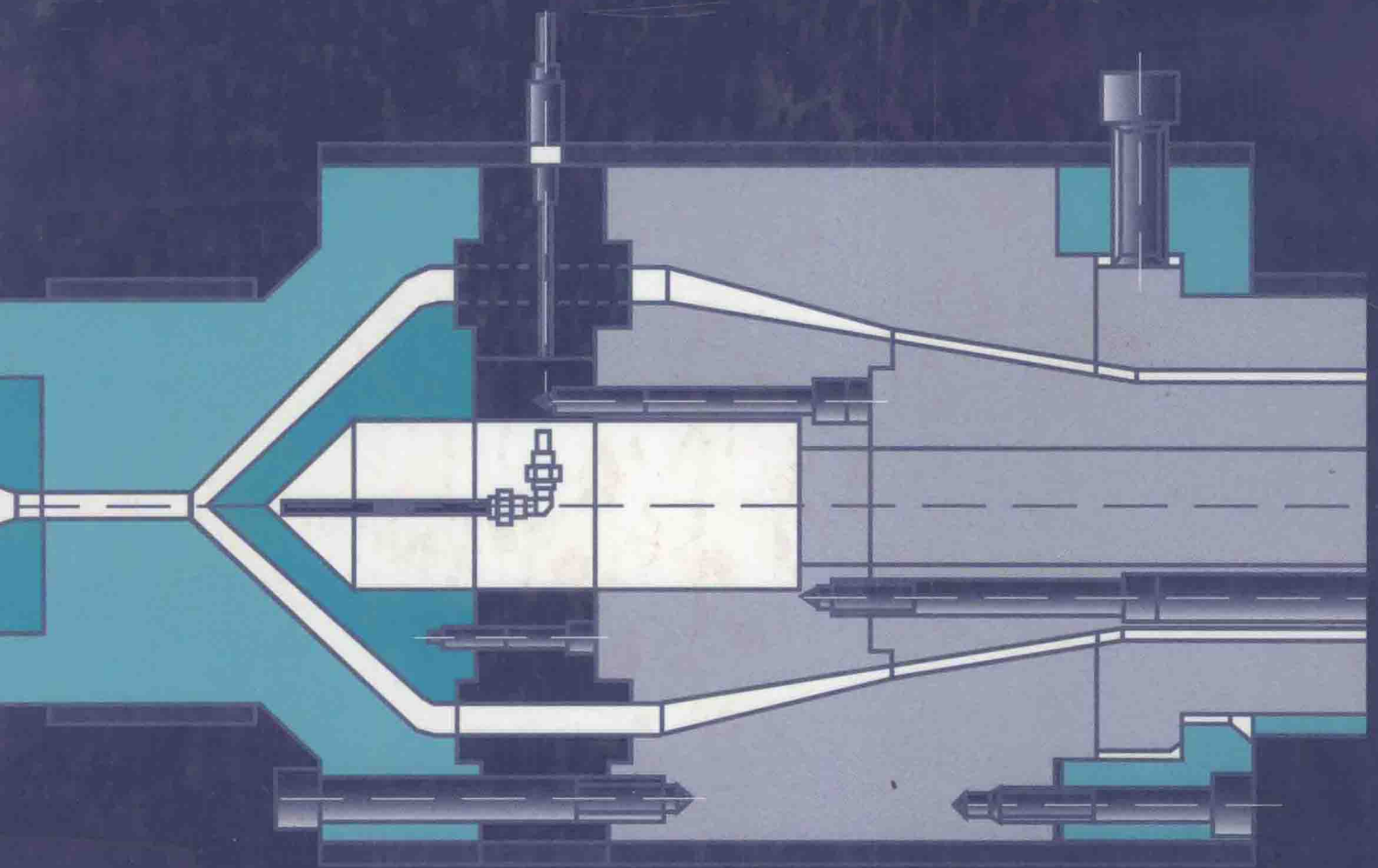


Polymer Processing

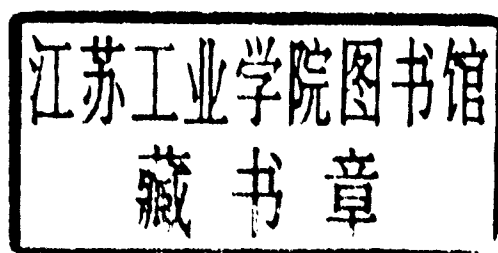
Principles and Design

Donald G. Baird
Dimitris I. Collias



Polymer Processing Principles and Design

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Dimitris I. Collias



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Polymer Processing

Preface

This book is intended to serve as an introduction to the design of processes for thermoplastics. It is intended to meet the needs of senior chemical, mechanical, and materials engineers who have been exposed to fluid mechanics, heat transfer, and mass transfer. With some supplements, the book can also be used by graduate students. For example, by providing more sophisticated coverage of nonlinear constitutive equations and by adding a discussion on finite element methods in Chapters 2 and 3 the book can be used in more advanced courses.

A large number of chemical and mechanical engineers are employed in the polymer industry. They are asked to improve existing processes or to design new ones to provide polymeric materials with a certain level of properties (e.g., mechanical, optical, electrical, or barrier). Although one used to believe that when a given polymer system did not meet the desired requirements a new polymer had to be used, it is becoming more apparent that the properties of the given polymer can be altered by processing or by adding other materials such as other polymers, fillers, glass fibers, or plasticizers. Certainly, a large number of these activities are carried out by trial and error (Edisonian research) approaches. The time to carry out the experiments can be reduced considerably by quantitative design work aimed at estimating the processing conditions that will provide the desired properties. Yet, engineers receive little or no training in the design of polymer processes during their education, partly because they have an inappropriate background in transport phenomena and in the mathematical knowledge required to solve the equations that arise in the design of polymer processes. One aim of this book is to strengthen the background of engineering students in transport phenomena as applied to polymer processing, and the other is to introduce them to numerical simulation.

There are several books available on the processing of polymers with an emphasis on thermoplastics, and one may ask how this book meets the described needs any differently or better than existing books? First of all we cannot revolutionize the area of teaching polymer processing as the principles do not change. What we have done, however, is to make the material more accessible for solving polymer processing design problems. Many times there may be several theories available to use in the modeling of a process. Rather than discuss all the different approaches, we choose what we think is the best theory (but pointing out its limitations and shortcomings) and show how to use it in solving design problems. Another important feature is that we provide the mathematical tools for solving the equations. Other books leave the student with the equations and a description of how they were solved. This does not help someone who has a slightly different set of equations and needs an answer. In this book, as much as possible, we offer the student several methods for getting a solution. Included is also a selection of the subroutines from the International Mathematics and Statistical Libraries (IMSL) (Visual Numerics Inc., Houston, TX) to solve various types of equations that arise in the design of polymer processes. The subroutines have been made relatively "user-friendly," and by following the examples and the descriptions of each subroutine given in Appendix D, solutions are readily available to a number of complex problems. The book does not totally depend on the use of a computer, but certain problems just cannot be solved without resorting to numerical techniques. Rather than dwell on the numerical techniques, we choose to use them in somewhat of a "black box" form. However, sufficient documentation is available in the References if the reader needs to understand the numerical technique. Many will criticize this approach. However, in the time it takes them to voice their objection, the equations will be solved and an answer will be available. With

practice the student will learn when the "black box" has spit out senseless results.

