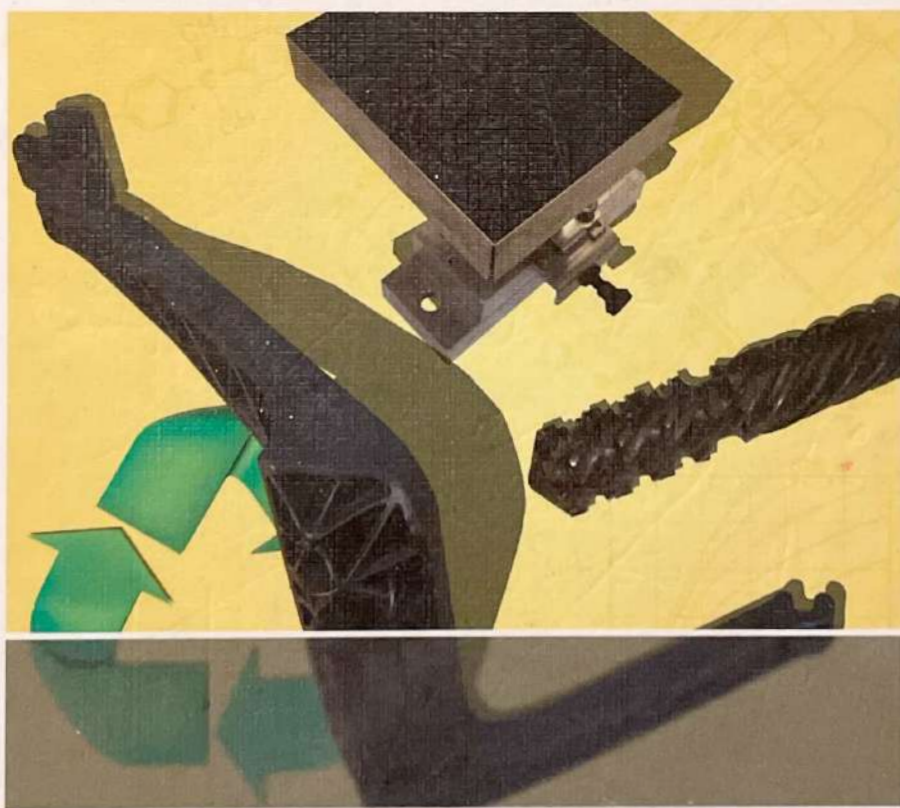


Tim A. Osswald
Georg Menges

Materials Science of Polymers for Engineers



3rd Edition

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Georg Menges

Material Science of Polymers for Engineers

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Preface to the First Edition

This book is designed to provide a polymer materials science background to engineering students and practicing engineers. It is written on an intermediate level for students, and as an introduction to polymer materials science for engineers. The book presents enough information that, in conjunction with a good design background, it will enable the engineer to design polymer components.

Materials Science of Polymers for Engineers is based on the German textbook, *Werkstoffkunde Kunststoffe* (G. Menges, Hanser Publishers, 1989), and on lecture notes from polymer materials science courses taught at the Technical University of Aachen, Germany, and at the University of Wisconsin-Madison.

The chapters on thermal and electrical properties are loose translations from *Werkstoffkunde Kunststoffe*, and many figures throughout the manuscript were taken from this book. We have chosen a unified approach and have divided the book into three major sections: Basic Principles, Influence of Processing on Properties, and Engineering Design Properties. This approach is often referred to as the four P's: polymer, processing, product and performance. The first section covers general topics such as historical background, basic material properties, molecular structure of polymers and thermal properties of polymers. The second section ties processing and design by discussing the effects of processing on properties of the final polymer component. Here, we introduce the reader to the rheology of polymer melts, mixing of polymer blends, development of anisotropy during processing and solidification processes. In essence, in this section we go from the melt (rheology) to the finished product (solidification). The third section covers the different properties that need to be considered when designing a polymer component, and analyzing its performance. These properties include mechanical properties, failure of polymers, electrical properties, optical properties, acoustic properties, and permeability of polymers. The authors cannot acknowledge everyone who helped in one way or another in the preparation of this manuscript. We would like to thank the students of our polymer materials science courses who in the past few years endured our experimenting and trying out of new ideas. The authors are grateful to the staff and faculty of the Mechanical Engineering Department at the University of Wisconsin-Madison, and the Institut für Kunststoffverarbeitung (IKV) at the Technical University of Aachen for their support while developing the courses which gave the base for this book. We

are grateful to Richard Theriault for proofreading the entire manuscript. We also thank the following people who helped proofread or gave suggestions during the preparation of the book: Susanne Belovari, Bruce A. Davis, Jeffrey Giacomini, Paul J. Gramann, Matthew Kaegebein, Gwan-Wan Lai, Maria del Pilar Noriega E., Antoine C. Rios B., Linards U. Stradins and Ester M. Sun, Susanne Belovari and Andrea Jung-Mack are acknowledged for translating portions of *Werkstoffkunde Kunststoffe* from German to English. We also thank Tara Ruggiero for preparing the camera-ready manuscript. Many of the figures were taken from class notes of the mechanical engineering senior elective course Engineering Design with Polymers. Special thanks are offered to Lynda Litzkow, Philipp Ehrenstein and Bryan Hutchinson for the superb job of drawing those figures. Matthias Mahlke of Bayer AG in Leverkusen, Germany, Laura Dietsche, Joseph Dooley and Kevin Hughes of Dow Chemical in Midland, Michigan, and Mauricio DeGreif and Juan Diego Sierra of the ICIPC in Medellín, Colombia, are acknowledged for some of the figures. Thanks are due to Marcia Sanders for copy editing the final manuscript. We are grateful to Wolfgang Glenz, Martha Kürzl, Ed Immergut and Carol Radtke of Hanser Publishers for their support throughout the development of this book. Above all, the authors thank their wives for their patience.

Summer 1995

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Preface to the Third Edition

The first edition of this book was adopted by several universities in North and South America, Europe, and Asia as a textbook to introduce engineering students to the materials science of polymers. The book was also translated into Japanese in 1998, Korean in 1999, and Spanish in 2008. The professors who taught with the first and second editions as well as their students liked the unified approach we took. The changes and additions that were introduced in this edition are based on suggestions from these professors and their students, as well as from our own experience using it as a class textbook.

After two revisions and two decades of teaching it has become clear that sustainability and profits are important when dealing with polymeric materials. Therefore the 4P's of the first edition have expanded to the 6P's in the third edition: polymer, processing, product, performance, post-consumer life, and profit. In the last 18 years, this book has become a reference for many practicing engineers, most of whom were introduced to the book as students. The first and second editions were praised because of the vast number of graphs and data that can be used as references. We have further strengthened this attribute by expanding a comprehensive table in the appendix that contains material property graphs for several polymers. Furthermore, in this edition we added color to the figures and graphs, making the book more appealing to the reader.

With this edition we owe our gratitude to Dr. Christine Strohm for editing the book and catching those small typos and inconsistencies in the text and equations. We thank Dr. Nadine Warkotsch and Steffen Joerg of Hanser Publishers for their cooperation during the production of this book. We are grateful to Luz Mayed D. Noguez and Tobias Mattner for the superb job drawing the figures, and to Tobias Mattner for his suggestions on how to make many of the figures more understandable. A special thanks to Katerina Sánchez for the graphs related to recycling of plastics in Chapter 1 and to Nora Catalina Restrepo for generating the polymer statistic graphs in Chapter 2. My graduate students Roberto Monroy, Luisa López, Tom Mulholland, Jakob Onken, Camilo Pérez, Daniel Ramírez, Jochen Wellekoetter and Yuxiao Zhang, organized by William Aquite, supplied extra problems and solutions for the third edition; thank you. Special thanks to Diane for – as always – serving as a sounding board and advisor during this project.

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Madison, Wisconsin, USA

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Appendix IV – Balance Equations

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Momentum Balance

Momentum Equation in Terms of τ

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3

Structure of Polymers

■ 3.1 Macromolecular Structure of Polymers

Polymers are macromolecular structures that are generated either synthetically or through natural processes. Cotton, silk, natural rubber, ivory, amber, and wood are a few materials that occur naturally with an organic macromolecular structure, whereas natural inorganic materials include quartz and glass. The other class of organic materials with a macromolecular structure is represented by synthetic polymers, which are generated through addition or *chain growth polymerization*, and condensation or *radical initiated polymerization*.

In the course of addition polymerization, monomers are added to each other by breaking the double-bonds between carbon atoms, allowing them to link to neighboring carbon atoms to form long chains. The simplest example is the addition of ethylene monomers, schematically shown in Fig. 3.1, to form polyethylene molecules, as shown in Fig. 3.2. Polyethylene may be depicted schematically as in Fig. 3.2 or using a symbolic representation as in Fig. 3.3. Here, the subscript n represents the number of repeat units, which determines the molecular weight of a polymer. The number of repeat units is more commonly referred to as the degree of polymerization. Other examples of addition polymerization include polypropylene, polyvinyl chloride, and polystyrene. The side groups, such as CH_3 for polypropylene and Cl for polyvinyl chloride, are sometimes referred to as the *X groups*.

Another technique to produce macromolecular materials is condensation polymerization. Condensation polymerization occurs when mixing two components with end-groups that react with each other. When they are stoichiometric, these end-groups react, linking them to chains leaving a by-product such as water. A common polymer made by condensation polymerization is polyamide, where diamine and diacid groups react to form polyamide and water, as explained in Chapter 2.

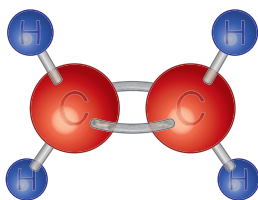


Figure 3.1 Schematic representation of an ethylene monomer

At the molecular level, there are several forces that hold a polymeric material together. The most basic forces present are covalent bonds that hold together the backbone of a polymer molecule, such as the -C-C bond. The energy needed to hold together two carbon atoms is about 350 kJ/mol, which when translated would result in a polymer component strength between 1.4×10^4 and 1.9×10^4 MPa. However, as will be seen in Chapter 9, the strength of polymers only ranges between 10 and 100 MPa.

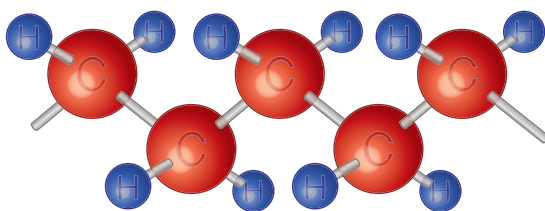


Figure 3.2 Schematic representation of a polyethylene molecule

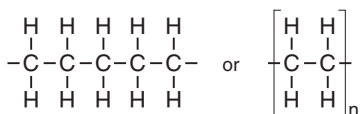


Figure 3.3 Symbolic representation of a polyethylene molecule

■ 3.2 Molecular Bonds and Inter-Molecular Attraction

Because of the comparatively low strength found in polymer components, it can be deduced that the forces holding a polymer component together do not come from the -C-C bonds but from intermolecular forces, or the so-called *Van-der-Waals forces*. The energy that generates the inter-molecular attraction between two polymer molecules increases as the molecules come closer to each other by

$$F \sim \frac{1}{r^6} \quad (3.1)$$

where $F < 10$ kJ/mol and r is the distance between the molecules. Thus, it becomes clear that as a polymer sample is heated, the distance between the molecules increases as the vibration amplitude of the molecules increases. The vibration amplitude increase allows the molecules to move more freely, enabling the material to flow at the macroscopic level.

Another important point is that as solvents are introduced between the molecules, the inter-molecular separation increases, which leads to a reduction in stiffness. This concept can be implemented by introducing *plasticizers* into the material, thus lowering the glass transition temperature below room temperature and bringing out rubber elastic material properties.

■ 3.3 Molecular Weight

A polymeric material may consist of polymer chains of various lengths or repeat units. Hence, the molecular weight is determined by the average or mean molecular weight, which is defined by

$$\bar{M} = \frac{W}{N} \quad (3.2)$$

where W is the weight of the sample and N the number of moles in the sample.

The properties of polymeric materials are strongly linked to the molecular weight of the polymer, as shown schematically in Fig. 3.4. A polymer such as polystyrene is stiff and brittle at room temperature with a degree of polymerization of 1,000. However, at a degree of polymerization of 10, polystyrene is sticky and soft at room temperature. Figure 3.5 shows the relation between molecular weight, temperature, and properties of a typical polymeric material. The stiffness properties reach an asymptotic maximum, whereas viscosity and the flow temperature increase

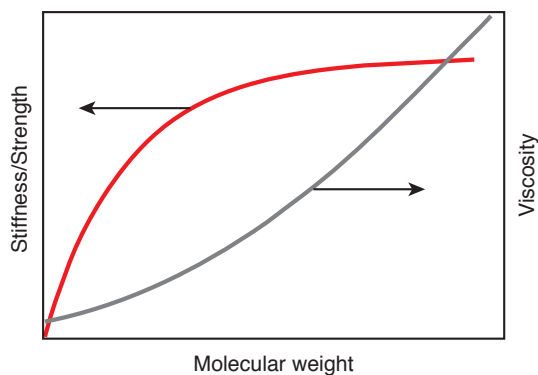


Figure 3.4 Influence of molecular weight on mechanical properties

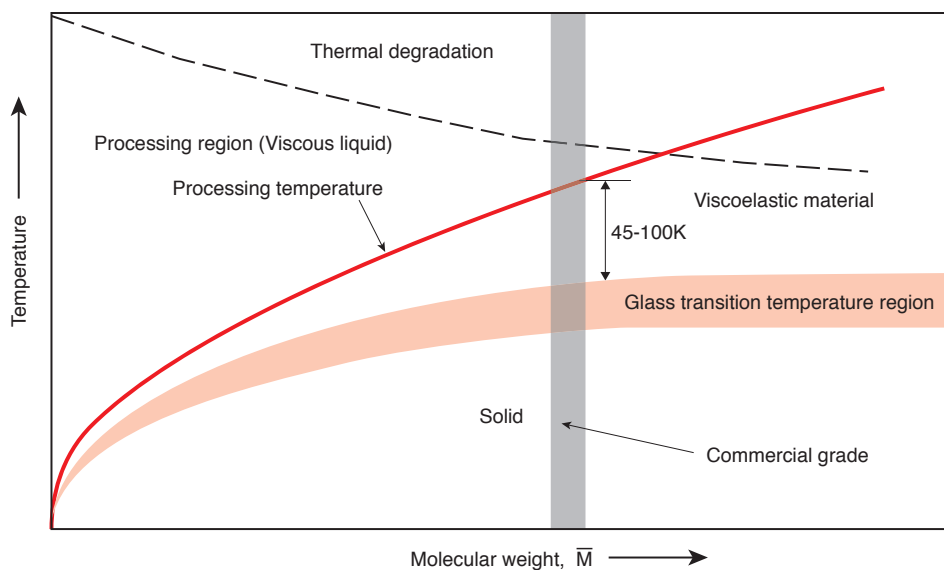


Figure 3.5 Diagram representing the relation between molecular weight, temperature, and properties of a typical thermoplastic

with molecular weight. On the other hand, the degradation temperature steadily decreases with increasing molecular weight. Hence, it is necessary to find the molecular weight that renders ideal material properties for the finished plastic product, while ensuring flow properties that make it easy to shape the material during the manufacturing process. It is important to mention that the temperature scale in Fig. 3.5 corresponds to a specific time scale, e.g., time required for a polymer molecule to flow through an extrusion die. If the time scale is reduced (e.g., by increasing the extruder throughput), the molecules have more difficulty sliding past each other. This would require a somewhat higher temperature to assure flow. In fact, at a specific temperature, a polymer melt may behave as a solid when the time scale is reduced sufficiently. Hence, for this new time scale the stiffness properties and flow temperature curves must be shifted upward on the temperature scale. A limiting factor is the fact that the thermal degradation curve remains fixed, limiting processing conditions to remain above certain time scales. This relation between time, or time scale, and temperature will be discussed in more detail later in this chapter.

With the exception of maybe some naturally occurring polymers, most polymers have a molecular weight distribution such as shown in Fig. 3.6. For such a molecular weight distribution function, we can define a number average, weight average, and viscosity average¹. The number average is the first moment and the weight

¹ There are other definitions of molecular weight that depend on the type of measuring technique.

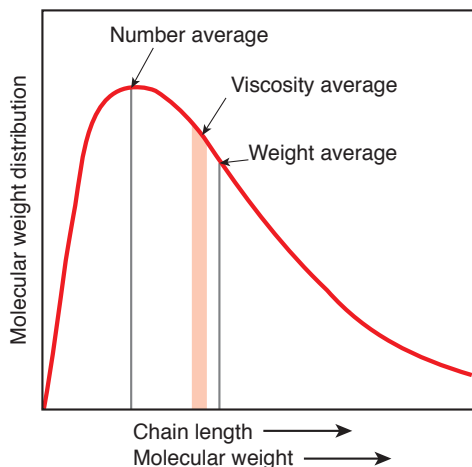


Figure 3.6 Molecular weight distribution of a typical thermoplastic

average the second moment of the distribution function. In terms of mechanics this is equivalent to the center of gravity and the radius of gyration as first and second moments, respectively. The number average is defined by

$$\bar{M}_n = \frac{\sum m_i}{\sum n_i} = \frac{\sum n_i M_i}{\sum n_i} \quad (3.3)$$

where m_i is the weight, M_i the molecular weight and n_i the number of molecules with i repeat units. The weight average is calculated using

$$\bar{M}_w = \frac{\sum m_i M_i}{\sum m_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} \quad (3.4)$$

Another form of molecular weight average is the *viscosity average*, which is calculated using

$$\bar{M}_v = \left(\frac{\sum m_i M_i^{\alpha+1}}{\sum m_i} \right)^{1/\alpha} \quad (3.5)$$

where α is a material dependent parameter which relates the *intrinsic viscosity*, $[\eta]$, to the molecular weight of the polymer. This relation is sometimes referred to as *Mark-Houwink relation* and is written as

$$[\eta] = k \bar{M}_v^\alpha \quad (3.6)$$

Figure 3.7 [1] presents the viscosity of various undiluted polymers as a function of molecular weight. The figure shows how for all these polymers the viscosity goes from a linear dependence for $\alpha = 1$ to a power law dependence for $\alpha = 3.4$ at some

critical molecular weight. The linear relation is sometimes referred to as Staudinger's rule [2] and applies to a perfectly *monodispersed polymer*². For monodispersed polymers we can write

$$\bar{M}_w = \bar{M}_n = \bar{M}_v \tag{3.7}$$

and for a polydispersed polymer³

$$\bar{M}_w > \bar{M}_v > \bar{M}_n \tag{3.8}$$

A measure of the broadness of a polymer's molecular weight distribution is the *polydispersity index* defined by

$$PI = \frac{\bar{M}_w}{\bar{M}_n} \tag{3.9}$$

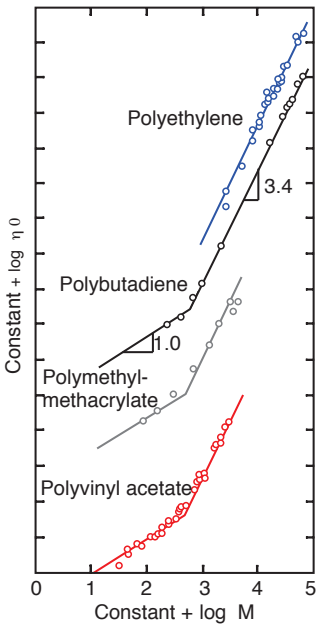


Figure 3.7 Zero shear rate viscosity η_0 for various polymers as a function of weight average molecular weight

Figure 3.8 [3] presents a plot of flexural strength versus melt flow index⁴ for polystyrene samples with three different polydispersity indices. The figure shows that low polydispersity index grade materials render higher strength properties and flowability, or processing ease, than high polydispersity index grades. Table 3.1 summarizes relations between polydispersity index, processing, and material

² A monodispersed polymer is composed of a single molecular weight species.
³ In most cases, polymers are polydispersed systems containing a range of molecular weights.
⁴ The melt flow index is the mass (grams) extruded through a capillary in a 10-min. period while applying a constant pressure. Increasing melt flow index signifies decreasing molecular weight. The melt flow index is discussed in more detail in Chapter 5.

properties of a polymer. Figure 3.9 is a graphical representation of the influence of number average and weight average on properties of polymers. The arrows in the diagram indicate an increase in any specific property.

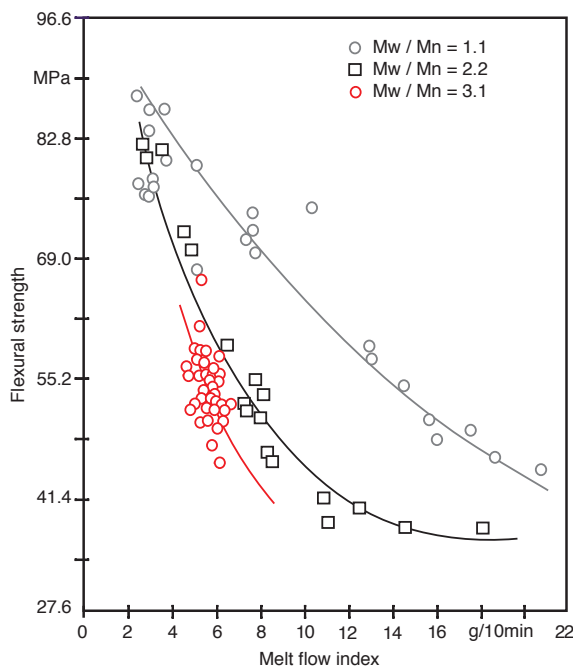


Figure 3.8 Effect of molecular weight on the strength-melt flow index interrelationship of polystyrene for three polydispersity indices

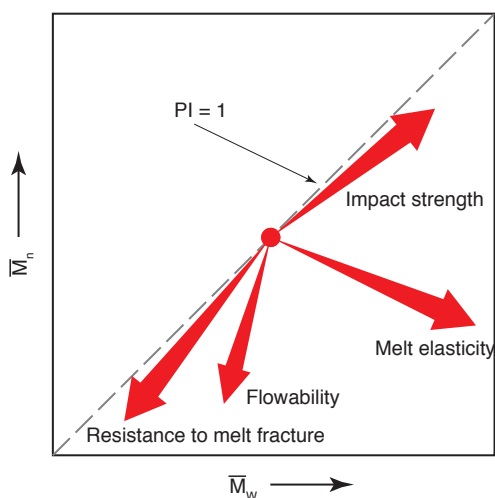


Figure 3.9 Influence of molecular weight number average and weight average on properties of thermoplastic polymers

Table 3.1 Effect of Molecular Weight on Processing and Properties of Polymers

$\overline{M}_w / \overline{M}_n > 1$ Processing	$\overline{M}_w / \overline{M}_n = 1$ Properties
<i>Injection Molding:</i> Longer cycle times caused by slow crystallization and low thermal conductivity.	Narrow distribution leads to higher impact strength. Short molecules lead to easy ripping.
<i>Extrusion:</i> Melt fracture is less likely to occur as short molecules act as lubricants.	
	Higher degree of extrudate swell caused by the long molecules.

■ 3.4 Conformation and Configuration of Polymer Molecules

The conformation and configuration of the polymer molecules have great influence on the properties of the polymer component.

