-24) as it passes through the deposition zone [38]. This process could be prone to generating dust, as the accumulation of aluminum on the mask flaked off and also there was a limit to the fineness of the lines that could be produced.

The newer process (Fig. 14-25) is to print on the polymer web some low vapor pressure oil [39]. This oil is printed onto the areas where the aluminum is not required. The process is designed to print just enough oil such that the polymer is virtually dry of oil once the polymer has passed through the deposition zone. What happens is that the aluminum, as it deposits onto the oil, does not stick and it re-evaporates. As it deposits on the oil surface, it will also heat and evaporate off some of the oil and so, eventually, all the oil will be removed. If too little oil is printed on the surface, there will be some aluminum deposition, if too much oil is deposited there will be residual oil and this will contaminate the roll as it gets re-wound.

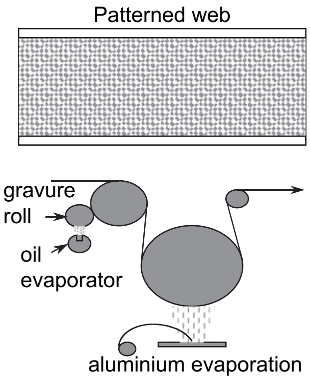

Fig. 14-25 A schematic showing the much more versatile oil printing process for the production of finer and more detailed patterns.

This pattern metallization process of Fig. 14-25 has been used for flexible electronic circuits such as RFID antenna, capacitor films, microwave susceptors (including fused susceptors), demetallized security holograms and packaging films (Fig. 14-26).

In packaging films, there has always been competition between hot or cold stamped foil and pattern metallization. Both techniques are designed to put the metal only where it is desired, rather than metallizing the whole surface and overprinting with an opaque ink to hide the metallization in areas where it is not required.

Trends

The cost of existing packaging is constantly under competitive or manufacturing cost pressure, which is passed on through the supply chain. The demand is for lower cost substrates, metallization, lamination and printing. One of the ways that some of this cost reduction has been achieved has been by down gauging (thinning the substrate). In down gauging, the substrate thickness is reduced but with the expectation that the overall substrate performance is not reduced at all. This is not without problems, as it is generally harder to handle thinner substrates. Also, managing the heat load through the deposition zone, during metallization, can be more difficult. The other aspect of down gauging can be the reduction of layers in packaging laminates.

A good example of this would be coffee packaging, where the initial packaging material was an aluminum foil laminate (Fig. 14-27a). A competitive material was

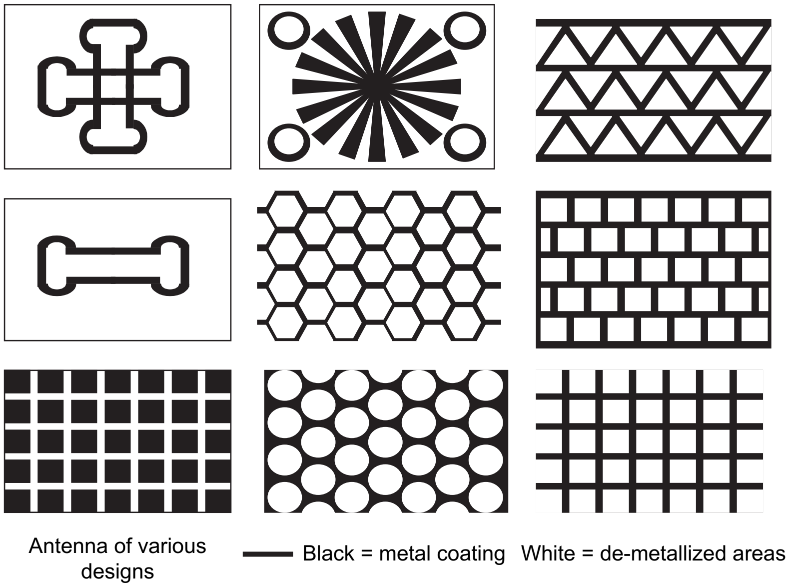

Fig. 14-26 A schematic of various antenna shapes for microwave applications that could be produced by the oil printing pattern metallization technique.

produced that replaced the aluminum foil with a metallized polymer film as a part of the triple layer laminate (Fig. 14-x27b). This triple layer packaging material was still thick at approximately 110 μm total thickness, so there was a demand for down gauging. The triple layer barrier laminate was later successfully replaced by a thinner, two-layer laminate of equivalent performance (Fig. 14-27c). This down-gauging process continued and the double layer laminate was further reduced in thickness from 85 μm down to 60 μm (Fig. 27d). It is believed possible to reduce further the laminate thickness and still meet the required barrier performance [40, 41]. The reason why further thickness reductions are not yet used is because of the mechanical performance of the thinner laminate. With the reduction in overall laminate thickness comes a reduction in stiffness, making forming and filling the package more difficult. Thus, any future down gauging will probably also include a further material change, such as a change to oriented polypropylene. Some packaging machines use a horizontal form and fill process that requires the package to be stiffer than a vertical form and fill process and so it is likely that there will be many different products for this single application.

The other critical part to many down-gauged packages is heat-sealing. It has been found that the limitation to further down gauging is most likely to be due to problems with the heat-sealing integrity and not with the performance of the metallization or deposition of the transparent barrier coatings [41]. Metallized biaxially oriented polypropylene (BOPP) thickness has been successfully reduced from 20 μm of BOPP with a 40 nm metallized coating to a 12 μm BOPP with the same metallized coating thickness.

Down gauging is not exclusive to polymer films but also applies to paper where it is used for high barrier

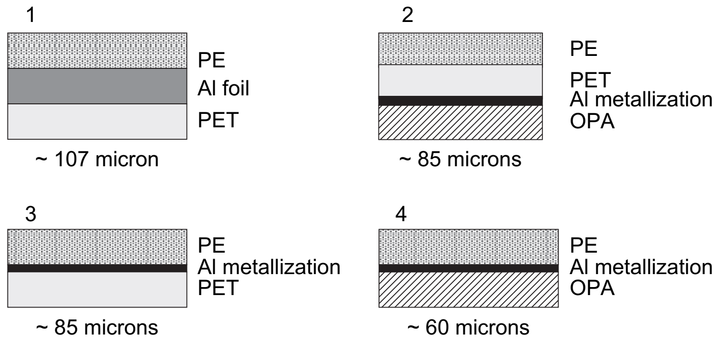

Fig. 14-27 A schematic of the progression, (a–d), from the original foil packaging for coffee to the triple layer replacement and then to the double layer and then the thinner double layer current product.

applications. Similar to the polymer versions, the paper laminates started with aluminum foil as the high barrier layer that was substituted with a metallized polymer film (Fig. 14-28). Typically, the approximately 10 µm aluminum foil is replaced by a metallized polymer film of at least 12 µm thickness. In this case, the initial total thickness is increased but the cost of the laminate is reduced [42].

Because polymer films can be produced as white films and not just transparent films, it is also possible not only to replace the aluminum foil, but to also to replace the paper with polymer film too while maintaining the overall product ascetics.

The trend of replacing aluminum foils has been established for a number of years [44]. The metallized films used as replacements are not true replacements in that they rarely match the aluminum foil barrier performance. However, it is often the case that the foil has a barrier performance beyond what is required for the product shelf-life and so the metallized film can meet the specification, although, technically, it does not match the performance of the foil it replaces [45]. Where the thinner metallized films can often outperform the foil is where the package is to be folded. The aluminum foil will crack or begin to perforate (pinhole) under dead fold conditions. As the technical understanding increases on how to produce more perfect barrier layers that do really approach the barrier performance of foil, then the environmental pressures will continue the drive to replace foils with metallized films. This is driven by the fact that laminations with metallized films are lighter in weight, take less energy to produce and to transport which lowers the total energy requirements of the packaging.

A further target for developing these multilayer films relates to recycling. It can be seen in the above examples that many of the laminates have mixed polymer content. While it is possible to recycle these films, the value of the recycled polymer is lower than if each of the layers were to be based around the same polymer and could be recycled as a single polymer type.

Recycling is also impacted by the adhesives, lacquers and inks that are used. Some materials may need to be heavily cross-linked to make them effective, but this may make the recycling more difficult. Thus, in the future, some material choices may appear to be taking a step backwards in performance but may enable either a lower carbon footprint or a lower recycling cost or penalty for the packaging.

An example of this would be the lidding material used as shown schematically in Fig. 14-29. The product in Fig. 14-29 has an amorphous polyethylene terephthalate (APET) tray and the lidding has a structure comprising a coextruded, heat-sealable PET film adhesive laminated to a transparent aluminum oxide coated PET film. This allows the lidding to be transparent and the whole package to be recycled as a single polymer [18]. Using a coextruded PET allows the use of an amorphous PET layer which can be heat-sealed, while retaining the film dimensional stability by using a coextruded crystalline PET layer. In this way, the amorphous polymer replaces an alternative polymer heat-seal coating.

Currently, many mixed polymer structures are used to reduce packaging costs. Polyethylene (PE) film does not have PET's mechanical performance but is lower in cost. To use a thicker single film of PET would be very expensive, whereas using a PE– PET laminate can be aimed at giving the best of both materials but at a reduced cost. As the recycling and disposal costs continue to rise and become a much more significant part of the total cost in the packaging process, the number of materials will be simplified. To continue to achieve the expected performance, we will have to use every possible technique to continue to improve the performance, using the reduced number of materials available.

We know that the film surface quality is critical in producing good barrier films and that, in theory, we only need the polymer carrier substrate and a perfect coating to achieve a perfect barrier. This requires the polymer substrate to be perfect, including the cleanliness, chemistry of the film production, minimization of any additional filler or additives as well as any optimized pretreatments. Currently, many products are made but only controlling one or two of these factors. This means that there is room for improvements by control of the rest of the factors. What currently stops this from being done tends to be the cost. It is always more expensive to clean film or to produce a smoother surface with fewer residues or additives. As the costs change to meet the

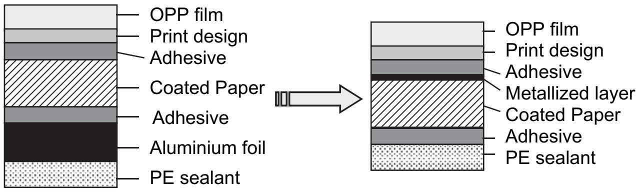

Fig. 14-28 A schematic of an aluminum foil/paper label with a replacement label that uses a metallized polymer that replaces the paper and foil [43].

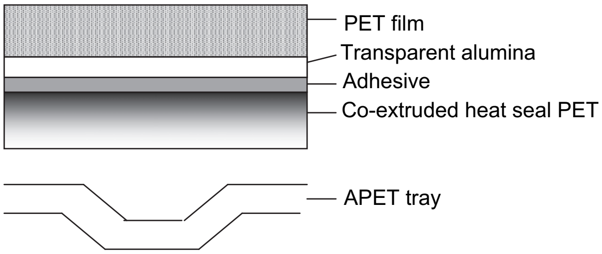

Fig. 14-29 PET heat-seal laminate barrier-lidding material.

environmental regulations, it is likely to become economically favourable to re-evaluate some of these factors. This could mean having to consider paying more for higher quality substrates that would enable superior products to be achieved.

Metallized papers for packaging, like aluminum foils, are also in decline. The metallized paper volumes have remained constant, despite the metallized packaging market increasing [44]. The bulk of the use for metallized paper is for labels. The removal of labels from glass bottles using high temperature liquids, that may also clean the bottles, is regarded as an easier process than removing polymer labels. With the increase in polymer bottles, either direct printing or polymer labelling is increasing. Although there are many niche markets that will always prefer metallized paper or board, it would be expected that metallized paper volumes will not only continue flat but will start to decline in volume.

In calculating the shelf-life of a product, it is possible to separate out the gas diffusion rate through the barrier film, but this is not the only source of the gas. There may be some gas captured within the package as it is filled and sealed. There are several methods of eliminating this gas including vacuum, modified gas atmosphere and scavenging or a combination of several of these mechanisms.

Shelf-life for some products may be adversely affected by oxygen and simply applying a barrier layer to the packaging may not achieve the required shelf-life. In some cases, it has been possible to add a scavenging chemical that preferentially getters, or absorbs the gas, further extending the shelf-life. The quantity of the scavenger used can be sufficient to remove any of the gas left in the package, after it was sealed, plus sufficient material to getter all the gas diffusing through the barrier material over the desired lifetime. Recently, there has been work to change these scavengers from powders, included in a porous sachet, to incorporate them in the structure as part of the vacuum deposition process becoming a more integral part of the lamination [46]. An example would be the use of palladium added towards the end of the electron beam deposition of silica.

Summary

Good quality vacuum deposited coatings start by using high quality substrates. Ideal barrier coatings are only achieved through minimizing the film surface contamination, optimizing the surface chemistry and maximizing the surface smoothness. By having a clean, smooth surface and then maximizing the surface energy before vacuum coating, the deposition material will wet the surface and produce a continuous, low defect coating at the thinnest coating thickness. This care of the surface and increased wetting will also help maximize the coating adhesion. If aluminum coatings are allowed to age and oxidize before use, the metal surface will have a tougher oxide surface and this will help protect the metal against any damage from subsequent handling.

Following the above recommendation will provide a high quality barrier material that can then be a core layer that the rest of the packaging can be designed around.

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Chapter 15

15

PE based multilayer film structures

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[2] E. I. DuPont

Introduction

Flexible packaging is used to deliver a product from the manufacturer or distributor to the retailer or ultimate consumer and protect that product during shipping, display, and storage. Multilayer flexible packaging is the combining of two or more layers into a composite web or tube that provides functional, protective or decorative properties. The introduction of new polymers, the development of new processing equipment technology and the emergence of new packaging applications has resulted in good growth rates in coextruded and laminated structures. Whatever the application or use, polymer materials are selected and the entire packaging structure is designed to meet the performance requirements specific to that particular application. These could include one or more of the following:

- specific performance properties
- reduced cost
- reduce number of processes.

The requirement for *specific performance properties* sometimes cannot be met by one polymer or even with polymer blends extruded in a monolayer film. Blending may not be desirable if the polymers are incompatible. Coextrusion with a high strength or high barrier polymer can allow significant down gauging, while maintaining or improving key properties. Heat seal polymers can be incorporated into a film structure to improve packaging line efficiency or speed.

Multilayer flexible packaging structures can *lower the cost* of many film structures by reducing the expensive polymer used, increasing the less costly polymers, using recycled material or reducing film thickness. Competitive advantages can be achieved for many film structures ranging from the high technology barrier food packaging films to the heavy duty shipping bag market.

Coextrusion can *reduce the number of process* operations required when several polymers are needed to obtain the desired properties [1]. Eliminating process steps saves labor, equipment overhead and reduces turnaround time. The more operations that can be combined into a single process means more space available for other equipment and less scrap generated with multiple process steps [2]. Coextrusion can eliminate the use of solvent-based adhesives. This may provide some raw material cost savings and, with increasing regulations on solvent use and disposal, the incineration or recovery cost could be high.

The polymers available for extrusion have increased in recent years [3]. There are several polymers to choose from with attributes, such as:

- high barriers
- selected permeation rates
- adhesion
- high strength sealants
- easy opening (peelable) sealants
- low temperature sealants
- high hot tack sealants

Multilayer Flexible Packaging; ISBN: 9780815520214

- high tensile strength
- high impact strength
- high tear strength
- high modulus
- high temperature resistance
- low temperature impact
- high clarity
- abrasion resistant
- chemical resistant
- low taste and odor
- high cling
- low slip
- stabilized
- degradable
- antistatic
- antifog
- pigmented
- thermoformable.

This list of polymer performance attributes will continue to grow as application requirements are identified.

A critical factor in developing successful flexible packaging applications has always been a good understanding of the target application. The performance properties required by the application and economic comparisons should be evaluated against the many alternative structures. Performance requirements may include all user requirements in the chain of use. For consumers, this may mean that the packaging:

- protects the product
- identifies the product
- is easy to open.

For retailers the packaging may provide:

- eye-catching graphics that help sell the product
- is of the proper physical form for display purposes.

For the packager, flexible packaging may need to provide:

- high packaging speeds
- low scrap rates
- meet the functional requirements for protecting the product inside the package.

Specific performance requirements will vary greatly from one package to another but, in every case, meeting the performance requirements will help assure proper protection of the goods being packaged.

Polymer films may be manufactured by blown film or cast film extrusion or by extrusion coating a polymer onto another substrate, such as paper or aluminum foil. Blown films are made by melting and pumping polymer through an annular die [4]. Cast films are made by melting and pumping polymer through a flat die. The extrusion coating process is similar to the cast film process except that the molten polymer is coated directly onto another material. The manufacturing process selected is governed by factors such as:

- the job size
- the packaging material to be made
- end-user packaging performance requirements
- equipment availability.

Cast film extrusion typically operates at much higher output rates than blown film so, for larger volume production, it has an advantage with high usage single use films such as stretch film. Blown film extrusion typically runs at a lower rate and may result in film with improved physical properties. Blown film also allows for bubble size adjustment and thus the film width produced. This is a key advantage when many different film widths must be produced on the same machine. There are many existing coextrusion processes ranging from two-layer to eleven-layer capability.

The coextrusion process is used to combine multiple materials into a single film [5–7]. Both blown films and cast films may be coextruded in three, five, seven, nine, or more layers. The combination of multiple materials in a single film allows a cost-effective means of combining the performance properties of several polymers in a single film [8]. One example would be the coextrusion of a barrier polymer such as ethylene vinyl alcohol (EVOH) or polyvinylidene chloride (PVDC) with a sealant resin such as linear low density polyethylene (LLDPE), ethylene vinyl acetate (EVA) or a polyolefin plastomer. Coextrusion is widely used in producing high performance packaging films, such as those used to package foods. It is also widely used to produce industrial films, such as stretch film, and is increasingly used in producing industrial films.