The first five chapters of the book are concerned with the background needed to design polymer processes, and the last five chapters cover the specifics of various types of processes. Chapter 1 contains an overview of polymer processing techniques to help the reader understand the examples and problems used in the next four chapters. Furthermore, a case study presented at the end of Chapter 1 shows how the properties of blown film strongly depend on the processing conditions. Each of the remaining chapters starts with a design problem that provides insights into the material presented in the chapter. In Chapters 2 and 3 we present the basics of non-Newtonian fluid mechanics, which are crucial to the design of polymer processes. In Chapter 4 we introduce the topic of mass transfer as applied to polymeric systems. Finally, in Chapter 5 we discuss the nonisothermal aspects of polymer processing, and the interrelation between processing, structure, and properties is emphasized. These first five chapters contain all the background information the reader needs, including examples illustrating the use of the IMSL subroutines. Mixing is so important to the processing of polymers that we have devoted a full chapter, Chapter 6, to this topic. In the remaining chapters we present the factors associated with the design of various processing methods. We have tried to arrange the subject matter by process similarities. In each chapter we are careful to make it known what aspects of design the readers should be able to execute based on their educational level. In many books on polymer processing it is not clear to the readers just what part of the design they should be able to carry out.

All but the first chapter contain problem sets. The problems are grouped into four classes: *Class A*: These problems can be solved by using equations or graphs given in the chapter and usually involve arithmetic manipulations. *Class B*: These problems require the development of equations and serve to reinforce knowledge acquired about the major subject matter in the chapter. *Class C*: These problems require the use of the computer and are aimed at making direct use of the IMSL subroutines. *Class D*: These problems are design problems and, as such, have a number of solutions. They require the use of all the previous subject matter covered but with an emphasis on the material presented in the given chapter. We have attempted to integrate the problems with the subject matter in an effort to reinforce the material in the given chapter. Furthermore, most of the problems have been motivated by situations that can be encountered in industry.

The coverage of the material in this book requires from 45 to 60 lectures. The number of lectures depends on the background of the students and the depth in which one covers the last five chapters of the book. In most cases, it is recommended to teach the material in Chapter 5 first before teaching Chapter 4, as understanding the heat transfer topics facilitates the teaching of mass transfer. If only 30 lectures are available for teaching the material, then we recommend eliminating Chapters 4 and 6. However, this depends on the specific preference of the instructor.

The book has evolved out of teaching a senior level course in polymer processing at Virginia Polytechnic Institute and State University, Blacksburg, teaching numerical methods to undergraduate chemical engineers, and consulting experiences. First, it was evident that we needed to reinforce the students's knowledge of transport phenomena before we could begin to teach polymer processing. Second, we recognized that B.S. engineers are required to deliver answers and don't have time to weigh out all the variations and perturbations in the various theories. Third, undergraduate engineers are becoming

computer literate and have less fear of using computers than many professors. With these ideas in mind we tried to write a book on polymer processing that provides the necessary tools to do design calculations and informs the students exactly what they can be expected to do with the level of the material at hand.

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Without the contributions of a number of people our efforts in writing this book would have been fruitless. First, one of us (D. G. B.) would specifically like to thank the Department of Chemical Engineering and the College of Engineering at Virginia Polytechnic Institute and State University for a study leave during the spring semester of 1992 so that a full effort could be devoted to writing the book. Diane Cannaday

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Finally, we would like to thank our families, especially our wives, Patricia and Eugenia, for their patience and consideration during times when it seemed that all that mattered was writing the book.

Blacksburg, VA

Donald G. Baird
Dimitris I. Collias

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IMPORTANCE OF PROCESS DESIGN

In this chapter we intend not merely to present the technology of polymer processing but also to initiate the concepts required in the design of polymer processes. A knowledge of the types of polymers available today and of the methods by which they are processed is certainly needed, but this is available in several sources such as *Modern Plastics Encyclopedia* (Green, 1992) and the *Plastics Engineering Handbook* (Frados, 1976). In this chapter we present primarily an overview of the major processes used in the processing of thermoplastics. In Section 1.1 we begin by classifying the various processes and point out where design is important. In Section 1.2 we present a case study on film blowing to illustrate how the final physical properties are related all the way back to the melt flow of a polymer through the die. Finally, in Section 1.3 we summarize the principles on which polymer process design and analysis are based.

1.1. CLASSIFICATION OF POLYMER PROCESSES

The major processes for thermoplastics can be categorized as follows: extrusion, postdie processing, forming, and injection molding. We describe specific examples of some of the more common of these processes here.

The largest volume of thermoplastics is probably processed by means of *extrusion*. The *extruder* is the main device used to melt and pump thermoplastics through the shaping device called a *die*. There are basically two types of extruders: single- and twin-screw. The *single-screw extruder* is shown in Fig. 1.1. The single-screw extruder basically consists of a screw (Fig. 1.2) that rotates within a metallic barrel. The length-to-diameter ratio (L:D) usually falls in the range of 20 to 24 with diameters between 1.25 cm and 50 cm. The primary design factors are the screw pitch (or helix angle, θ) and the channel depth profile. The main function of the plasticating extruder is to melt solid polymer and to deliver a homogeneous melt to the die at the end

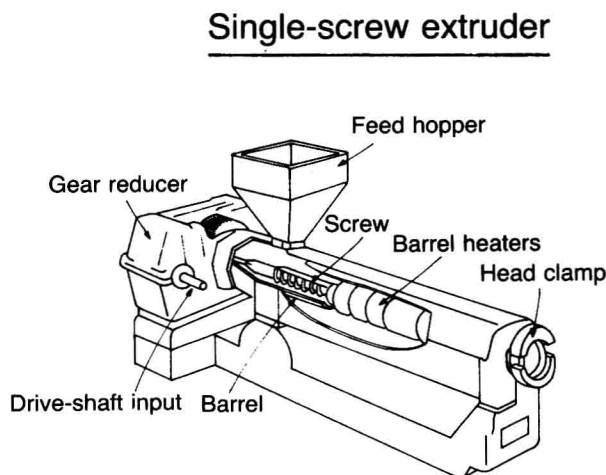


Figure 1.1 Typical single-screw extruder. (Reprinted by permission of the publisher from S. Middleman., *Fundamentals of Polymer Processing*, McGraw-Hill, Company, New York, 1977.)

Extruder screw geometry

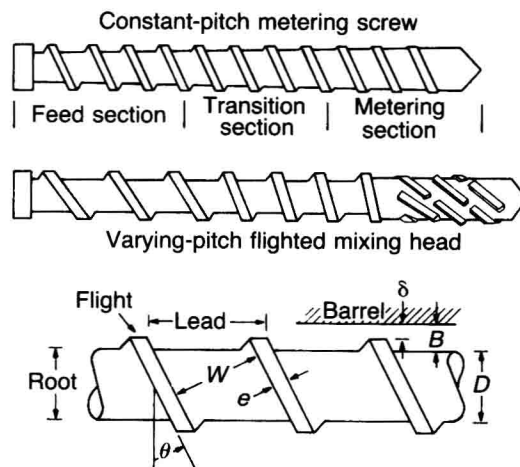


Figure 1.2 Two different extruder screw geometries along with the various geometric factors describing the characteristics of the screw. (Reprinted by permission of the publisher from S. Middleman, *Fundamentals of Polymer Processing*, McGraw-Hill, Company, New York, 1977.)

of the extruder. The extruder can also be used as a mixing device, a reactor, and a devolatilization tool (see Chapter 8).