The conformation describes the preferential spatial positions of the atoms in a molecule, which is described by the polarity flexibility and regularity of the macromolecule. Typically, carbon atoms are tetravalent, which means that they are surrounded by four substituents in a symmetric tetrahedral geometry.

The most common example is methane, CH₄, schematically depicted in Fig. 3.10. As the figure demonstrates, the tetrahedral geometry sets the bond angle at 109.5°. This angle is maintained between carbon atoms on the backbone of a polymer mol-

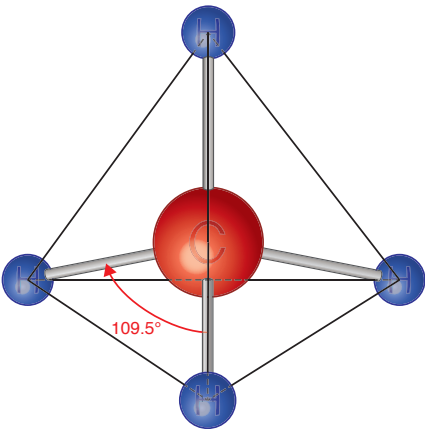


Figure 3.10 Schematic of tetrahedron formed by methane (CH₄)

ecule, as shown in Fig. 3.11. The figure also illustrates that each individual axis in the carbon backbone is free to rotate.

The configuration provides information about the distribution and spatial organization of the molecule. During polymerization it is possible to place the X groups on the carbon-carbon backbone in different directions. The order in which they are arranged is called the *tacticity*. The polymers with side groups that are placed in a random matter are called *atactic*. The polymers whose side groups are all on the same side are called *isotactic*, and those molecules with regularly alternating side groups are called *syndiotactic*.

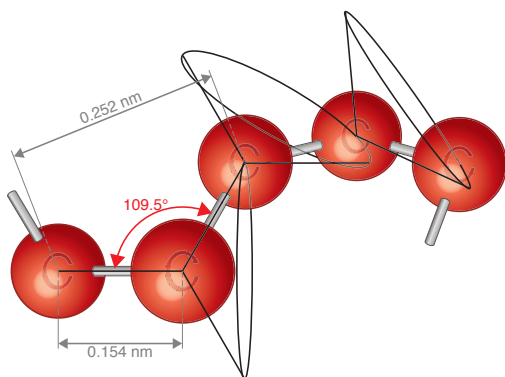
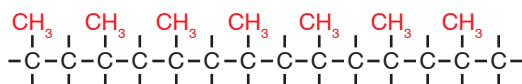
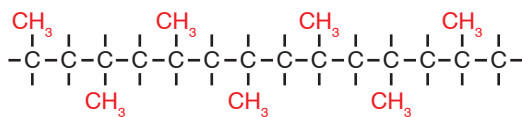


Figure 3.11 Random conformation of a polymer chain's carbon-carbon backbone

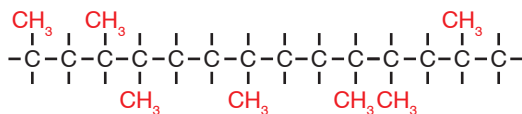
Figure 3.12 shows the three different tacticity cases for polypropylene. The tacticity in a polymer determines the degree of crystallinity that a polymer can reach. For example, polypropylene with a high isotactic content will reach a high degree of crystallinity and as a result will be stiff, strong, and hard.



Isotactic



Syndiotactic



Atactic

Figure 3.12 Different polypropylene structures

Another type of geometric arrangement arises with polymers that have a double bond between carbon atoms. Double bonds restrict the rotation of the carbon atoms about the backbone axis. These polymers are sometimes referred to as geometric isomers. The X groups may be on the same side (cis-) or on opposite sides (trans-) of the chain, as schematically shown for polybutadiene in Fig. 3.13. The arrangement in a cis-1,4-polybutadiene results in a very elastic rubbery material, whereas the structure in the trans-1,4-polybutadiene results in a leathery and tough material. A cis-1,4-polybutadiene can be used to manufacture the outer tread of an automotive tire. A trans-1,4-polybutadiene can be used to make the outer skin of a golf ball. The same geometric arrangement is found in natural rubber, polyisoprene. The cis-1,4-polyisoprene is the elastic natural rubber used for the body of a tire, and the latex used to manufacture “rubber” gloves and condoms. The trans-1,4-polyisoprene, or the so-called *gutta percha* or *ebony*, was used to make dentures, statues, and other decorative items in the 1800s.

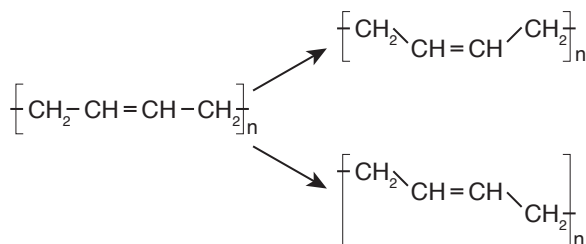


Figure 3.13 Symbolic representation of cis-1,4- and trans-1,4-polybutadiene molecules

Branching of the polymer chains also influences the final structure, crystallinity, and properties of the polymeric material. Figure 3.14 shows the molecular architecture of high density, low density, and linear low density polyethylene.

High density polyethylene has between 5 and 10 short branches every 1000 carbon atoms. The low density material has the same number of branches as HDPE; however, they are much longer and are usually branched themselves. LLDPE has between 10 and 35 short chains every 1000 carbon atoms. Polymer chains with fewer and shorter branches can crystallize with more ease, resulting in higher density.

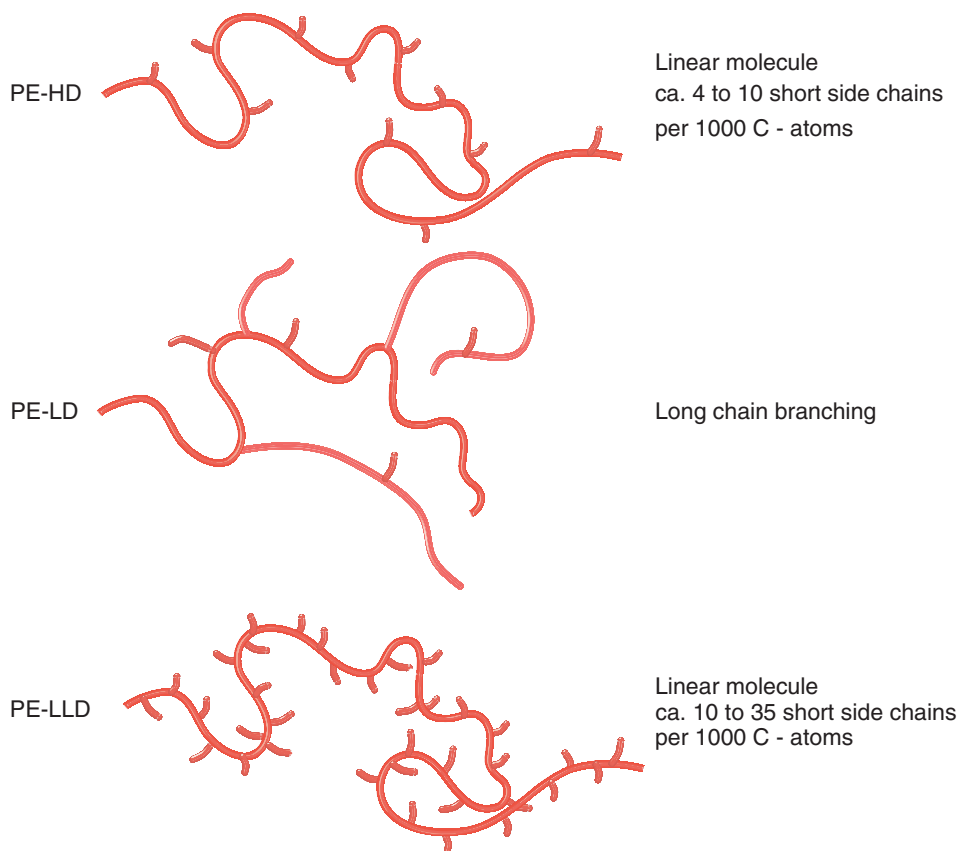


Figure 3.14 Schematic of the molecular structure of polyethylene with different densities

■ 3.5 Arrangement of Polymer Molecules

As mentioned in Chapter 1, polymeric materials can be divided into two general categories: thermoplastics and thermosets. Thermoplastics are materials that have the ability to remelt after they have solidified, and thermosets are those that solidify via a chemical reaction that causes polymer molecules to cross-link. These cross-linked materials cannot be remelted after solidification.

As thermoplastic polymers solidify, they take on two different types of structure: amorphous or semi-crystalline. Amorphous polymers are those where the molecules solidify in a random arrangement, whereas some of the molecules in semi-crystalline polymers align with their neighbors, forming regions with a three-dimensional order. In semi-crystalline polymers, the molecules that do not align into crystals remain amorphous structures.

3.5.1 Thermoplastic Polymers

The formation of macromolecules from monomers occurs if there are unsaturated carbon atoms (carbon atoms connected with double bonds), or if there are monomers with reactive end-groups. The double bond, say in an ethylene monomer, is split, which frees two valences per monomer and leads to the formation of a macromolecule such as polyethylene. This process is often referred to as polymerization. Similarly, monomers (R) that possess two reactive end-groups (bifunctional) can react with other monomers (R') that also have two other reactive end-groups that can react with each other, also leading to the formation of a polymer chain. A list of typical reactive end-groups is given in Table 3.2.

Table 3.2 List of Selected Reactive End-Groups

Hydrogen in aromatic monomers	–H
Hydroxyl group in alcohols	–OH
Aldehyde group as in formaldehyde	$\begin{array}{c} \text{H} \\ \\ -\text{C} \\ \\ \text{O} \end{array}$
Carboxyl group in organic acids	$\begin{array}{c} \text{OH} \\ \\ -\text{C} \\ \\ \text{O} \end{array}$
Isocyanate group in isocyanates	–N=C=O
Epoxy group in polyepoxys	$\begin{array}{c} \text{CH} - \text{CH}_2 \\ \quad \diagup \\ \text{O} \end{array}$
Amido groups in amides and polyamides	–CO–NH ₂
Amino groups in amines	–NH ₂

3.5.2 Amorphous Thermoplastics

Amorphous thermoplastics, with their randomly arranged molecular structure, are analogous to a bowl of spaghetti. Due to their random structure, the characteristic size of the largest ordered region is on the order of a carbon-carbon bond. This dimension is much smaller than the wavelength of visible light and so generally amorphous thermoplastics are transparent.

Figure 3.15 [4] shows the shear modulus⁵, G' , versus temperature for polystyrene, one of the most common amorphous thermoplastics. The figure shows two general

⁵ The dynamic shear modulus, G' , is obtained using the dynamic mechanical properties test described in Chapter 9.

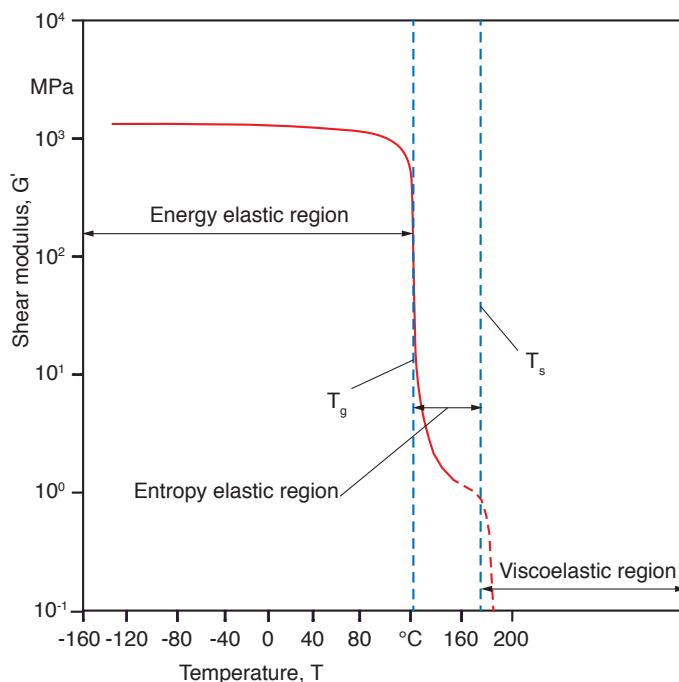


Figure 3.15 Shear modulus of polystyrene as a function of temperature

regions: one where the modulus appears fairly constant⁶, and one where the modulus drops significantly with increasing temperature. With decreasing temperatures, the material enters the glassy region where the slope of the modulus approaches zero. At high temperatures the modulus is negligible and the material is soft enough to flow. Although there is not a clear transition between “solid” and “liquid”, the temperature that divides the two states in an amorphous thermoplastic is referred to as the *glass transition temperature*, T_g . For the polystyrene in Fig. 3.15 the glass transition temperature is approximately 110 °C. At temperatures below the glass transition temperature the material behaves like a viscoelastic solid, the area in the curve denoted as *energy elastic region*. Once the material is above the glass transition temperature, it enters the so-called *entropy elastic region*. At this point the material can be more easily deformed, such as is done during the thermoforming process. However, in order for the material to flow, its temperature must be above a softening temperature, T_s , at which point it behaves like a viscoelastic fluid. The softening temperature defines the point where the viscous forces during deformation (loss) exceed the elastic forces during deformation (storage), and for amorphous thermoplastics it typically ranges about 50 K

⁶ When plotting G' versus temperature on a linear scale, a steady decrease of the modulus is observed.

above the glass transition temperature. Storage and loss moduli are discussed in more detail in Chapter 10.

It should be mentioned here that the curve shown in Fig. 3.15 was measured at a constant frequency. If the frequency of the test is increased – reducing the time scale – the curve is shifted to the right, because higher temperatures are required to achieve movement of the molecules at the new frequency. Figure 3.16 [5] demonstrates this concept by displaying the elastic modulus as a function of temperature for polyvinyl chloride at various test frequencies. The relation between time scale and temperature, also known as the *time-temperature superposition principle*, is discussed in detail Chapter 9. A similar effect as observed with time scale and temperature can be seen when the molecular weight of the material is increased. The longer molecules have more difficulty sliding past each other, thus requiring higher temperatures to achieve “flow.”

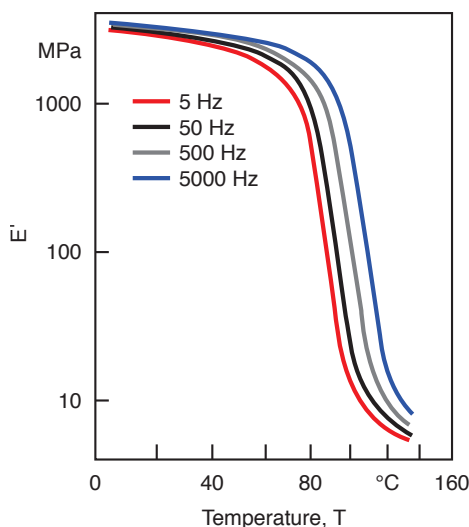


Figure 3.16 Modulus of polyvinyl chloride as a function of temperature at various test frequencies

3.5.3 Semi-Crystalline Thermoplastics

Semi-crystalline thermoplastic polymers show more order than amorphous thermoplastics. The molecules arrange in an ordered crystalline form as shown for polypropylene in Fig. 3.17. The crystalline structure shown in the photograph is composed of *spherulites*, which are formed by *lamellar crystals*. The formation of spherulites during solidification of semi-crystalline thermoplastics is covered in Chapter 8. The schematic in Fig. 3.18 shows the general structure and hierarchical arrangement in semi-crystalline materials, using polyethylene as an example. The spherulitic structure is the largest domain with a specific order and has a characteristic size of 50 to 500 μm . Some of the polypropylene spherulites in the

micrograph presented in Fig. 3.17 are about 150 μm in diameter. The size of spherulites is much larger than the wavelength of visible light, making semi-crystalline materials translucent and not transparent.

However, the crystalline regions are very small with molecular chains comprised of both crystalline and amorphous regions. The degree of crystallinity in a typical thermoplastic will vary from grade to grade. For example, in polyethylene the degree of crystallinity depends on the branching and the cooling rate. A low density polyethylene (LDPE) with its long branches (Fig. 3.14) can only crystallize to approximate 40 – 50 %, whereas a high density polyethylene (HDPE) crystallizes to up to 80 %. The density and strength of semi-crystalline thermoplastics increase with the degree of crystallinity, as demonstrated in Table 3.3 [6], which compares low and high density polyethylene. Figure 3.19 shows the different properties and molecular structure that may arise in polyethylene plotted as a function of degree of crystallinity and molecular weight.

Table 3.3 Influence of Crystallinity on Properties for Low and High Density Polyethylene

Property	Low density	High density
Density (g/cm^3)	0.91 – 0.925	0.941 – 0.965
% crystallinity	42 – 53	64 – 80
Melting temperature ($^{\circ}\text{C}$)	110 – 120	130 – 136
Tensile modulus (MPa)	17 – 26	41 – 124
Tensile strength (MPa)	4.1 – 16	21 – 38

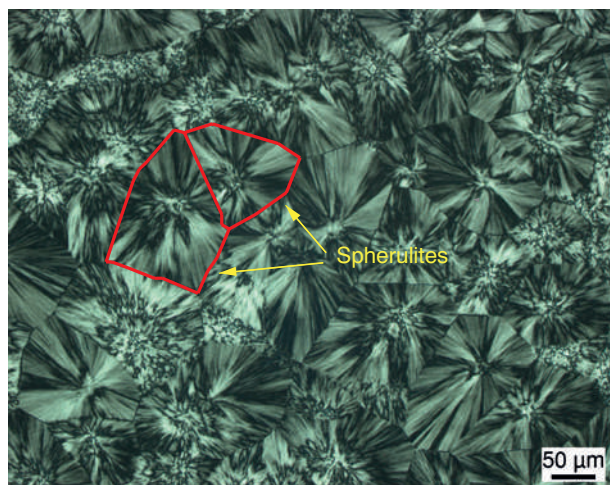


Figure 3.17 Micrograph of the spherulitic crystalline structure in a polypropylene polymer (Courtesy of the Institute of Plastics Technology, LKT, University of Erlangen-Nuremberg)

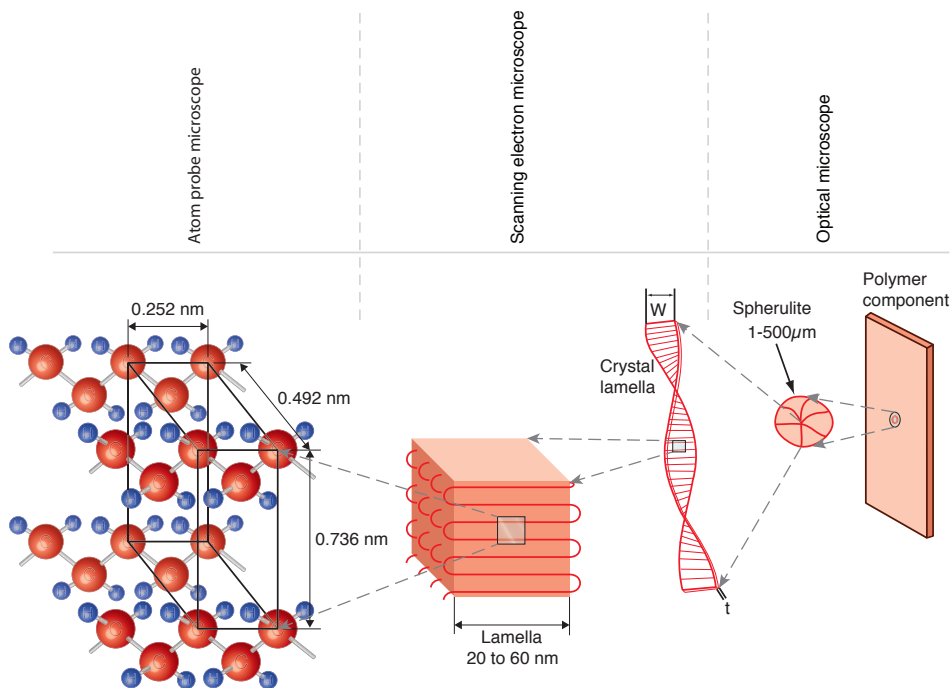


Figure 3.18 Schematic representation of the general molecular structure and arrangement of typical semi-crystalline materials

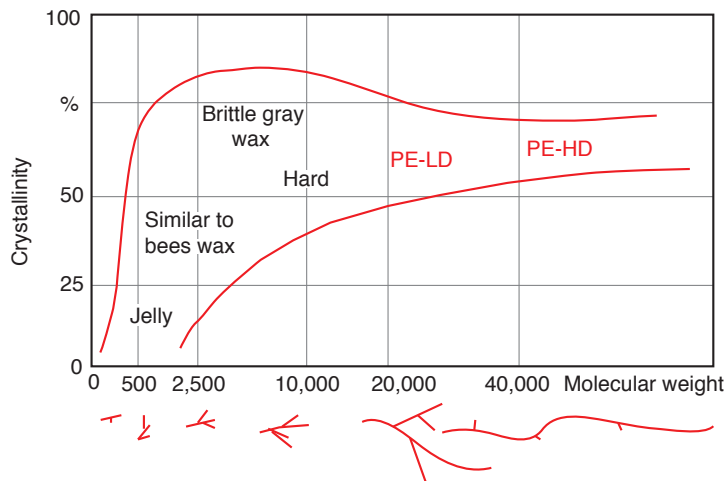


Figure 3.19 Influence of degree of crystallinity and molecular weight on different properties of polyethylene

Figure 3.20 [4] shows the dynamic shear modulus versus temperature for a high density polyethylene, the most common semi-crystalline thermoplastic. Again, this curve presents data measured at one test frequency. The figure clearly shows two distinct transitions: one at about $-110\text{ }^{\circ}\text{C}$, the *glass transition temperature*, and another near $140\text{ }^{\circ}\text{C}$, the *melting temperature*. Above the melting temperature, the shear modulus is negligible and the material will flow. Crystalline arrangement begins to develop as the temperature decreases below the melting point. Between the melting and glass transition temperatures, the material behaves like a leathery solid. As the temperature decreases below the glass transition temperature, the amorphous regions within the semi-crystalline structure solidify, forming a glassy, stiff, and in some cases brittle polymer.

To summarize, Table 3.4 presents the basic structure of several amorphous and semi-crystalline thermoplastics with their melting and/or glass transition temperatures.

Furthermore, Fig. 3.21 [7] summarizes the property behavior of amorphous, crystalline, and semi-crystalline materials using schematic diagrams of material properties plotted as functions of temperature.