As coextrusion technology has evolved over that last 30 years, the number of layers has increased [9]. Whereas 5–10 years ago a five-layer line was state-of-the art, now it is common to see seven-layer and higher lines installed [10–12]. In addition to the advantages described earlier around combining different polymer materials, the extra layer capability gives the converter greater flexibility and control over their process [13, 14]. For example, if a five-layer line was designed to produce five layers of equal thickness, it may be a challenge to produce an unbalanced structure such as a barrier cereal liner: (60% high density polyethylene (HDPE)/5% tie/ 5% EVOH/5% tie/25% EVA) [9]. The line may have to be slowed down to achieve the desired HDPE thickness because of extruder output limitations. At low line speed, however, controlling the thin layer thickness can be difficult since the extruders may be oversized. Making the same structure on a seven- or nine-layer line is easier. The HDPE layer can be split into more than one layer and fed by multiple extruders, allowing for greater output and control over the process.

Another advantage of greater layer capability is the ability to split barrier layers into two or more layers [15]. For example, a simple Nylon barrier film (polyamide (PA)/tie/LLDPE) may be split into (PA/tie/PA/tie/LLDPE). Separating the barrier layers insures barrier continuity – if a pinhole develops in one layer, the second layer still may be intact. Thin layer orientation and property non-linearity with thickness suggests that two thin layers may have better barrier performance than a single layer of the same total thickness [16].

Polymer films may be stretched, or oriented, to impart improved properties useful for packaging applications. Oriented film is produced by a double bubble or tenter frame process. A thick film or sheet is manufactured, typically 250–1000 µm (10–40 mils) and is subsequently oriented (stretched) in a semi-solid state to many times its original dimensions [17]. The multiple step production is normally done in a continuous operation [18]. The sheet stretching or orientation may occur sequentially in the machine and transverse directions or the stretching may occur simultaneously. After orienting, the films are typically 12.5–25 µm (0.5–1.0 mil) thick. The film is typically supplied in roll form. Biaxially oriented polypropylene (BOPP) is most often manufactured with a tenter frame process. Oriented polyethylene films are usually manufactured using a double bubble process. Polyvinyl chloride (PVC) films may also be oriented. Some oriented films are cross-linked further to enhance their performance. Compared to other films, oriented films typically provide improved optical properties, higher stiffness and increased shrinkage during packaging, which leads to improved package appearance. Coextruded barrier films may also be oriented, typically using a double bubble process. Applications include shrink bags and sausage casings.

Lamination is used to combine two or more films into a single packaging structure [19]. It allows materials that cannot be coextruded to be combined. An example would be an aluminum foil and a polyethylene sealant film lamination. More complicated laminations may include different polymer films, paper and foil. Laminations are usually either adhesive laminations or extrusion laminations. In adhesive laminations, the substrates are combined using an adhesive material [20]. In extrusion laminations, the substrates are adhered together using a molten polymer, often low density polyethylene is used as the adhesive layer. Lamination can also protect the printing ink by placing it between layers, thus providing superior graphics to surface printed packages. For example, glossy stand-up pouches have a reverse printed outer layer laminated to structural and sealant materials. Laminations are also used to provide oxygen, moisture or light barrier. The barrier functionality may be provided by foil or a barrier polymer such as EVOH or PVDC. Most high value processed meat and cheese packages are laminations. This allows for combining various materials into the packaging structure and for superior graphic properties when using reverse printing. Since laminations are more costly than coextruded or monolayer films, laminations are generally reserved for use in higher value applications.

Metallization is used to apply a thin coating, typically aluminum, to a polymer film. This provides improved oxygen and water barrier properties as well as light barrier. The major use for metallized film is potato chip bags. Metallized films are also used for nuts and salty snacks. Metallized films may be coated to provide sealability or may be laminated to another polymer film to provide improved properties, such as seal integrity. Other coatings, whether to provide barrier properties or other functionality, may also be applied to polymer films used in flexible packaging.

Polymer selection

Polymers are selected for the specific performance that they provide and are combined in the final package design to meet all the requirements for the specific application in which they are being used. Often, there are many different materials combinations or film constructions that will meet an application's minimum performance requirements [21]. In these cases, the packaging structure selected may be based on considerations such as availability from multiple suppliers and ability to provide differentiation over competitive packaging. For example, a box with an inner liner or a stand-up pouch may be used, each combination providing the minimum requirements for product protection and safety. One consumer goods company may select to use a box and inner liner and another consumer goods company may elect to package their product in a stand-up pouch for the same product or one manufacturer may choose to use a stand-up pouch and another manufacturer may choose to use a pillow pouch for the same product.

Polymers are chosen for individual layers to achieve specific performance properties. For example, polymers could be selected to contribute to the film's:

- tensile strength
- permeation resistance
- sealability
- adhesion
- optics
- formability
- machinability
- economics.

An individual layer could consist of virgin polymer, blends of polymers, regrind/recycled material or high levels of additives [22]. Most thermoplastic polymers can be coextruded together. Polyethylene is the largest thermoplastic used in flexible packaging applications. There are many polyethylene homopolymers and copolymers that are available for use. Some common polymers used in flexible packaging structures are included in Table 15-1.

Some of the key performance requirements for high performance flexible packaging include the following:

- *Barrier properties:* to keep oxygen, water, light, flavor or grease from entering the package or from leaving the package. Barrier properties may be characterized by measuring the oxygen and water vapor permeation through the packaging material.
- *Selective permeability:* to allow oxygen and carbon dioxide to permeate through the package at a calculated rate to extend the shelf life of fresh-cut produce. Oxygen, carbon dioxide and water vapor permeability are frequently measured and specified.
- *Abuse resistance:* to prevent damage to the packaging material and its contents during shipping and storage. Abuse resistance may include puncture resistance, tear strength, impact strength and modulus. Some packages require good toughness at refrigerated or freezer temperatures.
- *Sealability:* to allow packages to be made at high packaging speeds and keep the product secure by preventing the package seams from failing. Sealability may be characterized by heat seal and hot tack strength, heat seal and hot tack initiation temperatures, seal-through-contamination performance, caulkability and seal integrity. Hot tack refers to the seal strength while still in the molten state. It is critically important for packages where the product drops into the package while the seal is still partly molten, but also for horizontally filled packages involving gussets where the spring-back nature of the folded film creates an opening force. Caulkability refers to the ability of the sealant material to flow, filling in gaps around folds, wrinkles or product contaminants.
- *Machineability:* to allow the packaging films to be easily run on high speed automatic packaging equipment. Machineability is governed largely by film modulus, film thickness, seal properties and coefficient of friction.
- *Consumer appeal:* package appearance is an important factor driving product preference by consumers. Appeal is largely related to print quality and package gloss. Film thickness and modulus may also impact consumer appeal.

Table 15-1 Common polymers used for flexible packaging applications

Polymer name	Abbreviation	Density (g/cc)
Ethylene acrylic acid	EAA	0.925–0.950
Ethylene carbon monoxide	ECO	0.930
Ethylene ethyl acrylate	EEA	0.925–0.950
Ethylene metha acrylic acid (ionomer)	ION	0.940–0.950
Ethylene metha acrylic acid	EMAA	0.925–0.950
Ethylene methyl acrylate	EMA	0.930–0.950
Ethylene vinyl acetate	EVA	0.925–0.945
Ethylene vinyl alcohol	EVOH	1.14–1.16
Grafted maleic anhydride (grafted PE?)	PE-g-MAH	0.91–0.940
High density polyethylene	HDPE	0.940–0.965
High molecular weight-HDPE	HMW-HDPE	0.940–0.962
Linear low density polyethylene	LLDPE	0.915–0.940
Low density polyethylene	LDPE	0.915–0.925
Medium density polyethylene	MDPE	0.925–0.940
Metallocene polyethylene	m-LLDPE	0.865–0.960
Polyolefin plastomer/elastomer	POP/POE	0.856–0.915
Enhanced polyethylene	EPE	0.900–0.925
Polyamide (Nylon)	PA	1.12–1.14
Polybutylene	PB	0.909
Polycarbonate	PC	1.2
Polyethylene terephthalate	PET	1.3
Polypropylene	PP	0.89–0.902
Polystyrene	PS	1.04
Polyvinyl chloride	PVC	1.16
Polyvinylidene chloride	PVDC	1.7
Ultra low density polyethylene	ULDPE	0.90–0.915

Mechanical properties

Most published film data sheets are developed from monolayer films. A coextruded structure's mechanical strength may be estimated using the law of mixtures as shown in equation (15.1), i.e. the summation of the tensile strength per unit layer thickness, multiplied by its thickness, divided by the total thickness.

$$M = \frac{(t_1 \cdot M_1) + (t_2 \cdot M_2) + \mathrm{K} + (t_n \cdot M_n)}{t_1 + t_2 + \mathrm{K} + t_n} \tag{15.1}$$

Where:

M	=	estimate of coextruded film mechanical property;
t_1	=	polymer layer thickness;
M_1	=	polymer mechanical property/unit thickness;
n	=	layer number.

Determining multilayer film properties with equation (15.1) does not account for any interactions (positive or negative) between layers or the influence of fabrication variables or orientation. Sometimes unfavorable interactions can lead to interlayer destruction, such as when a very ductile layer is adhered to a brittle layer, resulting in the film exhibiting the properties of the brittle layer [23]. Fig. 15-1 shows the effect of a LDPE core versus a HDPE core in a three-layer coextrusion structure (A/B/A) with increasing LLDPE polymer content in the skin layers on dart impact.

In the first case, the dart impact strength is a linear function of LLDPE content and can be approximated by the law of mixtures. However, in the second case dart impact is non-linear and is disproportionately negatively influenced by the HDPE content. The LLDPE polymer is a highly elastic material, which allows it to absorb high levels of impact energy. The LDPE, while not as elastic as LLDPE, does not detract from the impact strength. High density polyethylene is more brittle than the LLDPE polymer and tends to form localized stress concentration sites resulting in lower dart impact values for the film structure.

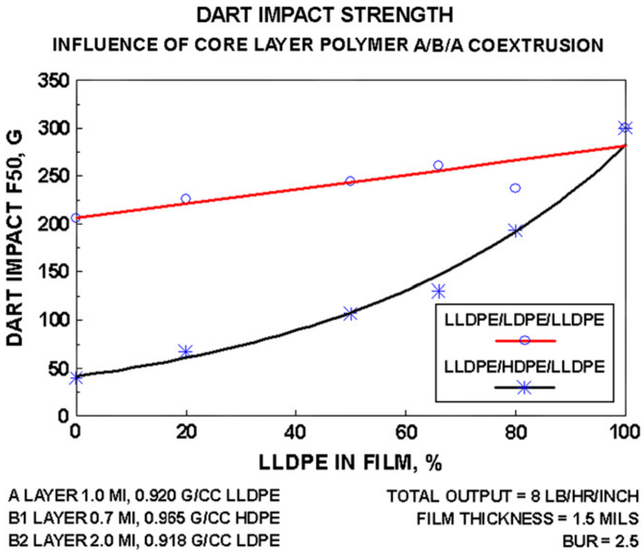

Fig. 15-1 Influence of polymer in core layer.

Another reason mechanical property data from monolayer film can be misleading is because some properties have a bias versus tested thickness, i.e. there may not be a linear relationship between the mechanical property and film thickness. Also, the film making process itself can impart differences between coextruded films and monolayer films. For example, the stress history may differ due to quenching differences between mono- and multilayer films, resulting in differences in orientation and properties [24]. Therefore, the law of mixtures for coextruded films may be used for estimates and film properties should be measured.

Film stiffness affects:

- machinability on packaging equipment
- wrinkling
- the hand or feel of the final package
- and, in some cases, the package function (e.g. a stand-up pouch).

Multilayer film stiffness is a function of the stiffness (modulus), thickness and position of each layer. Morris and Vansant [25] showed that the outermost layers in a multilayer film have the greatest impact on stiffness. Like an I-beam, separating stiff layers in a structure is an effective way to impart stiffness to the structure. Thus, using a stiff sealant layer can help build in stiffness and allow the total structure to be down gauged. Furthermore, the converting process can impact stiffness. In some cases, extrusion laminating two stiff films may build-in greater stiffness than adhesive lamination, since extrusion lamination allows the layers to be separated further apart.

Barrier properties

Flexible packaging films are used to provide barrier to gases such as:

- oxygen
- nitrogen
- carbon dioxide
- water vapor.

Other applications may require taste and odor resistance properties. Permeation occurs in polymer films and this mechanism allows interaction with the environment. Molecules may permeate through a package in a three-step process. First, the molecules must dissolve into the film structure. Then the molecules will diffuse through the film layers. And, finally, the molecule will desorb on the opposite side. The molecule can move either from outside the film into the package or from inside to outside. This permeation happens due to a concentration or pressure gradient and is sensitive to temperature and, for many polymers, relative humidity. The permeation rate of a material through a polymer is a function of the diffusivity at steady state times solubility in the polymer as shown in equation (15.2). Diffusivity is also a function of solubility especially at the low solubility levels.

$$P = D \bullet S \tag{15.2}$$

Where:

P = permeability of a material through a polymer (g/s-cm);
D = diffusivity of a material through a polymer (cm^2/s);
S = solubility coefficient of a material in a polymer (g/cm^3).

Permeation rates are usually measured at steady state conditions. The adsorption of a material can significantly influence the permeation rates and, if the adsorption mechanisms are of sufficiently long duration, this may prevent steady state conditions from being reached during the expected shelf-life of the package. Thus, in these instances, the polymer location in a film structure could influence actual permeation rates during a package's shelf-life.

The gas transmission rate at steady state through a given polymer is inversely proportional to the layer thickness. The permeation coefficient through a multilayer film structure may be estimated by summing the permeation resistance of each layer as shown in equation (15.3):

$$\frac{1}{P} = \frac{f_1}{P_1} + \frac{f_2}{P_2} + \cdots + \frac{f_n}{P_n} \tag{15.3}$$

Where:

P = coextruded film permeation coefficient;
f_n = polymer n layer thickness ratio;
P_n = polymer n permeation coefficient.

The actual transmission through a coextruded film is then calculated as shown in equation (15.4).

$$TM = \frac{P}{t_t} \tag{15.4}$$

Table 15-2 Sample calculation of moisture transmission rate

Basis		
At steady state conditions		
HDPE	HDPE	EVA
0.9	0.8	0.3 mils
45%	40%	15%
P(HDPE)	= 0.6 g*mil/100 in^2/day	
P(EVA)	= 2.0 g*mil/100 in^2/day	
1/P	= [(0.45/0.6) + (0.4/0.6) + (0.15/2.0)]=1.49	
P	= 0.67	
TM	= 0.674/2.0 = 0.34 g/ 100 in^2/day moisture transmission	

Where:

TM = transmission of film;
t_t = total thickness of coextruded film.

Table 15-2 shows a sample calculation of moisture transmission rates based on permeability factors for a three-layer film typical for a cereal liner application using equations (15.3) and (15.4). This apparent two-layer film is a typical cereal liner structure which is generally made on a three-layer blown film line with the HDPE layer split into two layers due to extruder size limitations.

For many high barrier films, the overall permeability rate is controlled by the highest barrier polymer. Permeability rates are sensitive to temperature and will increase as ambient temperature increases and follow the Arrhenius equation. Some polymer's permeability rates are also a function of relative humidity and increase with increasing relative humidity. Table 15-3 lists some oxygen permeability data for various polymers ranked from the lowest to the highest measured at 1.0 mil, 23 °C and 0% relative humidity.

Table 15-4 lists the moisture transmission rate data for various polymers from the lowest permeation to the highest measured at 1.0 mil, 100 °F (37.8 °C) and 90% relative humidity.

Understanding the package environment during filling, processing, distribution and storage is required to determine the permeation needs of a multilayer flexible package. Inadequate understanding of the product barrier requirements poses a design problem in predicting shelf-life from gas transmission data. Packagers must rely

Table 15-3 Oxygen permeability coefficients for various polymers

Oxygen permeability coefficients

1. 0 mil, 73 °F (23 °C), 0% RH

Polymer type	**Oxygen permeability coefficient ($cc^{*}mil/100\ in^{2*}day^{*}atm$)**
PVOH	0.03–0.06 [26]
EVOH	0.02
PVDC	0.15
PA	2.6
PET	3.5
PVC	5–20
PLA	30 [27, 28]
PP	150
HDPE	150
EAA	200–500
EMAA	200–500
ION	200–500
PS	350
PB	385
LDPE	420
LLDPE	440
EPE	500–800
EVA	600–1000
EMA	600–1000
ULDPE	600–950
POP/POE	600–2000

Table 15-4 Moisture permeability coefficients

Moisture vapor transmission rates (MVTR) 1.0 mil, 100 °F (37.8 °C), 90% RH

Polymer type	**$MVTRg^{*}mil/100\ in^{2*}day$**
PVDC	0.10
PP	0.7
HDPE	0.4–0.8
LLDPE	0.8–1.2
ULDPE	1.2–1.5
LDPE	1.0–1.2
PB	1.0–1.2
EVA	1.0–5.5
EAA	1.0–1.6
EMAA	1.0–1.6
ION	1.0–1.6
EMA	1.0–9.0
POP	1.3–2.0
EPE	0.9–1.2
POE	2.0–3.0
PET	2.0–3.3
PVC	0.9–5.1
EVOH	2.0–4.5
PS	7.0–10.0
PA	10.0–20.0
PLA	40 (51)

MVTR: moisture vapor transmission rate

on extensive shelf-life testing of individual food products to evaluate barrier film performance requirements.

Taste and aroma barrier can be very important in some packaging applications. It is not possible to predict from common gas transmission data the polymer aroma and flavor barrier to other chemicals. The chemical component molecular size and solubility will determine the permeation rates in the polymer.

Economics is a critical concern in all flexible packaging applications. Many factors are involved in determining the value a polymer is providing. For example, when comparing the cost of two barrier polymers, the comparison should be based on an equal transmission rate and package surface areas at the target application conditions (temperature and humidity). Use equation (15.5) to determine the best barrier polymer value:

$$TR = P \bullet \frac{A}{100} \bullet \frac{1}{t} \tag{15.5}$$

Where:

TR	=	transmission rate of a gas through film (cc/[day*atm]);
P	=	premeability coefficient of a gas through polymer (cc*mil/[100 in 2 *day*atm]);
t	=	thickness of polymer (mills);
A	=	surface area of polymer exposed to a gas (in^2).

