POLYMER PROCESSING
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Since the appearance of the first edition of this textbook in 1995 the main changes that have occurred in the field of polymer processing are the use of polymers from renewable resources and more interest in recycling and reprocessing of polymers (i.e., green engineering). Furthermore, processing technology for the most part has not changed significantly except for a technique referred to as “microinjection molding,” a process designed to deliver extremely small parts (∼1.0 mg in mass). Hence, the coverage of material as outlined in the original preface can still be followed. We outline the major changes in the textbook below.

Because the field of polymer processing has not changed drastically since the appearance of the first edition of this book nearly 20 years ago, there are no major changes in the overall thrust and purpose of the book. The goal of the book remains unchanged and is to teach the basic principles needed in the design of polymer processing operations for thermoplastics. The main change in the field has been in the area of microinjection molding in which objects such as miniature gears and biomedical devices weighing only a fraction of a gram are produced. Although the general features of the process rely on injection molding, there are still some differences in the design considerations of the process because of the high shear rates and high temperatures required during processing. We have added discussion of the microinjection molding process in Chapter 10.

The major change in the field of polymer processing is the polymers that are processed, which is driven by the need to practice “green engineering.” There is a greater interest in the processing of polymers from renewable resources and reprocessing (i.e., recycling) of polymers that have already been subjected to a processing history. For this reason a new chapter, Chapter 11, has been added to the book, which is concerned with the recycling of thermoplastics and the processing of renewable polymers. Because the decision to recycle a polymer or to use a polymer from renewable resources cannot be made without the appropriate analysis guided by the purpose to recycle, we introduce the concept of life cycle assessment (LCA), which provides a systematic method for determining whether recycling and which form of recycling is the proper environmental choice. Furthermore, we include background, which considers material and energy flows associated with various types of recycling streams as it is important that more energy not be used in recycling plastics than is required in the conversion of raw materials to virgin resin. Chapter 11 also includes discussion of the processing of new-to-world renewable polymers (i.e., polymers that come from renewable resources, e.g., carbohydrates, and are not identical to today’s petroleum-derived polymers). Examples of these polymers are poly(lactic acid) (PLA), thermoplastic starch (TPS), and polyhydroxyalkanoate (PHA). The other category of renewable polymers is that of identical renewable polymers (also called biodegradable polymers), but these polymers require no new knowledge for processing as these renewable polymers have identical structure, performance, and processing to petroleum-derived polymers, with examples being bio-HDPE, bio-PP, and biopoly(butylene succinate) (bio-PBS). The teaching of the subject matter in Chapter 11 can require five or six lectures to do it completely. However, the very basics such as those in Sections 11.1 and 11.2 coupled with an overview of the other sections can be done in two or three lectures. It is recommended that the students at least be exposed to the green engineering topics in Chapter 11.

The other additions to the book include discussion of the rheology of polymers containing fibers that serve to reinforce the solid polymer and the role of sparse long chain branching on the rheology of polymer melts. These topics are discussed
in Chapter 3, and additional problems using the theory are found there also. Fiber suspensions have always been of interest and are included in books on processing of fiber composites. However, because these materials are processed by means of equipment used for thermoplastics and because of their importance in the generation of lightweight parts, we have included the subject matter in this book. Furthermore, the significant changes in the rheology and processing of polymers containing sparse long chain branching, that is, chains with less than about 10 long branches per chain (greater than the critical entanglement molecular weight), justify the inclusion of a brief coverage of this topic in Chapter 3.

Finally, in the first edition of this book we included numerical subroutines (International Mathematics and Statistical Libraries, IMSL, from Visual Numerics). However, the use of these subroutines requires knowledge of a higher level programming language, such as Fortran, which is typically not taught in the engineering curriculums any more. Hence, we have removed from the numerical examples the use of these specific subroutines and report only the numerical results that may have been obtained by means of either the IMSL subroutines or Excel or MATLAB. These solutions are available on the Wiley website (http://booksupport.wiley.com) and are listed via the example number and which numerical method is employed. Many engineering students have been exposed to MATLAB and certainly have access to Excel. The discussion of the use of the IMSL subroutines is also given on the website, but the subroutines are no longer included with the book.