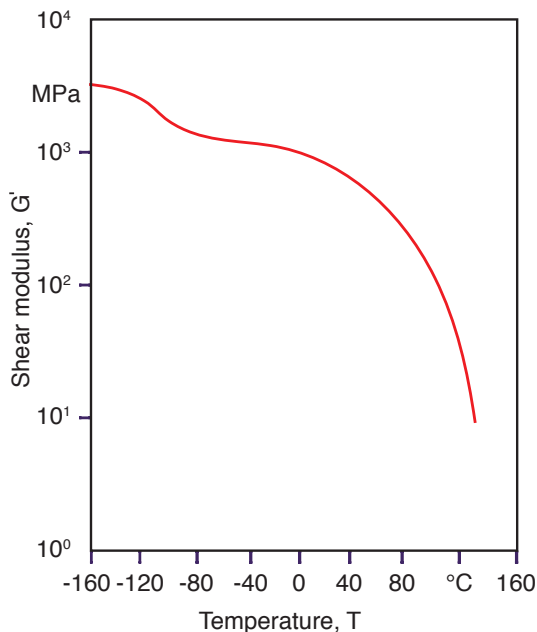


Figure 3.20 Shear modulus of a high density polyethylene as a function of temperature

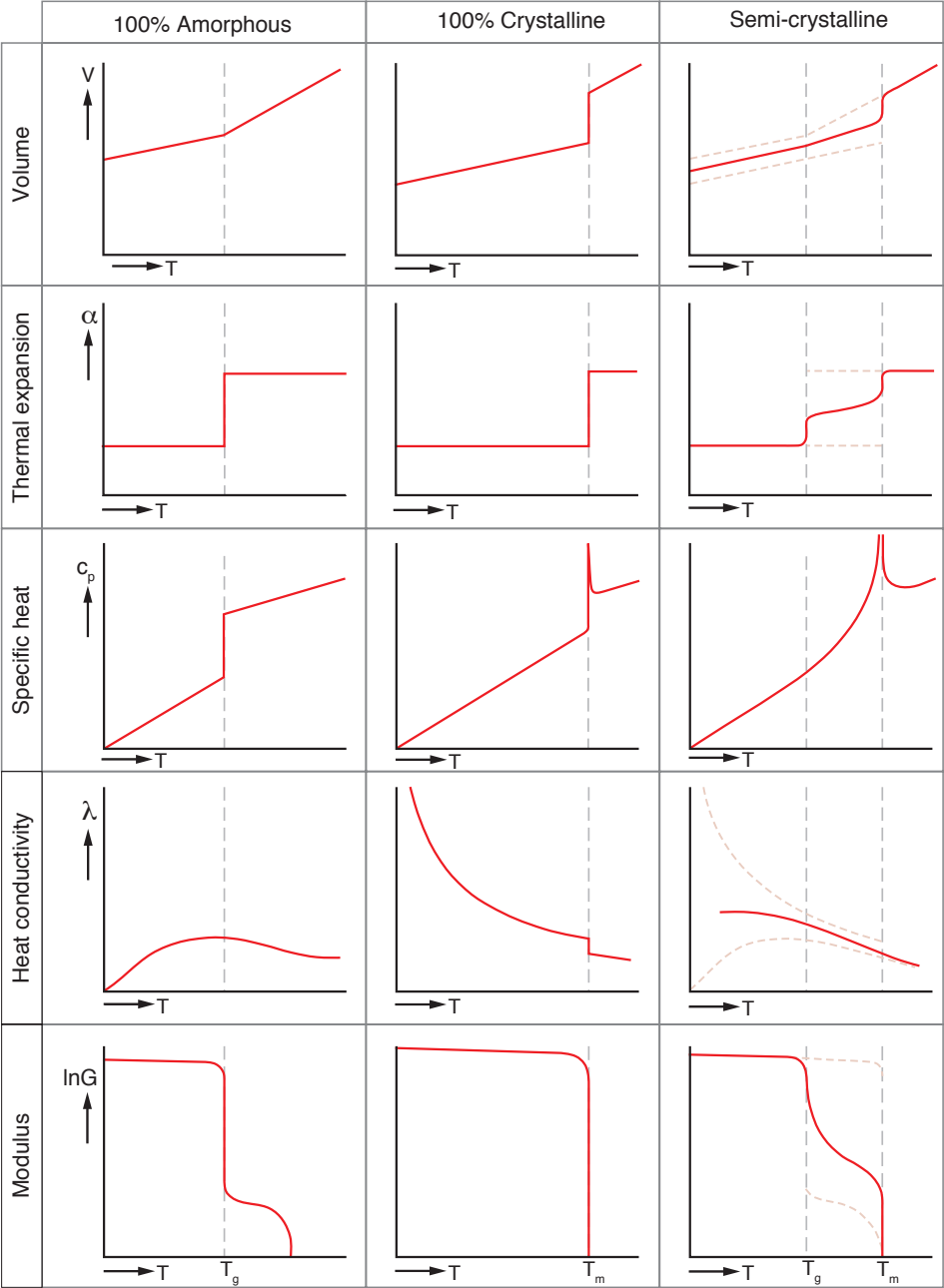


Figure 3.21 Schematic of the behavior of some polymer properties as a function of temperature for different thermoplastics

Table 3.4 Structural Units for Selected Polymers with Glass Transition and Melting Temperatures

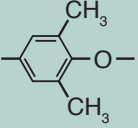
Structural unit	Polymers	
$-\text{CH}_2-\text{CH}_2-$	Linear polyethylene	$T_g = -125\text{ }^\circ\text{C}$ $T_m = 135\text{ }^\circ\text{C}$
$-\text{CH}_2-\underset{\text{CH}_3}{\underset{ }{\text{CH}}}-$	Isotactic polypropylene	$T_g = -20\text{ }^\circ\text{C}$ $T_m = 170\text{ }^\circ\text{C}$
$-\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\underset{ }{\text{CH}}}-$	Isotactic polybutene	$T_g = -25\text{ }^\circ\text{C}$ $T_m = 135\text{ }^\circ\text{C}$
$-\text{CH}_2-\underset{\text{CH}-\text{CH}_3}{\underset{ }{\text{CH}}}-$ $\quad\quad\quad $ $\quad\quad\quad\text{CH}_3$	Isotactic poly-3-methylbutene-1	$T_g = 50\text{ }^\circ\text{C}$ $T_m = 310\text{ }^\circ\text{C}$
$\begin{array}{c} \\ \text{CH}_2 \\ \\ \text{CH}-\text{CH}_2-\underset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_3 \\ \end{array}$	Isotactic poly-4-methylpentene-1	$T_g = 29\text{ }^\circ\text{C}$ $T_m = 240\text{ }^\circ\text{C}$
$-\text{CH}_2-\underset{\text{C}_6\text{H}_5}{\underset{ }{\text{CH}}}-$	Isotactic polystyrene	$T_g = 100\text{ }^\circ\text{C}$ $T_m = 240\text{ }^\circ\text{C}$
	Polyphenyleneether (PPE)	$T_g = 210\text{ }^\circ\text{C}$ $T_m = 261\text{ }^\circ\text{C}$

Table 3.4 Structural Units for Selected Polymers (*continued*)

Structural unit	Polymers	
$\begin{array}{c} \text{—O—CH—} \\ \\ \text{CH}_3 \end{array}$	Polyacetaldehyde	$T_g = -30\text{ }^\circ\text{C}$ $T_m = 165\text{ }^\circ\text{C}$
$\text{—O—CH}_2\text{—}$	Polyformaldehyde (polyacetal, polyoxymethylene)	$T_g = -85\text{ }^\circ\text{C}$ $T_m \approx 190\text{ }^\circ\text{C}$
$\begin{array}{c} \text{—O—CH—CH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$	Isotactic polypropyleneoxide	$T_g = -75\text{ }^\circ\text{C}$ $T_m = 75\text{ }^\circ\text{C}$
$\begin{array}{c} \text{CH}_2\text{—Cl} \\ \\ \text{—O—CH}_2\text{—C—CH}_2\text{—} \\ \\ \text{CH}_2\text{—Cl} \end{array}$	Poly-[2.2-bis-(chloromethyl)- trimethylene-oxide]	$T_g = 5\text{ }^\circ\text{C}$ $T_m = 181\text{ }^\circ\text{C}$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{—CH}_2\text{—C—} \\ \\ \text{CO}_2\text{—CH}_3 \end{array}$	Isotactic polymethylmeth- acrylate	$T_g = 50\text{ }^\circ\text{C}$ $T_m = 160\text{ }^\circ\text{C}$
$\begin{array}{cc} \text{Cl} & \text{F} \\ & \\ \text{—C—} & \text{—C—} \\ & \\ \text{F} & \text{F} \end{array}$	Polychlorotrifluoroethylene	$T_g = 45\text{ }^\circ\text{C}$ $T_m = 220\text{ }^\circ\text{C}$
$\text{—CF}_2\text{—CF}_2\text{—}$	Polytetrafluoroethylene	$T_{g1} = -113\text{ }^\circ\text{C}$ $T_{g2} = 127\text{ }^\circ\text{C}$ $T_m = 330\text{ }^\circ\text{C}$

Table 3.4 Structural Units for Selected Polymers (*continued*)

Structural unit	Polymers	
$\begin{array}{c} \text{Cl} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{Cl} \end{array}$	Polyvinylidenechloride	$T_g = -19\text{ }^\circ\text{C}$ $T_m = 190\text{ }^\circ\text{C}$
$\begin{array}{c} \text{F} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{F} \end{array}$	Polyvinylidene fluoride	$T_g = -45\text{ }^\circ\text{C}$ $T_m = 171\text{ }^\circ\text{C}$
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{Cl} \end{array}$	Polyvinylchloride (PVC) - amorphous	$T_g = 80\text{ }^\circ\text{C}$ $T_m = -$
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{Cl} \end{array}$	Polyvinylchloride (PVC) - crystalline	$T_g = 80\text{ }^\circ\text{C}$ $T_m = 212\text{ }^\circ\text{C}$
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{F} \end{array}$	Polyvinyl fluoride (PVF)	$T_g = -20\text{ }^\circ\text{C}$ $T_m = 200\text{ }^\circ\text{C}$
$-\text{CO}_2-\text{C}_6\text{H}_4-\text{CO}_2-\text{CH}_2-\text{CH}_2-\text{O}-$	Polyethyleneterephthalate (PET) (linear polyester)	$T_g = 69\text{ }^\circ\text{C}$ $T_m = 245\text{ }^\circ\text{C}$
$-\text{CO}-[\text{CH}_2]_4-\text{CO}-\text{NH}-[\text{CH}_2]_6-\text{NH}-$	Polyamide 66	$T_g = 57\text{ }^\circ\text{C}$ $T_m = 265\text{ }^\circ\text{C}$

Table 3.4 Structural Units for Selected Polymers (*continued*)

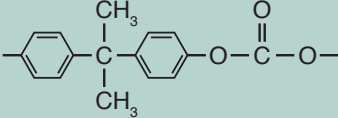
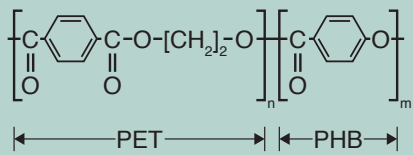
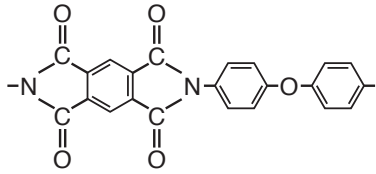
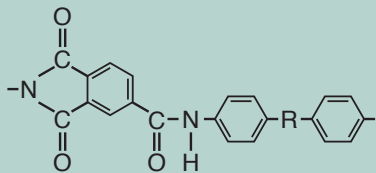
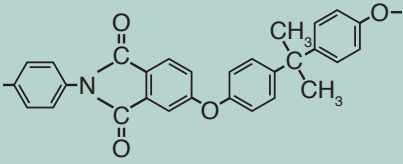
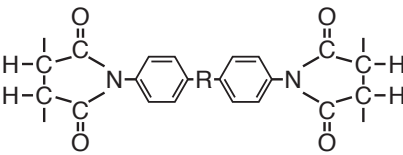
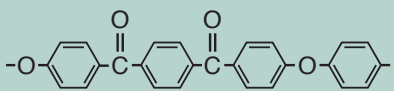
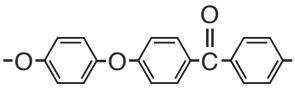
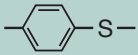
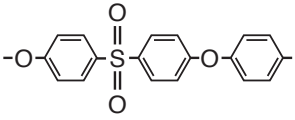
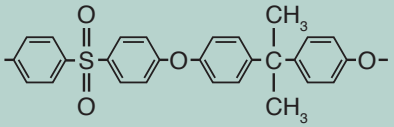
Structural unit	Polymers	
$-\text{CO}-[\text{CH}_2]_8-\text{CO}-\text{NH}-[\text{CH}_2]_6-\text{NH}-$	Polyamide 610	$T_g = 57\text{ }^\circ\text{C}$ $T_m = 265\text{ }^\circ\text{C}$
$-\text{CO}-[\text{CH}_2]_5-\text{NH}-$	Polycaprolactam, Polyamide 6	$T_g = 75\text{ }^\circ\text{C}$ $T_m = 233\text{ }^\circ\text{C}$
	Polycarbonate (PC)	$T_g = 149\text{ }^\circ\text{C}$ $T_m = 267\text{ }^\circ\text{C}$
$-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$	Poly-(p-xylylene) (Parylene R)	$T_g = -$ $T_m = 400\text{ }^\circ\text{C}$
	Polyethyleneterephthalate / p-Hydroxybenzoate- copolymers LC-PET, polymers with flexible chains	$T_g = 75\text{ }^\circ\text{C}$ $T_m = 280\text{ }^\circ\text{C}$
	Polyimide (PI)	T_g : up to $400\text{ }^\circ\text{C}$
	Polyamidimide (PAI)	$T_g \approx 260\text{ }^\circ\text{C}$

Table 3.4 Structural Units for Selected Polymers (*continued*)

Structural unit	Polymers	
	Polyetherimide (PEI)	$T_g \approx 215\text{ }^{\circ}\text{C}$
	Polybismaleinimide (PBI)	$T_g \approx 250\text{ }^{\circ}\text{C}$
	Polyoxybenzoate (POB)	$T_g \approx 290\text{ }^{\circ}\text{C}$
	Polyetherketone (PEEK)	$T_g = 145\text{ }^{\circ}\text{C}$ $T_m = 335\text{ }^{\circ}\text{C}$
	Polyphenylene-sulfide (PPS)	$T_g \approx 230\text{ }^{\circ}\text{C}$
	Polyethersulfone (PES)	$T_g = 85\text{ }^{\circ}\text{C}$ $T_m = 280\text{ }^{\circ}\text{C}$
	Polysulfone (PSU)	$T_g \approx 180\text{ }^{\circ}\text{C}$

3.5.4 Thermosets and Cross-Linked Elastomers

Thermosets, and some elastomers, are polymeric materials that have the ability to crosslink. The crosslinking causes the material to become heat resistant after it has solidified. A more in-depth explanation of the chemical crosslinking reaction that occurs during solidification is given in Chapter 8.

The crosslinking usually is a result of the presence of double bonds that break, allowing the molecules to link with their neighbors. One of the oldest thermosetting polymers is phenol-formaldehyde, or phenolic. Figure 3.22 shows the chemical symbol representation of the reaction, and Fig. 3.23 shows a schematic of the reaction. The phenol molecules react with formaldehyde molecules to create a three-dimensional crosslinked network that is stiff and strong. The by-product of this chemical reaction is water.

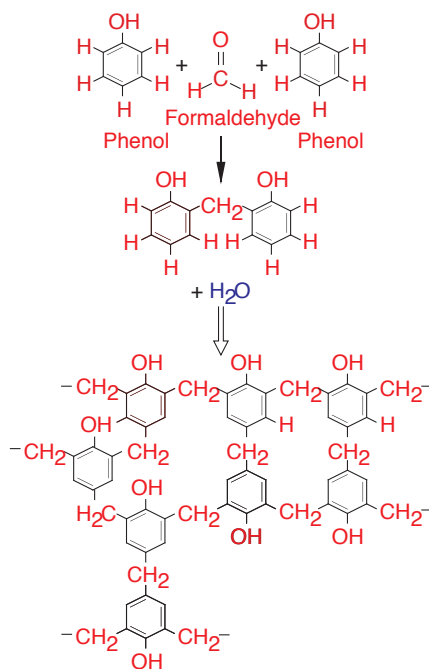


Figure 3.22 Symbolic representation of the condensation polymerization of phenol-formaldehyde resins

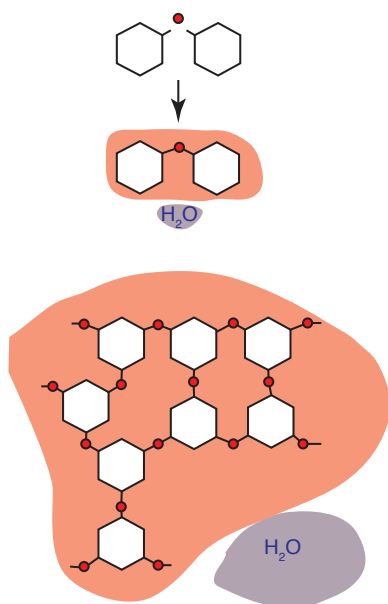


Figure 3.23 Schematic representation of the condensation polymerization of phenol-formaldehyde resins

■ 3.6 Copolymers and Polymer Blends

Copolymers are polymeric materials with two or more monomer types in the same chain. A copolymer that is composed of two monomer types is referred to as a *bipolymer*, and one that is formed by three different monomer groups is called a *terpolymer*. Depending on how the different monomers are arranged in the polymer chain, one distinguishes between *random*, alternating, block, or *graft* copolymers. The four types of copolymers are schematically represented in Fig. 3.24.

A common example of a copolymer is ethylene-propylene. Although both monomers would result in semi-crystalline polymers when polymerized individually, the melting temperature disappears in the *randomly* distributed copolymer with ratios between 35/65 and 65/35, resulting in an elastomeric material, as shown in Fig. 3.25. In fact, EPDM⁷ rubbers are continuously gaining acceptance in industry because of their resistance to weathering. On the other hand, the ethylene-propylene *block* copolymer maintains a melting temperature for all ethylene/propylene ratios, as shown in Fig. 3.26.

Another widely used copolymer is high impact polystyrene (PS-HI), which is formed by grafting polystyrene to polybutadiene. Again, when styrene and buta-

⁷ The D in EP(D)M stands for the added unsaturated diene component which results in a crosslinked elastomer.

diene are randomly copolymerized, the resulting material is an elastomer called styrene-butadiene-rubber (SBR). Another classic example of copolymerization is the terpolymer acrylonitrile-butadiene-styrene (ABS).

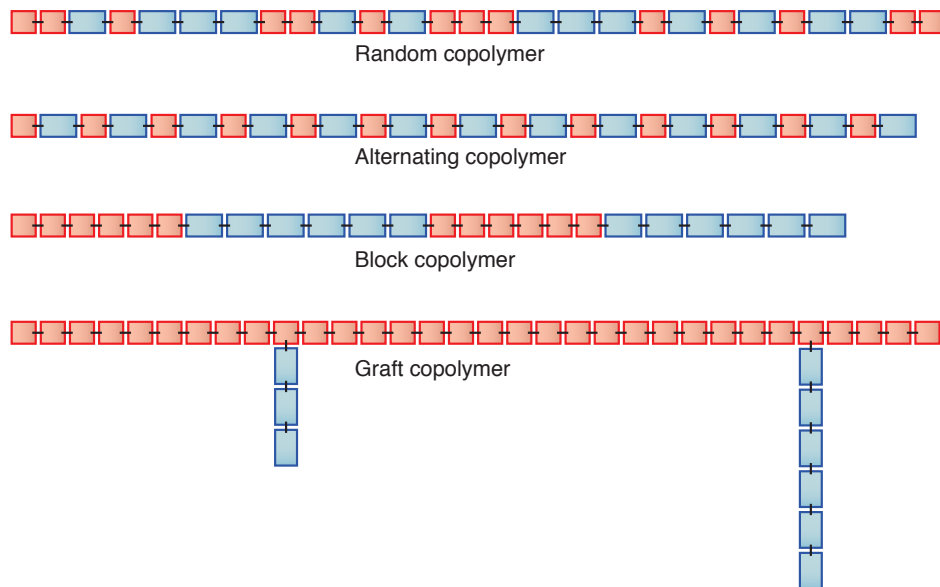


Figure 3.24 Schematic representation of different copolymers

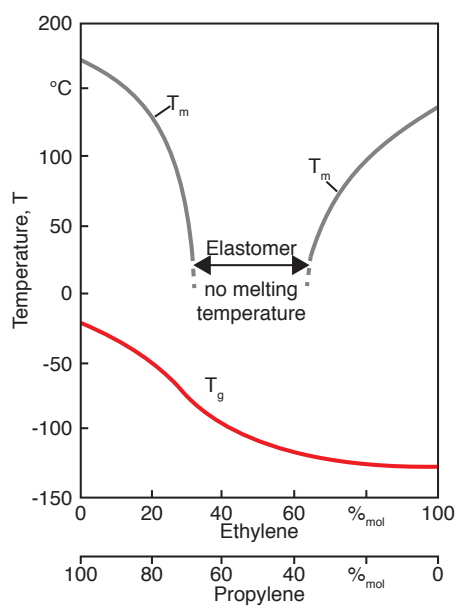


Figure 3.25 Melting and glass transition temperature for random ethylene-propylene copolymers

Polymer blends belong to another family of polymeric materials that are made by mixing or blending two or more polymers to enhance the physical properties of each individual component. Common polymer blends include PP-PC, PVC-ABS, and PE-PTFE.

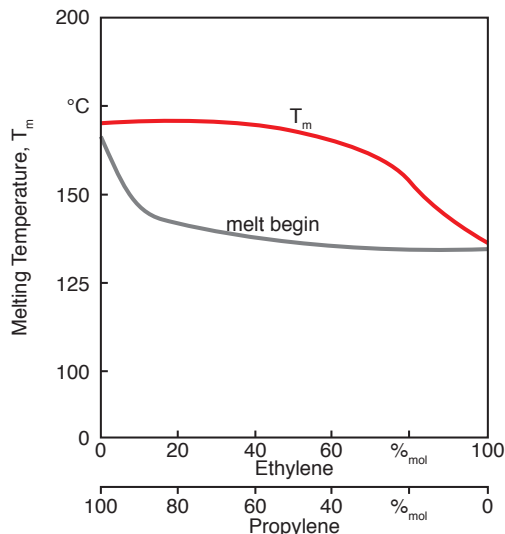


Figure 3.26 Melting temperature for ethylene-propylene block copolymers

■ 3.7 Polymer Additives

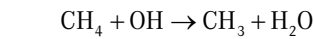
There are many polymer additives that are mixed into a polymer to improve the mechanical, optical, electrical, and acoustic – to name a few – performance of a component.

3.7.1 Flame Retardants

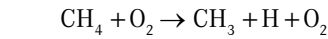
Since polymers are organic materials, most of them are flammable. The flammability of polymers has always been a serious technical problem. A parameter that can be used to assess the flammability of polymers is the *limiting oxygen index* (LOI), also known as the *critical oxygen index* (COI). This value defines the minimum volume percent of oxygen concentration, mixed with nitrogen, needed to support combustion of the polymer under the test conditions specified by ASTM D 2863. Since air contains 21 % oxygen by volume, only those polymers with an LOI greater than 0.21 are considered self-extinguishing. In practice, an LOI value higher than 0.27 is recommended as the limiting self-extinguishing threshold. Table 3.5 presents LOI values for selected polymers.

It is impossible to make a polymer completely inflammable. However, some additives containing halogens, such as bromine, chlorine, or phosphorous, reduce the possibility of either starting combustion within a polymer component or, once ignited, reduce the rate of flame spread. When rating the performance of flame retardants, bromine is more effective than chlorine.