Table 15-5 shows the calculations required to compare two barrier polymers. First, the equivalent thickness of each polymer that will provide the same barrier property is determined using equation (15.5). Then, the cost of each polymer is determined based on the equivalent barrier properties. The data needed are:

- the required transmission rate (TR)
- permeability coefficient (P_1 and P_2)
- package surface area (A).

Oil resistance of a polymer is influenced by its polarity and crystallinity. Polar polymers, such as Nylon and polyester, have good oil resistance. Among polyolefins and ethylene copolymers, PP and HDPE generally have the best oil resistance due to their high crystallinity. For PE, when the density is reduced by introducing comonomers, its oil resistance decreases. An exception is ionomers, which have excellent oil and grease resistance because of their polarity. Oil penetration generally increases with increasing temperature.

Table 15-5 Calculation of the most cost effective barrier polymer

Polymer	Thickness	Package cost
1	$t_1 = P_1 \bullet \frac{A}{100} \bullet \frac{1}{TR}$	$C_{Polymer\ 1} = \frac{t_1}{1000} \bullet A \bullet \rho_{Polymer\ 1} \bullet \$_{Polymer\ 1}$
2	$t_2 = P_2 \bullet \frac{A}{100} \bullet \frac{1}{TR}$	$C_{Polymer\ 2} = \frac{t_2}{1000} \bullet A \bullet \rho_{Polymer\ 2} \bullet \$_{Polymer\ 2}$

t_n	=	required polymer thickness (mills);
P_n	=	permeability coefficient;
A	=	package area (in^2);
ρ_n	=	polymer density (1b/in^3);
TR	=	transmission rate required to protect package contents;
C_n	=	polymer cost per package;
$\$_n$	=	polymer n price ($/1b).

Polymer sealability

Heat sealability is a critical property for many packaging applications. Fig. 15-2 shows a typical heat seal strength as a function of seal bar temperature. A polymer that exhibits low temperature sealability and maintains seal integrity over a broad seal temperature, dwell time and seal pressure can significantly increase packaging line speeds, improve efficiencies and minimize seal failures. Such a polymer may be unacceptable, however, for packages requiring heat resistance as in applications such as retort, boil-in-bag or microwave cooking.

Heat seal properties are influenced by a polymer's thermal and rheological properties as well as factors such as [29]:

- seal bar temperatures
- seal bar pressure
- dwell time
- sealing bar configuration
- package design.

Table 15-6 shows some heat seal data that compares the minimum seal bar temperature required to obtain a 3.5 N/cm (2.0 lb/inch) seal strength for monolayer films at the prescribed conditions. Ethylene copolymers have low melting temperatures and are often used as sealants; generally, the higher the copolymer content, the lower the seal initiation temperature. Stehling and Meka [30] showed that the fusion seal initiation temperature and the temperature for maximum seal strength of polyolefins and ethylene copolymers strongly correlate with their crystallinities. The seal interface strength is due to molecular chain interpenetration across the

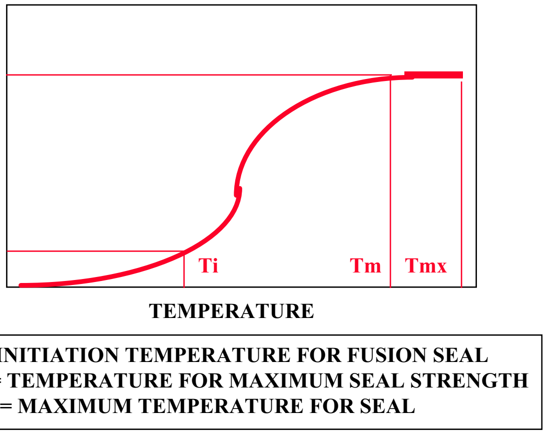

Fig. 15-2 Heat seal strength versus seal bar temperature.

Table 15-6 Polymer thermal and sealing properties

Polymer type	Melting point °C (F)	Vicat softening point °C (F)	Fusion seal temp^{+} °C (F)
EMA (20%)	80 (176)	59 (138)	82 (189)
POP (0.902 g/cc)	94 (201)	80 (176)	88 (190)
EVA (12%)	90 (194)	81 (178)	91 (195)
ION	93 (200)	72 (161)	99 (210)
EAA (9% AA)	98 (208)	83 (181)	93 (200)
ULDPE (0.912 g/cc)	121 (250)	105 (221)	101 (215)
LDPE (0.920 g/cc)	110 (230)	92 (198)	107 (225)
LLDPE (0.920 g/cc)	122 (252)	110 (230)	118 (245)
HDPE (0.960 g/cc)	135 (275)	125 (257)	121 (250)
PP	168 (334)	133 (271)	149 (300)
PS	120 (248) *		
PVDC	160 (320)*		
EVOH	160 (320)		
PA	216 (420)		
PC		154 (310)	

$^{+}$ Hot tack sealer, 50 μm (2.0 mil) film with 50 μm (2.0 mil) PET backing, 0.5 sec dwell, 275 KPa (40 psi) pressure; * Tg.

interface. Only after the polymer fully melts does enough penetration occur to ensure maximum seal strength. Qureshi, et al [31] show that molecular architecture of LLDPE plays a role: homogeneous copolymers have a more rapid seal strength increase than do heterogeneous (Zieger–Natta) polymers, presumably due to their faster diffusion rates. They estimate that, for PE to achieve its maximum seal strength, its chains must penetrate a distance on the order of its radius of gyration, a characteristic length scale of the polymer molecule in its random coiled configuration. Morris [32] found that ionomers only require penetration of a fraction of their radius of gyration to establish maximum seal strength. He attributes this to the longer range ionic forces present in ionomers. These same forces, however, contribute to slower diffusion rates for ionomers.

Morris also looked at the interrelationship between seal bar temperature, dwell time and package design on heat seal performance [32]. Thicker packaging structures require longer dwell times for a given seal bar temperature to reach the same heat seal strength as thinner structures. Nominally, this is due to heat transfer considerations; it takes longer for the heat to transfer through thicker films. Simple heat transfer modeling was not enough to account for seal performance differences. By coupling a polymer diffusion model with heat transfer analysis, Morris [32] was able to predict packaging performance. He found that, at least for the slow diffusing ionomers, seal strength increases at the interface after the heat seal jaws are removed as the film slowly cools to room temperature.

Another critical sealability property is hot tack strength, the ability to maintain seal integrity while still hot and a load is applied. Hot tack is important in vertical form-fill-seal (VFFS) machines since the product weight puts a force on the bottom seal while it is still hot [33]. It can also be important in horizontal form-fill-seal (HFFS) applications, particularly in gusseted areas where the films are folded. A film's dead fold or 'spring-back' nature exerts an opening force that must be countered by good hot tack strength to avoid channel leakers. Hot tack derives from two competing mechanisms. The first is polymer diffusion and penetration; as in the case for heat seal performance, strength at the interface is built by polymer inter-diffusion and entanglement. The second is melt strength, which is related to polymer viscosity. Diffusion increases with increasing temperature whereas melt strength decreases. Thus, hot tack strength versus sealing temperature typically goes through a maximum. Fig. 15-3 compares hot tack for ionomer versus polyolefin plastomer (POP). Ionomer has a broad hot tack range and polyolefin plastomer has a narrow hot tack range.

The maximum hot tack strength, the peak hot tack temperature and the hot tack range can all be consequential in end-use. The hot tack range versus temperature can be particularly important since it indicates how much flexibility packers may have in their packaging operation. Often, seal bar temperatures are not well controlled or the line speed is ramped up and down during the day, which affects the seal bar temperature. The molecular architecture and polymer chemistry play

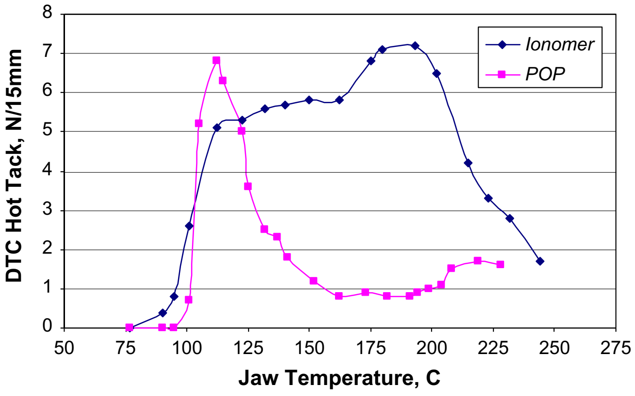

Fig. 15-3 Hot tack performance (from de Garavilla [34]).

a role in the hot tack curve shape. Some polyolefin plastomers have very high maximum hot tack strengths near their melting points that tail off quickly at higher temperatures. Strain induced crystallization in these homogeneous polymers has been proposed for the unusually high hot tack strength [35]. Poor hot tack at elevated temperatures is due to lower melt strength. Heterogeneous LLDPE and ULDPE tend to have broader hot tack curves. Broader yet are acid copolymers and, finally, ionomers, which have exceptionally high melt strength due to their unique ionic morphology [36].

Caulking or flow into cavities formed by wrinkles or gussets is sometimes required. Polymer flow is characterized by its viscosity, which is a function of temperature and shear rate. Higher sealing temperatures results in more flow and caulking. However, if the temperature is too high, the sealant may be squeezed out of the seal area, resulting in poor seal performance. Heat sealing is generally a very low shear process. The zero shear viscosity at the sealing temperature is a good starting point when comparing different polymers for their ability to caulk. Melt index, a flow measure typically used in the industry, is only a crude indicator for caulking since it does not account for a polymer's viscosity as a function of temperature and shear rate.

Seal bar pressure is another heat seal variable we have not discussed yet. A general guideline is to use just enough pressure to get by. Some pressure is needed to ensure the film surfaces are in intimate contact for interfacial penetration to occur. Too much pressure, however, may result in squeeze-out of the sealant from the seal area.

In some packaging applications, such as potato chip pouches, an easy opening seal is desired. There are three general methods used to control the seal strength for easy-open or peel–seal performance:

- an interfacial peel–seal mechanism where the sealant is often blended with another polymer that 'contaminates' the seal strength
- a delamination peel–seal mechanism, sometimes known as a 'burst' peel where adjusting the sealant layer adhesion to the adjacent layer controls the seal strength. The opening force tears through the sealant layer and the seal fails along the sealant/adjacent layer interface
- blending something into the sealant so that it has poor cohesive strength so that the seal fails within the sealant layer during opening.

Adhesive polymers

For a coextruded structure to function during manufacture, packaging, distribution and storage over the product life cycle, there must be sufficient adhesion between the layers. Interlayer adhesion is affected by:

- the structure design
- the individual layer properties
- the process by which it is put together
- the manner in which it is used [37].

The structure design and, in particular, the individual layers' compatibility, will determine whether specialized adhesive polymers or tie layers are needed [4]. For two polymers to bond to one another they first must come into intimate contact. In coextrusion, this is achieved as the molten polymer streams are combined in the die or feedblock. For coatings and laminations, this requires good wetting, which is a function of viscosity, polarity and surface tension. Once good contact is achieved, molecular segments may diffuse across the interface provided:

- the molecules are compatible
- the polymers are above their glass transition or melting temperature to allow chain segment mobility
- there is sufficient time and temperature for diffusion to occur.

As discussed above, diffusion is the primary mechanism for heat sealing a sealant to itself. Even if conditions are not favorable for diffusion, good adhesion can be obtained as a result of chemical reaction at the interface.

Table 15-7 gives some examples of the adhesion between some typical layer combinations found in coextruded packaging films. For those cases where adhesion is poor, specialized adhesive polymers or tie resins have been developed [38]. Tie resins are typically a polyolefin or ethylene copolymer matrix resin, with

Table 15-7 Chart of adhesion between polymers

Polymer	HDPE	PP	PS	PA	EVOH	PVDC	PC
LDPE	G	P	P	P	P	P	P
LLDPE	G	G	P	P	P	P	P
ECO	F	P	X	P	P	G	F
EVA	G	G	G	P	P	G	F
EMA	G	G	X	P	P	G	F
EAA	F	P	P	G	P	P	P
ION (Na)	P	P	P	P	P	P	P
ION (Zn)	P	P	P	G	P	P	P
PE-g-MAH	G	P	P	G	G	P	F

G = good; F = fair; P = poor; X = no data

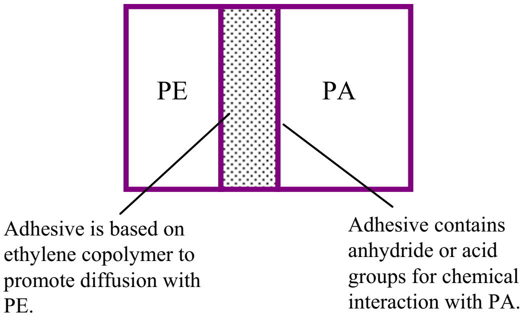

Fig. 15-4 Coextrusion adhesive technology.

chemical functionality and sometimes a toughener added. The matrix resin is chosen for its compatibility with one bonded layer to take advantage of the diffusion mechanism in adhesion. In Fig. 15-4, PE is being adhered to PA. In this case, the matrix resin can be PE, EVA or other ethylene copolymer which bonds to the PE layer. Chemical functionality is incorporated into the adhesive polymer via copolymerization, grafting reaction or alloying. Some common examples of chemical functionality are given in Table 15-8. In the example in Fig. 15-4, either acid or anhydride functionality is typically chosen. The acid or anhydride groups react with the PA amine end groups to achieve good adhesion. Finally, various tie resin manufacturers often blend in proprietary modifiers, such as rubber, that impact the tie resin physical properties and its peel strength performance. The most common tie resins used today are anhydride modified polyolefins for bonding to Nylon and EVOH in barrier film structures.

When selecting an appropriate tie resin, several factors come into play besides the adhesion performance. The adhesive must comply with appropriate government regulations, such as Food and Drug Administration (FDA) regulations for food packaging in the USA. It must have the proper flow properties for the given converting process and sufficiently match the flow properties of adjacent layers to avoid flow instabilities during coextrusion. The tie resin may also be called upon to impart other properties, such as moisture barrier, toughness or clarity. Selecting an appropriate tie resin matrix will often accomplish this. For example, an HDPE-based tie resin will have a lower moisture vapor transmission rate (MVTR) than one based on EVA. Finally, as with any polymer, the product quality and consistency is important for achieving good performance.

Table 15-8 List of commonly used functional groups in tie resins

Functionality	Adheres to
Acid	PA, Al foil
Anhydride	PA, EVOH
VA	PVDC, PP, PET
Acrylate	Some inks
Epoxy	PET
Silane	Glass

Tie resin thickness in the packaging structure can influence adhesion performance, as can coating thickness in extrusion coating [39]. Adhesion is most often measured by pulling the structure apart in a peel strength test. Peel strength is a function of fracture energy, or energy to create new surfaces as the peel front advances. At the advancing edge, the adhesive deforms, creating an energy loss that contributes to the measured fracture energy. Increasing the adhesive thickness may increase the deformation zone, increasing the fracture energy. It may also increase the energy to bend the peel arm during the peel test, although this effect is small for flexible films. In theory, the fracture energy will increase with increasing thickness until a critical value is reached where the deformation zone becomes small compared to the thickness. At this point, the fracture energy plateaus [40]. In many flexible packaging structures, the adhesive thickness is below this critical thickness so that reducing thickness reduces the peel strength performance. There are also practical limits on how low the thickness can be for a given converting process and still ensure adhesive layer continuity. For most processes, 2–3 μm (0.1 mil) is the lower adhesive layer thickness limit.

How the film is fabricated can have a significant impact on adhesion. Typically, less orientation and greater contact time at higher temperatures favors adhesion. Several processing parameters are important for optimizing adhesion performance [38]:

- adhesion generally increases with increasing processing temperatures. Both diffusion and chemical interaction are favored at higher temperatures
- increasing melt contact time generally improves adhesion. Combination technology (feedblock or die design), the order in which layers are brought together and die land length can affect adhesion
- increasing line speed generally reduces adhesion. In studying the blown film process, Morris [41, 42] found that the peel strength of an anhydride modified polyolefin to EVOH increased ten-fold by changing the process time, which is inversely related to line speed. He attributed this to a decrease in stress imparted during quenching. Morris [43, 44] found similar behavior in coextrusion cast film and coextrusion coating, although the nature of the process time versus peel strength behavior suggests time for reaction may play a role. He related the

differences between blown and cast film/extrusion coating back to fundamental differences in the time and temperature at which new interfacial area is created during drawing of the resin in the processes [43]. By scaling the process time by the characteristic relaxation time of the tie resin and the peel strength by the modulus of the tie resin, he was able to develop a single relationship that describes the effect of processing and material parameters on peel strength in both blown and cast film [44]

- orientation decreases adhesion. Increasing blow up ratio in blown film, or increasing draw down ratio in cast film can reduce adhesion. Orientation processes such as double bubble processes can substantially reduce adhesion by increasing stress, reducing thickness and creating new interfacial area (decreasing bond density)
- thermoforming can reduce adhesion by some of the same mechanisms as orientation.

Finally, the manner in which the structure is used can impact adhesion [37]. End-use storage conditions (temperature, RH) and the environment the package is subjected to, both physical (e.g. cook-in meats, post-packaging sterilization or pasteurization) and chemical can alter adhesion. The product itself can contain chemical species that migrate to the interface and destroy adhesive bonds. A well-known example is the effect an acid species in orange juice and condiments has on LDPE or EAA adhesion to foil [45–50]. It is critically important to test structures under conditions that closely simulate the end-use before finalizing a packaging structure.