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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 the supplementing of certain parts, the book can also be used by graduate students. In particular by supplementing the material in Chapters 2 and 3 with a more sophisticated coverage of nonlinear constitutive equations and the addition of topics in finite element methods, 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 with the intent of providing polymeric materials with a certain level of properties: for example, mechanical, optical, electrical, or barrier. Although there has been a belief that when a given polymer system does not meet the desired requirements that a new polymer must be used, it is becoming more apparent that the properties of the given polymer can be altered by the method of processing or the addition of 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 which will provide the desired properties. Yet, engineers receive little or no training in the design of polymer processes during their education. Part of the reason is they have an inappropriate background in transport phenomena, and the other is the lack of the mathematical tools required to solve the equations which 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.

As there are several books available concerned with the processing of polymers with an emphasis on thermoplastics, the question is: How does this book meet the needs as described in the above paragraph 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 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 leave the student with several methods for getting a solution. Included with this book are a selection of the subroutines from the International Mathematics and Statistical Libraries (IMSL) (Visual Numerics Inc., Houston, TX) for the solution of various types of equations which 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 is not totally dependent on the use of the computer, but there are certain problems which just can’t 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 it becomes necessary to understand the numerical technique. Although there are many who will criticize this approach, during the time of 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 book is organized in such a way that the first five chapters are concerned with the background needed to design polymer processes while the last five chapters are concerned with the specifics of various types of processes. Chapter 1 contains an overview of polymer processing techniques with the intent of facilitating examples and problems used throughout 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 is started with a design problem which serves to motivate the material presented in the chapter. Chapters 2 and 3 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 the interrelation between processing, structure, and properties is emphasized. These first five chapters contain all the background information 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. The remaining chapters are devoted to the factors associated with the design of various processing methods. We have tried to arrange the subject matter by similarities in the process. In each chapter we are careful to make it known what aspects of design the student should be able to execute based on their educational level. In many books on polymer processing it is not clear to the student just what part of the design he or she 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 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 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 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 which might 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 to 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 the heat transfer topics facilitate the teaching of mass transfer. If only 30 lectures are available for teaching the material, then it is recommended to eliminate Chapters 4 and 6. However, this depends on the specific preference of the instructor.

Finally, the book has evolved out of teaching a senior level course in polymer processing at Virginia Tech, the teaching of numerical methods to undergraduate chemical engineers, and consulting experiences. First, it was apparent that a reinforcement of transport phenomena was needed before one could begin to teach polymer processing. Second, it was 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 which provides the necessary tools to do design calculations and at the same time informs the student exactly what he or she can be expected to do with the level of material at hand.

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Dimitris I. Collias

Blacksburg, Virginia
February 1993
Without the contributions of a number of people our efforts in writing this book would have been fruitless.

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 providing study leave during the Spring Semester of 1992 so that a full effort could be devoted to writing the book.

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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 the writing of the book.

D. G. B.

D. I. C.
The intention of this chapter is not merely to present the technology of polymer processing but to initiate the concepts required in the design of polymer processes. A knowledge of the types of polymers available today and 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 concerned with 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 screws. The single-screw extruder is shown in Figure 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 falling in the range of 1.25 to 50 cm. The primary design factors are the screw pitch (or helix angle, $\theta$) 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 of the extruder. The extruder can also be used as a mixing device, a reactor, and a devolatilization tool (see Chapter 8).

There are an equal number of twin-screw extruders in use as single-screw extruders today. There are many different configurations 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 is 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-screw and corotating twin-screw extruders is affected by resistance to flow offered by the die. Hence, we cannot separate extruder design from the 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 that lead to the desired final shape, and the production of a smooth extrudate free of surface irregularities. Some of these design problems are accessible at this level of material while others are still research problems (see Chapter 6).

There are many types of extrusion die geometries including those for producing sheet and film, pipe and tubing, rods
IMPORTANCE OF PROCESS DESIGN

FIGURE 1.1 Typical single-screw extruder. (Reprinted by permission of the author from Middleman, 1977.)