In the *radical trap* theory of flame retardancy it is believed that bromine or phosphorous containing additives compete in the reaction of a combustion process. To illustrate this we examine two examples of typical combustion reactions. These are:



and



where OH and H are active chain carriers. With the presence of HBr the following reaction can take place



Table 3.5 LOI Values for Selected Polymers

Polymer	LOI
Polyformaldehyde	0.15
Polyethylene oxide	0.15
Polymethyl methacrylate	0.17
Polyacrylonitrile	0.18
Polyethylene	0.18
Polypropylene	0.18
Polyisoprene	0.185
Polybutadiene	0.185
Polystyrene	0.185
Cellulose	0.19
Polyethylene terephthalate	0.21
Polyvinyl alcohol	0.22
Polyamide 66	0.23
Epoxy	0.23
Polycarbonate	0.27
Aramid fibers	0.285
Polyphenylene oxide	0.29
Polysulfone	0.30
Phenolic resins	0.35

Table 3.5 LOI Values for Selected Polymers (*continued*)

Polymer	LOI
Polychloroprene	0.40
Polyvinyl chloride	0.42
Polyvinylidene fluoride	0.44
Polyvinylidene chloride	0.60
Carbon	0.60
Polytetrafluoroethylene	0.95

where the active chain carrier was replaced by the less active Br radical, helping with flame extinguishment. Similarly, with the presence of Br the following reaction can take place

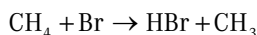


Table 3.6 [8] lists selected polymers and commonly used flame retardants.

Table 3.6 Selected Polymers with Typical Commercial Flame Retardants

Polymer	Flame retardants
Acrylonitrile butadiene styrene	Octabromodiphenyl oxide
High impact polystyrene	Decabromodiphenyl oxide
Polyamide	Dechlorane plus
Polycarbonate	Tetrabromobisphenol A carbonate oligomer
Polyethylene	Chlorinated paraffin
Polypropylene	Dechlorane plus
Polystyrene	Pentabromocyclododecane
Polyvinyl chloride	Phosphate ester

3.7.2 Stabilizers

The combination of heat and oxygen will bring about thermal degradation in a polymer. Heat or energy will produce free radicals that will react with oxygen to form carbonyl compounds, which give rise to yellow or brown discolorations in the final product.

Thermal degradation can be slowed by adding stabilizers such as antioxidants or peroxide decomposers. These additives do not eliminate thermal degradation, but they slow down the reaction process. Once the stabilizer has been consumed by the reaction with the free radicals, the protection of the polymer against thermal degradation ends. The time period over which the stabilizer renders protection

against thermal degradation is called *induction time*. A test used to measure thermal stability of a polymer is the *Oxidative Induction Time* (OIT) by differential scanning calorimetry (DSC). The OIT test is defined as the time it takes for a polymer sample to thermally degrade in an oxygen environment at a set temperature above the polymer's transition temperature. The transitions must occur in a nitrogen environment. The standard test is described by ASTM D 3895. Another test used to measure the thermal stability of a polymer and its additives is the thermal gravimetric analysis (TGA) discussed in Chapter 4.

Polyvinyl chloride is probably the polymer most vulnerable to thermal degradation. In polyvinyl chloride, scission of the C-Cl bond occurs at the weakest point of the molecule. The chlorine radicals will react with their nearest CH group, forming HCl and creating new weak C-Cl bonds. A stabilizer must therefore neutralize HCl and stop the auto-catalytic reaction, as well as prevent corrosion of the processing equipment.

3.7.3 Antistatic Agents

Since polymers have such low electric conductivity, they can build-up electric charges quite easily. The amount of charge build-up is controlled by the rate at which the charge is generated compared to the charge decay. The rate of charge generation at the surface of the component can be reduced by reducing the intimacy of contact, whereas the rate of charge decay is increased through surface conductivity. Hence, a good antistatic agent should be an ionizable additive that allows charge migration to the surface, at the same time as creating bridges to the atmosphere through moisture in the surroundings. Typical antistatic agents are nitrogen compounds, such as long chain amines and amides, polyhydric alcohols, among others.

3.7.4 Fillers

Fillers can be divided into two categories: those that reinforce the polymer and improve its mechanical performance and those that are used to take up space and so reduce the amount of actual resin to produce a part – sometimes referred to as *extenders*. A third, less common, category of filled polymers are those where fillers are dispersed into the polymer to improve its electric conductivity.

Polymers that contain fillers that improve their mechanical performance are often referred to as *composites*. Composites can be divided into two further categories: composites with *high performance* reinforcements, and composites with *low performance* reinforcements. In high performance composites the reinforcement is

placed inside the polymer in such a way that optimal mechanical behavior is achieved, such as unidirectional glass fibers in an epoxy resin. High performance composites usually have 50–80% reinforcement by volume and the composites are usually laminates, tubular shapes containing braided reinforcements, etc. In low performance composites the reinforcement is small enough that it can be dispersed well into the matrix, allowing to process these materials the same way their unreinforced counterparts are processed. The most common filler used to reinforce polymeric materials is glass fiber. However, wood fiber, which is commonly used as an extender, also increases the stiffness and mechanical performance of some thermoplastics. To improve the bonding between the polymer matrix and the reinforcing agent, *coupling agents*, such as *silanes* and *titanates* are often added. Polymer composites and their performance are discussed in more detail in Chapters 8 and 9.

Extenders, used to reduce the cost of the component, often come in the form of particulate fillers. The most common particulate fillers are calcium carbonate, silica flour, clay, and wood flour or fiber. As mentioned earlier, some fillers also slightly reinforce the polymer matrix, such as clay, silica flour, and wood fiber. It should be pointed out that polymers with extenders often have significantly lower toughness than the unfilled resin. This concept is covered in more detail in Chapter 10.

3.7.5 Blowing Agents

The task of blowing or foaming agents is to produce cellular polymers, also referred to as expanded plastics. The cells can be completely enclosed (closed cell) or they can be interconnected (open cell). Polymer foams are produced with densities ranging from 1.6 kg/m³ to 960 kg/m³. There are many reasons for using polymer foams, such as their high strength/weight ratio, excellent insulating and acoustic properties, and high energy and vibration absorbing properties.

Polymer foams can be made by mechanically whipping gases into the polymer, or by either chemical or physical means. Some of the most commonly used foaming methods are [9]:

- Thermal decomposition of chemical blowing agents, which generates nitrogen and/or carbon monoxide and dioxide. An example of such a foaming agent is *azodicarbonamide*, which is the most widely used commercial polyolefin foaming agent.
- Heat induced volatilization of low-boiling liquids such as pentane and heptane in the production of polystyrene foams, and methylene chloride when producing flexible polyvinyl chloride and polyurethane foams.

- Volatilization by the exothermic reaction of gases produced during polymerization. This is common in the reaction of isocyanate with water to produce carbon dioxide.
- Expansion of the gas dissolved in a polymer upon reduction of the processing pressure.

The basic steps of the foaming process are nucleation of the cells, expansion or growth of the cells, and stabilization of the cells. The nucleation of a cell occurs when, at a given temperature and pressure, the solubility of a gas is reduced, leading to saturation, expelling the excess gas to form a bubble. Nucleating agents are used for initial formation of the bubbles. The bubble reaches an equilibrium shape when the pressure inside the bubble balances with the surface tension surrounding the cell.

Examples

1. What is the maximum possible separation between the ends of a high density polyethylene molecule with an average molecular weight of 100,000.

Our first task is to estimate the number of repeat units, n , in the polyethylene chain. Each repeat unit has 2 carbon and 4 hydrogen atoms. The molecular weight of carbon is 12 and that of hydrogen 1. Hence,

$$\text{MW/repeat unit} = 2(12) + 4(1) = 28.$$

The number of repeat units is computed as

$$n = \text{MW}/(\text{MW/repeat unit}) = 100,000/28 = 3,571 \text{ units.}$$

Using the diagram presented in Fig. 3.27, we can now estimate the length of the fully extended molecule using

$$l = 0.252 \text{ nm}(3571) = 890 \text{ nm} = 0.89 \mu\text{m}$$

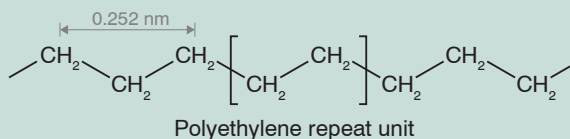


Figure 3.27 Schematic diagram of a polyethylene molecule

As we know, even high density polyethylene molecules are branched and therefore our result is an overprediction.

Problems

- 1. Estimate the degree of polymerization of a polyethylene with an average molecular weight of 150,000. The molecular weight of an ethylene monomer is 28.
- 2. What is the maximum possible separation between the ends of a polystyrene molecule with a molecular weight of 160,000?
- 3. To enhance processability of a polymer, why would you want to decrease its molecular weight?
- 4. Why would an uncrosslinked polybutadiene flow at room temperature?
- 5. What role does the cooling rate play in the morphological structure of semi-crystalline polymers?
- 6. Explain how crosslinking between the molecules affect the molecular mobility and elasticity of elastomers.
- 7. Increasing the molecular weight of a polymer increases its strength and stiffness, as well as its viscosity. Is too high of a viscosity a limiting factor when increasing the strength by increasing the molecular weight? Why?
- 8. Given two polyethylene grades, one for extrusion and one for injection molding, which one should have the higher molecular weight? Why?
- 9. A fractional analysis of a commercial polypropylene sample has a distribution of chain lengths from which the following data is obtained:

Table 3.7 Chain Length Distribution of a Commercial Polypropylene

Degree of Polymerization	Mole fraction
200	0.08
400	0.12
600	0.15
900	0.34
1500	0.16
2000	0.15

What is the number-average molecular weight? What is the weight average molecular weight and what is the polydispersity index of the sample? Derive the equations that can also represent these molecular weights using the mole fraction (x_i) and weight fraction (w_i) of polymers with similar molecular weight.

- 10. Which broad class of thermoplastic polymers densifies the least during cooling and solidification from a melt state into a solid state? Why?
- 11. What class of polymers would you probably use to manufacture frying pan handles? Even though most polymers could not actually be used for this particular application, what single property do all polymers exhibit that would be considered advantageous in this particular application.

12. In terms of recycling, which material is easier to handle, thermosets or thermoplastics? Why?
13. Polymers are considered flammable materials. How can flammability of a polymer be reduced? Can the flammability of a polymer be measured?
14. What type of general polymerization technique is used to make PA, PE, PET, POM, PP, PS, and PVC?
15. Given a typical polymer, is the polydispersity index greater than one, smaller than one, or equal to one?
16. For a low $\bar{M}_w$ polymer with a PI close to 1, name typical properties that go with this trend.

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- [1] Berry, G.C., and Fox, T.G., *Adv. Polymer Sci.*, 5, 261, (1968).
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4

Thermal Properties of Polymers

The heat flow through a material can be defined by Fourier's law of heat conduction. Fourier's law can be expressed as¹

$$q_x = -k_x \frac{\partial T}{\partial x} \quad (4.1)$$

where q_x is the energy transport per unit area in the x direction, k_x the thermal conductivity and $\frac{\partial T}{\partial x}$ is the temperature gradient. At the onset of heating the polymer responds solely as a heat sink, and the amount of energy per unit volume, Q , stored in the material before reaching steady state conditions can be approximated by

$$Q = \rho C_p \Delta T \quad (4.2)$$

where ρ is the density of the material, C_p the specific heat, and ΔT the change in temperature.

Using the notation found in Fig. 4.1 and balancing the heat flow through the element via conduction, including the transient, convective, and viscous heating effects, the energy balance can be written as

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \underline{\mathbf{v}} \cdot \nabla T = (\nabla \cdot \underline{\mathbf{k}} \cdot \nabla T) + \mu (\underline{\dot{\gamma}} : \underline{\dot{\gamma}}) + \rho \dot{Q} \quad (4.3)$$

where on the left are the transient and convective terms, and on the right the conductive term, viscous heating, and an arbitrary heat generation term. The full form of the energy equation is found along with the continuity equation and momentum balance in Tables IV and V of the appendix of this book.

The material properties found in Eqs. 4.1–4.3 are often written as one single property, namely the thermal diffusivity, α , which for an isotropic material is defined by

$$\alpha = \frac{k}{\rho C_p} \quad (4.4)$$

¹ For more detailed information on transport phenomena the reader can refer to: Bird, R. B., Stewart, W. E. and Lightfoot, E. N., *Transport Phenomena*, John Wiley & Sons, (1960).

Typical values of thermal properties for selected polymers are shown in Table 4.1 [1]. For comparison, the properties for stainless steel are also shown at the end of the list.

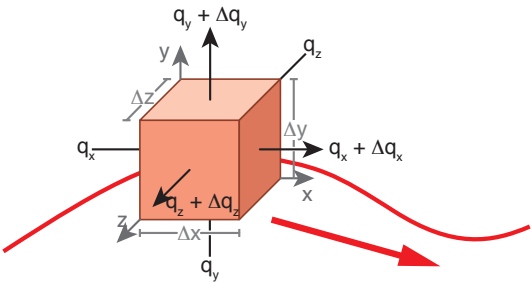


Figure 4.1 Heat flow through a differential material element

Table 4.1 Thermal Properties for Selected Polymeric Materials

Polymer	Specific gravity	Specific heat (kJ/kg°C)	Thermal conductivity (W/m/K)	Coeff. of therm. exp. (μm/m/K)	Thermal diffusivity (m ² /s)x10 ⁻⁷	Max temperature (°C)
ABS	1.04	1.47	0.3	90	1.7	70
Acetal (homo-pol.)	1.42	1.47	0.2	80	0.7	85
Acetal (co-pol.)	1.41	1.47	0.2	95	0.72	90
Acrylic	1.18	1.47	0.2	70	1.09	50
Cellulose acetate	1.28	1.50	0.15	100	1.04	60
Epoxy	1.90	–	0.23	70	–	130
Mod. PPO	1.06	–	0.22	60	–	120
PA 66	1.14	1.67	0.24	90	1.01	90
PA 66 +30% GF	1.38	1.26	0.52	30	1.33	100
PET	1.37	1.05	0.24	90	–	110
PET +30% GF	1.63	–	–	40	–	150
Phenolic	1.40	1.30	0.35	22	1.92	185
PC	1.15	1.26	0.2	65	1.47	125
u-Polyester	1.20	1.20	0.2	100	–	–
PP	0.905	1.93	0.24	100	0.65	100
PS	1.05	1.34	0.15	80	0.6	50
LDPE	0.92	2.30	0.33	200	1.17	50
HDPE	0.95	2.30	0.63	120	1.57	55
PTFE	2.10	1.00	0.25	140	0.7	50
u-PVC	1.40	1.00	0.16	70	1.16	50
p-PVC	1.30	1.67	0.14	140	0.7	50
SAN	1.08	1.38	0.17	70	0.81	60
PS-foam	0.032	–	0.032	–	–	–
Steel	7.854	0.434	60.00	–	14.1	800

It should be pointed out that the material properties of polymers are not constant and may vary with temperature, pressure or phase changes. This chapter will discuss each of these properties individually and present examples of some of the most widely used polymers and measurement techniques. For a more in-depth study of thermal properties of polymers the reader is encouraged to consult the literature [2–4].

■ 4.1 Material Properties

4.1.1 Thermal Conductivity

When analyzing thermal processes, thermal conductivity, k , is the most commonly used property that helps quantify the transport of heat through a material. By definition, energy is transported proportionally to the speed of sound. Accordingly, thermal conductivity follows the relation

$$k \approx C_p \rho u l \quad (4.5)$$

where u is the speed of sound and l the molecular separation. Amorphous polymers show an increase in thermal conductivity with increasing temperature, up to their glass transition temperature, T_g . Above T_g , the thermal conductivity decreases with increasing temperature. Figure 4.2 [3] presents the thermal conductivity, below the glass transition temperature, for various amorphous thermoplastics as a function of temperature.

Due to the increase in density upon solidification of semi-crystalline thermoplastics, the thermal conductivity is higher in the solid state than in the melt. In the melt state, however, the thermal conductivity of semi-crystalline polymers reduces to that of amorphous polymers, as can be seen in Fig. 4.3 [5]. Furthermore, it is not surprising that the thermal conductivity of melts increases with hydrostatic pressure. This effect is clearly shown in Fig. 4.4 [6]. As long as thermosets are unfilled, their thermal conductivity is very similar to that of amorphous thermoplastics.

Anisotropy in thermoplastic polymers also significantly influences their thermal conductivity. Highly drawn semi-crystalline polymer specimens may have a much higher thermal conductivity as a result of the orientation of the polymer chains in the direction of the draw. For amorphous polymers, the thermal conductivity in the direction of the draw can increase by a factor of two. Figure 4.5 [3] presents the thermal conductivity in the directions parallel and perpendicular to the draw direction for high density polyethylene, polypropylene, and polymethyl methacrylate.

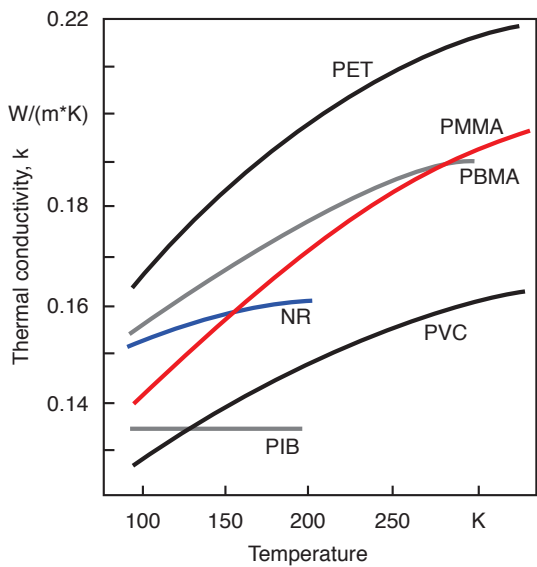


Figure 4.2 Thermal conductivity of various materials

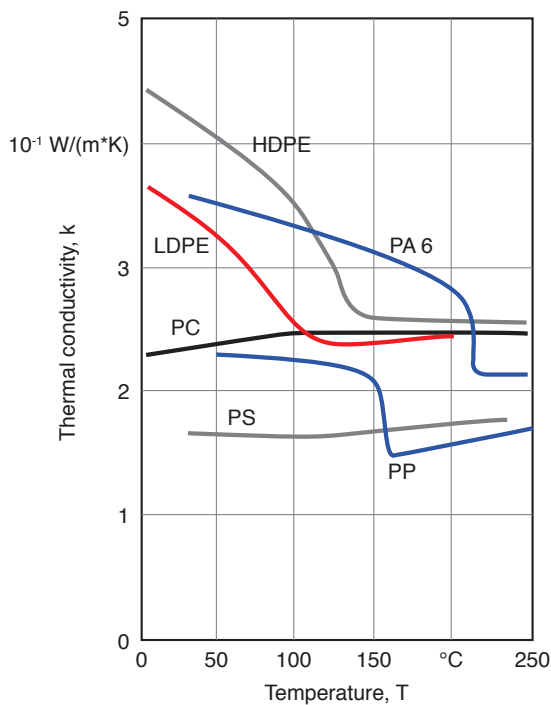


Figure 4.3 Thermal conductivity of various thermoplastics

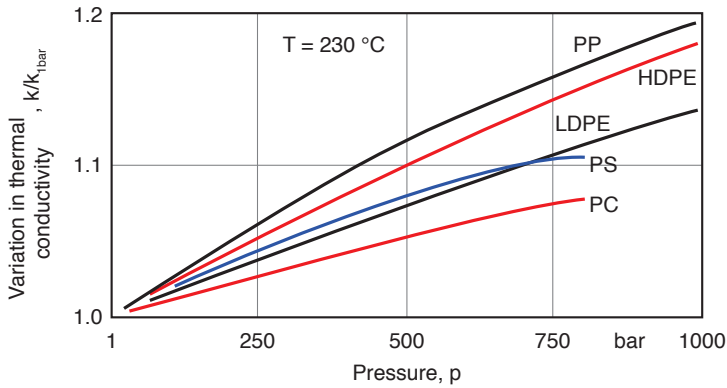


Figure 4.4 Influence of pressure on thermal conductivity of various thermoplastics

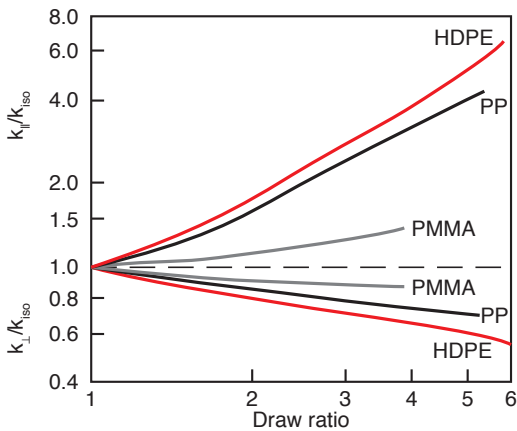


Figure 4.5 Thermal conductivity as a function of draw ratio in the directions perpendicular and parallel to the draw direction for various oriented thermoplastics

A simple relation exists between anisotropic and the isotropic thermal conductivity [7]; it can be written as

$$\frac{1}{k_{\parallel}} + \frac{2}{k_{\perp}} = \frac{3}{k} \quad (4.6)$$

where the subscripts $\parallel$ and $\perp$ represent the directions parallel and perpendicular to the draw direction, respectively.