There are as many *twin-screw extruders* as single-screw extruders in use today. Many different configurations are available, including corotating and counterrotating screws (see Fig. 1.3) and intermeshing and nonintermeshing screws. These extruders are primarily adapted to handling difficult-to-process materials and are used for compounding and mixing operations. The analysis and design of these devices are quite complicated and somewhat out of the range of the material level in this text. However, some of the basic design elements are discussed in Chapter 8.

The extruder feeds a shaping device called a die. The performance of the single- and corotating twin-screw extruders is affected by resistance to flow offered by the die. Hence, we cannot separate extruder design from die design. Problems in die design include distributing the melt flow uniformly over the width of a die, obtaining a uniform thermal history, predicting the die dimensions, which lead to the desired final shape, and producing a smooth extrudate free of surface irregularities. Some of these design problems are accessible at this level of material, but others are still research issues (see Chapter 7).

There are many types of extrusion die geometries, including those for producing sheet and film, pipe and tubing, rods and fiber, irregular cross sections (profiles), and coating wire. As an example, a wire-coating die is shown in Fig. 1.4. Here metal wire is pulled through the center of the die with melt being pumped through the opening to encapsulate

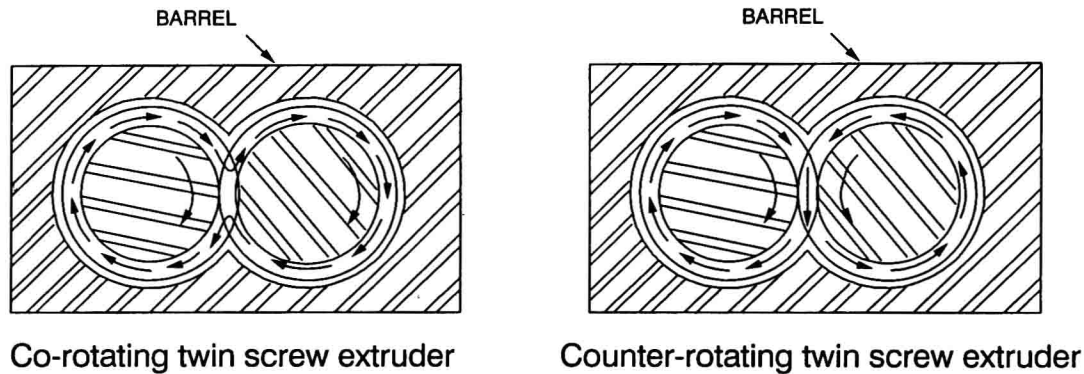


Figure 1.3 Cross-sectional view of corotating and counterrotating twin-screw extruders.

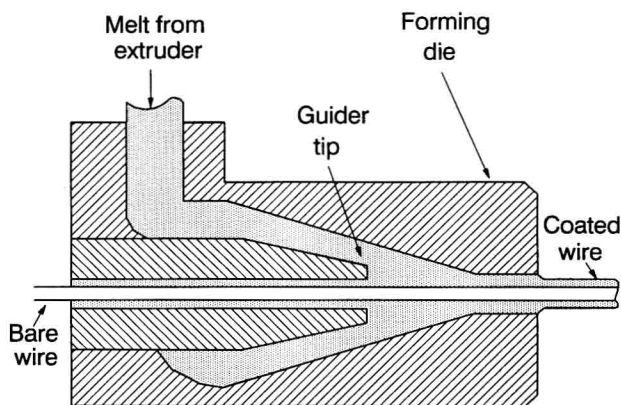


Figure 1.4 Cross-head wire-coating die. (Reprinted by permission of the publisher from Tadmor & Gogos, 1979.)

the wire. The design problems encountered here are concerned with providing melt flowing under laminar flow conditions at the highest extrusion rate possible and to give a coating of polymer of specified thickness and uniformity. At some critical condition, polymers undergo a low Reynolds number flow instability, called *melt fracture*, which leads to a nonuniform coating. Furthermore, the melt expands on leaving the die, leading to a coating that can be several times thicker than the die gap itself (this is associated with the phenomenon of die swell). The problems are quite similar for other types of extrusion

processes even though the die geometry is different. The details associated with die design are presented in Chapter 7.

We next turn to *postdie* processing operations. Examples of these processes include *fiber spinning* (Fig. 1.5), film blowing (Fig. 1.6), and *sheet forming* (Fig. 1.7). These processes share a number of similarities. In particular they are free-surface processes in which the shape and thickness or diameter of the extrudate are determined by the rheological (flow) properties of the melt, the die dimensions, cooling conditions, and take-up speed relative to the extrusion rate. The physical and, in the case of film blowing and sheet forming, the optical properties are determined by both the conditions of flow in the die and the cooling rates and stretching conditions of the melt during the cooling process. Furthermore, slight changes in the rheological properties of the melt can have a significant effect on the final film or fiber properties. Design considerations must include predictions of conditions that provide not only the desired dimensions but also the optical and physical properties of the film, fiber, or sheet.

The third category of processing of thermoplastics is *forming*. Three examples of this type of process are blow molding, thermoforming, and compression molding. *Blow molding* (Fig. 1.8) is primarily employed for making containers used to package a wide variety of fluids. Although polyolefins, such as high-density polyethylene (HDPE) or polyethyleneterephthalate (PET), both of which can be considered as commodity resins, are commonly used, there is growing interest in using this technique for the processing of higher-performance engineering thermoplastics. Essentially, a parison that has been extruded or injection-molded is inflated with air until it fills the mold cavity. The inflated parison is held in contact with the cold mold walls until it is solidified.

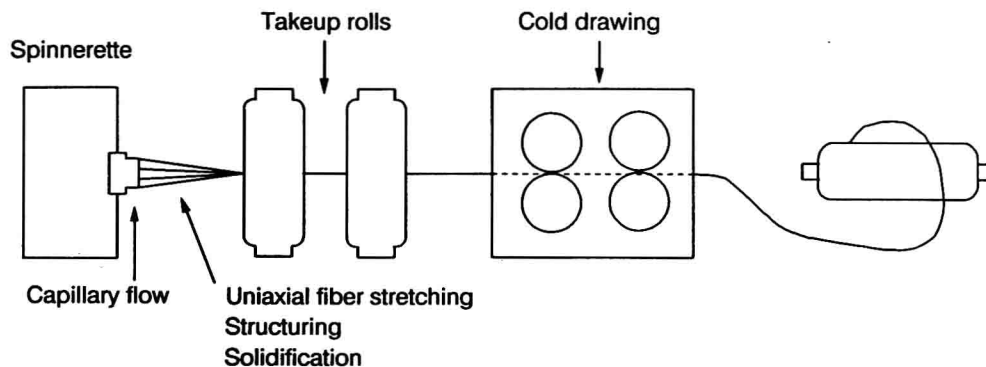


Figure 1.5 Fiber melt-spinning process. (Reprinted by permission of the publisher from Tadmor & Gogos, 1979.)