Applications for flexible packaging film structures

Packages may be formed in-line by several techniques or may be supplied to the packer as pre-formed pouches or bags. Packaging may be created by wrapping or shrinking a basic film around a bundle of goods. In-line packaging forming examples include vertical form/fill/seal (VFFS), horizontal form/fill/seal (HFFS) and thermoform/fill/seal. In VFFS operations, film from a roll is guided through rollers and then shaped by a forming collar into a tube. The film moves in a vertical direction (down) over a filling tube. A vertical seal is made, forming the film into a continuous tube. As the film continues through the machine, a horizontal seal is made, perpendicular to the film machine direction, forming the bottom end-seal of the bag being formed and the top seal of the previously filled bag. The product is dropped into the partially formed bag, advanced to the seal bars and the next bottom and top end-seal is made. The process may operate in a step-wise or continuous manner. One example of a product normally packaged on VFFS equipment is fresh-cut produce. In HFFS operations, the film moves in a horizontal direction during the packaging step, reducing the need for high hot tack strength. One application that typically uses HFFS equipment is chunk cheese. In thermoform/fill/seal operations, a bottom web is formed, product is added and the top web, which is normally flat, is sealed to the bottom web. Thermoform/fill/seal packaging is frequently used for bacon and processed meats. Stand-up pouches and other types of packaging may be formed in-line with the filling equipment, or may be fully or partially pre-fabricated prior to the filling step.

Markets for flexible packaging films have continued to grow in many applications. Polyethylene and the various copolymers account for more than 75% of the flexible packaging film. Some major market segments where coextruded film is used include [51]:

- medical packaging
- food packaging
- heavy duty shipping bags
- stretch wrap
- trash bags
- condiments – OPET/print/LDPE/Al/EAA/LDPE and variations
- aseptic packaging OJ – juice boxes – print/LDPE/paperboard/LDPE/Al/EMAA/LDPE and variations
- towlettes – OPET/print/LDPE/Al/ION and variations
- condoms – similar structures as towlettes
- laminates for toothpaste tubes – PE-film/(LDPE-EAA)/Al/(EAA/LDPE)/PE-film
- stand-up pouches – OPET/print/adh/m-OPP/adh/(LLDPE-HDPE-LLDPE) and variations.

Medical packaging

A wide variety of structures are used in the medical packaging area (Table 15-9). The structure requirements include:

- sterilization capability
- microbial barrier
- linear tear properties
- puncture resistance.

Sterilization methods used for medical packaging film include ethylene oxide gas or radiation. The package is typically a forming web and a non-woven fabric (like TYVEK®) which lets the ethylene oxide in and out of the package. Medical packaging usually does not require oxygen barrier properties so EVOH is normally not required in medical packaging structures. Coextrusion processes are growing in this market. Blown film, cast film and extrusion coating processes are used in

Table 15-9 Medical device packaging structures

<table>
<tr><th colspan="9">3-layer structure</th><th>Layers (%)</th><th>Gauge (μm)</th></tr>
<tr><td>EVA</td><td></td><td></td><td>ION</td><td></td><td></td><td>EVA</td><td></td><td></td><td>20 | 60 | 20</td><td>50–400</td></tr>
<tr><td>ION</td><td></td><td></td><td>EAA</td><td></td><td></td><td>EVA</td><td></td><td></td><td>30 | 30 | 40</td><td>50–400</td></tr>
<tr><td>Paper</td><td></td><td></td><td>PE</td><td></td><td></td><td>Foil</td><td></td><td></td><td>Lamination</td><td></td></tr>
<tr><th colspan="9">5-layer structure</th><th></th><th></th></tr>
<tr><td>LLDPE</td><td>Tie</td><td></td><td>PA</td><td></td><td>Tie</td><td></td><td>LLDPE</td><td></td><td>40 |5|10|5| 40</td><td>50–400</td></tr>
<tr><td>m-LLDPE</td><td>Tie</td><td></td><td>PA</td><td></td><td>Tie</td><td></td><td>m-LLDPE</td><td></td><td>40 |5|10|5| 40</td><td>50–400</td></tr>
<tr><td>LLDPE</td><td>Tie</td><td></td><td>PA</td><td></td><td>Tie</td><td></td><td>PA</td><td></td><td>70 |5|10|5| 10</td><td>50–400</td></tr>
<tr><td>LDPE</td><td>Paper</td><td></td><td>LDPE</td><td></td><td>Foil</td><td></td><td>LDPE</td><td></td><td>Lamination</td><td></td></tr>
<tr><td>PET</td><td>adh</td><td></td><td>LDPE</td><td></td><td>EVA</td><td></td><td>ION</td><td></td><td>Lamination</td><td></td></tr>
<tr><th colspan="9">7-layer structure</th><th></th><th></th></tr>
<tr><td>LLDPE</td><td>Tie</td><td>PA</td><td>EVOH</td><td>PA</td><td>Tie</td><td></td><td>LLDPE</td><td></td><td>30 |5|10|10|10|5| 30</td><td>50–400</td></tr>
<tr><th colspan="9">9-layer structure:</th><th></th><th></th></tr>
<tr><td>PE</td><td>Tie</td><td>PA</td><td>Tie</td><td>PE</td><td>Tie</td><td>PA</td><td>Tie</td><td>PE</td><td>20 |5|10|5| 20 |5|10|5| 20</td><td>50–400</td></tr>
<tr><td>LLDPE</td><td>LDPE</td><td>Tie</td><td>PA</td><td>EVOH</td><td>PA</td><td>Tie</td><td>LDPE</td><td>LLDPE</td><td>10/15/10/10/10//10/10/15/10</td><td>50–400</td></tr>
</table>

producing flexible packaging structures for medical packaging applications. Films ranging from three layers to eleven layers are now available. These markets are typically small and require many years to meet the required qualifications.

The forming webs were historically three-layer EVA and ionomer films as shown in the syringe package in Fig. 15-5. Heavy gauge films were sometimes produced by combining a three-layer film to form six layers. Newer film structures have seen more layers being used and incorporating polyamide (PA) to replace ionomer in film structures to address economic issues.

Consumer and industrial heath care packaging includes:

Fig. 15-5 Multilayer film used for syringe package.

- medical disposables
- surgical instruments – structures similar to disposables
- resterilization packaging
- syringes and hypodermic needles
    - forming web
    - non-forming web
- sutures
- pharmaceutical
- condoms and towlettes.

Lidding stock is normally produced by extrusion coating and/or lamination processes and combines paper, polymers and foil to form multilayer structures. Sachets for condom and towelette packaging typically use the structure OPET/print/LDPE/Al/ION and variations, with ionomers used as the sealant for its chemical flex crack resistance.

Food packaging

Primal meat packaging (Shrink)

Packaging primal and sub-primal meat requires a package that must:

- provide high shrinkage to fully collapse around irregular shapes
- have excellent optical properties

- shrink at low temperature to prevent product damage
- impart good softness and elasticity
- provide excellent oxygen, moisture, odor and grease barrier protection
- prevent freezer burn
- facilitate using individual cuts by food preparers
- help reduce purge loss
- extend shelf-life
- after easy disposal
- have good machinability
- have an oxygen transmission rate (OTR) less than 1.0 cc/100 in^2-day-atm (non-frozen only).

A shrinkable film used in this application is a PVDC barrier film with the sealant layer designed to provide toughness and puncture resistance. These films must be oriented to provide acceptable shrink properties using a double bubble process. Table 15-10 shows some typical film structures used in shrink film for primal and sub-primal meat packaging.

Processed meat packaging

Processed and cook-in meat such as:

- luncheon meat
- ham
- bologna
- salami

are packaged in barrier films that are designed to keep oxygen from entering the package. This extends shelf-life and gives the retailer extended product display time. It also allows the consumer to keep the product in their refrigerator, unopened, for some time after purchase. These packages are often printed with eye-catching graphics to increase sales. These films may contain:

- a barrier polymer
- printing surface, such as PET or nylon, that also provides thermal resistance during sealing and helps provide abuse resistance during distribution
- LLDPE or ULDPE toughness layers
- a sealant layer that could be LLDPE, a polyolefin plastomer or an ionomer.

The processed meat package comprises a forming film and a backing film. The forming film is thermoformed to the meat product shape. In addition, low oxygen permeability, abuse resistance and seal integrity are critical to maintaining the proper atmosphere inside the package. Optical properties, such as high gloss and high clarity, are important on the backing film where reverse printed PET is used to create consumer appeal. Barrier requirements for processed meats range from 0.2–1.0 cc/100 in^2-day-atm for OTR and 0.2–0.5 g/100in^2-day for water vapor transmission rates (WVTR). Table 15-11 shows some typical film structures used in processed meat packaging.

Poultry/fish packaging

Moisture barrier properties are more critical. The packages are normally vacuum packaged (Fig. 15-6) with a good sealant polymer such as EVA, ionomer or LLDPE (Table 15-12).

Cereal box liners

Cereal box liners (Fig. 15-7) also require good moisture barrier properties to provide good taste and freshness protection. High density polyethylene polymers are typically used to provide moisture barrier. Sealant polymers such as EVA, ionomer or blends are used for low temperature seals, form-fill-seal packaging and easy opening seals, respectively. Certain products have additional requirements, such as puncture resistance to keep the product from poking through the packaging film and flavor and aroma barrier for highly flavored cereals. Most cereal box liners contain HDPE for its moisture barrier properties and a sealant layer which may be EVA, ionomer or POP (Table 15-13). Heat seal initiation temperatures of 90 °C and below

Table 15-10 Primal and sub-primal meat packaging

5-layer structure					**Layers (%)**	**Gauge (μm)**
ULDPE	EVA	PVDC	EVA	ULDPE	40 |5|10|5| 40	50–120
m-LLDPE	EVA	PVDC	EVA	m-LLDPE	40 |5|10|5| 40	50–120
m-LLDPE	LLDPE	Tie	EVOH	PA	30 | 40 |10|10|10	50–120
ION	LLDPE	Tie	EVOH	PA	30 | 40 |10|10|10	200–300
ION	EVA	LLDPE	/PVDC/	o-PA	20 | 30 | 35 |5|10	50–100

Note: /PVDC/ is an adhesive lamination with PVDC. See appendix for convention used.

Table 15-11 Processed meat packaging film structures

Product Structure	Layers (%)	Gauge (μm)
Ground beef		
LLDPE/Tie/PA	(75/5/20)	150–200
LLDPE/Tie/EVOH/PA	(75/5/10/10)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	40–150
Barrier overwrap		
m-LLDPE/LLDPE/Tie/EVOH	(30/40/10/10/10)	150–200
m-LLDPE/LDPE/LDPE/Tie/PA/EVOH/PA	(20/15/15/10/15/10/15)	150–200
Chub films		
LLDPE/ PVDC//PA	(75//5//20)	150–200
Foodservice portion: steaks/chops/roasts		
Forming web		
LLDPE/Tie/EVOH/PA	(75/5/5/15)	150–200
ION/Tie/EVOH/PA	(75/5/5/15)	150–200
LLDPE/Tie/PA	(75/5/20)	150–200
ION/PA	(80/20)	150–200
ION/EVA//PVDC/PA	(60/10//5/25)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	150–200
Non-forming web		
LLDPE/Tie/EVOH/PA	(70/10/10/10)	50–80
ION/Tie/EVOH/PA	(70/10/10/10)	50–80
LLDPE//PVDC//o-PET	(85//5//10)	50–80
ION//PVDC//o-PET	(85//5//10)	50–80
ION/Tie/PA	(80/10/10)	50–80
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–80
Skin packaging forming web		
ION/Tie/EVOH//Tie/EVA	(35/10/10//10/35)	150–250
Skin packaging non-forming web		
ION/Tie/EVOH//Tie/EVA	(35/10/10//10/35)	50–80
Luncheon meat		
Forming web		
LLDPE/Tie/EVOH/PA	(75/5/5/15)	150–200
ION/Tie/EVOH/PA	(75/5/5/15)	150–200
m-LLDPE/Tie/EVOH/PA	(75/5/5/15)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	150–200

(*Continued*)

Table 15-11 Processed meat packaging film structures —*cont'd*

Product Structure	Layers (%)	Gauge (μm)
Non-forming web		
LLDPE/EVA/PVDC//o-PET	(60/10/5//25)	50–100
m-LLDPE/tie/EVOH//o-PET	(60/10/5//25)	50–100
ION/Tie/EVOH//o-PET	(60/10/5//25)	50–100
LLDPE/Tie/EVOH/PA	(60/10/5/25)	50–100
LLDPE//PVDC//o-PA	(60/10//5//25)	50–100
LLDPE/Tie/PA/EVOH/PA	(60/10/10/10/10)	50–100
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Frankfurters		
Forming web		
LLDPE/Tie/EVOH/PA	(75/5/5/15)	150–200
m-LLDPE/EVOH/PA	(75/5/5/15)	150–200
ION/EVOH/PA	(75/5/5/15)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	150–200
Non-forming web		
LLDPE-EVA//PVDC//o-PA	(60/25//5//10)	50–100
m-LLDPE/tie/EVOH/o-PET	(60/15/10/15)	50–100
ION//PVDC//o-PET	(85//5//10)	50–100
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–10
Sausage		
Forming web		
LLDPE/LDPE/Tie/EVOH/PA/Tie/EVA	(30/5/10/10/10/5/30)	150–200
m-LLDPE/Tie/EVOH/PA	(75/5/5/15)	150–200
ION/Tie/EVOH/PA	(75/5/5/15)	150–-200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	150–200
Non-forming web		
ION//PVDC/o-PET	(80//5/15)	50–100
LLDPE/Tie/EVOH//o-PET	(60/15/10//15)	50–100
m-LLDPE/Tie/EVOH/PA	(60/15/10/15)	50–100
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Shrink bags		
EVA/EVOH/EVA	(48/5/47)	50–80
EVA/PVDC/EVA	(48/5/47)	50–80

Table 15-11 Processed meat packaging film structures —*cont'd*

Product Structure	Layers (%)	Gauge (μm)
Ham		
Forming web		
LLDPE/Tie/EVOH/PA	(60/15/10/15)	150–200
ION/Tie/EVOH/PA	(60/15/10/15)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Non-forming web		
LLDPE//PVDC//PA	(70//5//25)	50–80
ION//PVDC//PA	(70//5//25)	50–80
LLDPE//PVDC//o-PET	(70//5//25)	50–80
ION//PVDC//o-PET	(70//5//25)	50–80
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Shrink bags		
EVA/EVOH/EVA	(48/5/47)	50–80
EVA/PVDC/EVA	(48/5/47)	50–80
m-LLDPE/Tie/EVOH/Tie/m-LLDPE	(30/10/10/10/30)	50–80
Bacon		
ION/TiE/EVOH/PA	(50/10/10/30)	30–60
ION/PA	(50/50)	30–60
Deli meats		
Shrink bags		
EVA/EVOH/EVA	(48/5/47)	50–80
EVA/PVDC/EVA	(48/5/47)	50–80
m-LLDPE/Tie/EVOH/Tie/m-LLDPE	(30/10/10/10/30)	50–80
Forming web		
LLDPE/Tie/EVOH/PA	(80/5/5/10)	200–250
ION/Tie/EVOH/PA	(80/5/5/10)	200–250
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Non-forming web		
LLDPE//Tie/PA/EVOH/EVA	(40//10/10/20/30)	50–80
ION/Tie/EVOH/PA	(60/15/10/15)	50–80
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Casings		
LLDPE//o-PA	(70//30)	50–80
LLDPE//o-PA//PVDC	(70//20//10)	50–80

Fig. 15-6 Poultry packaging.

Fig. 15-7 Cereal boxes.

are commonly required. Moisture vapor transmission rates less than or equal to 0.1 g/100in^2-day-atm are often required. Packages requiring aroma or taste barrier properties will contain either Nylon or EVOH polymers.

Snack food packaging

Potato chips are often packaged in structures that contain metallized films (Table 15-14). Polymer film metallization provides oxygen barrier, moisture barrier and light barrier. The light barrier is to protect the potato chips from ultraviolet radiation that initializes an oxidation mechanism. Seal strength must be optimized to provide a secure package that can be easily opened by the consumer. Seal integrity and consumer appeal are also critical.

Salty snack packaging

Salty snacks are frequently high in fat content and may require a package that provides an oxygen barrier in order to prevent the fat in the food from going rancid. They may also require grease resistance to keep the package from leaving an oily spot. Salty snacks may be packaged in barrier films containing foil, a metallized polymer film or a barrier polymer such as EVOH or PVDC and are gas flushed with nitrogen to maintain a low oxygen concentration inside the package (Table 15-15).

Bakery

Moisture barrier is normally the critical property in bakery applications. Polymers used for moisture barrier include LDPE, LLDPE, HDPE or PP. Typically, EVA polymers are used for sealability and optics. Applications, such as the cake mix pouch, will require aroma, taste and moisture barrier properties. Nylon is used for taste and aroma barrier. In bread bags, the LLDPE polymer's toughness allows down gauging, while LDPE allows good optics and printability (Table 15-16).

Cheese packaging

Most cheese sold in the USA is prepackaged in flexible packaging. The cheese packaging includes:

- individually wrapped slices (IWS) of processed cheese
- chunk cheese
- shredded cheese.

Both chunk cheese and shredded cheese require substantial oxygen barrier to prevent mold growth and

Table 15-12 Poultry/fish packaging

7-layers structure	Layers (%)							Gauge (μm)
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	25	10	10	10	10	10	25	40–150
LLDPE/Tie/PA/EVOH/PA/Tie/Ion	25	10	10	10	10	10	25	40–150

Table 15-13 Cereal packaging

Market Structure	Layers (%)	Gauge (μm)
Bag-in-box		
HDPE/HDPE/EVA	45 | 45 |10	40–60
HDPE/HDPE/ION	45 | 45 |10	40–60
Bag-in-box (peelable seal)		
HDPE/HDPE/EVA+ION	45 | 45 |10	40–60
Bag-in-box (barrier bag)		
HDPE/Tie/EVOH/Tie/EVA	60 |10|10|10|10	40–60
HDPE/Tie/PA/Tie/EVA	60 |10|10|10|10	40–60

spoilage. Ethylene vinyl alcohol, PVDC or PVOH may provide the oxygen barrier. While EVOH is generally coextruded into the film structure, PVDC or PVOH may be coated on a film via a coating process. Cheese packaging also requires excellent seal integrity and abuse resistance to prevent the controlled atmosphere inside the package from being lost. Cheese packages are often laminations made with reverse printed outer webs containing PET or nylon for superior graphical presentation. They may also be extrusion coated structures where the sealant layer has been extrusion coated onto the outer layer. Sealant layers may consist of EVA, an ionomer or a polyolefin plastomer. Low heat seal initiation temperature (90 °C or below) and good seal through contamination performance are required. Processed cheese typically requires films with OTR of 0.6–1.0 cc/100in^2-day-atm and WVTR of 1.0 g/100in^2-day (Table 15-17).