The higher thermal conductivity of inorganic fillers increases the thermal conductivity of filled polymers. Nevertheless, a sharp decrease in thermal conductivity around the melting temperature of crystalline polymers can still be seen with filled materials. The effect of fillers on thermal conductivity of various thermoplastics is shown in Figs. 4.6 to 4.9. Figure 4.6 [8] shows the effect of fiber orientation as well as the effect of quartz powder on the thermal conductivity of low density polyethylene. Figures 4.7 to 4.9 show the effect of various volume fractions of glass fiber in polyamide 6, polycarbonate, and ABS, respectively. Figure 4.10 demonstrates

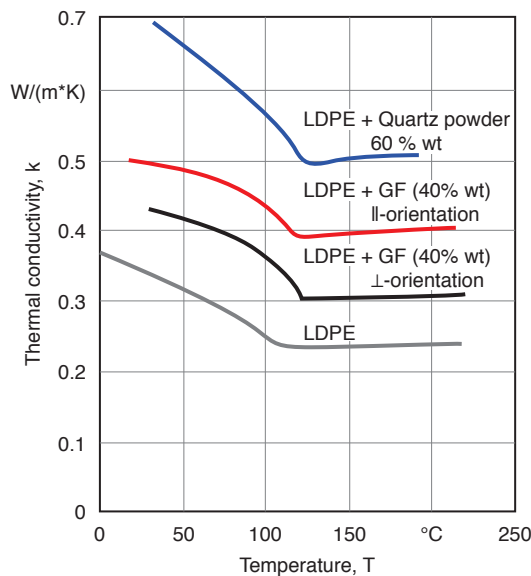


Figure 4.6 Influence of filler on the thermal conductivity of LDPE

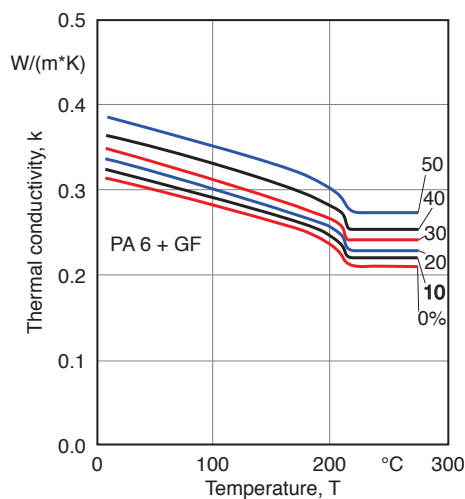


Figure 4.7 Influence of glass fiber on the thermal conductivity of polyamide 6 (Courtesy of Bayer AG, Germany)

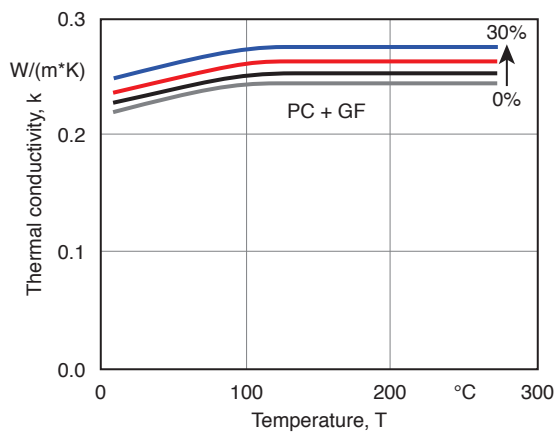


Figure 4.8 Influence of glass fiber on the thermal conductivity of polycarbonate (Courtesy of Bayer AG, Germany)

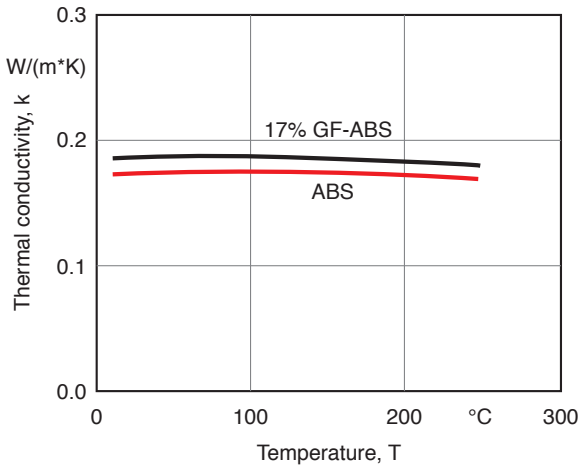


Figure 4.9 Influence of glass fiber on the thermal conductivity of ABS (Courtesy of Bayer AG, Germany)

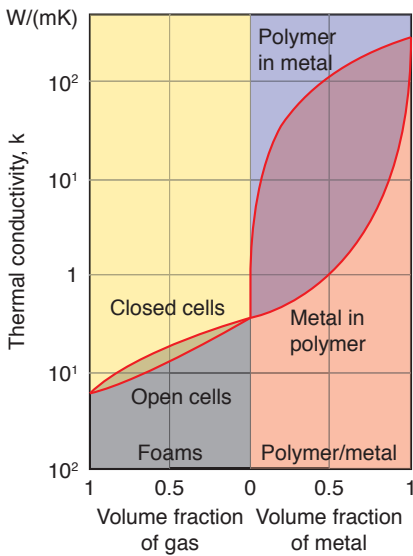


Figure 4.10 Thermal conductivity of plastics filled with glass or metal

the influence of gas content on thermal conductivity of expanded or foamed polymers, and the influence of mineral content on thermal conductivity of filled polymers. There are various models available to compute the thermal conductivity of foamed or filled plastics [7, 9, 10]. A rule of mixtures, suggested by Knappe [7], commonly used to compute thermal conductivity of composite materials is written as

$$k_c = \frac{2k_m + k_f - 2\phi_f(k_m - k_f)}{2k_m + k_f + \phi_f(k_m - k_f)} k_m \quad (4.7)$$

where, ϕ_f is the volume fraction of filler, and k_m , k_f and k_c are the thermal conductivity of the matrix, filler and composite, respectively. Figure 4.11 compares Eq. 4.7

with experimental data [11] for an epoxy filled with copper particles of various diameters. The figure also compares the data to the classic model given by Maxwell [9], which is written as

$$k_c = \left(1 + 3\phi_f \left(\frac{k_f / k_m - 1}{k_f / k_m + 2} \right) \right) k_m \quad (4.8)$$

In addition, a model derived by Meredith and Tobias [10] applies to a cubic array of spheres inside a matrix. Consequently, it cannot be used for volumetric concentration above 52% because the spheres will touch at that point. However, their model predicts the thermal conductivity very well up to 40% by volume of particle concentration.

When mixing several materials the following variation of Knappe's model applies

$$k_c = \frac{1 - \sum_{i=1}^n 2\phi_i \frac{k_m - k_i}{2k_m + k_i}}{1 - \sum_{i=1}^n \phi_i \frac{k_m - k_i}{2k_m - k_i}} k_m \quad (4.9)$$

where k_i is the thermal conductivity of the filler and ϕ_i its volume fraction. This relation is useful for glass fiber reinforced composites (FRC) with glass concentrations up to 50% by volume. This is also valid for FRC with unidirectional reinforcement. However, one must differentiate between the direction longitudinal to the fibers and that transverse to them. For high fiber content one can approximate the thermal conductivity of the composite by the thermal conductivity of the fiber.

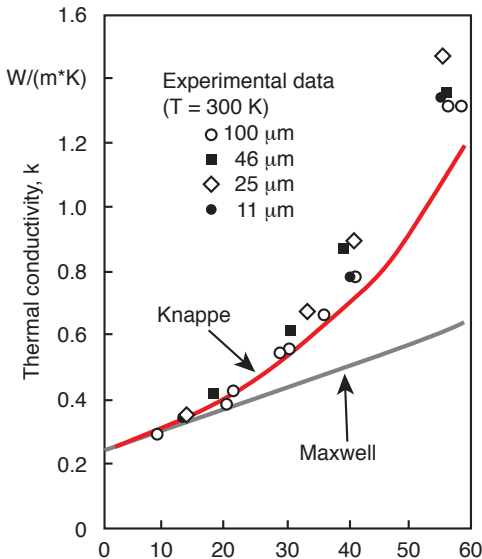


Figure 4.11 Thermal conductivity versus volume concentration of metallic particles of an epoxy resin. Solid lines represent predictions using Maxwell and Knappe models

Thermal conductivity can be measured using the standard tests ASTM C177 and DIN 52612. A new method is currently being balloted, ASTM D20.30, which is preferred by most people today.

4.1.2 Specific Heat

The specific heat, C , represents the energy required to change the temperature of a unit mass of material by one degree. It can be measured at either constant pressure, C_p , or constant volume, C_v . Since the specific heat at constant pressure includes the effect of volumetric change, it is higher than the specific heat at constant volume. However, the volume changes of a polymer with changing temperatures have a negligible effect on the specific heat. Hence, one can usually assume that the specific heat at constant volume or constant pressure is the same. It is usually true that specific heat only changes modestly in the range of practical processing and design temperatures of polymers. However, semi-crystalline thermoplastics display a discontinuity in their specific heat at the melting point of the crystallites. This jump or discontinuity in specific heat includes the heat that is required to melt the crystallites which is usually called the *heat of fusion*. Hence, specific heat is dependent on the degree of crystallinity. Values of heat of fusion for typical semi-crystalline polymers are shown in Table 4.2.

Table 4.2² Heat of Fusion of Various Thermoplastic Polymers

Polymer	Δ (kJ / kg)	T_m (°C)
Polyethylene	268–300	141
Polypropylene	209–259	183
Polyvinyl chloride	181	285
Polybutadiene	170–187	148
Polyamide 6	193–208	223
Polyamide 66	205	265

The chemical reaction that takes place during solidification of thermosets also leads to considerable thermal effects. In a hardened state, their thermal data are similar to those of amorphous thermoplastics. Figure 4.12 shows the specific heat graphs for the three polymer categories.

For filled polymer systems with inorganic and powdery fillers a rule of mixtures³ can be written as

2 The values for heat of fusion were computed using data taken from: van Krevelen, D. W., and Hoftyzer, P. J., *Properties of Polymers*, Elsevier Scientific Publishing Company, Amsterdam, (1976).
3 Valid up to 65% filler content by volume.

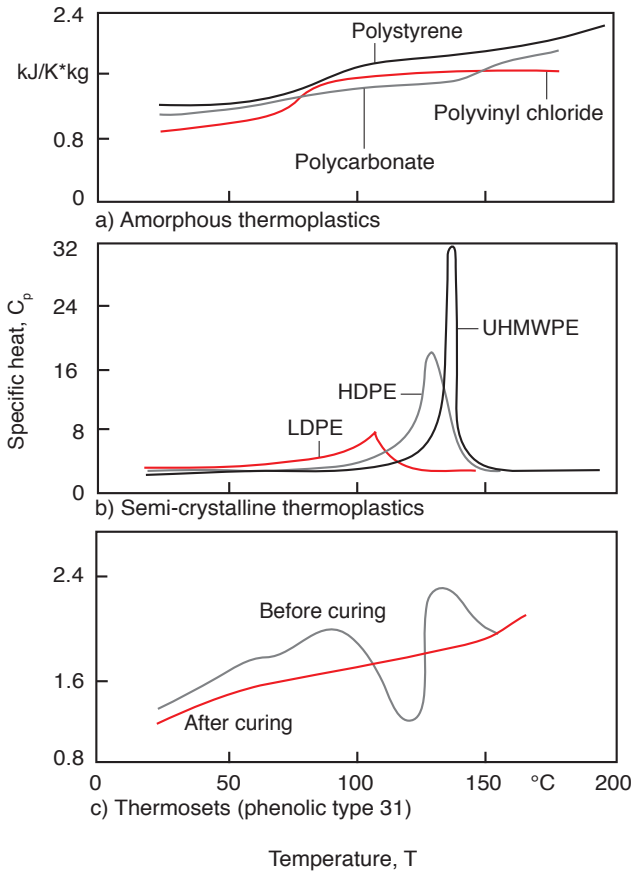


Figure 4.12 Specific heat curves for selected polymers of the three general polymer categories

$$C_p(T) = (1 - \psi_f)C_{PM}(T) + \psi_f C_{Pf}(T) \quad (4.10)$$

where ψ_f represents the weight fraction of the filler and C_{PM} and C_{Pf} the specific heat of the polymer matrix and the filler, respectively. As an example for the application of Eq. 4.10, Fig. 4.13 shows a specific heat curve of an unfilled polycarbonate and its corresponding computed specific heat curves for 10%, 20%, and 30% glass fiber content. In most cases, temperature dependence of C_p of inorganic fillers is minimal and need not be taken into consideration.

The specific heat of copolymers can be calculated using the mole fraction of the polymer components.

$$C_{p\text{copolymer}} = \sigma_1 C_{p1} + \sigma_2 C_{p2} \quad (4.11)$$

where σ_1 and σ_2 are the mole fractions of the comonomer components and C_{p1} and C_{p2} the corresponding specific heat values.

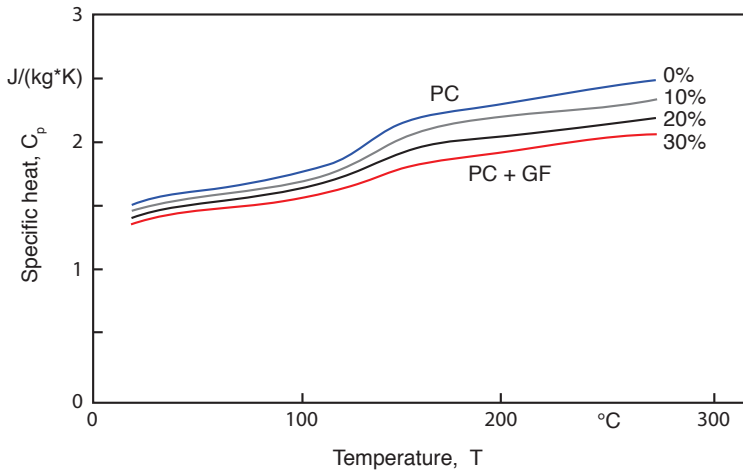


Figure 4.13 Generated specific heat curves for a filled and unfilled polycarbonate (Courtesy of Bayer AG, Germany)

4.1.3 Density

The density or its reciprocal, the specific volume, is a commonly used property for polymeric materials. The specific volume is often plotted as a function of pressure and temperature in what is known as a p-v-T diagram. Using polycarbonate as an example, a typical p-v-T diagram for an unfilled and a filled amorphous polymer is shown, in Figs. 4.14 to 4.16. The two slopes in the curves represent the specific volume of the melt and of the glassy amorphous polycarbonate, separated by the glass transition temperature. Figure 4.17 presents the p-v-T diagram for polyamide 66 as an example of a typical semi-crystalline polymer. Figure 4.18 shows the p-v-T

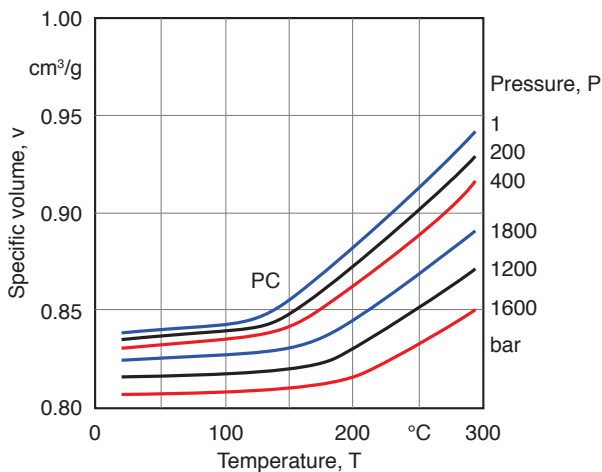


Figure 4.14 p-v-T diagram for a polycarbonate (Courtesy of Bayer AG, Germany)

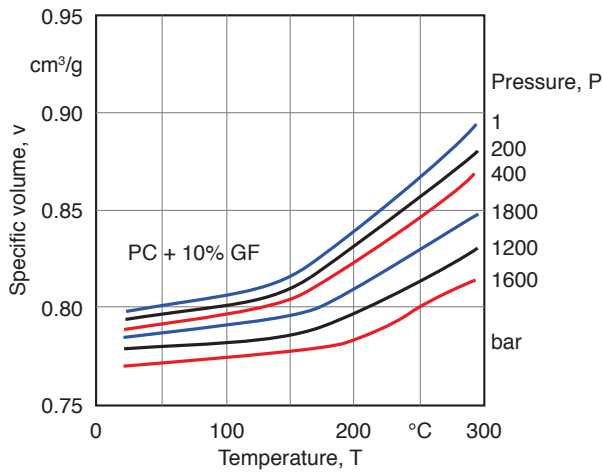


Figure 4.15 p-v-T diagram for a polycarbonate filled with 10% glass fiber (Courtesy of Bayer AG, Germany)

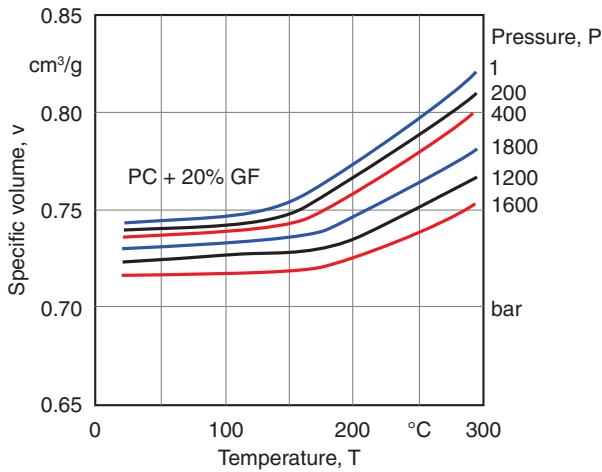


Figure 4.16 p-v-T diagram for a polycarbonate filled with 20% glass fiber (Courtesy of Bayer AG, Germany)

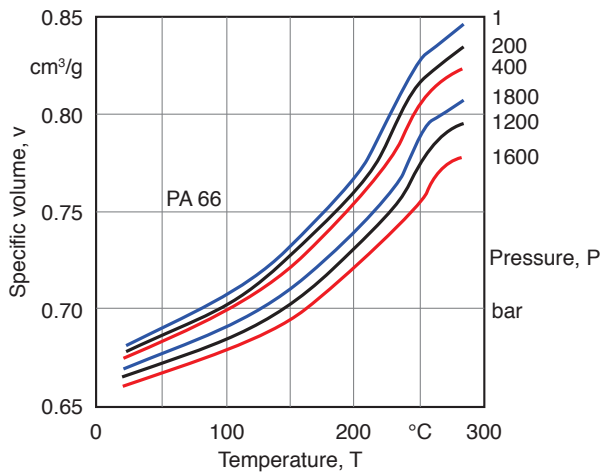


Figure 4.17 p-v-T diagram for a polyamide 66 (Courtesy of Bayer AG, Germany)

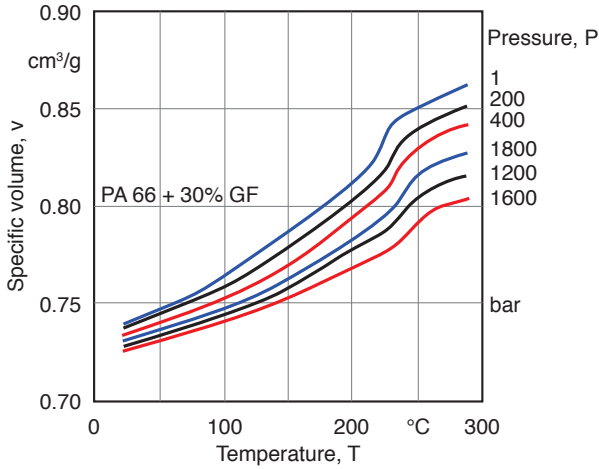


Figure 4.18 p-v-T diagram for a polyamide 66 filled with 30% glass fiber (Courtesy of Bayer AG, Germany)

diagram for polyamide 66 filled with 30% glass fiber. The curves clearly show the melting temperature (i.e., $T_m \approx 250^\circ\text{C}$ for the unfilled PA 66 cooled at 1 bar, which marks the beginning of crystallization as the material cools). It should also come as no surprise that the glass transition temperatures are the same for the filled and unfilled materials.

When carrying out die flow calculations, the temperature dependence of the specific volume must often be dealt with analytically. At constant pressures, the density of pure polymers can be approximated by

$$\rho(T) = \rho_0 \frac{1}{1 + \alpha_t (T - T_0)} \quad (4.12)$$

where ρ_0 is the density at reference temperature T_0 , and α_t is the linear coefficient of thermal expansion.

For amorphous polymers, Eq. 4.12 is valid only for the linear segments (i.e., below or above T_g), and for semi-crystalline polymers it is only valid for temperatures above T_m .

The density of polymers filled with inorganic materials can be computed at any temperature using the following rule of mixtures

$$\rho_c(T) = \frac{\rho_m(T) \rho_f}{\psi \rho_m(T) + (1 - \psi) \rho_f} \quad (4.13)$$

where ρ_c , ρ_m and ρ_f are the densities of the composite, the polymer and the filler, respectively, and ψ is the weight fraction of the filler.

4.1.4 Thermal Diffusivity

Thermal diffusivity, defined in Eq. 4.4, is the material property that governs the process of thermal diffusion over time. The thermal diffusivity in amorphous thermoplastics decreases with temperature. A small jump is observed around the glass transition temperature due to the decrease in heat capacity at T_g . Figure 4.19 [3] presents the thermal diffusivity for selected amorphous thermoplastics.

With increasing temperature, a decrease in thermal diffusivity, is also observed in semi-crystalline thermoplastics. These materials show a minimum at the melting

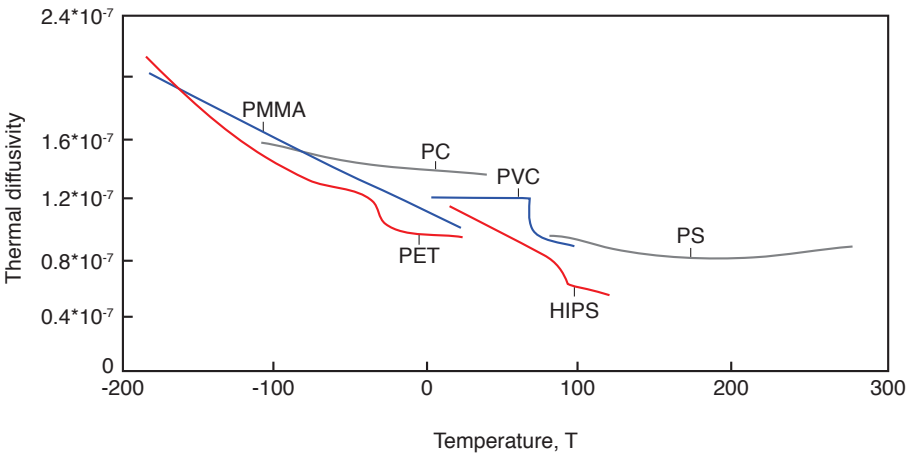


Figure 4.19 Thermal diffusivity as a function of temperature for various amorphous thermoplastics

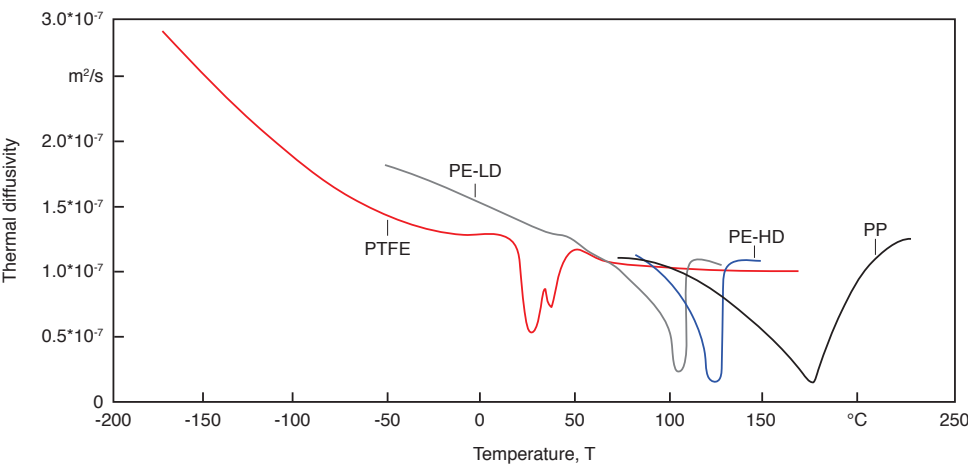


Figure 4.20 Thermal diffusivity as a function of temperature for various semi-crystalline thermoplastics

temperature as demonstrated in Fig. 4.20 [3] for a selected number of semi-crystalline thermoplastics. It has also been observed that the thermal diffusivity increases with increasing degree of crystallinity and that it depends on the rate of crystalline growth, hence, on the cooling speed.