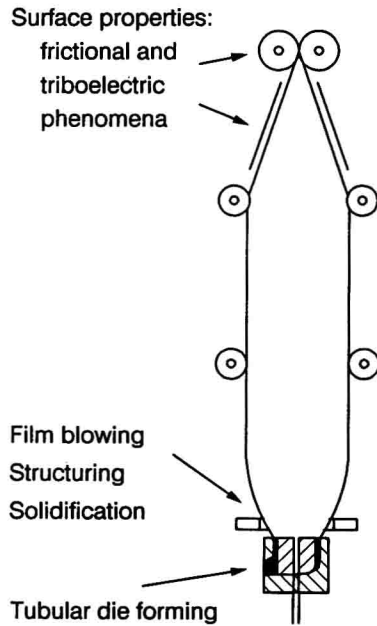


Figure 1.6 Film-blowing process. (Reprinted by permission of the publisher from P. N. Richardson, *Introduction to Extrusion*, Society of Plastics Engineers Inc., Greenwich, CT, 1974.)

In *thermoforming* (Fig. 1.9) a sheet of polymer is heated by radiation (and sometimes cooled intermittently by forced convection) to a temperature above its glass transition temperature or in some cases above the crystalline melting temperature and then pressed into the bottom part of the mold (female part) by mechanical force or pressure or by pulling a vacuum. The key flow property is the extensional flow behavior of the melt which controls the uniformity of the part's thickness. Sometimes the deformation is applied at a temperature just below the onset of melting, in which case the process is referred to as

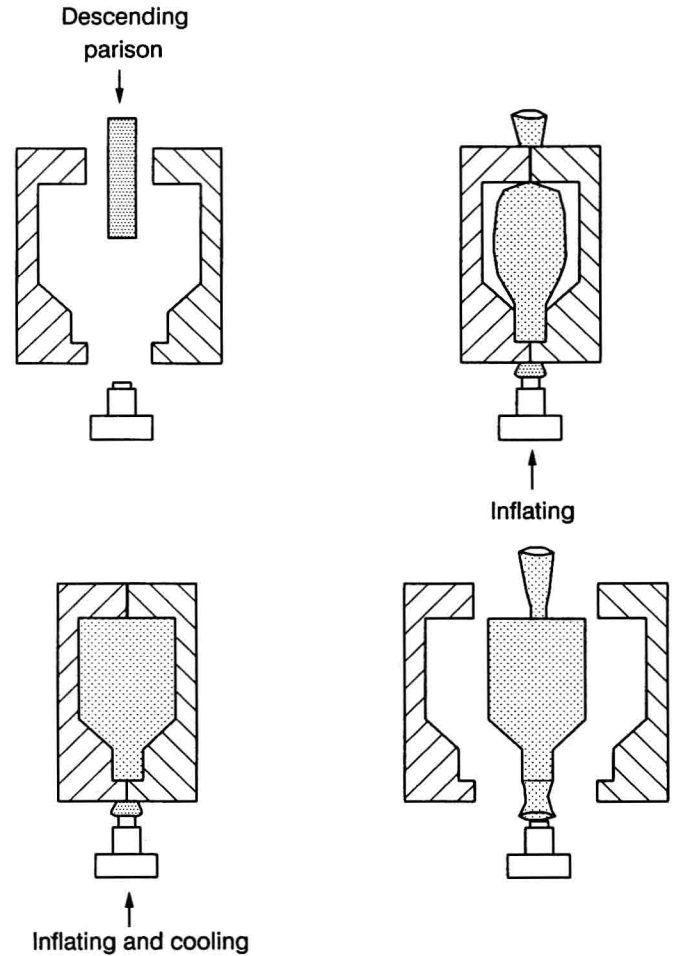


Figure 1.8 Blow-molding process. (Reprinted by permission of the publisher from W. A. Holmes-Walker, *Polymer Conversion*, Elsevier, London, 1975.)

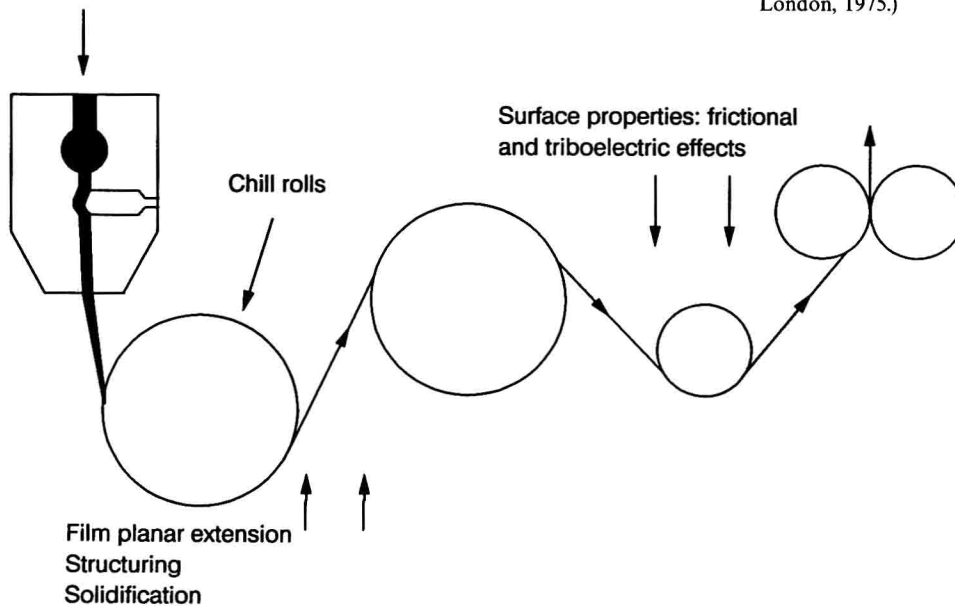


Figure 1.7 Flat film and sheet process. (Reprinted by permission of the publisher from Tadmor & Gogos, 1979.)

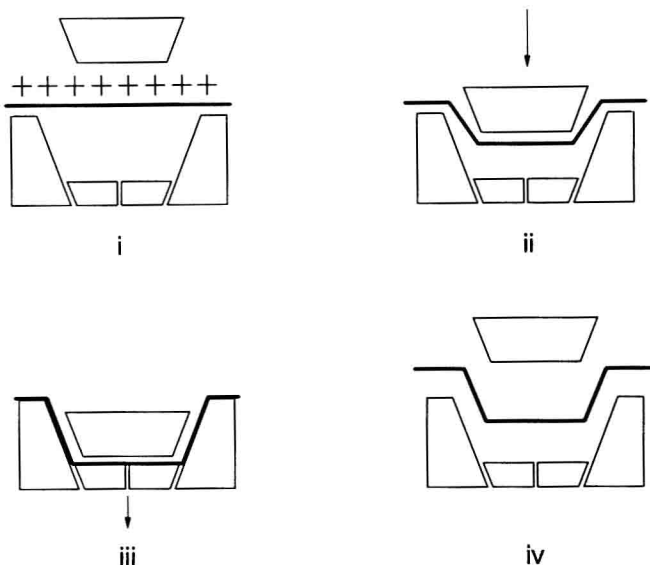


Figure 1.9 Plug-assisted vacuum thermoforming. (Reprinted by permission of the publisher from R. Greene, ed., *Modern Plastics Encyclopedia*, Vol. 53, McGraw-Hill, New York, 1977.)

solid-phase forming. At other times the sheet is extruded directly to the forming unit and is formed before it cools down (this is called scrapless, or continuous, thermoforming). Some of the key design considerations are the time required to heat the sheet, the final thickness of the part, especially around sharp corners, and the cooling rate that controls the amount and type of crystallinity.