Table 15-14 Snack food packaging films

Structure	Layers (%)	Gauge (μm)
Potato chips (OTR 2.0, MVTR 0.02)		
o-PP//met o-PP	50 || 50	20–60
o-PP//LDPE//MET o-PP	25 || 50 || 25	20–60
EVA/HDPE//Met-o-PP	15 | 70 || 15	40–80
Tortilla and corn chips (OTR<2.0, MVTR<0.35)		
o-PP//LDPE//o-PP	25 || 50 || 25	20–60
o-PP//PVDC//o-PP	50 //p/5|| 45	20–60
Pretzels (OTR<2.0, MVTR<0.5)		
o-PP//LDPE//o-PET	25 || 50 || 25	30–80
o-PP//LDPE//o-PP	25 || 50 || 25	30–80
o-PP//PVDC//o-PP	45 ||5|| 50	30–60
Meat snacks		
LDPE//PVDC//o-PET	45 ||5|| 50	30–60
LLDPE/Tie/EVOH/PA	60 |10|10|10|10	40–80

MVTR: moisture vapor transmission rate; OTR: oxygen transmission rate
Note: p stands for primer

Table 15-15 Snack nuts packaging

Structure	Layers (%)	Gauge (μm)
o-PP//LDPE//o-PP	20 || 60 || 20	40–60
o-PP//LDPE//Foil//LDPE	10|| 20 ||5|| 65	40–60

An acrylic, PVOH coated OPP film is also used in cheese packaging in both extrusion and adhesive laminations. It is an ExxonMobil product called Bicor AOH. Acrylic is coated on one side and PVOH on the other side.

Milk pouches

LLDPE or LDPE/LLDPE blends provide the sealant in both milk powder and liquid pouches (Table 15-18). If oxygen barrier is required for long shelf-life, then Nylon could be used.

Frozen food

Frozen foods (Fig. 15-8) are packaged in a variety of packaging types. Examples of frozen foods packaged in flexible packaging include:

- frozen fruits
- vegetables
- French fries
- individually quick frozen chicken breasts.

Many frozen foods are packaged in surface printed polyethylene films. Some higher value added items are packaged in laminations, which may be shaped into stand-up pouches. Most frozen food bags are made on standard VFFS machinery.

Table 15-16 Bakery packaging

Structure	Layers (%)	Gauge (μm)
cPP/PP/cPP	10| 80 |10	30–60
EVA/PP	20 | 80	30–60
HDPE/EAA/PA/EAA	70 |10|10|10	30–70
LLDPE/PP/LLDPE	10| 80 |10	30–60
LLDPE/Tie/PA/EVOH/PA	30 |10| 20 |10| 20	100–160

Table 15-17 Cheese packaging

Structure	Layers (%)	Gauge (μm)
Natural chuck cheese pouches		
LLDPE/Tie/EVOH//o-PET	75 |10||15	40–60
LLDPE//PVDC//o-PP	75 |10||15	50–60
LLDPE//PVDC//o-PET	75 |10||15	45–50
EVA//PVDC	95 ||5	50–60
LLDPE//PVDC//o-PA	75 |10||15	45–50
Vacuum bags for aging		
EVA//PVDC//o-PA	85 ||5||10	40–100
LLDPE/Tie/PA	80 |10|10	40–100
EVA/Tie/PA	80 |10|10	40–100
Shredded cheese		
PVDC//PA//LDPE	5|| 20 || 75	80–100
PVDC//PET//LDPE	5|| 20 || 75	80–100
PA/EVOH/Tie/LDPE	10|10|10| 70	80–100
Processed cheese slices		
o-PP//EVA	50 || 50	20
PP/EVA	20 | 80	35–40

Key requirements for frozen food packaging are:

- low temperature toughness
- modulus
- high hot tack strength
- high seal strength.

Some packages are clear and require good clarity, while others are pigmented and require good gloss. Linear low density polyethylene, ULDPE, EVA and POP resins are all commonly used in creating frozen food packaging. Stiffness must be adequate for high speed packaging and packaging films must have tear and puncture strength high enough to prevent package damage during transportation and storage (Table 15-19).

Table 15-18 Milk packaging

Structure	Layers (%)	Gauge (μm)
LLDPE/Tie/PA/Tie/LLDPE	35 |10|10|10| 35	40–70
HDPE/(LDPE + LLDPE)	40 | 60	40–80

Fresh-cut produce

Key performance requirements for fresh-cut produce packaging include proper oxygen and carbon dioxide

Fig. 15-8 Frozen food packaging.

Table 15-19 Frozen food packaging

Structure	Layers (%)	Gauge (μm)
EVA/LLDPE/EVA	15 | 70 | 15	40–80
PET//Tie//LDPE/ION	15 ||5|| 40 | 40	40–80
m-LLDPE/LLDPE/m-LLDPE	15 | 70 | 15	40–80
HDPE/MDPE/EVA	15 | 70 | 15	40–80

permeability, seal integrity, machinability and consumer appeal. Consumer appeal includes both feel and appearance. Feel is generally determined by film thickness and modulus while appearance is governed by print quality and film optical properties, such as clarity, haze and gloss. In order to extend the shelf-life of the produce being packaged, films must provide the proper oxygen permeability that is matched to the packed produce respiration rate. Cut produce respires after harvesting, consuming oxygen and giving off carbon dioxide. By controlling the permeation of gases through the package, the environment inside the package is controlled, respiration is slowed and shelf-life is extended. The bags must have complete seal integrity in order to prevent the unplanned transfer of gases between the bags and the environment. Bags may contain PP, LLDPE, ULDPE, EVA or POP. Oxygen transmission rate requirements vary widely depending on the produce being packaged, but common items range from about 100 cc/100in^2-day-atm for Caesar salad mixes, 150–200 cc/100in^2-day-atm for iceberg salad mixes and 200–350 cc/100 in^2-day-atm for specialty salad mixes such as baby greens and exotic lettuces. Perforation may be used to obtain high transmission rates for some applications.

Retortable pouches

A growing flexible packaging use is in the replacement of metal cans with retortable pouches. These pouches are typically laminations containing biaxially oriented nylon for toughness, foil for oxygen barrier and a polypropylene sealant film. These pouches may contain items like tuna, pet food and soup. The food items are held at elevated temperature after packaging, so the packages must remain intact at elevated temperatures. In addition to temperature resistance, toughness, seal strength and barrier properties are critically important.

Edible oil packaging

The packaging of cooking oil uses nylon to provide oxygen barrier properties. Ethylene acrylic acid is typically used as the sealant layer. The seal type determines the nylon layer location (Table 15-20).

Bag-in-box

Coextruded films containing oxygen barrier polymers are replacing some metallizing laminates where flex crack resistance is required. Linear low density polyethylene or EVA polymers are used as sealants (Table 15-21).

Stretch wrap

Stretch film, or stretch/cling film, is used to unitize goods for transportation. A thin film is stretched, either by machine or by hand and wrapped around packages to hold the goods together. The film clings to itself and to the pallet, securing the load. In its most common form, stretch/cling film is applied to a stacked pallet using a power pre-stretch pallet wrapper in an automated operation (Fig. 15-9). In this operation, the film is stretched, between 100 and 300%, by rollers turning at different speeds and is then applied to a loaded pallet which sits atop a moving turntable. Machine wrap film is typically supplied on rolls that are 20 or 30 inches (51 or 76 cm) wide. Hand wrap film is supplied on smaller rolls. Stretch/cling films may be manufactured by either a cast film or blown film process. Most stretch/cling films are coextruded structures containing three to seven layers. Most cast film lines are now being installed with

Table 15-20 Edible oil packaging

Structure	Layers (%)	Gauge (μm)
PA/Tie/EAA	10| 15| 75	50–150
EAA/Tie/PA/Tie/ EAA	30 |10|10|10| 35	50–150
EAA/PA/EAA	40 | 20 | 40	50–150

Table 15-21 Bag-in-box

Structure	Layers (%)					Gauge (μm)
LLDPE/Tie/PA/Tie/LLDPE	35	10	10	10	35	40–80
EVA/Tie/PA/ Tie/EVA	35	10	10	10	35	40–80
LLDPE/Tie/EVOH/Tie/LLDPE	35	10	10	10	35	40–80

five-layer capability and blown film coextruded films are typically three layers. Linear low density polyethylene is the primary component in most stretch films. For specialized applications, coextrusions containing minor PP, EVA, POP, m-LLDPE, EPE or ULDPE layers may be employed (Table 15-22). For most stretch film structures, a resin with good inherent cling is used on either one or both surface layers. A tackifier, such as polyisobutylene, can also be added to the structure to provide the desired cling force. Stretch film is used to unitize entire or partial pallets stacked with products such as resin bags, fertilizer bags, consumer goods and food products during distribution. Most stretch film is removed by the retailer prior to displaying the packaged items for sale. Stretch films must have:

- good cling
- stretchability
- load retention
- puncture resistance.

Heavy duty bags (Shipping Bags)

Heavy duty shipping sacks are used to transport items such as:

- resin
- salt
- pet food
- fertilizer
- chemicals
- topsoil
- bark mulch
- compressed bales of fiberglass insulation.

Fig. 15-9 Rotary pallet stretch cling wrapper.

When filled they weigh 40 pounds (18 kg) or more. Heavy duty shipping sacks may be supplied as preformed bags or as roll stock, which is formed into bags in a continuous VFFS operation. Special machinery is required to form heavy duty shipping sacks on VFFS machinery in a high-speed continuous operation. These bags need moderate COF because they must easily pass through the packaging equipment, but stacked bags must not slide off each other. Bags filled with hot products, such as salt, must also withstand the filling temperatures without excessive stretching or dimpling. Film toughness and creep resistance are also important in many heavy duty shipping sack applications. Linear low density polyethylene has allowed significant gauge reduction. Low density polyethylene is used to reduce creep and improve processability. High density polyethylene and PP are used for stiffness and higher end-use temperature resistance. Ethylene vinyl acetate polymers are used for low temperature sealability in form-fill-seal applications (Table 15-23).

Trash bags

Linear low density polyethylene introduction accelerated using coextrusion in trash (or refuse) bags (Table 15-24). Down gauging and using recycled material allows for improved economics and environmental concerns. High molecular weight-HDPE polymers are also finding increased usage due to further down gauging opportunities. This is the largest coextruded film market segment.

Grocery sacks (merchandise bags)

High molecular weight -HDPE coextruded with LLDPE provides improved sealability with good down gauging potential (Table 15-25). This film is typically made on high stalk HDPE blown film coextrusion lines.

High clarity shrink film (oriented)

Oriented, high clarity shrink film is used to protect and display high value consumer goods. It is distinguished

Table 15-22 Stretch cling pallet wrap

Structure	Layers (%)					Gauge (μm)
Stretch cling film						
EVA/ULDPE/LLDPE	10		80		10	15–30
ULDPE/LLDPE/ULDPE	10		80		10	15–30
ULDPE/LLDPE/m-LLDPE/LLDPE/ULDPE	10	25	30	25	10	15–30
One-side cling film						
m-LLDPE/LLDPE/LMDPE	10		80		10	15–30
EMA/LLDPE/PP	10		80		10	15–30
POP/LLDPE/PP	10		80		10	15–30
ULDPE/LLDPE/LLDPE/ e-LLDPE/PP	10	20	30	30	10	10–30

from regular shrink film by its superior clarity and appearance, as well as increased shrinkage properties and higher stiffness. Goods are packaged by wrapping the film loosely around the goods, sealing the film to make a completely enclosed bag and then shrinking the film in a shrink tunnel or oven. Small holes may be poked in the film before wrapping to allow air to escape while the film is shrinking. As in industrial shrink film, heat causes the polymer molecules to relax, causing the film to return to its original unoriented size and shrink tightly around the packaged goods. Since the polymer molecules in oriented shrink film are much more highly oriented, greater shrinkage may be obtained. Boxed software and stationery products are often wrapped with high clarity shrink film. Ice cream cartons and other food products are also wrapped in high clarity shrink film. Optical properties, seal properties, shrinkage and holding force are key requirements for oriented shrink film. These structures are normally biaxially oriented films of LLDPE and PP (Table 15-26).

Summary

It is critical for the flexible packaging film producer to understand their market. Even within a given market segment there are usually several film structures that are used. The film producer must evaluate the alternative film structures to determine the best fit for the market identified and for his production capabilities. Market trends should be analyzed to determine strategy. The market studies will dictate which coextrusion/lamination equipment design will be optimum. Economic evaluation

Table 15-23 Heavy duty bags

Structure	Layers (%)			Gauge (μm)
LLDPE/EPE/LLDPE+LDPE	20	60	20	100–200
EPE/PP/EPE	20	60	20	100–200

Table 15-24 Trash bag coextrusion structures

Structure	Layers (%)			Gauge (μm)
LLDPE/LLDPE	50		50	15–70
LLDPE/RECYCLE/LLDPE	33	34	33	15–70
LLDPE/HMW-HDPE/LLDPE	10	80	10	15–25

Table 15-25 Grocery bags

Structure	Layers (%)			Gauge (μm)
LLDPE/HMW-HDPE/LLDPE	10	80	10	12–20

Table 15-26 High clarity shrink film

Structure	Layers (%)			Gauge (μm)
PP/LLDPE/PP	25	50	25	15-25

of each market should include the cost incurred in scrap recycle (or disposal). The average production run size and the polymer changes will determine the off-spec film produced. A new consideration for today's market place may also include some thoughts into after-use disposal of the multilayer film. The design and testing of multilayer film, particularly in the barrier films, will require more manpower and overhead costs than typical monolayer film.

The markets identified for multilayer flexible packaging should value higher performance properties and high value films. In addition to performance properties, some markets may have other barriers to entry such as qualification cost, experience in the market or lack of business relationships. These considerations must be evaluated. The multilayer coextrusion line design requires knowledge of the specific structures and polymers to be produced. It is recommended that mutual discussions with the equipment supplier and polymer suppliers be made to insure that proper consideration is given to all critical aspects.

New applications continue to be developed for multilayer films and film structures continue to evolve as new market drivers come into play. The structures highlighted in this chapter are intended only as examples and may not represent where packaging is headed in the future. For example, sustainability has recently garnered attention in the marketplace. For packaging, this may mean a number of things, such as down gauging to reduce the carbon footprint or the use of new bio-sourced or biodegradable polymers. No matter what the market driver, the principles developed in this chapter remain true. Combining high performance polymers and low cost polymers will expand market opportunities. Understanding how to combine easily the properties of new polymers and knowledge of the market needs and trends will lead to development of more coextrusion applications.

Table 15-27 gives a list of conversion factors.

Table 15-27 Conversion factors.

Property	To convert from:	To:	Multiply by:
Density	g/cc	lb/ft^3	62.43
Pressure	lb/in^2	MPa	0.00689
Output	lb/h	kg/h	0.45359
Output	lb/h	g/s	0.125997
Length	inch	mm	25.4
Specific output	lb/h/inch-c	kg/h/mm-c	0.017858
Specific output	lb/h/inch-c	kg/h/mm-d	0.055245
Viscosity	poise	MPa-s	0.1
Viscosity	poise	lb-s/in^2	68947
Stress	lb/in^2	KPa	6.8947
Stress	lb/in^2	dynes/cm^2	68947
MVTR	g*mil/100 in^2/day	g*mm/m^2/day	0.394
Permeability	cc*mil/100 in^2/day/atm	cc*mm/mm^2/sec/atm	4.56E-06
Permeability	cc*mil/in^2/day/atm	cc*mil/m^2/day/atm	15.5
Weight	lb	kg	0.4536
Peel or seal strength	lb/in	g/in	454
Peel or seal strength	g/in	N/15mm	0.0059

MVTR: moisture vapor transmission rate

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Chapter 16

16

Multilayer oriented films

Jürgen Breil

Introduction

Chapter 11 discussed orientation technology and showed examples of the most widespread film types (biaxially oriented polypropylene (BOPP), biaxially oriented polyethylene terephthalate (BOPET), biaxially oriented polyamide (BOPA), biaxially oriented polystyrene (BOPS) and others). Emphasis was given in particular to the enhancement of the mechanical, optical and permeation characteristics by means of selective orientation of molecule chains. While monolayer biaxial stretching is most suitable for certain applications, many applications utilize multilayer film structures. The reason is that, as a rule, diverse specific film requirements are necessary and a single layer film cannot fulfil those requirements. They can only be met with the different combinations possible in a multilayer structure. In a multilayer film, the benefits of different resins are applied in order to attain the required mechanical properties as well as the sliding, seal and barrier properties. Fig. 16-1 shows a five-layer film structure. Besides meeting the technical requirements, multilayer films provide economic benefits as either recycled or lower-priced raw materials are incorporated in the main layers.

The surface layers essentially serve to define:

- the sliding characteristics – friction value, surface roughness
- sealing properties
- treatment or surface energy for printing and coating adhesion strength
- hot tack
- antistatic activity
- metallizing properties
- optical properties (haze, gloss).
- whiteness
- stiffness
- barrier properties.

The application of high barrier layers (e.g. ethylene vinyl alcohol (EVOH)) usually requires a tie layer/bonding agent to the base layers, thus resulting in five- or seven-layer structures.

In principle, multilayer configurations can be generated in-line or off-line. In-line processes shall be further explained in this chapter; off-line processes are required as converting steps and therefore shall not be elaborated here.

Technology for multilayer oriented films

The in-line process involves three different methods:

- in-line coating
- in-line lamination
- coextrusion.