4.1.5 Linear Coefficient of Thermal Expansion

The linear coefficient of thermal expansion is related to volume changes that occur in a polymer due to temperature variations; it is well represented in the p-v-T diagram. For many materials, thermal expansion is related to the melting temperature of that material, clearly demonstrated for a number of important materials in Fig. 4.21. Although the linear coefficient of thermal expansion varies with temperature, it can be considered constant within typical design and processing conditions. It is especially high for polyolefins, for which it ranges from $1.5 \times 10^{-4}/\text{K}$ to $2 \times 10^{-4}/\text{K}$; however, fibers and other fillers significantly reduce thermal expansion. A rule of mixtures is sufficient to calculate the thermal expansion coefficient of polymers that are filled with powdery and small particles as well as with short fibers. For this case, the rule of mixtures is written as

$$\alpha_c = \alpha_p(1 - \phi_f) + \alpha_f \phi_f \quad (4.14)$$

where ϕ_f is the volume fraction of the filler, and α_c , α_p and α_f are coefficients for the composite, the polymer, and the filler, respectively. In case of continuous fiber

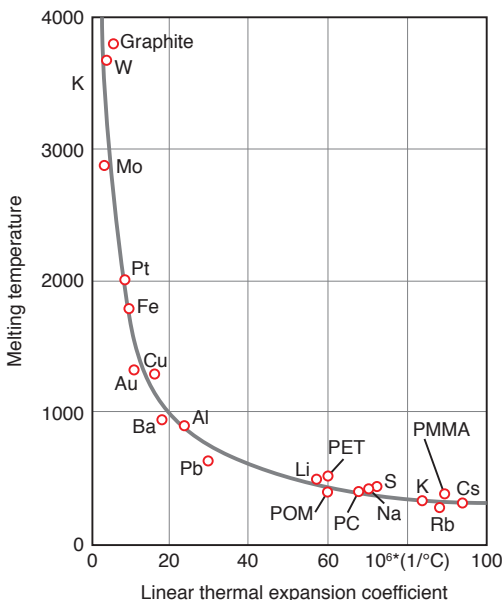


Figure 4.21 Relation between thermal expansion of some metals and plastics at 2°C and their respective melting temperatures

reinforcement, the rule of mixtures presented in Eq. 4.14 applies for the coefficient perpendicular to the reinforcing fibers. Parallel to the fiber direction, however, the thermal expansion of the fibers determines the linear coefficient of thermal expansion of the composite. Extensive calculations are necessary to determine coefficients in layered laminated composites.

4.1.6 Thermal Penetration

In addition to thermal diffusivity, the thermal penetration number is of considerable practical interest. It is given by

$$b = \sqrt{kC_p\rho}$$

(4.15)

If the thermal penetration number is known, the contact temperature T_c , which results when two bodies A and B that are at different temperatures touch, can easily be computed using

$$T_c = \frac{b_A T_A + b_B T_B}{b_A + b_B}$$

(4.16)

where T_A and T_B are the temperatures of the touching bodies and b_A and b_B are the thermal penetrations for both materials. The contact temperature is very important for many objects in daily use (e.g., from the handles of heated objects or drinking cups made of plastic, to the heat insulation of space crafts). It is also very important for the calculation of temperatures in tools and molds during polymer processing. The constants used to compute temperature dependent thermal penetration numbers for common thermoplastics are given in Table 4.3 [12].

Table 4.3 Thermal Penetration of Some Plastics

Plastic	Coefficients to calculate thermal penetration $b = a_b T + b_b$ (W/s ^{1/2} /m ² K)	
	a_a	b_b
HDPE	1.41	441.7
LDPE	0.0836	615.1
PMMA	0.891	286.4
POM	0.674	699.6
PP	0.846	366.8
PS	0.909	188.9
PVC	0.649	257.8

4.1.7 Glass Transition Temperature

The glass transition temperature, T_g , is closely related to the secondary forces. Typical values for the glass transition temperature of common thermoplastics are listed in Chapter 3. If a polymer is mixed with a solvent, the glass transition temperature can be lowered and we can compute it with the following rule of mixtures⁴

$$T_{gM} = \frac{\phi_p \alpha_{ip} T_{gp} - (1 - \phi_p) T_{gs}}{\alpha_{ip} \phi_p + (1 - \phi_p) \alpha_{is}} \quad (4.17)$$

where α_{ip} and α_{is} are the linear coefficients of thermal expansion for the polymer and the solvent, respectively; T_{gM} , T_{gp} and T_{gs} are the glass transition temperatures of the mixture, the polymer, and the solvent, respectively; and ϕ_p is the volume fraction of polymer in the mixture. Stabilizers, plasticizers, and similar auxiliary processing agents work the same way. Usually, the rule of thumb applies that 1 % by volume of plasticizer reduces the glass transition temperature by 2 K.

When mixing two incompatible polymers, two glass transition temperatures result, which are visible when measuring the elastic or loss modulus of the polymer blend.

4.1.8 Melting Temperature

The melting temperature, T_m , is the highest temperature at which crystalline structures can exist. Above this temperature the polymer can be considered a viscous or viscoelastic liquid, depending on the molecular weight of the polymer and the time scale associated with its deformation. An interesting observation to be noted is the relation between the melting and the glass transition temperatures. This relation can be written as

$$\frac{T_g}{T_m} \approx \frac{2}{3} \quad (4.18)$$

where the temperatures are expressed in degrees Kelvin.

■ 4.2 Measuring Thermal Data

Thanks to modern analytical instruments it is possible to measure thermal data with a high degree of accuracy. These data provide good insight into chemical and manufacturing processes. Accurate thermal data or properties are necessary for

⁴ This rule of mixtures only applies for compatible or miscible materials.

everyday calculations and computer simulations of thermal processes. Such analyses are used to design polymer processing installations and to determine and optimize processing conditions.

Over the last twenty years several physical thermal measuring devices have been developed to determine thermal data necessary to analyze processing and polymer component behavior.

4.2.1 Differential Thermal Analysis (DTA)

Differential thermal analysis tests are used to examine transitions and reactions that occur on the order between seconds and minutes, and involve a measurable energy differential of less than 0.04 J/g. Usually, measuring is done dynamically (i.e., with linear temperature variations in time). However, in some cases isothermal measurements are also done. DTA is mainly used to determine the transition temperatures. The principle is shown schematically in Fig. 4.22. Here, the sample, S , and an inert substance, I , are placed in an oven that has the ability to raise its temperature linearly. Two thermocouples that monitor the samples are connected opposite to one another such that no voltage is measured as long as S and I are at the same temperature:

$$\Delta T = T_s - T_i = 0 \quad (4.19)$$

However, if a transition or a reaction occurs in the sample at a temperature T_c , then heat is consumed or released, in which case $\Delta T \neq 0$. This thermal disturbance in time can be recorded and used to interpret possible information about the reaction temperature, T_c , the heat of transition or reaction, ΔH , or simply about the existence of a transition or reaction.

Figure 4.23 presents the temperature history in a sample with an endothermic melting point (i.e., such as the one that occurs during melting of semi-crystalline

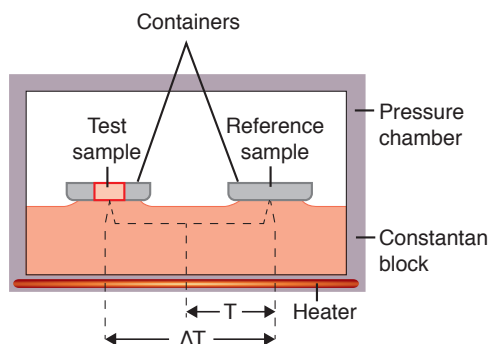


Figure 4.22 Schematic of a differential thermal analysis test

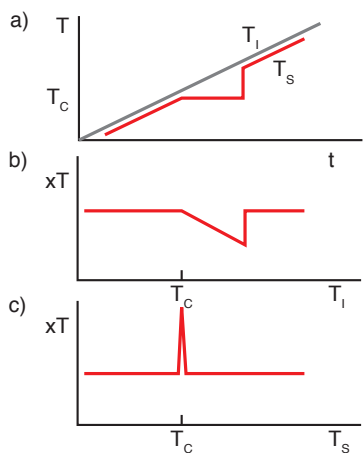


Figure 4.23 Temperature and temperature differences measured during melting of a semi-crystalline polymer sample

polymers). The figure also shows the functions $\Delta T(T_i)$ and $\Delta T(T_s)$ which result from such a test. A comparison between Figs. 4.23 (b) and (c) demonstrates that it is very important to record the sample temperature, T_s , to determine a transition temperature such as the melting or glass transition temperature.

4.2.2 Differential Scanning Calorimeter (DSC)

With the help of differential scanning calorimetry it is possible to determine thermal transitions of polymers in a range of temperatures between -180 and $+600$ °C. Other than in a DTA cell, in the DSC device thermocouples are not placed directly inside the sample or the reference substance. Instead, they are embedded in the specimen holder or stage on which the sample and reference pans are placed; the thermocouples make contact with the containers from the outside. A schematic diagram of a differential scanning calorimeter is very similar to the one shown in Fig. 4.22. Materials that do not show or undergo transition or react in the measuring range (e.g., air, glass powder, etc.) are placed inside the reference container. For standardization purposes typically materials whose properties are exactly known, such as mercury, tin, or zinc are used. In contrast to the DTA test, where samples larger than 10 g are needed, the DSC test requires samples that are in the mg range (< 10 mg). Although DSC tests are less sensitive than the DTA tests, they are the most widely used tests for thermal analysis. In fact, DTA tests are rarely used in the polymer industry.

Figure 4.24 [4] shows a typical DSC curve measured using a partly crystalline polymer sample. In the figure, the area enclosed between the trend line (bold) and the base line is a direct measurement for the amount of heat, ΔH , needed for transition. In this case, the transition is melting and the area corresponds to the *heat of fusion*.

The degree of crystallinity, x , is determined from the ratio of the heat of fusion of a polymer sample, ΔH_{sc} , and the enthalpy of fusion of a 100% crystalline sample ΔH_c .

$$\chi = \frac{\Delta H_{sc}}{\Delta H_c} \quad (4.20)$$

In a DSC analysis of a semi-crystalline polymer, a jump in the specific heat curve, as shown in Fig. 4.24, becomes visible; a phenomenon that can easily be traced with a DSC. The glass transition temperature, T_g , is determined at the inflection point of the specific heat curve. The release of residual stresses as a material's temperature is raised above the glass transition temperature is often observed in a DSC analysis.

Specific heat, C_p , is one of the many material properties that can be measured using DSC. During a DSC temperature sweep, the sample pan and the reference pan are maintained at the same temperature. This allows the measurement of the differential energy required to maintain identical temperatures. The sample with the higher heat capacity will absorb a larger amount of heat, which is proportional to the difference between the heat capacity of the measuring sample and the reference sample.

It is also possible to determine the purity of a polymer sample when additional peaks or curve shifts are detected in a DSC measurement.

Thermal degradation is generally accompanied by an exothermic reaction that may result from oxidation. Such a reaction can easily be detected in a DSC output. By further warming of the test sample, crosslinking may take place and, finally, chain breakage, as shown in Fig. 4.24.

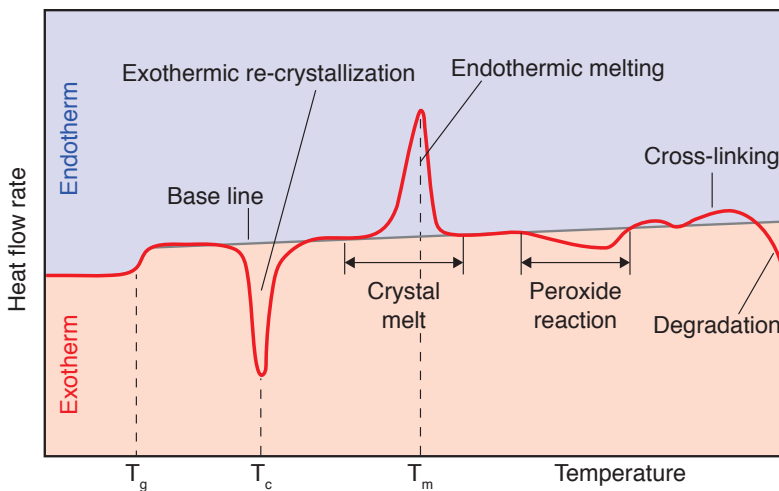


Figure 4.24 Typical DSC heat flow for a semi-crystalline polymer

An important aspect in DSC data interpretation is the finite heat flow resistance between the sample pan and the furnace surface. Studies by Janeschitz-Kriegl, Eder and co-workers [13, 14] have demonstrated that the heat transfer coefficient between the sample pan and furnace is of finite value, and cannot be disregarded when interpreting the data. In fact, with materials that have a low thermal conductivity, such as polymers, the finite heat transfer coefficient will significantly influence the temperature profiles of the samples.

4.2.3 Thermomechanical Analysis (TMA)

Thermomechanical analysis (TMA) measures shape stability of a material at elevated temperatures by physically penetrating it with a metal rod. A schematic diagram of TMA equipment is shown in Fig. 4.25. During TMA, the test specimen's temperature is raised at a constant rate, the sample is placed inside the measuring device, and a rod with a specified weight is placed on top of it. To allow for measurements at low temperatures, the sample, oven, and rod can be cooled with liquid nitrogen. TMA also allows the measurement of Vicat temperatures described in Chapter 9.

Most instruments are so precise that they can be used to measure the melting temperature of the material and, by using linear dilatometry to measure the thermal expansion coefficients. The thermal expansion coefficient can be measured using

$$\alpha_t = \frac{1}{L_0} \frac{\Delta L}{\Delta T} \quad (4.21)$$

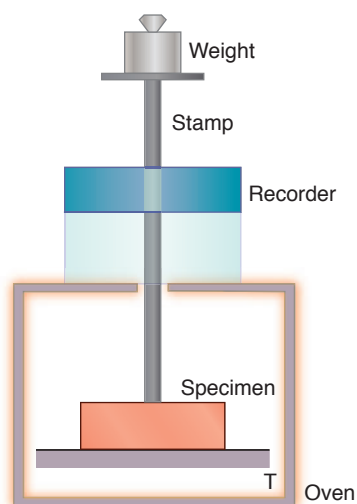


Figure 4.25 Schematic diagram of the thermomechanical analysis (TMA) device

where L_0 is the initial dimension of the test specimen, ΔL the change in size and ΔT the temperature difference. For isotropic materials a common relation between the linear and the volumetric thermal expansion coefficient can be used:

$$\gamma = 3\alpha_t \quad (4.22)$$

4.2.4 Thermogravimetry (TGA)

A thermogravimetric analyzer can measure weight changes of less than $10 \mu\text{g}$ as a function of temperature and time. This measurement technique, typically used to measure thermal stability, works on the principle of a beam balance. The testing chamber can be heated (up to approximately 1200°C) and rinsed with gases (inert or reactive). Measurements are performed on isothermal reactions or at temperature sweeps of less than 100 K/min . The maximum sample weight used during thermogravimetric analyses is 500 mg . Thermogravimetry is often used to identify the components in a blend or a compound based on the thermal stability of each component. Figure 4.26 shows results from a TGA analysis of a PVC fabric. The figure clearly shows the transitions at which the various components of the compound decompose. The percent of the original sample weight is recorded along with the change of the weight with respect to temperature. Five transitions representing (1) the decomposition of volatile components, (2) decomposition of the DOP plasticizer, (3) formation of HCl , (4) carbon-carbon scission, and (5) the forming of CO_2 , are clearly visible.

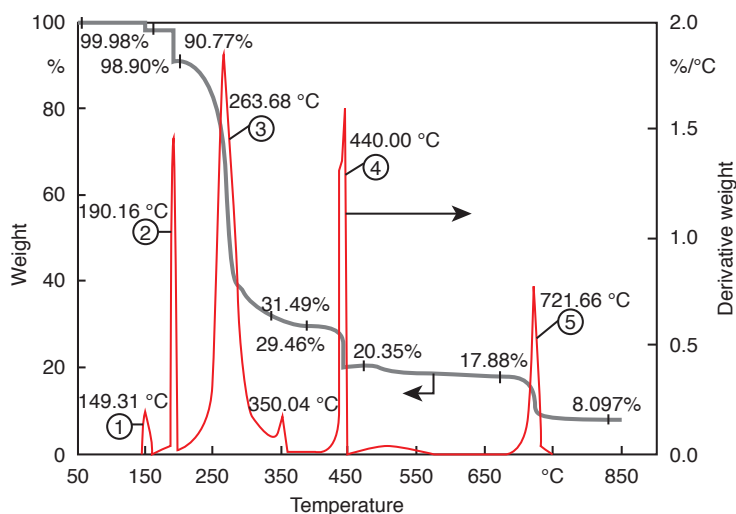


Figure 4.26 TGA analysis of a PVC fabric; (1) volatiles: humidity, monomers, solvents etc., (2) DOP plasticizer, (3) HCl formation, (4) carbon-carbon scission, and (5) CO_2 formation (Courtesy of the ICIPC, Medellín, Colombia)

4.2.5 Density Measurements

One simple form of calculating the density of a polymer sample is to first weigh the sample immersed in water. Assuming the density of water to be 1.0 g/cm^3 we can use the relation

$$\rho = \frac{m}{(m - m_i) \left(1 \text{ cm}^3/\text{g} \right)} \quad (4.23)$$

where m is mass of the specimen, m_i is the mass of the immersed specimen and $(m - m_i)$ is the mass of the displaced body of water.

Some common ways of determining density of polymeric materials are described by the test methods defined by ASTM D792, ISO 1183, and DIN 53 479 standards. Another common way of measuring density is the “through flow density meter”. Here, the density of water is changed to that of the polymer by adding ethanol until the plastic shavings are suspended in the solution. The density of the solution is then measured in a device that pumps the liquid through a U-pipe, where it is measured using ultrasound techniques. A density gradient technique is described by the standard ASTM D1505 test method.

Examples

1. A differential scanning calorimetry (DSC) test was performed on a 25 mg polyethylene terephthalate (PET) sample taken from the screw-top of a soda bottle. The test was performed using a heating rate of 5 K/min (5 K rise every minute). The DSC output is presented in Fig. 4.27.

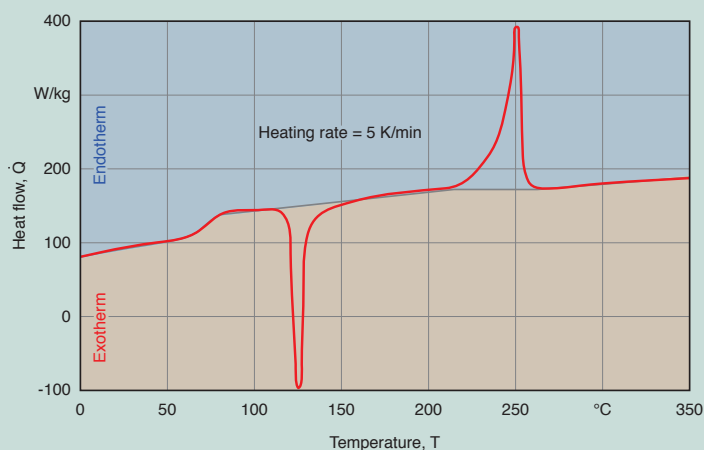


Figure 4.27 DSC scan of a PET bottle screw-top sample

Using the curve, estimate the glass transition temperature, T_g , the melting temperature, T_m , the crystallization temperature, T_c , and the heat of fusion, λ , for this specific PET sample during the temperature ramp-up.

If the heat of fusion for a hypothetically 100% crystalline PET sample is 137 kJ/kg [15], what was the degree of crystallinity in the PET bottle screw-top?

From the curve presented in Fig. 4.27 we can deduce that the glass transition temperature is approx. 72 °C, the crystallization temperature approx. 125 °C, and the melting temperature approx. 250 °C. Note that in all three cases there is range of temperatures at which each transition occurs. To compute the heat of fusion during the ramp-up we need to find the area between $\dot{Q}$ and the base-line for the endothermic deviation around the melting point, between 210 and 260 °C. To do this, we must first transform the temperature scale to time by dividing it by the heating rate as

$$t = \frac{T}{5 \text{ K/min}} \frac{60 \text{ s}}{1 \text{ min}}$$

Hence, 50 °C becomes 600 s, 100 °C becomes 1200 s, etc. The integral equals 37.8 kJ/kg, which represents the heat of fusion of the sample during the temperature ramp-up. However, one must consider that this melting energy includes the extra crystallization that occurs between 108 and 155 °C. The exothermic energy is computed by integrating the curve between those two temperatures in a transformed time scale. The integral equals 22.9 kJ/kg. We can also find the area under the curve by transforming the heat flow, $\dot{Q}$, to heat capacity, C_p , and integrating using the temperature scale instead of a time scale. Heat capacity can be computed using

$$C_p = \frac{\dot{Q}}{5 \text{ K/min}} \frac{60 \text{ s}}{1 \text{ min}}$$

The degree of crystallinity of the initial PET bottle screw-top can now easily be computed using

$$\chi = \frac{37.8 \text{ kJ/kg} - 22.9 \text{ kJ/kg}}{137 \text{ kJ/kg}} = 0.109 \text{ or } 10.9\%$$

Problems

1. Does the coefficient of linear expansion of a polymer increase or decrease after the addition of glass fibers?
2. Plot T_g versus T_m for several polymers. What trend or relation do you observe?
3. In a soda bottle, how does the degree of crystallinity in the screw-top region compare to the degree of crystallinity in the wall? Explain.
4. A 5 K/min heating and 5 K/min cooling differential scanning calorimetry (DSC) test (Fig. 4.28) was performed on a 10.8 mg sample of PE-LD. What is the specific heat of the PE-LD just after melting during heating

and just before crystallization during cooling? What is the degree of crystallinity of the initial and the final samples?

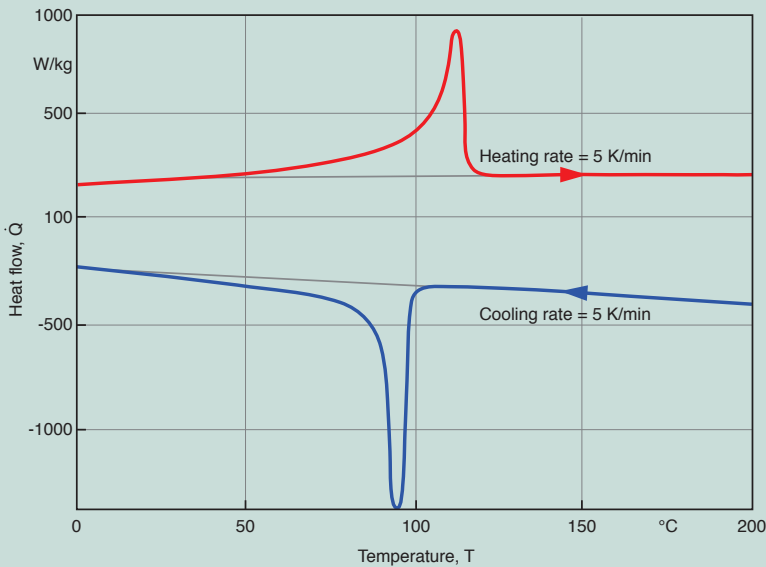


Figure 4.28 Heating and cooling DSC scans of a PE-LD sample

5. A differential scanning calorimetry (DSC) test was performed on an 11.4 mg polyethylene terephthalate (PET) sample using the standard ASTM D 3417 test method. The ASTM test calls for a temperature heating rate of 20 °C/min (20 °C rise every minute). The DSC output is presented below⁵.

Using the curve in Fig. 4.29, estimate the glass transition temperature, T_g , the melting temperature, T_m , the crystallization temperature, T_c and the heat of fusion, λ , for this specific PET sample during the temperature ramp-up. Note that the heat flow scale has already been transformed to heat capacity. How do T_g and T_m compare to the “book values”?