In *compression molding* (Fig. 1.10) a slug of polymer is heated, and then pressure is applied to squeeze the material into the remaining part of the mold. Some aspects of forming are discussed in Chapter 10.

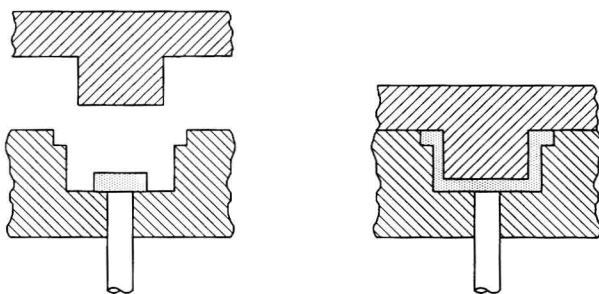


Figure 1.10 Compression-molding process. (Reprinted by permission of the publisher from Tadmor & Gogos, 1979.)

The last general category is *injection molding* (see Fig. 1.11). Polymer is melted and pumped forward just as in a screw extruder. The screw is then advanced forward by a hydraulic system that pushes the melt into the mold. Because of the high deformation and cooling rates, a considerable degree of structuring and molecular orientation occurs during mold filling. The physical properties of injection-molded parts can be significantly affected by processing conditions. Design considerations include the required injection pressure to fill the mold cavity, the location of weld lines (places where two melt fronts come together), cooling rates, length of hold time in the mold, and distribution of molecular orientation. Some of these factors are out of the realm of the material that can be covered by this book, but accessible aspects are presented in Chapter 10.

Although the majority of the material in this book is concerned with the processing of thermoplastics, the processing of *thermosetting* systems should also be mentioned for the sake of completeness. We describe three types of processes involving reactive processing: reaction injection molding (RIM), compression molding, and pultrusion.

Reaction injection molding is a process in which two liquid intermediates are metered separately to a mixing head where they are combined by high-pressure impingement mixing and subsequently flow into a mold where they are polymerized to form a molded part (see Fig. 1.12). A typical process consists of the reaction of diisocyanate and a polyol to form polyurethane. The important design factors are the degree of mixing and the appropriate heat transfer conditions to ensure uniform curing conditions in the mold. This process is discussed in more detail in Becker (1979).

Thermosetting composites can be processed by means of *compression molding* of uncured resin. Usually, fiber reinforcement is used to provide additional strength and stiffness. The application of pressure pushes the resin into the fiber reinforcement, and heat cross-links the resin to form a solid material. The critical factors are the flow of the uncured resin into and around the reinforcement and the uniform and complete cure of the resin throughout the part. This technique is used primarily in the aerospace and automobile industries.

Pultrusion is a process used for making continuous filament-reinforced composite extruded profiles (see Fig. 1.13). Reinforcing filaments, such as glass fiber roving, are saturated with catalyzed resin and then pulled through an orifice similar to an extrusion die. As the two materials pass through the die, polymerization of the resin occurs to continuously form a rigid cured profile corresponding to the die orifice shape. The materials are pulled through the die rather than being pumped. Although the primary resins used are of the thermosetting type such as polyester, vinyl ester, and epoxy, thermoplastic resins can be utilized in the same process. The major design considerations for thermosetting systems consist of dispersion of the resin in the reinforcement and the conditions for complete cure of the resin. The processing of thermosetting systems is discussed in Macosko (1990).

The intention in Section 1.1 was not merely to review the technology of polymer processing, but also to point out factors that

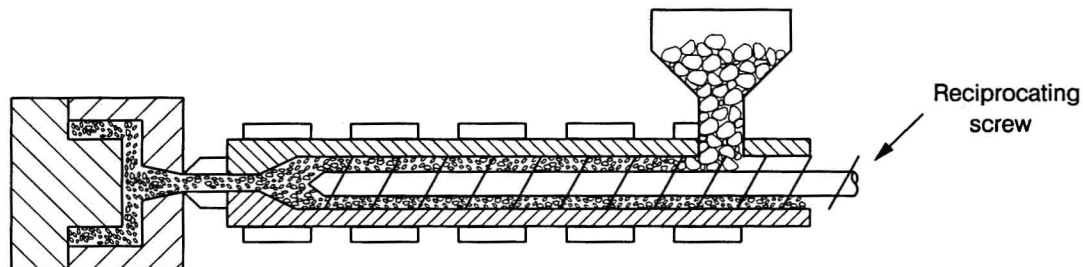


Figure 1.11 Typical injection-molding unit. (Reprinted by permission of the publisher from Tadmor & Gogos, 1979.)

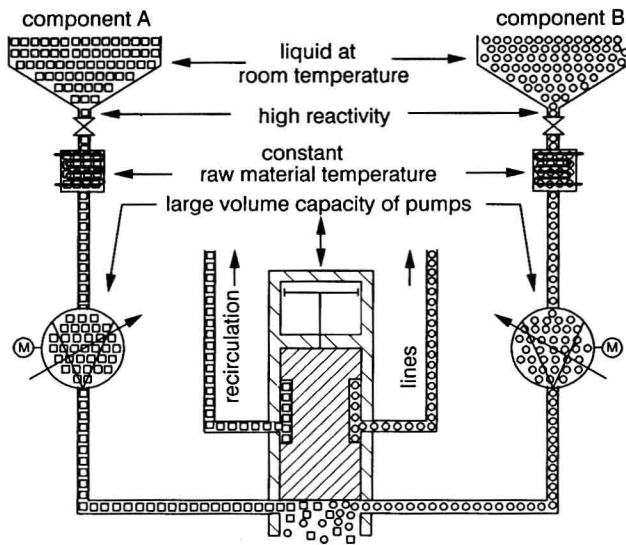


Figure 1.12 Reaction injection-molding (RIM) process. (Reprinted by permission of the publisher from Becker, 1979.)

must be considered in the design of polymer processes. However, because most students have little knowledge of the technology of polymer processing, some general introduction is of value. Furthermore, a physical picture of the various processes is required to facilitate the discussion of the material presented in the next four chapters.

1.2. FILM BLOWING: A CASE STUDY

In the preceding section we described the technology of polymer processing. In this section we illustrate the role of processing in affecting the properties of polymeric systems. In particular, the properties of

films of polybutylene (PB1) generated by film blowing are shown to be highly sensitive to processing conditions.

Most blown film is made from some form of polyethylene (PE), but polybutylene, PB1, has been considered because it is slightly cheaper to use in the production of film. However, one does not obtain the same physical properties without changing the processing conditions. Identifying the appropriate processing conditions is usually done by either a trial-and-error approach or through statistically designed experiments. If a model of film blowing was available, or if one could apply dimensional analysis concepts, then it might be possible to find the appropriate processing conditions without carrying out a lengthy set of costly experiments. The following example illustrates the many factors that affect the properties of blown PB1 film.