Thereby, the in-line coating-process involves either liquid coating or extrusion coating. During the latter process, an extruder has an extrusion coating device located either in front of the machine direction orienter or in front of the transverse direction orienter so that a melt film is applied to the already prior hardened/reinforced prefilm/base

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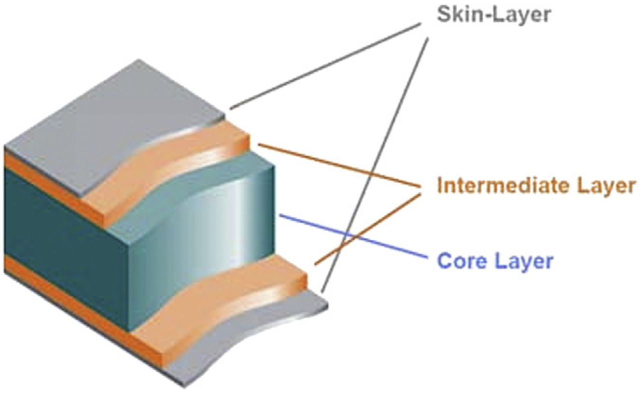


Fig. 16-1 A five-layer film structure.

film (Fig. 16-2). However, in view of the fact that this process is rather complex, it is very rarely used. The same applies for in-line lamination, where a second film is laminated prior to stretching. The in-line coating process with liquid coating is, however, widespread. Mainly aqueous solutions are applied with gravure or spray coating on the machine direction oriented film before the transverse direction orienter, thus, the required functional layers are generated on the surface. Biaxially oriented polypropylene and BOPET films can be coated with silicone coatings as release layers. Furthermore, for BOPET films, this process can provide a thin chemical treatment which improves the adhesion properties of printing inks, glue laminates and metallizing layers.

The coextrusion process represents by far the most widespread method for producing multilayer oriented films, as this combines all the benefits in terms of the largest flexibility for layer combination and maximum cost effectiveness/operating efficiency. Fig. 16-3 shows a typical extruder configuration for a five-layer BOPP film production line. The main extruder has a twin-screw additive feeder plus a melt pump and melt filter. This particular configuration has two single screw and two twin-screw coextruders. The setup can also utilize melt pumps to provide accurate flow of the thin coextruded layers. Twin-screw extruders ensure that the additives, recycling material and edge trim are well homogenized. Moreover, the specific energy consumption is reduced, a better degasification is achieved and, due to the self-purification, a shorter product switchover time is ensured. In the light of these advantages, over the last 10 years, many film stretching lines have twin-screw extruders. For BOPET lines, twin-screw extruders, both as main and coextruder, remove the need for complex resin drying.

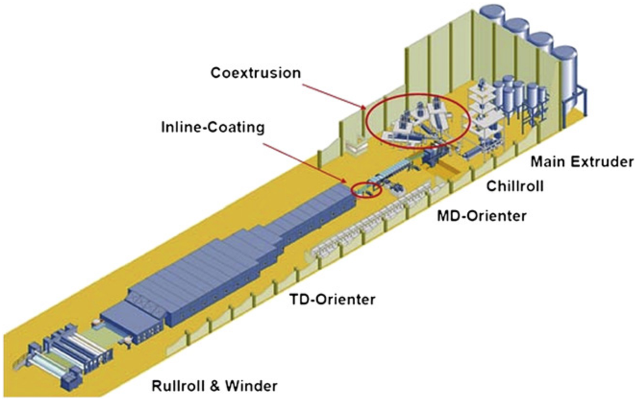


Fig. 16-2 Multilayer structures in Biaxially Orienting Lines.

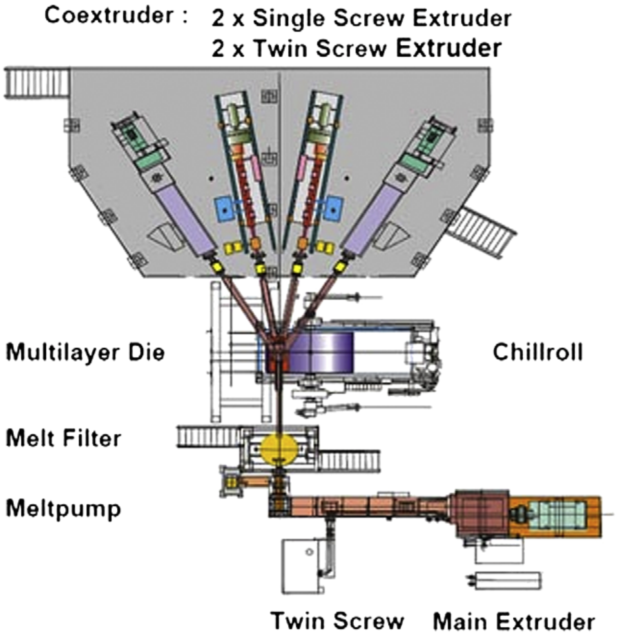


Fig. 16-3 A five-layer extruder configuration.

The melt flow from the main and coextruders is merged in multichannel dies or laminar flow adapters. Focus is placed on the adapter system flexibility. The concern is how many single layer combinations there are in the adapter system. Fig. 16-4a and b show the flow pattern for a combining plug with an adjustable vane adaptor and for a combining plug with a laminar flow adaptor.

Multichannel dies represent the most common alternative as one can attain a precisely-defined layer distribution over the working width. Single melt flows are merged via coat hanger distribution channels. These channels are specially designed for the resin viscosity and the desired layer width in the extrusion die. Fig. 16-5 shows a cross-section of a seven-layer multichannel die in a ABCDCBA configuration. The design criteria are for the film edge trim areas not to have coextrusion layers. This provides an advantage for in-line edge trim recycling, as is commonly practiced with BOPP.

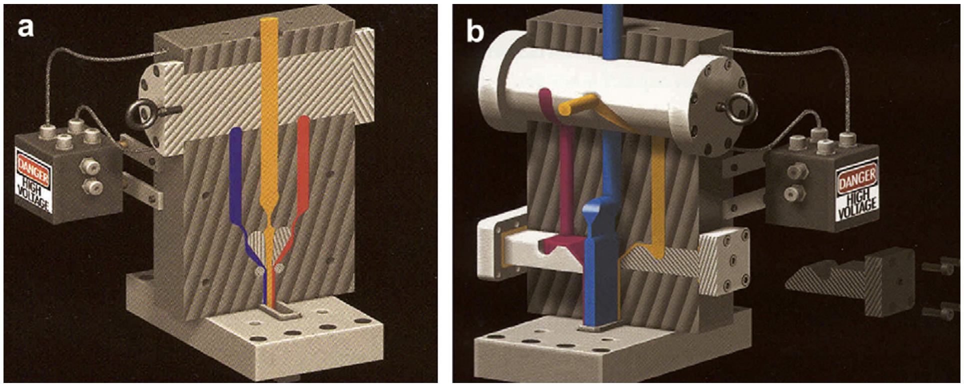


Fig. 16-4 (a) Combining plug with adjustable vane adapter; (b) combining plug with laminar adapter.

Each polymer that can be oriented has different process parameters. The machine and transverse direction stretch ratios and temperatures have to be carefully selected and adjusted so the utilizable process windows do not overlap.

Structures

Just as for non-oriented film types, such as cast film and blown film, coextrusion technology is also applied for oriented films, thus yielding a multitude of structures up to seven layers and therefore enhancing the product properties.

Some BOPP film examples and the main applications will be presented along with the beneficial features of multilayer technology.

In the 1970s, three-layer coextrusion technology was adopted for BOPP films to produce heat sealable film for the packaging industry. Polypropylene copolymers and PP terpolymers were applied to the outer layers with thicknesses ranging between 0.5 and 3 µm. These lower melting polymers provided lower heat sealing temperatures in a range that allowed the main PP homopolymer structure to remain geometrically stable. When these heat sealing polymers were developed, it was necessary not only to consider the seal ignition temperature but also provide adequate hot tack properties, in order to meet the demands made on high-speed packaging lines. Normally, antiblock and slip additives are applied to the outer layers, in order to attain the required sliding properties. Furthermore, special masterbatches are available which provide either glossy or matte surfaces. In order to attain different skin layers, the line configuration is designed to have one main extruder and two coextruders.

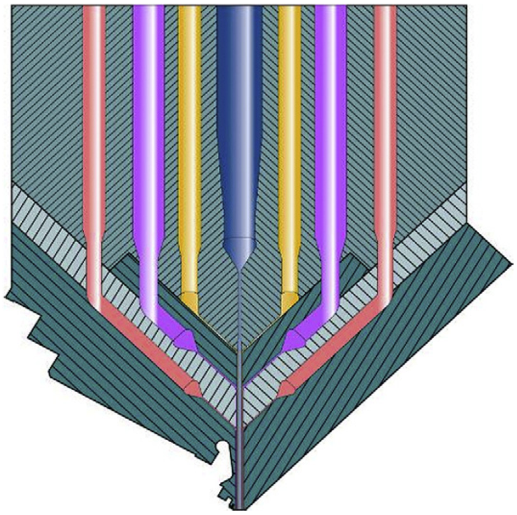


Fig. 16-5 Seven-layer coextrusion die.

Five-layer film structures allow for more flexibility by implementing intermediate layers between the main layers and skin layers (Fig. 16-6). The following benefits can be obtained:

- use special masterbatches for the main intermediate and skin layers to change optical properties
  - ○ a high opacity film, e.g. white opaque films
  - ○ provide high gloss or matte surfaces
- more cost-effective structures without impairing the optical film quality by using higher recycled material and reducing the additives
- increase the seal properties by adding low sealing copolymer onto a comparatively thick PP copolymer layer as an intermediate layer.

Fig. 16-7 shows the structure, advantages, applications and seal strength versus sealing jaw temperature for a five-layer low seal initiation temperature (SIT) BOPP film. A very high seal strength and sealed seam rigidity is achieved with this structure. This characteristic is vitally important for many packaging applications, since both the film and the sealed seam quality provide the

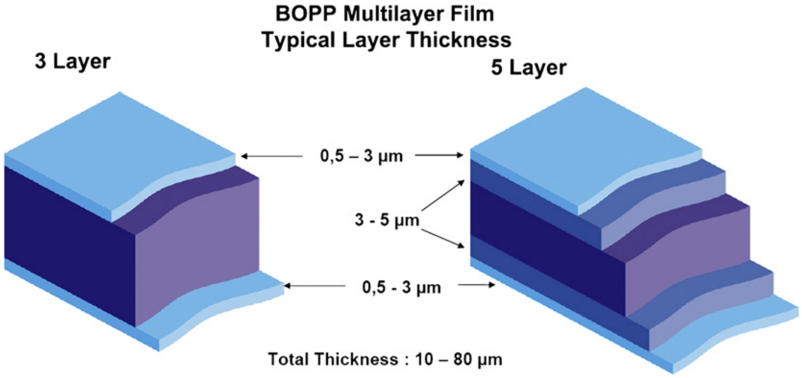


Fig. 16-6 Typical layer thickness of BOPP multilayer film.

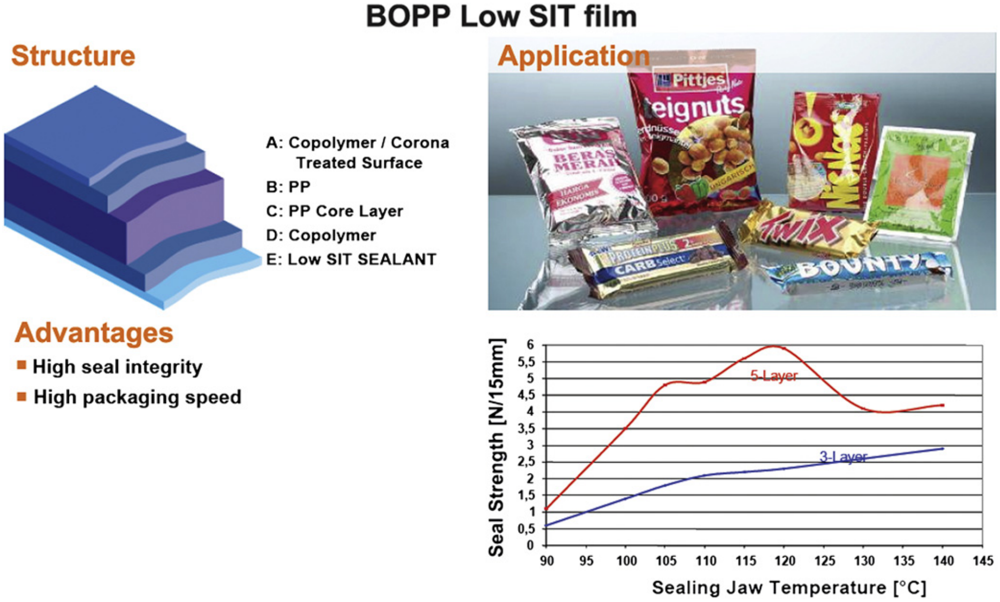


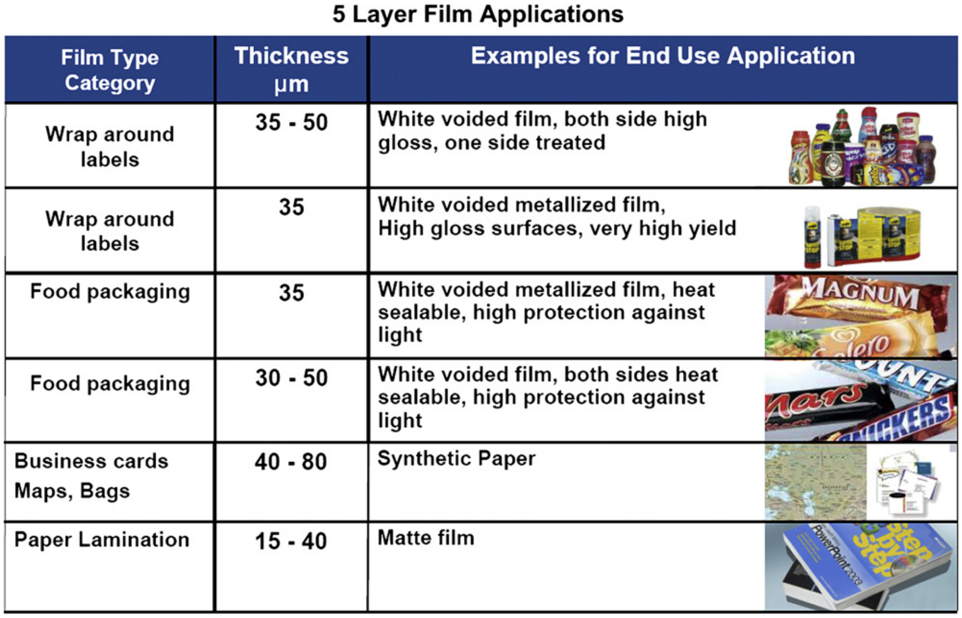
Fig. 16-7 Five-layer low seal initiation temperature (SIT) BOPP film structure advantages, applications and seal strength.

necessary product protection. Five-layer technology provides the design flexibility to produce films with excellent properties for various applications (Fig. 16-8).

Fig. 16-9 details a special film produced with a five-layer structure, an ultra-high barrier (UHB) metallized film. In this particular product design, the first surface is a polymer with a high surface energy (PA, EVOH and others). This polymer requires a tie or adhesive layer to bond to the PP main layer. The fourth D layer is also PP and is covered with a heat sealable copolymer skin. The metallized properties of this structure, compared to PP homopolymer or PP copolymer surfaces, show a much better adhesion strength and metallized surface uniformity. This results in 50 times better oxygen barrier values than obtained by standard metallized BOPP films.

The ultra-high barrier metallized film example shows that, when suitable barrier materials are combined, a considerable increase in the barrier properties is possible. Metallized film also provides a light barrier which means that the product inside the package is not visible. There is a demand for transparent barrier films which is being satisfied by clear barrier coatings, as described in Chapter 14, and seven-layer structures.

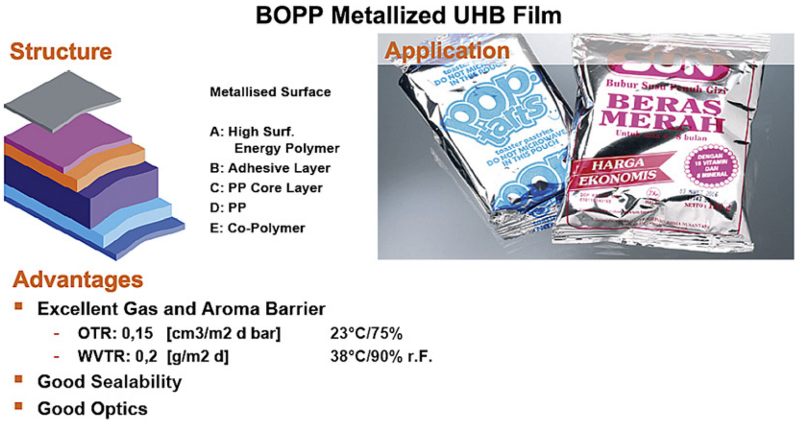
The seven-layer technology is particularly suitable for such films, since it is possible to attain the required barrier values, even without metallizing. In this case, preferentially EVOH as barrier material is applied in the middle of the main layer imbedded between tie layers. Furthermore, such symmetrical film layer configuration has the advantage that the occurrence of curling becomes less likely. A typical seven-layer configuration is shown in Fig. 16-10. As a rule, such seven-layer structures with the application of various polymers – such as, for example, PP and EVOH – can be manufactured not only with



5 Layer Film Applications

Film Type Category	Thickness µm	Examples for End Use Application
Wrap around labels	35 - 50	White voided film, both side high gloss, one side treated
Wrap around labels	35	White voided metallized film, High gloss surfaces, very high yield
Food packaging	35	White voided metallized film, heat sealable, high protection against light
Food packaging	30 - 50	White voided film, both sides heat sealable, high protection against light
Business cards Maps, Bags	40 - 80	Synthetic Paper
Paper Lamination	15 - 40	Matte film

Fig. 16-8 Five-layer film applications.