If the heat of fusion for a hypothetically 100% crystalline PET is 137 kJ/kg, what was the degree of crystallinity of the original PET sample?

In the graph of Fig. 4.29 sketch a hypothetical DSC output for the original PET sample with a temperature heating rate that is too fast to allow any additional crystallization during heating.

6. A typical injection pack/hold pressure during injection molding of polyamide 66 components is 1000 bar and the injection temperature is 280 °C. The gate freezes shut when the average temperature inside the mold reaches 225 °C.

Draw the process on the p-v-T diagram given in Fig. 4.17.

⁵ Courtesy of ICIPC, Medellín, Colombia.

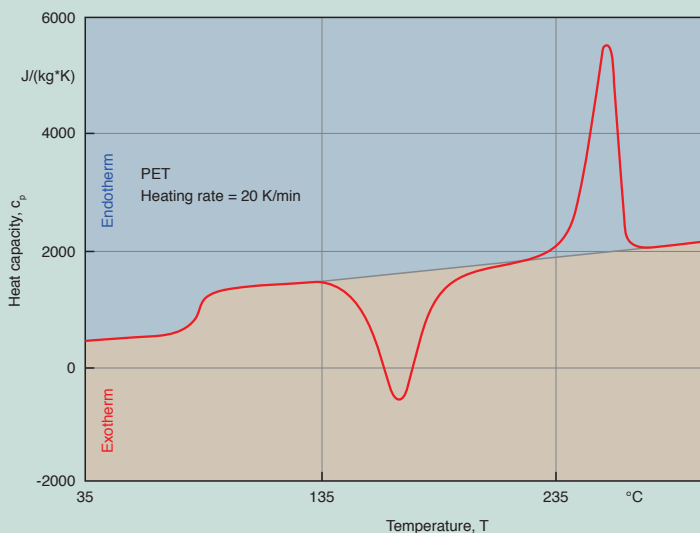


Figure 4.29 DSC scan of a PET sample

What volume shrinkage should be taken into account when designing the mold? Note that the shrinkage is mostly taken up by a thickness reduction.

7. Isothermal differential scanning calorimetry (DSC) tests were performed on three unsaturated polyester (UPE) samples at three different temperatures (100 °C, 110 °C, and 120 °C). The output for the three DSC tests is presented in the Fig. 4.30. On the graph, label which curve is associated with which test temperature. From the curves in Fig. 4.30 estimate the total heat of reaction, Q_T .

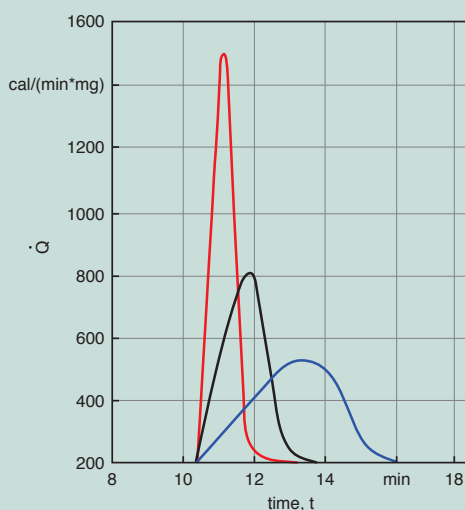


Figure 4.30 Isothermal DSC measurements of UPE samples (Courtesy of Gen-Corp Research, Akron, OH)

8. A differential scanning calorimetry (DSC) test (Fig. 4.31) was performed on an 18.3 mg sample of polystyrene. What is the glass transition temperature of the sample? Determine the specific heat of this PS just before the glass transition temperature has been reached. What is C_p just beyond T_g ? Why is the heat higher as the temperature increases?

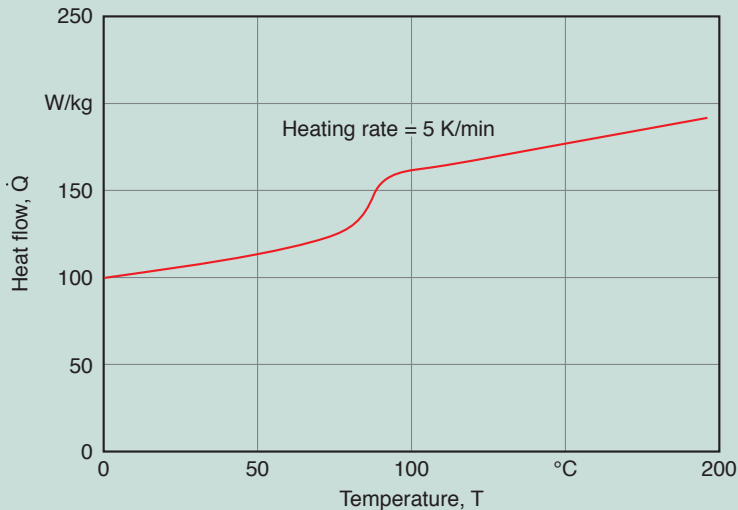


Figure 4.31 DSC scan of a PS sample

9. Sketch the p-v-T diagrams for a semi-crystalline polymer with a high and a low cooling rate.
10. A polystyrene sample is split in two and the glass transition temperature for each half is measured using DSC in two different laboratories. They reported the values for this property to be 96 °C and 106 °C, respectively. Suggest 3 possible explanations for this difference.

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5

Rheology of Polymer Melts

■ 5.1 Introduction

Rheology is the field of science that studies fluid behavior during flow-induced deformation. Of the variety of materials that rheologists study, polymers have been found to be the most interesting and complex. Polymer melts are shear-thinning, viscoelastic, and their flow properties are temperature dependent. Viscosity is the most widely used material parameter when determining the behavior of polymers during processing. Because the majority of polymer processes are shear rate dominated, the viscosity of the melt is commonly measured using shear deformation measurement devices. However, some polymer processes, such as blow molding, thermoforming, and fiber spinning, are dominated by either elongational deformation or by a combination of shear and elongational deformation. In addition, some polymer melts exhibit significant elastic effects during deformation. This chapter will concentrate on shear deformation models but, for completeness, elongational flows, concentrated suspensions, and viscoelastic fluids will also be covered. Modeling and simulation of polymer flows will be briefly discussed. For further reading on rheology of polymer melts, the reader should consult the literature [1–6]. For more detail on polymer flow and processing simulation the literature [7, 8] should also be reviewed.

5.1.1 Continuum Mechanics

When analyzing the flow or deformation of polymers during processing, a balance of energy, mass, and forces must be preserved.

Using the notation found in Fig. 5.1 and performing a mass balance on the differential element, for an incompressible liquid¹ one can write

¹ It is clear that a polymer melt is not incompressible. However, assuming incompressibility simplifies the analysis significantly without losing accuracy in flow predictions.

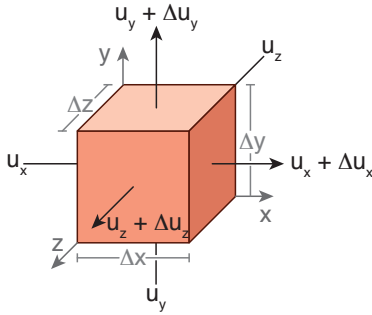


Figure 5.1 Differential element used for mass balance

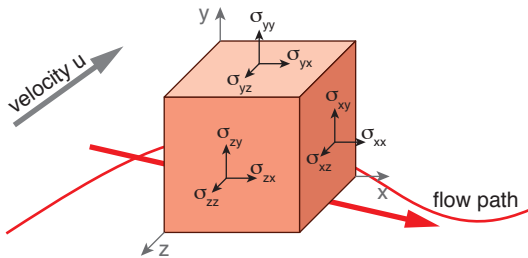


Figure 5.2 Differential element used for force balance

$$\nabla \cdot \underline{\mathbf{u}} = 0 \quad (5.1)$$

where Eq. 5.1 represents the divergence of the velocity vector and is presented in Appendix A in expanded form for various coordinate systems.

Using a similar differential element that is moving with the fluid, as shown in Fig. 5.2, a force balance results in

$$\rho \frac{D\underline{\mathbf{u}}}{Dt} = [\nabla \cdot \underline{\underline{\sigma}}] + \rho \underline{\underline{g}} \quad (5.2)$$

where the term on the left side represents the inertia of the polymer melt, the first term on the right is the divergence of the stress tensor and represents viscous and elastic forces, and the second term on the right represents the gravitational effects. The operator D/Dt is the *substantial* or *material derivative* defined by

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \underline{\mathbf{u}} \cdot \nabla \quad (5.3)$$

which represents a convective or embedded frame of reference that moves with a material particle.

The stress $\underline{\underline{\sigma}}$, sometimes referred to as the *total stress*, can be split into *hydrostatic pressure*, $\underline{\underline{\sigma}}_H$, and *deviatoric stress*, $\underline{\underline{\tau}}$. The hydrostatic pressure is a stress vector that acts only in the normal direction to the surfaces and can be represented by $-p\underline{\underline{\delta}}$, where p is the pressure and $\underline{\underline{\delta}}$ is a unit tensor. The momentum balance can now be written as

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p + [\nabla \cdot \underline{\underline{\tau}}] + \rho \mathbf{g} \quad (5.4)$$

The full form of Eq. 5.4 is presented in Table VI of the appendix.

5.1.2 The Generalized Newtonian Fluid

The viscosity of most polymer melts is *shear thinning* and temperature dependent. The shear thinning effect is defined as the reduction in viscosity at high rates of deformation. This phenomenon occurs because at high rates of deformation the molecules are stretched out, enabling them to slide past each other with more ease, hence, lowering the bulk viscosity of the melt. Figure 5.3 clearly shows the shear thinning behavior and temperature dependence of the viscosity for a selected number of thermoplastics. The figure also illustrates ranges of rate of deformation that are typical for various processing techniques. To take into consideration *non-Newtonian effects*, it is common to use a viscosity model that is a function of the strain rate and temperature to calculate the stress tensor² in Eq. 5.4:

$$\underline{\underline{\tau}} = \eta(\dot{\gamma}, T) \dot{\underline{\underline{\gamma}}} \quad (5.5)$$

where η is the viscosity and $\dot{\underline{\underline{\gamma}}}$ the *strain rate* or *rate of deformation tensor* defined by

$$\dot{\underline{\underline{\gamma}}} = \nabla \mathbf{u} + \nabla \mathbf{u}^t \quad (5.6)$$

where $\nabla \mathbf{u}$ represents the velocity gradient tensor. This model describes the *Generalized Newtonian Fluid*. In Eq. 5.5, $\dot{\gamma}$ is the magnitude of the strain rate tensor and can be written as

$$\dot{\gamma} = \sqrt{\frac{1}{2} II} \quad (5.7)$$

where II is the second invariant of the strain rate tensor defined by

$$II = \sum_i \sum_j \dot{\gamma}_{ij} \dot{\gamma}_{ji} \quad (5.8)$$

The strain rate tensor components in Eq. 5.8 are defined by

$$\dot{\gamma}_{ij} = \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \quad (5.9)$$

The temperature dependence of the polymer's viscosity is normally factored out as

$$\eta(T, \dot{\gamma}) = f(T) \eta(\dot{\gamma}) \quad (5.10)$$

² As will be shown later, this is only true when the elastic effects are negligible during deformation of the polymeric material.

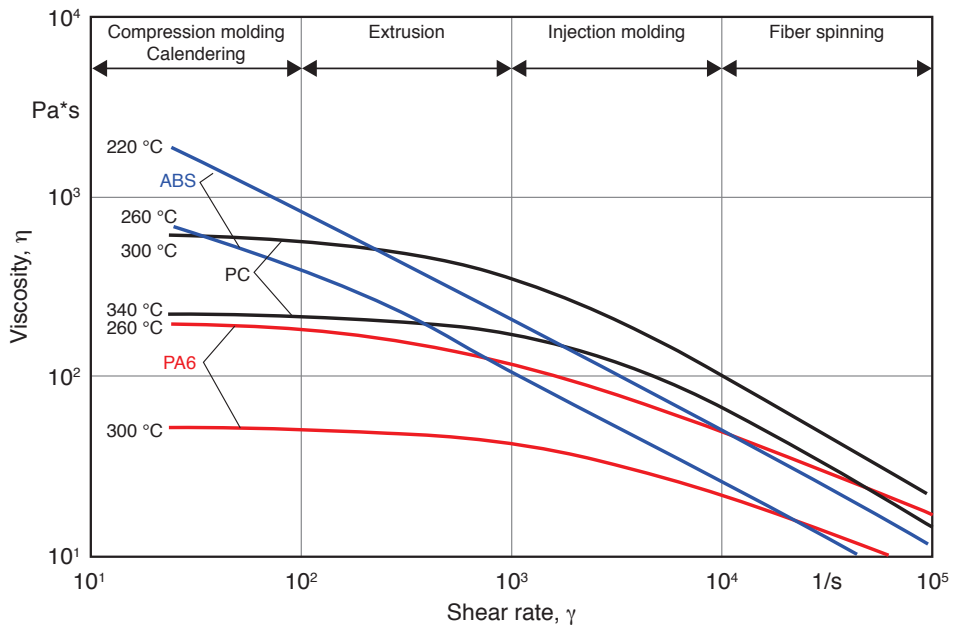


Figure 5.3 Viscosity curves for a selected number of thermoplastics

where for small variations in temperature, $f(T)$ can be approximated using an exponential function such as

$$f(T) = \exp(-a(T - T_0)) \quad (5.11)$$

However, a variation in temperature corresponds to a shift in the time scale. A shift commonly used for semi-crystalline polymers is the Arrhenius shift, which is written as

$$a_T(T) = \frac{\eta_0(T)}{\eta_0(T_0)} = \exp\left(\frac{E_0}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (5.12)$$

where E_0 is the activation energy, T_0 a reference temperature, and R the gas constant. Using this shift, the viscosity curves measured at different temperatures can be translated to generate a master curve at a specific temperature. Figure 5.4 [9] presents the viscosity of a low density polyethylene with measured values shifted to a reference temperature of 150 °C. For the shift in Fig. 5.4, an activation energy $E_0 = 54$ kJ/mol was used.

Several models that are used to represent the strain rate dependence of polymer melts are presented later in this chapter.

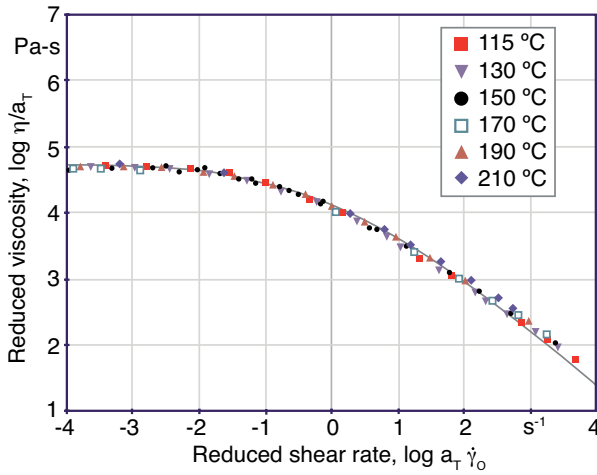


Figure 5.4 Reduced viscosity curve for a low density polyethylene at a reference temperature of 150 °C

5.1.3 Normal Stresses in Shear Flow

The tendency of polymer molecules to “curl-up” while they are being stretched in shear flow results in normal stresses in the fluid. For example, shear flows exhibit a deviatoric stress defined by

$$\tau_{xy} = \eta(\dot{\gamma})\dot{\gamma}_{xy} \quad (5.13)$$

Measurable normal stress differences, $N_1 = \tau_{xx} - \tau_{yy}$ and $N_2 = \tau_{yy} - \tau_{zz}$ are referred to as the *first* and *second normal stress differences*. The first and second normal stress differences are material dependent and are defined by

$$N_1 = \tau_{xx} - \tau_{yy} = -\psi_1(\dot{\gamma}, T)\dot{\gamma}_{xy}^2 \quad (5.14)$$

$$N_2 = \tau_{yy} - \tau_{zz} = -\psi_2(\dot{\gamma}, T)\dot{\gamma}_{xy}^2 \quad (5.15)$$

The material functions ψ_1 and ψ_2 are called the primary and secondary normal stress coefficients, and are also functions of the magnitude of the strain rate tensor and temperature. The first and second normal stress differences do not change in sign when the direction of the strain rate changes. This is reflected in Eqs. 5.14 and 5.15. Figure 5.5 [9] presents the first normal stress difference coefficient for the low density polyethylene melt shown in Fig. 5.4 at a reference temperature of 150 °C. The second normal stress difference is difficult to measure and is often approximated by

$$\psi_2(\dot{\gamma}) \approx -0.1\psi_1(\dot{\gamma}) \quad (5.16)$$

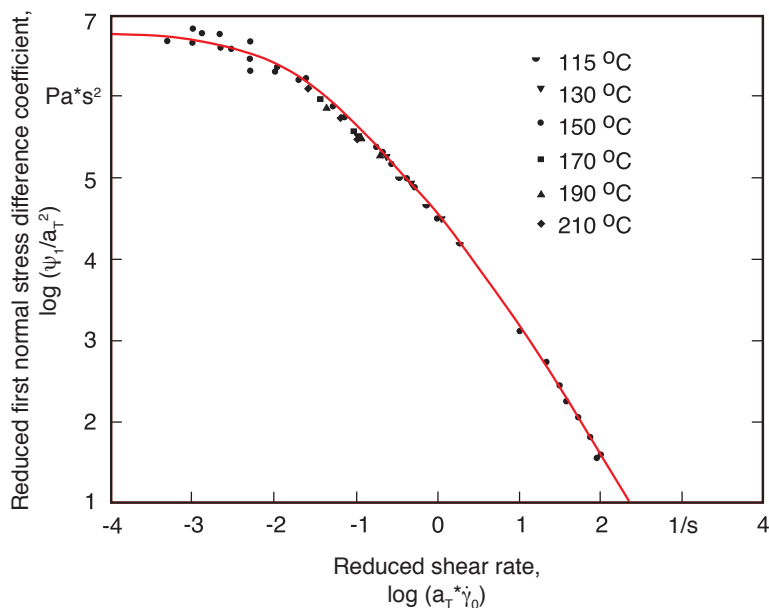


Figure 5.5 Reduced first normal stress difference coefficient for a low density polyethylene melt at a reference temperature of 150 °C

5.1.4 Deborah Number

A useful parameter often used to estimate the elastic effects during flow is the Deborah number³, De . The Deborah number is defined by

$$De = \frac{\lambda}{t_p} \quad (5.17)$$

³ From the Song of Deborah, Judges 5:5 – “*The mountains flowed before the Lord.*” M. Reiner is credited for naming the Deborah number; *Physics Today*, (January 1964).



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where λ is the relaxation time of the polymer and t_p is a characteristic process time. The characteristic process time can be defined by the ratio of characteristic die dimension and average speed through the die. A Deborah number of zero represents a viscous fluid and a Deborah number of ∞ an elastic solid. As the Deborah number becomes > 1 , the polymer does not have enough time to relax during the process, resulting in possible deviations in extrudate dimension or irregularities, such as *extrudate swell*⁴, *shark skin*, or even *melt fracture*.

Although many factors affect the amount of extrudate swell, fluid “memory” and normal stress effects are the most significant ones. However, abrupt changes in boundary conditions, such as the separation point of the extrudate from the die, also play a role in the swelling or cross section reduction of the extrudate. In practice, the fluid memory contribution to die swell can be mitigated by lengthening the land length of the die. This is schematically depicted in Fig. 5.6. A long die land separates the polymer from the manifold long enough to allow it to “forget” its past shape.

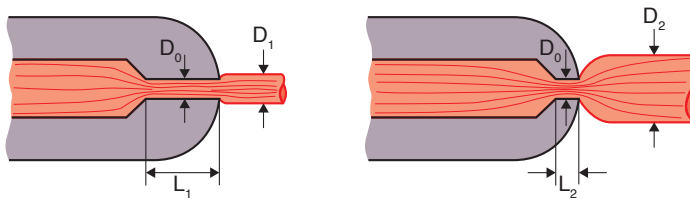


Figure 5.6 Schematic diagram of extrudate swell during extrusion

Waves in the extrudate may also appear as a result of high speeds during extrusion that do not allow the polymer to relax. This phenomenon is generally referred to as *shark skin* and is shown for a high density polyethylene in Fig. 5.7a [10]. It is possible to extrude at such high speeds that an intermittent separation of melt and inner die walls occurs, as shown in Fig. 5.7b. This phenomenon is often referred to as the *stick-slip effect* or *spurt flow* and is attributed to high shear stresses between the polymer and the die wall. This phenomenon occurs when the shear stress is near the critical value of 0.1 MPa [11–13]. If the speed is further increased, a helical geometry is extruded, as shown for a polypropylene extrudate in Fig. 5.7c. Eventually, the speeds become so high that a chaotic pattern develops, such as the one shown in Fig. 5.7d. This well-known phenomenon is called *melt fracture*. The

⁴ It should be pointed out that Newtonian fluids, which do not experience elastic or normal stress effects, also show some extrudate swell or reduction. A Newtonian fluid that is being extruded at high shear rates reduces its cross-section to 87% of the diameter of the die, whereas if extruded at very low shear rates, it swells to 113% of the diameter of the die. This swell is due to inertia effects caused by the change from the parabolic velocity distribution inside the die to the flat velocity distribution of the extrudate.

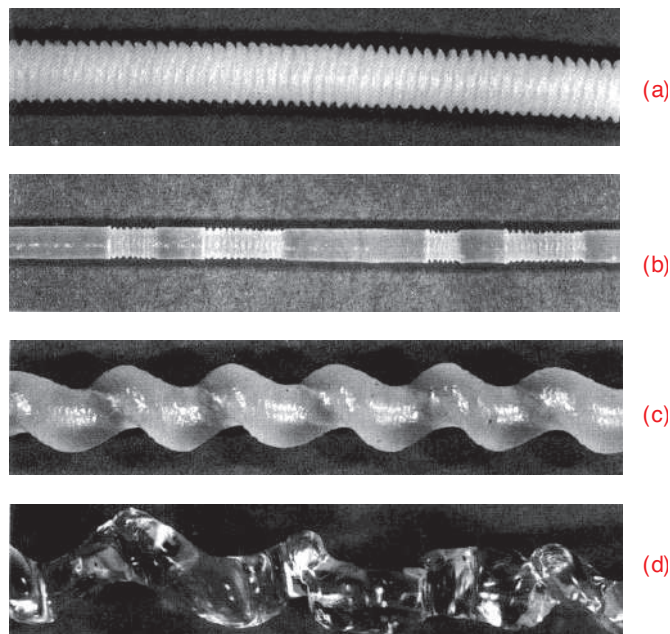


Figure 5.7 Various shapes of extrudates under melt fracture

shark skin effect is rarely experienced with linear polymers, which tend to experience spurt flow

It has been reported that the critical shear stress is independent of the melt temperature, but inversely proportional to the weight average molecular weight [14, 12]. However, Vinogradov et al. [15] presented results showing that the critical stress was independent of molecular weight, except for low molecular weights. Dealy and co-workers [16], and Denn [17] provide an extensive overview of various melt fracture phenomena that is recommended reading.