The film-blowing process is shown in Fig. 1.6. Polymer pellets are fed to the extruder in which melting, homogenization, and pumping occur. The melt then passes through the die, which is designed to subject the melt to both a uniform deformation and thermal history. Air is blown through the center of the die to expand the molten bubble to impart orientation of the molecules in the hoop direction. At the same time, the bubble is being stretched as a result of the take up velocity being greater than the average velocity of the melt leaving the die. The stretching imparted in the two directions controls the degree to which the molecules orient and, hence, affects the physical properties. Cooling air is blown along the bubble by an air ring that is placed around the outside of the die. This causes the film to solidify or crystallize and lock in the orientation imparted by the biaxial stretching process. The film is then taken up on a roller and either slit to make flat film or sealed and cut to make bags.

We now look at some of the factors that affect the physical properties of the blown film. The recommendations for the annular die gap opening for a desired film thickness are given in Table 1.1. It is probably clear why the die gap is larger than the desired film thickness as the film is to be drawn down to create molecular orientation. What is not clear is why it is recommended that the die land (the annular portion of the die) be shortened as the die gap increases. The physical properties based on the tear strength of the film are found to be

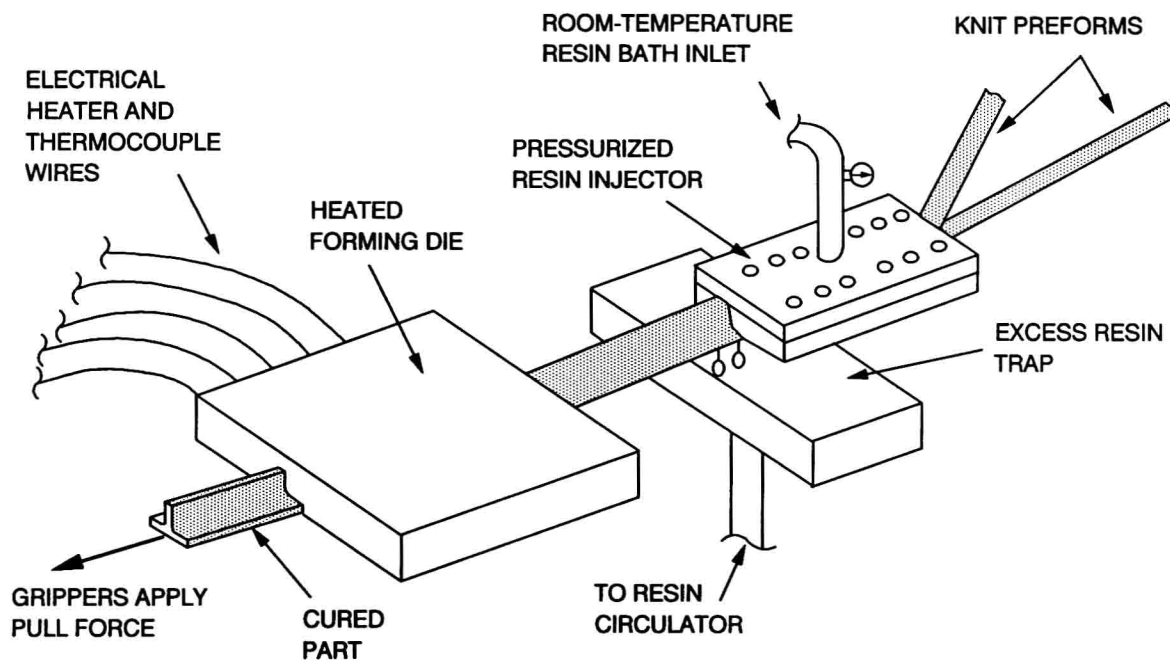


Figure 1.13 Pultrusion process.

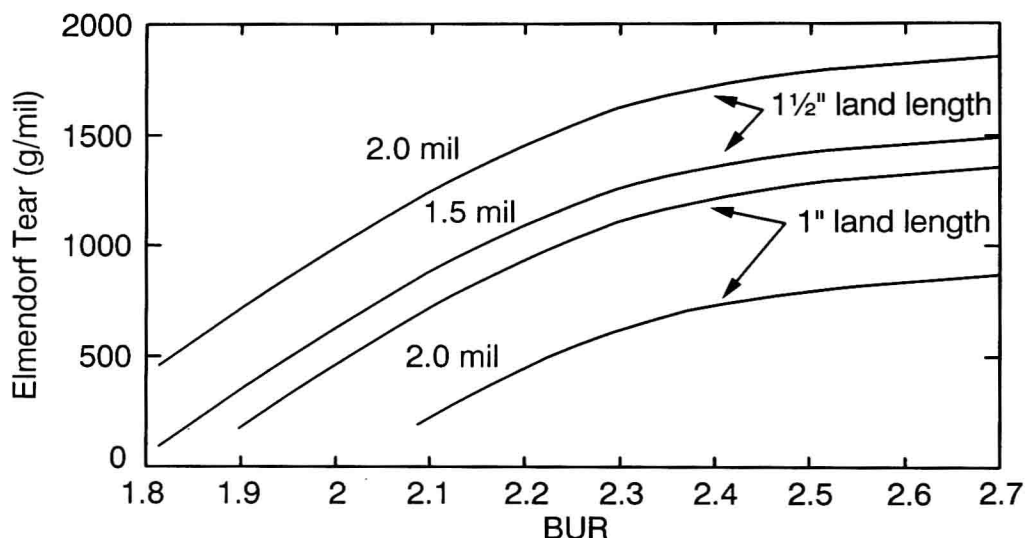


Figure 1.14 Effect of the annular die land length on the film tear strength of polybutylene extruded at the rate of 10 m/min for two different film thicknesses.

TABLE 1.1 Die Recommendations for the Blowing of PBI with a Blowup Ratio of 2.4 to 2.8 at a Melt Temperature of 370°F to 390°F

Film Thickness ($\times 10^3$ in.)	Die Gap (in.)	Land Length (in.)
0.5–1	0.015	$1\frac{1}{2}$ –2
1–2	0.018–0.023	$1\frac{1}{2}$
2–7	0.028–0.032	1
8–15	0.040–0.050	1
15–40	0.050–0.060	1

significantly affected by the length of the die land as shown in Fig. 1.14. Here the tear strength is plotted versus the blowup ratio (BUR), which is the ratio of the final film diameter to the die diameter (outer diameter). It is observed that there is of the order of a threefold difference in the tear strength for a 2.0×10^{-3} in. thick film when the die land is decreased from 1.5 in. to 1.0 in. One reason for this result is that more “die swell” (the expansion of a polymer melt on leaving a die) occurs for the die with the 1.0 in. land length, and hence a higher stretch ratio is required to draw the film down to 2.0×10^{-3} in. This leads to higher orientation of the molecules along the draw direction than in the case of the die with a 1.5 in. land length. Finally, the effect of the die gap on the tear strength measured along both the film length (the machine direction [MD]) and the circumference of the film (the transverse direction [TD]) is shown in Fig. 1.15. Here we see that the tear strength in the TD direction decreases significantly with an increase in die gap, whereas in the MD the effect is significant but nowhere near as large. Again, it is not clear what would cause the loss of properties in both directions as the die gap increases other than the longer time available for molecular relaxation due to the increase in time required for cooling of the film. Factors other than orientation must be involved in controlling the properties. For example, the amount of crystallinity and the size of the spherulitic regions may play a significant role.