BOPP Metallized UHB Film

Structure

Metallised Surface

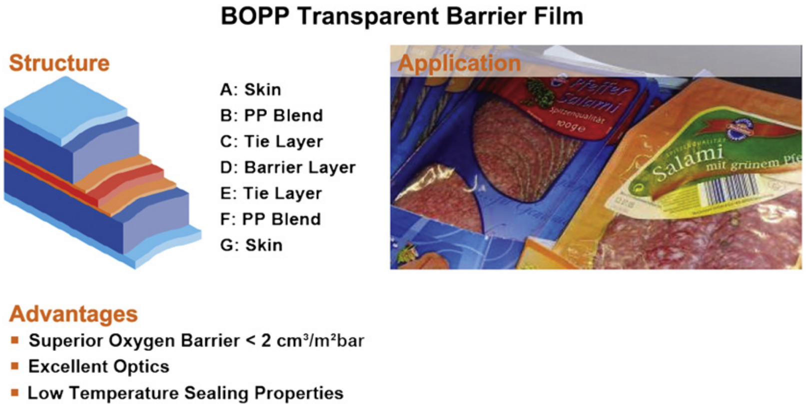
A: High Surf. Energy Polymer
B: Adhesive Layer
C: PP Core Layer
D: PP
E: Co-Polymer

Application

Advantages

- Excellent Gas and Aroma Barrier
  - OTR: 0,15 [cm3/m2 d bar] 23°C/75%
  - WVTR: 0,2 [g/m2 d] 38°C/90% r.F.
- Good Sealability
- Good Optics

Fig. 16-9 Five-layer metallized UHB BOPP film structure and advantages.



BOPP Transparent Barrier Film

Structure

A: Skin
B: PP Blend
C: Tie Layer
D: Barrier Layer
E: Tie Layer
F: PP Blend
G: Skin

Application

Advantages

- Superior Oxygen Barrier < 2 cm^3/m^2bar
- Excellent Optics
- Low Temperature Sealing Properties

Fig. 16-10 A typical seven-layer configuration.

sequential but also with simultaneous orientation technology. However, upon selection of the types of raw material to be used, one has to bear in mind the divergence of the various process requirements for the particular stretching process. The types of available EVOH resin have a distinct correlation the ethylene content with the stretchability on the one hand and, on the other hand, with the barrier values. Generally, it can be said that a higher ethylene proportion implicates a less complicated orientation process, permits higher stretching ratios and, furthermore, the implementation of the sequential orientation process. For the simultaneous orientation process, however, it is possible to stretch all types of EVOH with an ethylene content of 24–47%. Although the barrier properties of the EVOH types are increased, in view of the orientation process, the basic coherence remains that EVOH with a high ethylene content has considerably poorer barrier properties. This is illustrated in Fig. 16-11 showing an evaluation on the oxygen barrier with the use of various EVOH types and orientation with area-stretching ratio of almost 50. It can therefore be concluded that the use of EVOH types with an ethylene content of not more than 33% is particularly beneficial, since a good oxygen barrier of less than 2 $cm^3/m^2/d/bar$ can be attained with thin layers of 2 μm thickness. This value can easily compete with other high barrier film types, which are off-line-coated.

The examples of multilayer BOPP films demonstrate the wide variability of structures by implementing the coextrusion technology. This applies in general also to the other film types such as BOPET and BOPA.

There is a strong trend to enhance the barrier properties further with a minimum of packaging material, so there is no doubt that coextruded oriented films will continue with stable growth rates.

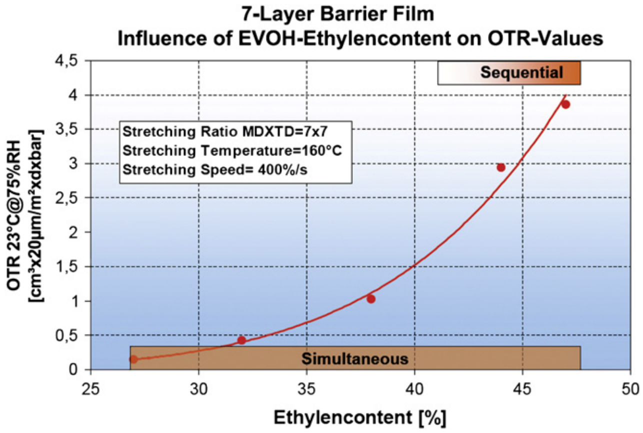


Fig. 16-11 Evaluation of the oxygen barrier with the use of various EVOH types.

Trends for Multi-Layer Oriented Films

In 2008, the worldwide production capacity of biaxially stretched films was over 12 million tons. Approximately 66 percent was BOPP and 25 percent BOPET.

As the packaging sector is the majority application for these films, one can analyze flexible film trends within the packaging industry and draw conclusions for future Research and Development challenges.

These trends can be split into the following categories:

- Cost Efficiency
- Consumer Requirement
- Sustainability

Cost Efficiency

Cost Efficiency consists of:

- Cost per package
- Packaging speed.

The prevailing global cost pressure necessitates that packaging experts not only focus their attention on utmost efficiency but also combine minimum material consumption with maximum packaging functionality.

In many cases, biaxially oriented films, especially multi-layer films, provide solutions such as downgaging to these challenges.

Also, high mechanical properties and excellent friction characteristics are required to attain high packaging speeds.

Many final packaging films are multi-layer laminates produced by combining two or more films. This lamination step strongly impacts the cost. Consequently, intense efforts are being made to combine as many property requirements as possible in one coextruded oriented film. Such endeavors are underway, in particular, combining mechanical properties with barrier, sealing and surface properties.

This trend will continue and the outcome will be that film stretching lines will become increasingly more complex and diverse. This will reduce, to a certain extent, the cost-intensive subsequent film converting.

Consumer Requirements

Consumer Requirements consist of:

- Convenience
- Product Identification
- Shelf life

Wrapping material has to satisfy the consumers' basic needs inasmuch as they should be easy to open and if possible, reclosable. Consequently, there is a demand for multi-layer composites with low tear resistance and reclosability. Consumers' requirements to see the package content and have long shelf life necessitate transparent barrier films. These film characteristics are ideally attained by coextruded oriented films with corresponding barrier layers. This applies in particular to transparent lidding film for products such as sausage and cheese in deep drawn trays that ensure the required shelf life.

Sustainability

Sustainability consists of:

- Energy consumption
- Raw material consumption
- Renewable sourced materials
- CO_2 footprints

The sustainability conversation has in recent years increasingly influenced the packaging industry and has been driven by large global retailers. In the course of such discussions, all aspects of sustainability have been analyzed and future consequences will increasingly be that energy consumption will be displayed and comparisons drawn. This in turn will result in that complex processes that comprise various production steps will be replaced by single step production processes that provide many end properties, such as coextruded orientation film. This will also support the trend towards replacing aluminum foil, since producing aluminum foil containing structures is more energy intensive compared to alternative barrier plastic films.

A further trend is the increased renewable sourced raw materials use, such as PLA. Development entails that the property characteristics necessary for wrappings can also be attained with this raw material. In many cases this is only possible by coextrusion and orientation.

It is to be expected that sustainability will gain importance, as relevant legal requirements are passed, be they on marking or on using certain material.

All these trends will definitely have a positive influence on extended use of coextruded oriented films in future.

Appendix

Writing guide for packaging films and other multilayer structures

Scott B. Marks

E.I. DuPont de Nemours & Company

A wide variety of multilayer structures are used in the flexible and rigid packaging industry, which are put together by an assortment of techniques including: extrusion lamination, adhesive lamination, extrusion coating, as well as coextrusion blown film, cast film, sheet and blow molding.

Currently, there does not exist a standard method for communicating structures in a written format between companies (and for the most part, even within companies). The guidelines described below are derived from formats used within DuPont. While no one method is best, we have found this guide to be useful in that it presents a systematic way to not only communicate the components of the structure but also the technology used to put it together. By following the guidelines, one can better understand whether, for example, a structure is manufactured using coextrusion or by tandem extrusion coating. Such concise writing can improve communication. Thus we offer these guidelines to the industry in the hope that they will increase communication effectiveness and understanding between all persons in our business.

The format guidelines allow for use in hand-written communication or for typing using a keyboard, which is especially important for the electronic communication methods in use today.

One commonly misunderstood character is the dash or minus sign. There are actually three different dashes available in most word processors. They are:

- The minus sign -
- An En dash – (a medium length dash) Ctrl+Num -
- An Em dash — (a long dash) Alt+Ctrl+Num -

In Microsoft Word they are shown on the Special Character tab of the symbol window.

In this guide the dash is called out for one symbol and is meant to have a space before and after the dash to make the code more legible. One can also use the En dash to replace the dash with the before and after spaces.

Note: The information contained herein is only a guide. The structures listed herein are a mixture of actual and potential applications, but users should not rely upon it absolutely for specific applications since performance properties will vary with processing and specific end-use conditions. It is given and accepted at user's risk and confirmation of its validity and suitability in particular cases should be obtained independently. We make no guarantees of results and assume no obligation or liability in connection with its advice. This publication is not to be taken as a license to operate under, or recommendation to infringe, any patents.

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Table A-1 Key definitions

Primer	A bonding agent that is applied in a liquid form to a solid surface. It is intended to promote the adhesion of another liquid or molten material that will subsequently be applied on top of the primer. Typically it is dried, prior to having the subsequent material applied to it. **(This is usually associated with extrusion coating.)** In some parts of the world these are referred to as anchor coatings (‘**AC**’). Adhesion generally increases after curing time.
Adhesive	A bonding agent that is applied in a liquid or paste form to one or more solid surfaces. It is intended to promote adhesion of the solid surfaces to one another. The adhesive is typically dried, and then the solid surfaces are brought together with heat and/or pressure to active the adhesive. **(This usually is associated with water based, solvent based, or solventless dry lamination.)** Adhesion generally increases after curing time. An adhesive can be abbreviated as “**ADH**”, or **“adh”.**

Table A-2 Key abbreviations

VM	A vacuum metallization process for applying a thin metal layer to a solid surface, such as OPET and OPP films. This can also be applied to paper, printed surfaces, and other materials. (**VM** can also be written, “**met**”.) The metal is usually aluminum, but can also be other metals such as copper, gold, tin, etc. (If it is not aluminum, please specify in your communication.)
VM	Vacuum metallized
met.	Metallized
SiOx	A silicon oxide coating that is typically applied to a film such as OPET. This usually transparent coating is applied in a vacuum deposition process.
O.L.	An overlacquer that is applied over ink to add scratch protection and gloss.
W.O.	White Opaque. This is a white pigmented material with higher opacity.
Tie	Generically indicates a coextrudable adhesive resin. This is used in structure notations when the resin brand or grade is unknown. If the tie material base resin is known then please indicate: e.g. LLDPE tie, EVA tie, PP tie, etc. If the brand is known, please indicate, such as DuPont Bynel®, or Mitsui Admer®. If the grade number is known, please indicate.
MB	A “masterbatch” or concentrate. This could be for pigments such as TiO_2 (white MB) or for slip and antiblock concentrates. e.g. white MB, slip MB, etc.

Table A-3 Key symbols

/	The boundary between a solid interface and a liquid or molten material being applied to it. For example: **OPET /ink/ primer/33μ EMAA** is an oriented polyester film, printed with one or more inks, and dried. A primer is applied to the printed surface, dried, then extrusion coated with 33 microns (μ) of an EMAA resin.
( )	A set of parentheses. These indicate that the materials within are being coextruded. Look for a dash “ **-** ” sign with spaces or and En dash “–” between materials.
“ **-** ”	Indicates the boundary between two molten materials being coextruded together. They should be enclosed in a set of parentheses, “**( )**”. Use a space on each side of the dash or an En dash. For example: **(1 mil LDPE–2 mil EAA)** is a two layer coextruded film of low density polyethylene and EAA.
[ ]	A set of straight sided brackets. These indicate that the materials within are being blended. If known, percentages by **weight ratio** for the materials being blended should be indicated. Look for a plus sign between the materials.
“ + ”	Indicates two materials being blended together. They should be enclosed in a set of straight-sided brackets, “**[ ]**”. Use a space on each side the plus. For example: **([75% Nylon 6 + 25% Amorphous PA] - tie - LLDPE)** is a blend of Nylon 6 and Amorphous Nylon, in the **weight ratios** indicated, is the outer layer of a three layer coextrusion. The middle layer is an unknown coextrudable adhesive resin, and the inner layer is a LLDPE.

Table A-3 Key symbols—Cont'd

//	Indicates the boundary between two solid surfaces, one is a film, and the other is a film that is often coated with an adhesive. (Typical for adhesive lamination.) For example: **OPET/ adhesive// 25μ ionomer film** an oriented polyester film that has an adhesive applied to it and dried. An ionomer film is then combined, typically with a heated nip roll to activate the adhesive.
"**//TL or BL//**"	Indicates the boundary between two warm solid layers that are joined together by only heat and pressure. Examples would be: **"//TL//"** Thermally laminated films. Two films (or one film and one foil), combined typically between rubber rolls, following preheating of one or both films. **"//BL//"** Blown films that are intentionally blocked in the collapsing nip. A "**B**locked **L**amination". In addition, surround the structure with braces or curly brackets, "**{ }**", to indicate a combined web. See examples in the following pages.
< or **>**	Indicates direction to which a surface treatment has been applied, such as; flame, corona, ozone, plasma. For Example: **Paper < flame / LDPE / foil / LDPE**

Table A-4 Materials (generic representations) for webs / films / substrates

OPET or BOPET	Biaxially oriented polyester film. (Occasionally called BOPET.) Using "OPET" will prevent confusion with extruded PET.
VM-OPET	Vacuum metallized OPET film. Metallization on the left.
OPET-VM	Vacuum metallized OPET film. Metallization on the right.
OPET-SiOx	OPET film with silicon oxide on the right side of the film.
SiOx-OPET	OPET film with silicon oxide on the left side of the film.
OPET-PVdC	Oriented polyester film with a PVdC coating on the right.
PVdC-OPET	Oriented polyester film with a PVdC coating on the left.
PVdC-OPET-PVdC	Oriented polyester film, two side coated with PVdC.
OPP or BOPP	Biaxially oriented polypropylene film.
VM-OPP	Oriented polypropylene film, with metallization on the left side
OPP-VM	Oriented polypropylene film, with metallization on the right side
OPP-A	Oriented polypropylene film, with an acrylic coating on the right side
A-OPP	Oriented polypropylene film, with an acrylic coating on the left side.
CPP	Cast polypropylene film
VM-CPP	Cast polypropylene film with metallization on the left side.
CPP-VM	Cast polypropylene film with metallization on the right side.
C-Nylon	Cast nylon film, also written as **Cast PA,** for cast polyamide film.
O-Nylon	Uniaxially oriented nylon film
BONy	Biaxially oriented nylon film
BOPA	Biaxially oriented polyamide (nylon) film
K-Nylon	Biaxially oriented nylon film, with PVdC on one side
BONy-PVdC	"K-Nylon", but written to specify PVdC on the right side.
Alu	Aluminum (Aluminium), can also be written as "**AL**".

(*Continued*)

Table A-4 Materials (generic representations) for webs / films / substrates—Cont'd

Foil	Usually thin aluminum. Can be other metals, if not aluminum, specify. Examples: tin foil, gold foil, (In Europe the word "foil" is used to indicate any thin film, and can cause communication issues globally.)
Cello	Plain, uncoated cellophane
K-Cello	Two-side PVdC coated cellophane
NC-Cello	Two-side nitrocellulose coated cellophane
Paper	Lightweight paper based webs. Please specify when possible: Kraft, Bleached Kraft, SBS, clay coated, etc.
Board	Heavy weight paper based webs. Please specify when possible.
Nonwoven	Nonwoven webs. If the brand is unknown, use nonwoven HDPE, nonwoven PP, and nonwoven PET. Use brand name if known; such as DuPont Tyvek®, BBA Group Reemay®, BBA Group Typar®
Woven Fabric	Fabric weaves. e.g. "tight weave"; woven PP, woven HDPE, woven PP
Scrim	Woven mesh type fabrics with an "open weave"; e.g. Scrim PP, Scrim PET, Scrim HDPE

Table A-5 Thickness or gauge representations

#	"pounds per ream" (a ream being 3000 square feet)
Mils	English measurement of 0.001 or 1/1000 of an inch.
Inches	English unit for thick layers, such as in bottles and sheet applications.
μ	Metric measurement (micron), 0.001 of a millimeter.
mm	Millimeters, metric unit used for thick layers, such as in bottle and sheet applications.
gsm	grams per square meter
pt.	"point", which is a unit of thickness for paperboard. (1 pt. approximately = 1 mil)
ga	"gauge" of a film in some systems. e.g. 100ga = 1 mil = 25.4μ: 48 ga = 12μ = 0.5 mils

Table A-6 Adhesives and primers

PUR	Polyurethane; **PUR adhesive** or **PUR primer**; can be solvent or water based.
PEI	Polyethylene-imine; **PEI primer**, usually a water based primer
EAA	Ethylene acrylic acid; **EAA primer** (water based)
EAC	Ethylene acrylate; **EAC primer** (water based) (there are several others such as organic titanates, etc.)

Table A-7 Surface treatments

Corona	Electron discharge excitement of atmospheric air over the film surface.
Plasma	Electron discharge excitement of a gas other than standard air over the film surface. Examples would include: nitrogen, argon, helium, neon, etc. (as well as gas mixtures.)
Flame	Surface treatment with burning gases. The gas mixture could be either an oxidizing flame, reducing flame, or stoichiometric flame.
Ozone	Molten web oxidation by exposing the polymer to a dry ozone flow created off-line and pumped to the molten web area, through a tube with small outlet holes along its length. Occasionally seen on extrusion coating lines.

Table A-8 Extrudable resins (generic names for when brand / grade is unknown.)