FIGURE 1.2 Two different extruder screw geometries along with the various geometric factors that describe the characteristics of the screw. (Reprinted by permission of the publisher from Middleman, 1977.)

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 and Gogos, 1979.)

and fiber, irregular cross sections (profiles), and coating wire. As an example, a wire coating die is shown in Figure 1.4. Here metal wire is pulled through the center of the die with melt being pumped through the opening to encapsulate 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, which is called melt fracture and 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 have 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 as well as 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 which provide not only the desired dimensions but 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 (Fig. 1.8), thermoforming (Fig. 1.9), and compression molding (Fig. 1.10). Blow molding 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, interest is growing in using this technique for the processing of higher performance engineering thermoplastics.
Essentially a parison, which has been extruded or injection molded, is inflated by air until it fills the mold cavity. The inflated parison is held in contact with the cold mold walls until it is solidified. Considering the process of thermoforming, 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) either using mechanical force, 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 thickness. Sometimes the deformation is applied at a temperature just below the onset of melting, in which case the process is referred to as 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 which controls the amount and type of crystallinity. In compression molding 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.

The last general category is that of injection molding, which is shown in Figure 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 affected significantly 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. In conventional injection molding, parts may vary from a few grams to many kilograms (e.g., a car hood or trunk).

In the last 10 to 15 years one of the major variations in the injection molding process has been microinjection molding (μIM), which appears to be one of the most efficient processes for the large-scale production of thermoplastic polymer microparts (Giboz et al., 2007). These microparts can be as small as 0.6 mg and possess dimensions in the micron range along with dimensional tolerances in the range of microns. Examples of microparts are microelectromechanical systems, which is the name given to the combination of miniaturized mechanical and electronic structures in a system, and miniature gears and lenses. Biomedical parts for insertion into the body such as heart stents and sensors are also produced by this method. Micromolding is still very much in its infancy as a new branch of injection molding.

As will be discussed in Chapter 10 (Section 10.1.3), it is not just about scaling everything down, but it is a specialized technique in its own right, with a different set of challenges. Some of these factors are out of the realm of the material that can be covered by this book, but those aspects that are accessible 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. RIM 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 diisocynate 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 elsewhere (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 crosslinks 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 elsewhere (Macosko, 1989).

The intention in Section 1.1 was more than just to review the technology of polymer processing, but to point out factors that must be considered in the design of polymer processes. However, since most students have little knowledge of the technology of processing of polymers, 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: CASE STUDY

The last section was merely concerned with describing the technology of polymer processing. This section is concerned with illustrating the role of processing in affecting the properties of polymeric systems. In particular, the properties of films of polybutylene (PB1) generated by means of 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, it does not lead to the same physical properties without changing the processing conditions. Identification of the appropriate processing conditions is usually done either by 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 was shown in Figure 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 such that as it leaves the die, the melt has been subjected to both a uniform deformation as well as 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, which is placed around the outside of the die. This serves to cause 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 as to 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 significantly affected by the length of the die land as shown in Figure 1.14. Here the tear strength is plotted versus the blow up ratio, BUR, which is the ratio of the final film diameter to the die diameter (outer diameter). It is observed that there is on the order of a threefold difference in the tear strength for a 2.0 \times 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 \times 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 both along the film length (this is called the machine direction, MD) and along the circumference of the film (this is called the transverse direction, TD) is shown in Figure 1.15. Here we see that the tear strength in the TD decreases significantly with an increase in die gap, while in the machine direction the effect is significant but nowhere near as large. Again it is not clear as to 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.

### Table 1.1: Die Recommendations for the Blowing of PB1 with a Blow Up Ratio of 2.4–2.8 at a Melt Temperature of 370–390 °F

<table>
<thead>
<tr>
<th>Film Thickness (× 10^3 in.)</th>
<th>Die Gap (inches)</th>
<th>Land Length (inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5–1</td>
<td>0.015</td>
<td>1 1/2–2</td>
</tr>
<tr>
<td>1–2</td>
<td>0.018–0.023</td>
<td>1 1/2</td>
</tr>
<tr>
<td>2–7</td>
<td>0.028–0.032</td>
<td>1</td>
</tr>
<tr>
<td>8–15</td>
<td>0.040–0.050</td>
<td>1</td>
</tr>
<tr>
<td>15–40</td>
<td>0.050–0.060</td>
<td>1</td>
</tr>
</tbody>
</table>

### 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.

### 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 blow up ratio is 2.8.
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 (mil here means 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 the poorer the tear strength in this direction. The other properties given here can be explained by similar arguments.