The melt extrusion temperature is also observed (Fig. 1.16) to have a significant effect on the physical properties as the tear strength in both directions increases with increasing melt temperature. This is probably due to lower levels of orientation as the result of lower stress

levels in the melt and shorter relaxation times allowing a rapid relaxation of molecular orientation.

The line speed, given in feet per minute (fpm), as shown in Table 1.2, has a very significant effect on the properties. For example, as the line speed increases from 14 fpm, the breaking strength in the MD increases from 4800 g/mil to 6600 g/mil but decreases in the TD from 5000 g/mil to 2300 g/mil (1 mil = 0.001 in.). This is mostly associated with the degree of molecular orientation. The more the molecules are oriented along the MD, the stronger the films are, but also the poorer the tear strength in this direction is. The other properties given here can be explained by similar arguments.

The BUR, can be used to obtain a better balance of properties, as shown in Fig. 1.17. As the BUR increases, the tear properties become more uniform in both directions. Biaxial orientation (i.e., orientation of molecules in two directions) is generated in the blowing process and leads to more uniform properties.

As one can imagine, the film-blowing process is very difficult to model, and hence very little quantitative design work has been done. Although the complete modeling of this process is beyond the level of the material in this book (or even an advanced book for that matter), the example serves to illustrate that the properties of a polymeric material highly depend on the processing conditions and to highlight some of the problems faced by the engineer. In designing a polymer process, one must be concerned not only with how much material per unit time can be produced but also with the quality of the properties of the material. In the next section we look at the fundamental principles on which the design and analysis of polymer processes are based.

1.3. BASICS OF POLYMER PROCESS DESIGN

In order to design and analyze polymer processes there are common steps associated with nearly every process. Following Tadmor and Gogos (1979), these basic steps are:

1. Handling of particulate solids
2. Melting, cooling, and crystallization
3. Pumping and pressurization
4. Mixing
5. Devolatilization and stripping
6. Flow and molecular orientation

TABLE 1.2 Line Speed versus Properties for PBI

(FPM) Line Speed	Break Strength (g/mil)		Yield Strength (g/mil)		Ultimate Elongation (%)		Dart Drop (g/m ² /s ²)	Tear Strength (g/mil)	
	MD	TD	MD	TD	MD	TD		MD	TD
14	4800	5000	2000	2000	220	260	350	1700	550
20	4600	3700	2100	2000	160	230	280	1500	550
30	5500	2800	2500	1900	110	170	190	680	390
40	6600	2300	3000	1900	80	150	90	80	270

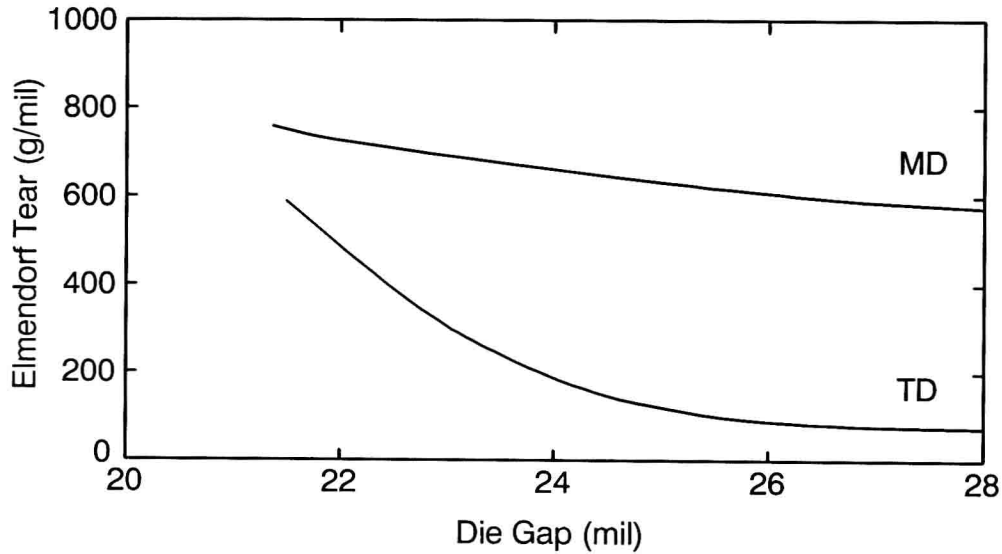


Figure 1.15 Effect of die gap on the film tear strength of polybutylene extruded at the rate of 10 m/min. The film thickness is 0.002 in., and the blowup ratio is 2.8.

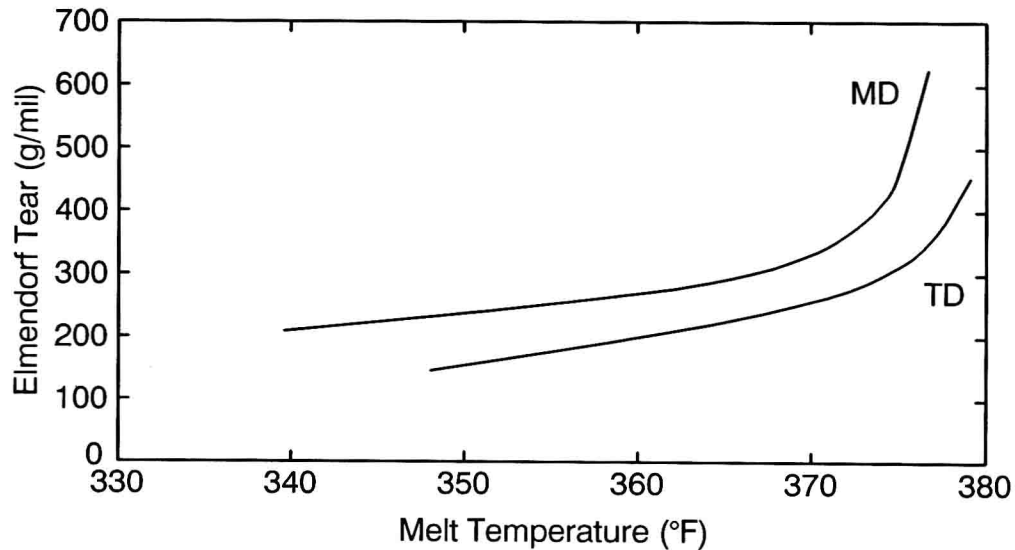


Figure 1.16 Effect of melt temperature on the film tear strength of polybutylene film extruded at the rate of 10 m/min. The film thickness is 0.002 in., and the blowup ratio is 2.8.