HDPE	High density polyethylene
HMW-HDPE	High molecular weight HDPE
MDPE	Medium density polyethylene
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
VLDPE	Very low density (linear) polyethylene (also- VLLDPE)
ULDPE	Ultra low density polyethylene (also- ULLDPE)
mPE	Metallocene polyethylene, generic.
mLMDPE	Metallocene linear medium density polyethylene
mLLDPE	Metallocene linear low density polyethylene
mVLDPE	Metallocene very low (linear) density polyethylene, (sometimes referred to as a ‘plastomer’).
PP	Polypropylene; (generic indication when minimal information is known).
CoPP	Copolymer polypropylene
HoPP	Homopolymer polypropylene
ACR	Acid copolymer resin, generic name for EAA and EMAA resins
EAA	Ethylene acrylic acid copolymer, such as DuPont Nucrel®, Dow Primacor®, and ExxonMobil Escor®.
EMAA	Ethylene methacrylic acid copolymer, such as DuPont Nucrel®
Ionomer	Ionomer copolymer resins, such as DuPont Surlyn®, and ExxonMobil Iotek®.
Acrylate	Acrylate copolymers, such as DuPont Elvaloy AC®, Arkema Lotryl®, Westlake EMAC®, ExxonMobil Optema®.
EBA	Ethylene butyl acrylate
EEA	Ethylene ethyl acrylate
EMA	Ethylene methyl acrylate
EMMA	Ethylene methyl methacrylate
EiBA	Ethylene iso-butyl acrylate
EnBA	Ethylene normal-butyl acrylate
EVA	Ethylene vinyl acetate; such as; DuPont Elvax®, AT-Plastics Ateva®, Equistar Ultrathene®, ExxonMobil Escorene Ultra®
PS	Polystyrene
EPS	Expanded (or foamed) polystyrene
HIPS	High impact polystyrene
GPPS	General purpose polystyrene
PVC	Polyvinyl chloride
PVdC	Polyvinylidene chloride. Most commonly seen as a coating on a film, but there are also extrudable grades, such as Dow Saran®, and SolVin Ixan®
PA	Polyamide, commonly called **Nylon**

(*Continued*)

Table A-8 Extrudable resins (generic names for when brand / grade is unknown.)—Cont'd

Nylon	Polyamide, when unspecified, quite often is **Nylon 6**
Nylon 6	Polymer from caprolactam (also written "**PA 6**")
Nylon 6,6	Polymer from adipic acid & hexamethylenediamine (also written "PA 6,6" or "PA 6:6" or "PA 66")
Nylon 6/6,6	Copolymer of 6 and 6,6 types of polyamide (also written "**PA 6/6,6**" or **PA 6:66**)
	other nylon polymers: Nylon 11, Nylon 12, Nylon 6/ 12, etc…
Amorphous PA	Amorphous nylon; DuPont Selar PA®, or EMS Grivory®
MXD6	Crystalline nylon; Mitsubishi Nylon-MXD6.
EVOH	Ethylene vinyl alcohol; Kuraray Eval®, Evalca Eval®, Nippon-Gohsei Soarnol®
PAN	**P**olyacrylontrile, sometimes written as 'ACN'
SAN	Styrene acrylonitrile copolymer
AN-MA	Acrylonitrile methyl acrylate copolymer (such as; Innovene, Barex®**)**
ABS	Acrylonitrile butadiene styrene copolymer
LCP	Liquid crystal polymer
COC	Cyclic olefin copolymer, such as TAP Topas®, or Mitsui Apel®
PUR	Polyurethane, extrudable type when seen in a coextrusion for example.
SBC	Styrene butadiene copolymer (such as Chevron Philips K-Resin®)
PET	Extruded polyester. Could be monolayer or in a coextrusion.
PET ext.ctg.	Extrusion coating of polyester
APET	Amorphous polyester
CPET	Crystalline polyester
PETG	Polyester copolymer with glycol
PEN	Polyethylene napthalate
PLA	Polylactic acid
PGA	Polyglycolic acid
PHA	Polyhydroxyalkanote

Table A-9 Terpolymers

EVACO	terpolymer of ethylene, vinyl acetate, and carbon monoxide
EnBACO	terpolymer of ethylene, normal-butyl acrylate, and carbon monoxide
EiBAMAA	terpolymer of ethylene, isobutyl acrylate, and methacrylic acid (*** there are various other terpolymers in the industry…)

Table A-10 Grafted resins

EVA-gMAh	Ethylene vinyl acetate with a graft of maleic anhydride
LLDPE-gMAh	LLDPE with a graft of maleic anhydride (*** there are various other grafted resins in the industry…)

Table A-11 Others

Peel Seal or Easy Peel	Generic name for a peelable sealant resin of unknown brand/grade. If brand is known, please indicate, such as DuPont Appeel®, Mitsui-DuPont CMPS®, Yasuhara Hirodyne®, or Toyo Topco®
H.S. lacquer	Generic name for a 'heat seal lacquer', usually applied by gravure.
Hot Melt	Generic name for a hot melt adhesive applied as a sealant.

Table A-12 Trademarks

AT-Plastics:	Ateva
BBA Group Fiberweb:	Reemay, Typar
Chevron Phillips Chemical:	K-Resin
Curwood Inc, Subsidiary of Bemis Company, Inc.:	EZ Peel
Dow Chemical:	Dowlex, Primacor, Elite, Affinity, Amplify, Saran
DuPont-Teijin Films	Mylar, Melinex
E.I. du Pont de Nemours & Co.	Appeel, Bynel, Conpol, Crystar, Elvaloy, Elvax, Entira, Fusabond, Nucrel, Selar, Surlyn, Trancend, Tyvek, Zytel
EMS Group:	Grivory, Grilon
Equistar Chemical:	Ultrathene, Petrothene, Plexar
ExxonMobil Chemical:	Iotek, Escor, Exact, Exceed, Escorene, Optema, Enable
Innovene:	Barex
Kuraray and Evalca Companies	Eval
Mitsui Chemical:	Apel, Admer
Mitsui-DuPont Chemical:	CMPS
Nippon Gohsei	Soarnol
SolVin (Solvay/BASF JV):	Ixan, Diofan
Topas Advanced Polymers:	Topas
Toyo Chemical:	Topco
Westlake Chemical:	EMAC, EBAC
Yasuhara Chemical:	Hirodyne, Hirotac

Table A-13 Structure examples (Structures should be written from "outside to inside", with regards to the order of layers, starting from the left.)

OPET / ink / adhesive // CPP An adhesive lamination of cast polypropylene film to reverse printed polyester film An unknown adhesive is applied to the printed polyester film surface.
OPET / primer / CoPP An extrusion coating of copolymer polypropylene on to an unprinted polyester film. There is an unknown primer applied to the OPET.
48ga OPET / ink / PEI primer / 28# LDPE A reverse printed 48 gauge OPET film that is primed with a PEI primer, and then extrusion coated with 28 pounds per ream of low density polyethylene.
15μ BONy / ink / PUR adh // 88μ LDPE An adhesive lamination of a LDPE film to a reverse printed biax nylon film. The PUR adhesive is applied to the reverse printed nylon film.
0.5 mils OPET-PVdC / ink / primer / 0.8 mils LDPE / 1.5 mils Peel Seal A 0.5mils OPET film with PVdC coating is reverse printed on the PVdC side. The printed side is then primed and extrusion coated with 0.8 mils LDPE. A 1.5 mils Easy Peel extrusion coating resin is applied onto the LDPE. This is done in either tandem or a two-pass extrusion coating.
12μ OPET / primer / 15μ LDPE / 6μ alu / (11μ EMAA – 25μ Easy Peel) A 12 micron OPET film is primed and extrusion laminated with 15 microns of LDPE to 6 micron aluminum foil. The bare aluminum side is then coextrusion coated with a two-layer coating that is 11 microns of EMAA and 25 microns of Easy Peel resin.
OPET / primer / (LDPE – [LDPE + white MB]- LDPE) / foil / EMAA An OPET film which is primed, and then has foil extrusion laminated to it using a three layer coextrusion, with the center layer containing a white masterbatch. The foil is then extrusion coated on the other side with EMAA.
20μ OPP / ink / adhesive // 7μ alu / 33 gsm EAA A 20 micron OPP film that is reverse printed, then adhesively laminated to 7 micron aluminum foil. The adhesive is applied to the printed surface, not the aluminum. The laminate is then extrusion coated with 33 grams per square meter of EAA.
20μ OPP-PVdC / low temp PUR primer / 35μ EVA PVdC coated OPP extrusion coated with an 18% EVA. A special low activation temperature PUR primer is used to allow for direct extrusion coating of an EVA at 235°C onto a primed film.
BONy / ink / solventless adh // (LLDPE – LDPE – Ionomer) A solventless adhesive lamination of a reverse printed biaxially oriented nylon film to a three layer coextruded film. The adhesive is applied to the printed surface of the nylon film.
(Nylon 6,6 – Tie A – Nylon 6 – Tie B – Ionomer) A five layer coextruded film. You will need to specify if this is made by a cast film or blown film process. In a straight coextrusion, this is helpful to know for physical property issues.
OPP < corona / solvent adhesive // (Nylon 6 – tie – LDPE – Ionomer) An OPP film that is corona treated in-line, then has a solventless adhesive applied to its surface. This film is then combined with a four layer coex film, likely with a typical heated pressure nip.
O.L. / ink / 40# Paper < flame/ 0.7 mils LDPE/ 0.35 mils alu/ 1.8 mils Ionomer A surface printed and overlacquered paper is flame treated, and extrusion laminated using LDPE to aluminum. The other side of the aluminum is then extrusion coated with the Ionomer. You will need to specify if this is done in a two-pass operation on a single station extrusion coating line, or one pass on a tandem extrusion coating line.
O.L./ ink / Paper / EMAA / alu / [Ionomer + Slip MB] A surface printed and overlacquered paper that is extrusion laminated to aluminum with EMAA. The other side of the aluminum is then extrusion coated with a blend of Ionomer and masterbatch.
(PP – tie A – Nylon 6 – EVOH – Nylon 6 – tie B – Ionomer) A seven layer coextruded film. The tie layer resins are not known, but it is known that there are two different grades being used in the one structure. You will need to specify whether it is made by a cast film or blown film process.
(Nylon – tie – Nylon – tie – LDPE – mPE – Ionomer) A seven layer coextruded film. The tie layers are believed to be the same, so are not labeled differently. A mPE is used to adhere the Ionomer to the LDPE. An upgrade would be to specify the mPE grade or density and the Ionomer grade. You will need to specify whether it is made by a cast film or blown film process.

Table A-13 Structure examples (Structures should be written from “outside to inside”, with regards to the order of layers, starting from the left.)—Cont’d

(15μ Nylon 6 – 5μ LLDPE tie – 45μ LLDPE) A three layer coextruded film. As each layer thickness is known, they are specified in the structure. While the tie resin grade is not known, it is known to be based on LLDPE. You will need to specify whether it is a cast film or blown film.
(20μ [Nylon 6 + Amorphous PA] – 4μ tie – 40μ LLDPE) A three layer coex film. The outer layer blend ratio is unknown. The layer thickness for each layer is specified. You will have to specify if this is made by a blown or cast film process.
([80% Nylon 6 + 20% Amorphous PA] – tie – EVOH – tie – LLDPE) A five layer coextruded film. The outer layer is an 80% Nylon 6 plus 20% amorphous nylon blend. You will need to specify if the film is made by a blown or cast process.
OPET / ink /adh // SiOx-OPET / primer / (LDPE – Ionomer) A reverse printed OPET is adhesively laminated to a silicon oxide coated OPET. The adhesive is applied to the printed surface of the outer OPET. Then the plain side of the silicon oxide coated OPET is primed and coextrusion coated with a two-layer LDPE and Ionomer coating.
OPET / ink / primer / met / adhesive // (Nylon - tie - LLDPE) A reverse printed OPET is primed on the ink surface, then metallized. This film is then adhesively laminated to a three-layer coex film. The adhesive is applied to the metallized surface.
OPET / ink / adhesive // OPET-VM / (LDPE – Ionomer) A reverse printed OPET is adhesively laminated to a metallized OPET. The adhesive is applied to the ink surface. The metallized layer is facing to the inside of the package structure, not the outside. The metallized surface is coex-extrusion coated with a two-layer LDPE and Ionomer coating.
OPP / ink / primer / LDPE / primer / VM-CPP A reverse printed OPP that is extrusion laminated using LDPE to a metallized cast polypropylene film. Primers are applied to the printed OPP, and the metallized CPP.
OPP / ink / primer / LDPE / VM-OPET // adhesive / CPP A reverse printed OPP that is extrusion laminated using LDPE to a metallized OPET. This is then adhesively laminated to a cast polypropylene film. The adhesive is applied to the CPP film.
OPET / ink / primer / LDPE / VM-OPET / adhesive // CPP A reverse printed OPET that is extrusion laminated using LDPE to a metallized OPET. This is then adhesively laminated to a cast polypropylene film. The adhesive is applied to the OPET film.
12μ OPET / met / adh // 15μ BONy / adhesive // corona > (20μ LLDPE–10μ LDPE–45μ EVA) An OPET that has been metallized, then adhesively laminated to BONy film. The other side of the nylon film is then adhesively laminated to a coex film which has been in-line corona treated (likely re-treated to burn off slip agents in the film).
OPET / ink / primer / LDPE / met-OPET / LDPE / LLDPE film A reverse printed OPET film that is coated with an unknown primer, and then extrusion laminated to metallized PET film using LDPE. The plain side of the PET film is then extrusion laminated to LLDPE film using LDPE.
20μ OPP / ink / primer / 15μ LDPE / 13μ met-OPET / 12μ LDPE / 12μ Ionomer A reverse printed OPP that is extrusion laminated to a metallized PET film. The plain side of the PET film is extrusion coated with LDPE, and the LDPE is extrusion coated with Ionomer.
(LLDPE – W.O. LLDPE – LDPE) film / EAA / alu / EAA / (LDPE – LLDPE) film An extrusion lamination with EAA of a three layer film to one side of the aluminum. The outer film is white, but the pigment is only in the middle layer. The other side of the aluminum has a two layer film extrusion laminated to it with an EAA.
50μ Blue EAA //TL// alu //TL// 50μ EAA A thermal lamination of blue pigmented EAA film to aluminum on one side. Another film of clear EAA is thermally laminated to the other side of the alu. (A cable shielding type structure.)
Green EAA / 200μ alu / EAA An extrusion coating of green pigmented EAA is applied to one side of the 200μ aluminum. A clear EAA is extrusion coated to the other side of the aluminum. (A cable shielding type structure.)
(LDPE – EAA) //TL// 150μ alu //TL// (EAA – LDPE) 150μ aluminum that has coex films thermally laminated to each side. (A cable shielding type structure.)

(*Continued*)

Table A-13 Structure examples (Structures should be written from “outside to inside”, with regards to the order of layers, starting from the left.)—Cont’d

{ (mLLDPE – LDPE – tie – Nylon – EVOH – Nylon – EVA tie) //BL// (EVA tie – Nylon – EVOH – Nylon – tie – LDPE – mLLDPE) } A thirteen layer structure that is made by intentionally blocking a coex blown film in the main collapsing nip. The film from the die is actually seven layers. In the main nip, the bubble is blocked on purpose. The nip rolls may be heated to help this. The tower height is usually very short so that the film is still quite warm entering the nips. The tie resin at the blocking interface is known to be an EVA based tie resin, but the exact grade is not known.
Cello / ink / primer / LDPE / alu / EMAA Cellophane that is reverse printed, primed, and extrusion laminated to aluminum with LDPE. The other side of the aluminum is then extrusion coated with EMAA.
K-Cello / ink / primer / LDPE / alu / Ionomer A PVdC coated cellophane (two side coated), that is reverse printed, primed, and extrusion laminated to aluminum with LDPE. The other side of the aluminum is then extrusion coated with an ionomer.
O.L. / Ink / 50gsm Paper / LDPE / 7μ Alu / 35μ EAA (made on a tandem extrusion line) Paper that is surface printed and overlacquered. It is extrusion laminated with LDPE to aluminum. The other side of the aluminum is extrusion coated with EAA. This is specified as being processed by tandem extrusion lamination instead of two-pass coating.
LDPE / ink / 18 pt. Board/ LDPE/ alu/ (EAA- LDPE) A surface printed 18 Point Paperboard that is surface extrusion coated with LDPE, and then extrusion laminated with LDPE to aluminum. The other side of the aluminum is then coextrusion coated with a combination of LDPE and EAA.
(850μ HDPE – 55μ HDPE tie – 55μ Nylon 6) A three-layer coextrusion, which by looking at the thickness, likely is a coex blow molded bottle. This layer thickness is often used for barrier bottles, such as for agricultural chemicals, where nylon is often used as the inner layer. Please indicate the application when drafting out structures such as this to prevent confusion, as this could also be a sheeting application.
(725μ HDPE – 12μ regrind – 55μ HDPE tie – 55μ Nylon 6) Similar to above structure for an agchem bottle, except with a layer of regrind material between the outer HDPE and the tie layer.
(225μ PP – PP tie – 35μ EVOH – PP tie – 175μ PP) A coextrusion that by the thickness is likely a sheet material. The structure may seem to indicate that it might be used to thermoform into a cup or tray. A description of the actual application for the structure should be included in any communication.
OPET/ primer/ LDPE/ sealant // TL // leather An oriented polyester film that is primed and extrusion coated with LDPE and then the sealant resin. This structure is then thermally laminated to leather. (The application may be for an emblem or other fabric decoration that requires surface protection.)
Ink/ 30μ alu < flame/ (EMAA – Easy Peel) A surface printed aluminum foil that is in-line flame treated, and then coextrusion coated with a two layer coextrusion. The EMAA would be for high foil adhesion. The ’easy peel’ is a sealant to various cup stock materials.

Table A-14 Sample structures for practice descriptions

K-Nylon < corona/ adhesive // (mLLDPE – 12% EVA – peel seal resin)
BONy-PVdC/ adhesive // (mLLDPE – mLLDPE – EMAA)
BONy-PVdC/ primer/ (LDPE – LDPE – EMAA)
OPET/ ink/ adh/ alu/ adhesive // (LLDPE – LLDPE – EMAA)
PET-VM/ adhesive // BONy/ adhesive // corona > (LLDPE - LDPE - EVA)
OPP/ ink/ adh // met-OPET/ primer/ (LDPE – Ionomer)
OPET-PVdC /ink/ adhesive/ (LDPE – EMAA – Ionomer)
PVdC-OPET-PVdC/ ink/ adhesive/ LLDPE

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