The blow up ratio, BUR, can be used to obtain a better balance of properties as shown in Figure 1.17. As 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, which 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 are highly dependent on the processing conditions and some of the problems faced by the engineer. In designing a polymer process one must be concerned with not only how much material per unit time can be produced but with the properties of the material. In the next section we look at the fundamental principles on which the design and analysis of polymer processes is 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 given below:

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

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

<table>
<thead>
<tr>
<th>Table 1.2: Line Speed Versus Properties for PB1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line Speed (fpm)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>14</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>40</td>
</tr>
</tbody>
</table>
4. Principles of mixing
5. Chemical reactions

In the first five chapters of this book we deal with the fundamental principles required in the design of polymer processes. The last six chapters are concerned with the details of specific types of processes and the reprocessing of polymers and the processing of renewable polymers.

REFERENCES


Richardson, P. N. 1974. Introduction to Extrusion (Society of Plastics Engineers, Inc., Greenwich, CT).
ISOTHERMAL FLOW OF PURELY VISCOS
NON-NEWTONIAN FLUIDS

DESIGN PROBLEM I
DESIGN OF A BLOW MOLDING DIE

A typical blow molding die is shown in Figure 2.1. The region of particular interest is shown in Figure 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 HDPE is to have a weight of 90 g with an outside diameter of 0.127 m and a wall thickness of \(3.81 \times 10^{-4}\) m. Consider only the conical region in your calculations. The angles \(\alpha\) and \(\theta\) 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 the limiting factor is melt fracture. (This occurs when the wall shear stress, \(\tau_w\), reaches \(1.4 \times 10^5\) Pa.) Use the rheological parameters given in Table 2.1. Determine the length of time required to extrude the parison.

(a) Use the lubrication approximation to determine a design equation (i.e., \(Q\) vs. \(\Delta P\)) 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 \(\Delta z\). Use the annular flow equations presented in Section 2.2.1 and the computer to get a solution. At 180°C (453 K), \(\rho = 965\) kg/m³.

The transport properties of polymeric materials which distinguish them most from other materials are their flow properties or rheological behavior. There are many differences between the flow properties of a polymeric fluid and typical low molecular weight fluids such as water, benzene, sulfuric acid, and other fluids, which we classify as Newtonian. Newtonian fluids can be characterized by a single flow property called viscosity (\(\mu\)) and their density (\(\rho\)). Polymeric fluids, on the other hand, exhibit a viscosity function that depends on shear rate or shear stress, time-dependent rheological properties, viscoelastic behavior such as elastic recoil (memory), additional normal stresses in shear flow, and an extensional viscosity that is not simply related to the shear viscosity, to name a few differences.

Because of these vastly different rheological properties, polymeric fluids are known to exhibit flow behavior that cannot be accounted for merely through a single rheological parameter such as the viscosity. Some of the differences in flow behavior include a nonlinear relation between pressure drop and volumetric flow rate for flow through a tube, swelling of the extrudate on emerging from a tube, the onset of a low Reynolds number flow instability called melt fracture, gradual relaxation of stresses on cessation of flow, and the ability of the molecules to orient during flow. These phenomena are discussed in more detail elsewhere (Bird et al., 1987; Larson, 1999).

The emphasis in this chapter is on the viscous behavior of polymeric fluids and in particular their pseudoplastic behavior. The chapter is arranged in the following manner. First, in Section 2.1 we review the definition of a Newtonian fluid, and then we present empiricisms for describing the viscosity of polymeric fluids. In Section 2.2
we use shell force or momentum balances to solve onedimensional flow problems commonly found in polymer processing. In Section 2.3 we generalize the force or momentum balances to give the equations of motion, and we generalize the constitutive equation presented in Section 2.1. In Section 2.4 we present two useful approximations for solving polymeric flow problems. Finally, in Section 2.5 the topics discussed in the previous sections are used to solve Design Problem I.