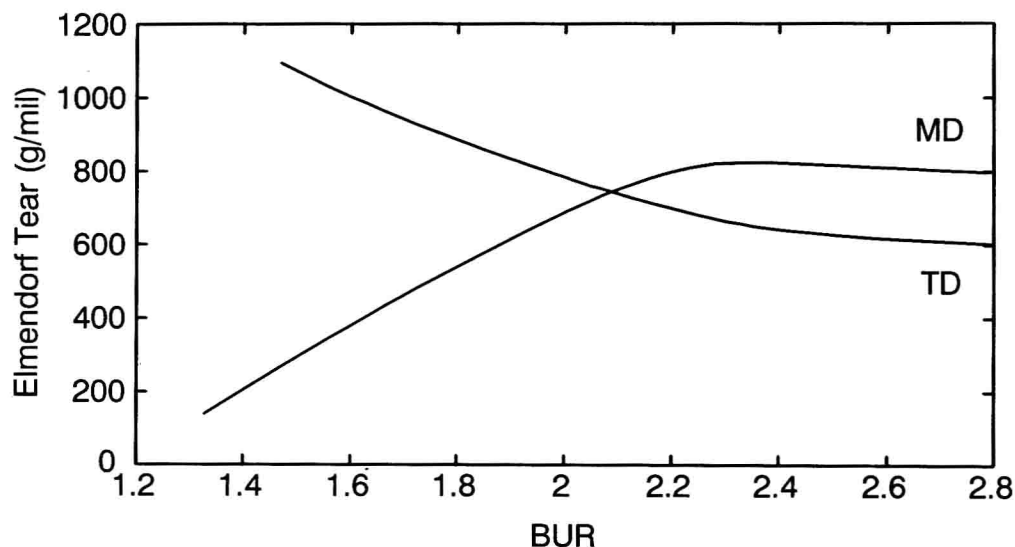


Figure 1.17 Effect of blowup ratio on the film tear strength measured along the machine (MD) and transverse (TD) directions.

These basic steps are based on the following concepts:

1. Transport phenomena: fluid mechanics, heat transfer, and mass transfer
2. Polymer rheology
3. Solid mechanics and flow

4. Principles of mixing
5. Chemical reactions

In the first five chapters of this book we present the fundamental principles required in the design of polymer processes. In the last five chapters we analyze specific types of processes in detail.

REFERENCES

- Becker, W. E., Ed. 1979. *Reaction Injection Molding* (Van Nostrand Reinhold, New York).
- Frados, J., Ed. 1976. *Plastics Engineering Handbook* (Van Nostrand Reinhold, New York).
- E. Green, Ed. 1992. *Modern Plastics Encyclopedia* (McGraw-Hill, New York).
- Macosko, C. W. 1989. *RIM: Fundamentals of Reaction Injection Molding* (Hanser, New York).
- Tadmor, Z., and C. G. Gogos 1979. *Principles of Polymer Processing* (Wiley, New York).

ISOTHERMAL FLOW OF PURELY VISCOUS NON-NEWTONIAN FLUIDS

DESIGN PROBLEM 1 Design of a Blow-Molding Die

A typical blow-molding die is shown in Fig. 2.1. The region of particular interest is shown in Fig. 2.2. The die exit is the region that controls the final dimensions of the parison, which is a cylindrically shaped tube of polymer. The parison consisting of high-density polyethylene (HDPE) is to have a weight of 90 g with an outside diameter of 0.127 m

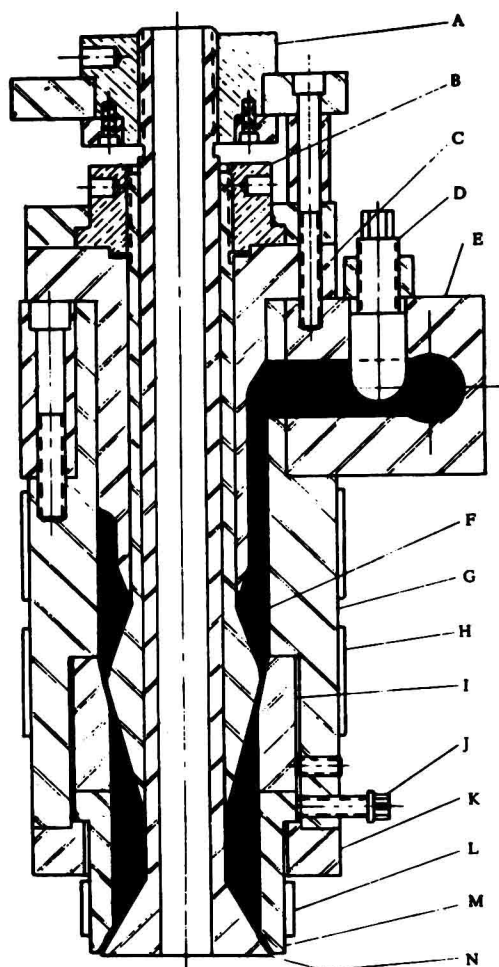


Figure 2.1 Typical blow-molding die: A, choke-adjusting nut; B, mandrel adjustment; C, feed throat; D, choke screw; E, die head; F, plastic melt; G, die barrel; H, heater band; I, choke ring; J, centering screw; K, clamp ring; L, die heater; M, die; N, mandrel. (Reprinted by permission of the publisher from J. D. Frankland, "A High Speed Blow Molding Process", *Trans. Soc. Rheol. (J. Rheol.)*, 19, 371, 1975.)

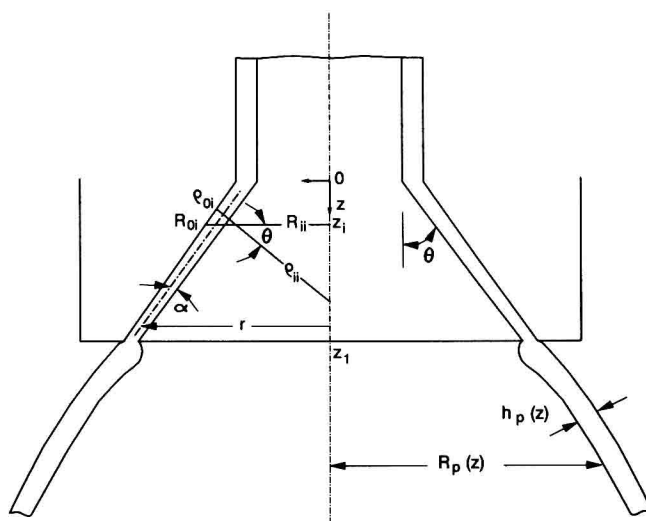


Figure 2.2 Details of the conical region of the blow-molding die.

TABLE 2.1 Power-Law and Ellis Model Parameters

	Graphically Obtained	From Nonlinear Regression Analysis
$m(\text{Pa}\cdot\text{s}^n)$	2.374 E+04	1.616 E+04
n	0.424	0.520
$\eta_0(\text{Pa}\cdot\text{s})$	1.33 E+04	
$\tau_{1/2}(\text{Pa})$	3.325 E+04	
$\alpha-1$	1.54	

and a wall thickness of 3.81×10^{-4} m. Consider only the conical region in your calculations. The angles α and θ are taken as 0° and 30° , respectively. The distance z_1 should be 20 times the gap thickness. Determine the remaining dimensions of the die required to produce the desired extrudate. At this point neglect die swell (i.e., the increase in diameter and thickness due to elastic recovery) in your calculations. Determine the maximum extrusion rate (m^3/s) and pressure drop assuming that the limiting factor is melt fracture. (This occurs when the wall shear stress, τ_w , reaches 1.4×10^5 Pa.) Use the rheological parameters given in Table 2.3. Determine the length of time required to extrude the parison.

(a) Use the lubrication approximation to determine a design equation (i.e., Q versus ΔP), and then provide the required information.

(b) Carry out the design calculations by breaking up the flow region into a series of cones of length Δz . Use the annular flow equations presented in Section 2.3.1 and the computer to get a solution. At 180°C (453°K), $\rho = 965 \text{ kg/m}^3$.