### 2.1 VISCOUS BEHAVIOR OF POLYMER MELTS

When a Newtonian fluid is placed between the two plates as shown in Figure 2.3 in which the top plate is moved to the right with constant velocity, \( V \), the relation between force, \( F \), divided by the area of the plates, \( A \), and the velocity divided by the separation distance, \( H \), is given as follows:

\[
F/A = \mu V/H
\]
The constant of proportionality, $\mu$, is called the viscosity of the fluid. The force, $F$, is the force required to keep the top plate moving with a constant velocity. The force per unit area acting in the $x$ direction on a fluid surface at constant $y$ by the fluid in the region of lesser $y$ is the shear stress, $\tau_{yx}$. Since the velocity of the fluid particles varies in a linear manner with respect to the $y$ coordinate, it is clear that $V/H = dv_y/dy$ as shown below:

$$\lim_{\Delta y \to 0} \frac{\Delta v_y}{\Delta y} = \frac{dv_y}{dy} = \frac{V - 0}{H - 0} = \frac{V}{H} \quad (2.2)$$

Equation 2.1 can be rewritten as

$$\tau_{yx} = -\mu (dv_y/dy) \quad (2.3)$$

This states that the shear force per unit area is proportional to the negative of the local velocity gradient and is known as Newton’s law of viscosity. The sign convention used here follows that of Bird et al. (2007).

$\tau_{yx}$ can also be interpreted in another fashion. $\tau_{yx}$ may be considered as the viscous flux of $x$ momentum in the $y$ direction. The idea here is that the plate located at $y = H$ transmits its $x$ momentum to the layer below, which in turn transmits momentum to the next layer. The momentum flux, $\tau_{yx}$, is negative in this case as the momentum is transferred in the negative $y$ direction. The sign convention follows the ideas used for heat flux in that heat flows from hot to cold or in the direction of a negative temperature gradient. This also makes the law of viscosity fit with the ideas of diffusion in which matter flows in the direction of decreasing concentration.

Probably the most frequently used notation, however, is that found in mechanics in which material at greater $y$ exerts force in the $x$ direction on a layer of fluid at lesser $y$. The shear stress, $\tau^{*}_{xy}$, is then related to that used above as follows:

$$\tau_{yx} = -\tau^{*}_{xy} \quad (2.4)$$

$\tau^{*}_{xy}$ is then defined as the force per unit area acting in the $x$ direction by fluid at $y$ on a surface of lesser $y$ with a unit outward normal in the $+y$ direction.

The flow behavior of most thermoplastics does not follow Newton’s law of viscosity. To quantitatively describe the viscous behavior of polymeric fluids, Newton’s law of viscosity is generalized as follows:

$$\tau_{yx} = -\eta \frac{dv_y}{dy} \quad (2.5)$$

where $\eta$ can be expressed as a function of either $dv_y/dy$ or $\tau_{yx}$. Some typical responses of polymeric fluids are shown in Figure 2.4, where $\tau_{yx}$ is plotted versus the velocity gradient. For a pseudoplastic fluid the slope of the line decreases with increasing magnitude of $dv_y/dy$, or in essence the viscosity decreases. Some polymeric fluids (in some cases polymer blends and filled polymers) exhibit a yield stress, which is the stress that must be overcome before flow can occur. When flow occurs, if the slope of the line is constant, then the fluid is referred to as a Bingham fluid. In many cases the fluid is still pseudoplastic once flow begins. Finally, in some cases the viscosity of the material increases with increasing velocity gradient. The fluid is then referred to as dilatant.

Many empiricisms have been proposed to describe the steady-state relation between $\tau_{yx}$ and $dv_y/dy$, but we mention only a few that are most useful for polymeric fluids. The first is the power law of Ostwald–de Waele:

$$\eta = m \left| \frac{dv_y}{dy} \right|^{n-1} \quad (2.6)$$

This is a two-parameter model in which $n$ describes the degree of deviation from Newtonian behavior. $m$, which has the units of Pa·s$^n$, is called the consistency. For $n = 1$ and $m = \mu$, this model predicts Newtonian fluid behavior. For $n < 1$, the fluid is pseudoplastic while for $n > 1$ the fluid is dilatant. The Ellis model is a three-parameter model and is defined as

$$\frac{\eta_0}{\eta} = 1 + \left( \frac{\tau_{yx}}{\tau_{1/2}} \right)^{n-1} \quad (2.7)$$
Here \( \eta_0 \) is the zero shear viscosity and \( \tau_{1/2} \) is the value of \( \tau_{yx} \) when \( \eta = \frac{1}{2} \eta_0 \). Actually most polymeric fluids exhibit a constant viscosity at low shear rates and then shear thin at higher shear rates (see Fig. 2.5). A model that is used often in numerical calculations, because it fits the full flow curve, is the Bird–Carreau model:

\[
\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[ 1 + (\lambda \dot{\gamma})^2 \right]^{(n-1)/2}
\]  

(2.8)

When the 2’s in the exponents in Eq. 2.8 are replaced by \( a \)’s, where \( a \) is a parameter that controls the width of the transition from constant viscosity into the shear-thinning region, then the model is referred to as the Carreau–Yasuda model. This Bird–Carreau model contains four parameters: \( \eta_0, \eta_\infty, \lambda, \) and \( n \). \( \eta_0 \) is the zero shear viscosity just as above. \( \eta_\infty \) is the viscosity as the shear rate (\( \dot{\gamma} \)) or \( dv_x/dy \) \( \rightarrow \infty \), and for polymer melts this can be taken as zero. \( \lambda \) has units of seconds and approximately represents the reciprocal of the shear rate for the onset of shear thinning behavior. \( n \) represents the degree of shear thinning and is nearly the same as the value in the power-law model. As a number of polymeric fluids exhibit yield stresses, models that include these are the Bingham and Hershel–Bulkley models. The Bingham model is given as

\[
\eta = \mu_0 + \frac{|\tau_0|}{dv_x/dy} \quad \text{if} \quad |\tau_{yx}| \geq |\tau_0| \quad (2.9)
\]

\[
\eta = \infty \quad \text{if} \quad |\tau_{yx}| < |\tau_0| \quad (2.10)
\]

Here \( \tau_0 \) is the yield stress and \( \mu_0 \) is the slope of the line of \( \tau_{yx} - \tau_0 \) versus \( dv_x/dy \). The Hershel–Bulkley model is given as

\[
\eta = m' \left| \frac{dv_x}{dy} \right|^{n'-1} + \frac{|\tau_0|}{dv_x/dy} \quad \text{if} \quad |\tau_{yx}| \geq |\tau_0| \quad (2.11)
\]

Here \( m' \) and \( n' \) are power-law parameters determined from \( \tau_{yx} - \tau_0 \) versus \( dv_x/dy \). This model describes fluids that are pseudoplastic once flow starts.

Example 2.1. Power-Law and Ellis Model Parameters for LLDPE

Determine the power-law (Eq. 2.6) and Ellis (Eq. 2.7) model parameters for LLDPE (NTA 101) at 170 °C using the rheological data given in the Appendix Tables A.7–A.9.

Solution. To find the parameters \( m \) and \( n \) in Eq. 2.6 we first plot \( \ln \eta \) versus \( \ln \dot{\gamma} \) as shown in Figure 2.6. The slope of the line in the linear region is \( n - 1 \) and is estimated to be \(-0.576\). Hence, \( n \) is 0.424. \( m \) is found by taking the natural logarithm of both sides of Eq. 2.6:

\[
\ln \eta = \ln m + (n - 1) \ln \dot{\gamma} \quad (2.12)
\]

and then arbitrarily selecting values of \( \eta \) and \( \dot{\gamma} \) in the linear region. For example, by substituting \( \dot{\gamma} = 140 \text{ s}^{-1} \) and \( \eta = 1.45 \times 10^3 \text{ Pa·s} \) into Eq. 2.12, we find \( m \) to be \( 2.374 \times 10^4 \text{ Pa·s}^{n'} \).