To summarize, the Deborah number and the size of the deformation imposed upon the material during processing determine how to most accurately model the system. Figure 5.8 [1] helps visualize the relation between time scale, deformation, and applicable model. At small Deborah numbers, the polymer can be modeled as a Newtonian fluid, and at very high Deborah numbers the material can be modeled as a Hookean solid. In between, the viscoelastic region is divided in two areas: the linear viscoelastic region for small deformations, and the non-linear viscoelastic region for large deformations. Linear viscoelasticity was briefly discussed in Chapter 2.

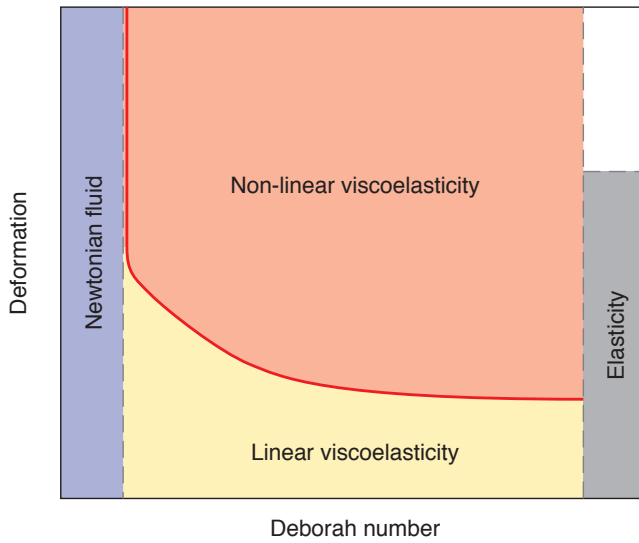


Figure 5.8 Schematic of Newtonian, elastic, linear, and non-linear viscoelastic regimes as a function of deformation and Deborah number during deformation of polymeric materials

■ 5.2 Viscous Flow Models

Strictly speaking, the viscosity η , measured with shear deformation viscometers, should not be used to represent the elongational terms located on the diagonal of the stress and strain rate tensors. Elongational flows are briefly discussed later in this chapter. A rheologist's task is to find the models that best fit the data for the viscosity represented in Eq. 5.5. Some of the models used by polymer processors on a day-to-day basis to represent the viscosity of industrial polymers are presented in the next section.

5.2.1 The Power Law Model

The power law model proposed by Ostwald [18] and de Waale [19] is a simple model that accurately represents the shear thinning region in the viscosity versus strain rate curve but neglects the Newtonian plateau present at small strain rates. The power law model can be written as follows:

$$\eta = m(T)\dot{\gamma}^{n-1} \quad (5.18)$$

where m is referred to as the *consistency index* and n the *power law index*. The consistency index may include the temperature dependence of the viscosity such as represented in Eq. 5.11, and the power law index represents the shear thinning behavior of the polymer melt. Figure 5.9 presents normalized velocity distributions inside a tube for a fluid calculated using the power law model with various power law indices. It should be noted that the limits of this model are

$$\eta \rightarrow 0 \text{ as } \dot{\gamma} \rightarrow \infty \text{ and } \eta \rightarrow \infty \text{ as } \dot{\gamma} \rightarrow 0$$

The infinite viscosity at zero strain rates leads to an erroneous result for regions of zero shear rate, such as at the center of a tube. This results in a predicted velocity distribution that is flatter at the center than the experimental profile. In computer simulation of polymer flows, this problem is often overcome by using a truncated model such as

$$\eta = m_0(T) \dot{\gamma}^{n-1} \text{ for } \dot{\gamma} > \dot{\gamma}_0 \text{ and} \quad (5.19a)$$

$$\eta = m_0(T) \text{ for } \dot{\gamma} \leq \dot{\gamma}_0 \quad (5.19b)$$

where m_0 represents a zero shear rate ($\dot{\gamma}_0$) viscosity. Table 5.1 presents a list of typical power law and consistency indices for common thermoplastics.

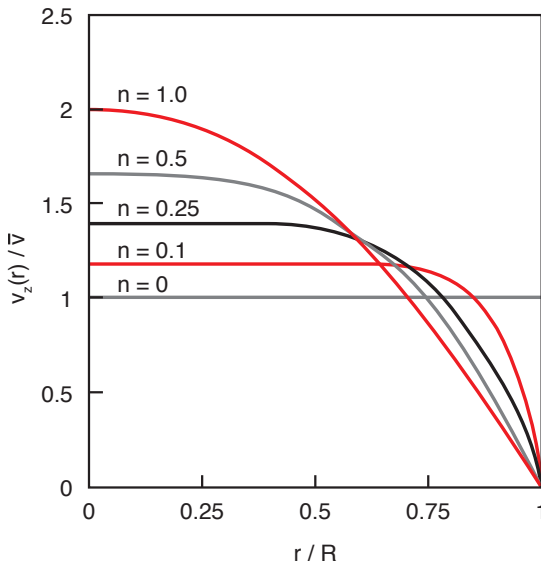


Figure 5.9 Pressure flow velocity distributions inside a tube for fluids with various power law indices

Table 5.1 Power Law and Consistency Indices for Common Thermoplastics

Polymer	m (Pa·s ^{n})	n	T (°C)
Polystyrene	2.80×10^4	0.28	170
High density polyethylene	2.00×10^4	0.41	180
Low density polyethylene	6.00×10^3	0.39	160
Polypropylene	7.50×10^3	0.38	200
Polyamide 66	6.00×10^2	0.66	290
Polycarbonate	6.00×10^2	0.98	300
Polyvinyl chloride	1.70×10^4	0.26	180

5.2.2 The Bird-Carreau-Yasuda Model

A model that fits the whole range of strain rates was developed by Bird and Carreau [20] and Yasuda [21]; it contains five parameters:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[1 + |\lambda \dot{\gamma}|^a \right]^{(n-1)/a} \quad (5.20)$$

where η_0 is the zero shear rate viscosity, η_∞ is an infinite shear rate viscosity, λ is a time constant, n is the power law index and a is a constant, which in the original Bird-Carreau model is $a = 2$. In many cases, the infinite shear rate viscosity is negligible, reducing Eq. 5.20 to a three parameter model. Equation 5.20 was modified by Menges, Wortberg, and Michaeli [22] to include a temperature dependence using a WLF relation. The modified model, which is used in commercial polymer data banks, is written as follows:

$$\eta = \frac{k_1 a_T}{[1 + k_2 \dot{\gamma} a_T]^{k_3}} \quad (5.21)$$

where the shift a_T applies well for amorphous thermoplastics and is written as

$$\ln a_T = \frac{8.86(k_4 - k_5)}{101.6 + k_4 - k_5} - \frac{8.86(T - T_5)}{101.6 + T - k_5} \quad (5.22)$$

Table 5.2 presents constants k_i for Carreau-WLF (amorphous) and Carreau-Arrhenius models (semi-crystalline) for various common thermoplastics. In addition to the temperature shift, Menges, Wortberg and Michaeli [22] measured a pressure dependence of the viscosity and proposed the following model, which includes both temperature and pressure viscosity shifts:

$$\log \eta(T, p) = \log \eta_0 + \frac{8.86(T^* - T_s)}{101.6 + T^* - T_s} - \frac{8.86(T - T_s + 0.02p)}{101.6 + (T - T_s + 0.02p)} \quad (5.23)$$

where p is in bar, and the constant 0.02 represents a 0.02 K shift per bar⁵. In the above equation, the first term represents a shift between the measured temperature T^* and the reference temperature T_s . The second term represents the temperature and pressure shifts between the actual temperature and the reference temperature, as well as between 1 bar and the actual pressure. Hence, in the above model a rise in pressure is equivalent to a drop in temperature.

Table 5.2 Constants for Carreau-WLF (Amorphous) and Carreau-Arrhenius (Semi-Crystalline) Models for Various Common Thermoplastic

Polymer	k_1 (Pa-s)	k_2 (s)	k_3	k_4 (°C)	k_5 (°C)	T_0 (°C)	E_0 (J/mol)
Polystyrene	1777	0.064	0.73	200	123	–	–
High density polyethylene	24198	1.38	0.60	–	–	200	22272
Low density polyethylene	317	0.015	0.61	–	–	189	43694
Polypropylene	1386	0.091	0.68	–	–	220	427198
Polyamide 66	44	0.00059	0.40	–	–	300	123058
Polycarbonate	305	0.00046	0.48	320	153	–	–
Polyvinyl chloride	1786	0.054	0.73	185	88	–	–

5.2.3 The Bingham Fluid

The Bingham fluid is an empirical model that represents the rheological behavior of materials that exhibit a “no flow” region below certain yield stresses, τ_y , such as polymer emulsions and slurries. Since these materials flow like a Newtonian liquid above the yield stress, the Bingham model can be represented by

$$\eta = \infty \quad \text{or} \quad \dot{\gamma} = 0 \quad \tau \leq \tau_y \tag{5.24a}$$

$$\eta = \mu_0 + \frac{\tau_y}{\dot{\gamma}} \quad \tau \geq \tau_y \tag{5.24b}$$

Here, τ is the magnitude of the deviatoric stress tensor and is computed in the same way as in Eq. 5.7.

5.2.4 Elongational Viscosity

In polymer processes, such as fiber spinning, blow molding, thermoforming, foaming, certain extrusion die flows, and compression molding with specific processing conditions, the major mode of deformation is elongational.

⁵ This constant can be in the range of 0.01 to 0.03.

To illustrate elongational flows, consider the fiber spinning process shown in Fig. 5.10.

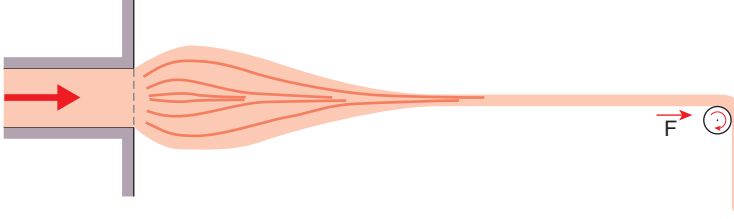


Figure 5.10 Schematic diagram of a fiber spinning process

A simple elongational flow is developed as the filament is stretched with the following components for the rate of deformation:

$$\dot{\gamma}_{11} = -\dot{\epsilon} \quad (5.25a)$$

$$\dot{\gamma}_{22} = -\dot{\epsilon} \quad (5.25b)$$

$$\dot{\gamma}_{33} = 2\dot{\epsilon} \quad (5.25c)$$

where $\dot{\epsilon}$ is the elongation rate, and the off-diagonal terms of $\dot{\gamma}_{ij}$ are all zero. The diagonal terms of the total stress tensor can be written as

$$\sigma_{11} = -p - \eta\dot{\epsilon} \quad (5.26a)$$

$$\sigma_{22} = -p - \eta\dot{\epsilon} \quad (5.26b)$$

and

$$\sigma_{33} = -p + 2\eta\dot{\epsilon} \quad (5.26c)$$

Since the only outside forces acting on the fiber are in the axial or 3 direction, for the Newtonian case, σ_{11} and σ_{12} must be zero. Hence,

$$p = -\eta\dot{\epsilon} \quad \text{and} \quad (5.27)$$

$$\sigma_{33} = 3\eta\dot{\epsilon} = \bar{\eta}\dot{\epsilon} \quad (5.28)$$

which is known as *elongational viscosity* or *Trouton viscosity* [23]. This is analogous to elasticity where the following relation between elastic modulus, E , and shear modulus, G , can be written

$$\frac{E}{G} = 2(1 + \nu) \quad (5.29)$$

where ν is Poisson's ratio. For the incompressibility case, where $\nu = 0.5$, Eq. 5.29 reduces to

$$\frac{E}{G} = 3 \tag{5.30}$$

Figure 5.11 [24] shows shear and elongational viscosities for two types of polystyrene. In the region of the Newtonian plateau, the limit of 3, shown in Eq. 5.28, is quite clear. Figure 5.12 presents plots of elongational viscosities as a function of stress for various thermoplastics at common processing conditions. It should be emphasized that measuring elongational or extensional viscosity is an extremely difficult task. For example, in order to maintain a constant strain rate, the specimen must be deformed uniformly exponentially. In addition, a molten polymer

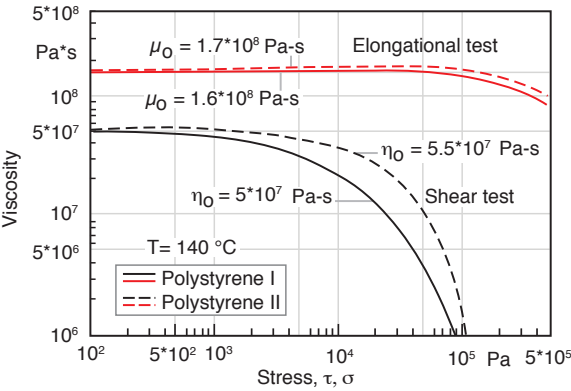


Figure 5.11 Shear and elongational viscosity curves for two types of polystyrene

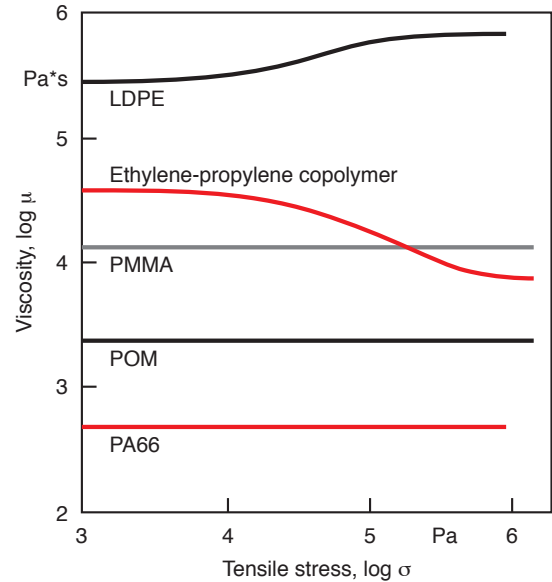


Figure 5.12 Elongational viscosity curves as a function of tensile stress for several thermoplastics

must be tested completely submerged in a heated, neutrally buoyant liquid at constant temperature.

5.2.5 Rheology of Curing Thermosets

The conversion or cure dependent viscosity of a curing thermoset polymer increases as the molecular weight of the reacting polymer increases. For the vinyl ester, whose curing history⁶ is shown in Fig. 5.13 [25], the viscosity behaves as shown in Fig. 5.14 [25]. Hence, a complete model for viscosity of a reacting polymer must contain the effects of strain rate, $\dot{\gamma}$, temperature, T , and degree of cure, c , such as

$$\eta = \eta(\dot{\gamma}, T, c) \quad (5.31)$$

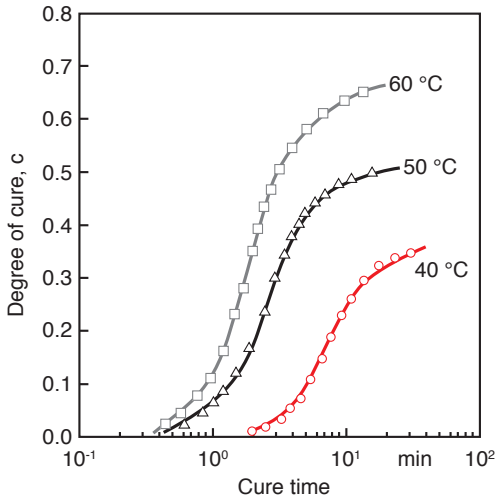


Figure 5.13 Degree of cure as a function of time for a vinyl ester at various isothermal cure conditions

There are no generalized models that include all these variables for thermosetting polymers. However, extensive work has been done on the viscosity of polyurethanes [26, 27] used in reaction injection molding processes. An empirical relation, sometimes referred to as the Castro-Macosko model, which models the viscosity of these mixing-activated polymers, given as a function of temperature and degree of cure, is written as

$$\eta = \eta_0 e^{\frac{E}{RT}} \left(\frac{c_g}{c_g - c} \right)^{C_1 + C_2 c} \quad (5.32)$$

⁶ A more in-depth view of curing and solidification processes of thermosetting polymers is given in Chapter 7.

where E is the activation energy of the polymer, R is the ideal gas constant, T is the temperature, c_g is the gel point⁷, c the degree of cure, and C_1 and C_2 are constants that fit the experimental data. Figure 5.15 shows the viscosity as a function of time and temperature for a 47 % MDI-BDO P(PO-EO) polyurethane, and Fig. 5.16 shows the viscosity as a function of degree of cure.

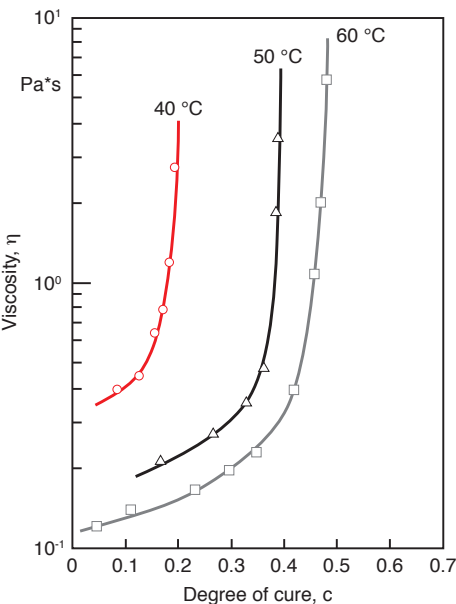


Figure 5.14 Viscosity as a function of degree of cure for a vinyl ester at various isothermal cure conditions

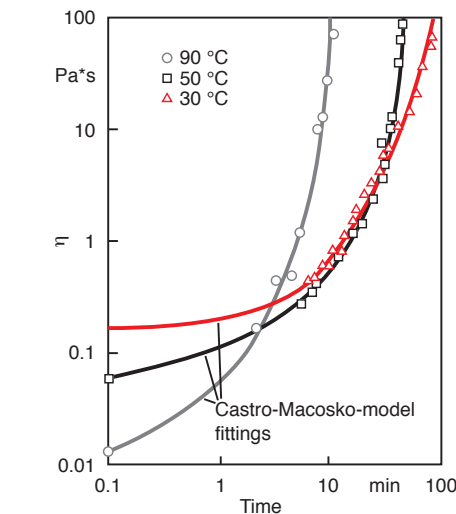


Figure 5.15 Viscosity as a function of time for a 47 % MDI-BDO P(PO-EO) polyurethane at various isothermal cure conditions

⁷ At the gel point the change of the molecular weight with respect to the degree of cure goes to infinity. Hence, it can be said that at this point all the molecules are interconnected.

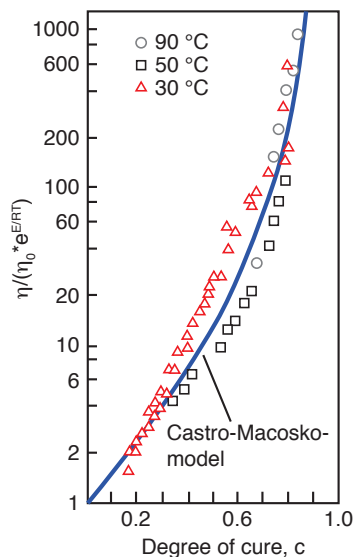


Figure 5.16 Viscosity as a function of degree of cure for a 47% MDI-BDO P(PO-EO) polyurethane at various isothermal cure conditions

5.2.6 Suspension Rheology

Particles suspended in a material, such as in filled or reinforced polymers, have a direct effect on the properties of the final article and on the viscosity during processing. Numerous models have been proposed to estimate the viscosity of filled liquids [28–32]. Most models proposed are a power series of the form⁸

$$\frac{\eta_f}{\eta_0} = 1 + a_1\phi + a_2\phi^2 + a_3\phi^3 + \dots \quad (5.33)$$

The linear term in Eq. 5.33 represents the narrowing of the flow passage caused by the filler that is passively entrained by the fluid and sustains no deformation, as shown in Fig. 5.17. For instance, Einstein's model, which only includes the linear term with $a_1 = 2.5$, was derived based on a viscous dissipation balance. The quadratic term in the equation represents the first-order effects of interaction between the filler particles. Geisbüsch suggested a model with a yield stress, where the strain rate of the melt increases by a factor κ as

$$\eta_f = \frac{\tau_0}{\dot{\gamma}} + \kappa\eta_0(\kappa\dot{\gamma}) \quad (5.34)$$

For high deformation stresses, which are typical in polymer processing, the yield stress in the filled polymer melt can be neglected. Figure 5.18 compares Geisbüsch's experimental data to Eq. 5.33 using the coefficients derived by Guth [30].

⁸ The model developed by Guth in 1938 best fits experimental: $\frac{\eta_f}{\eta_0} = 1 + 2.5\phi + 14.1\phi^2$

However, a full analysis of the first-order particle interactions gives an analytical value for the quadratic term of 6.96.

The data and Guth's model seem to agree well. A comprehensive survey on particulate suspensions was given by Gupta [33], and one on short-fiber suspensions by Milliken and Powell [34].

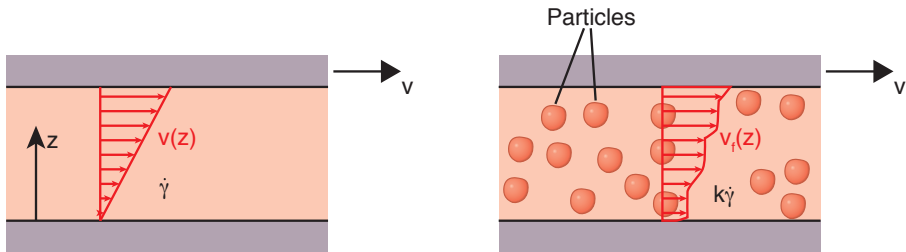


Figure 5.17 Schematic diagram of strain rate increase in a filled system

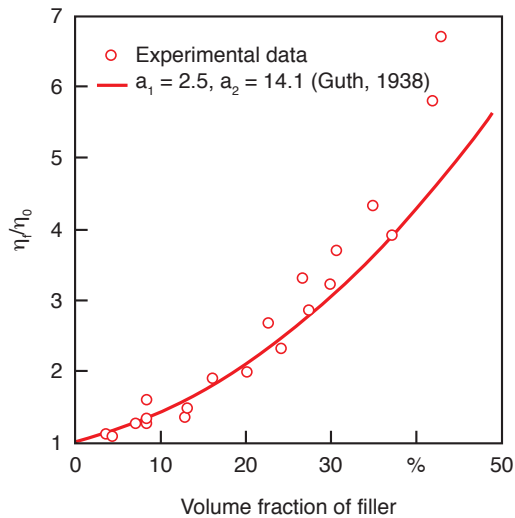


Figure 5.18 Viscosity increase as a function of volume fraction of filler for polystyrene and low density polyethylene containing spherical glass particles with diameters ranging between 36 μm and 99.8 μm

■ 5.3 Simplified Flow Models Common in Polymer Processing

Many polymer processing operations can be modeled using simplified geometries and material models. This section presents several isothermal flow models in simple geometries using a Newtonian viscosity and a power-law viscosity as described in Eq. 5.18. Although it is very common to simplify analyses of polymer processes by assuming isothermal conditions, most operations are non-isothermal because they include melting and are often influenced by viscous dissipation. Hence, the temperature of the polymer melt ranges between T_g (for amorphous polymers) or T_m (for semi-crystalline polymers) and the heater temperature T_w (the subscript w is often used for “wall”) and often exceeds T_w due to viscous dissipation. An estimate of the maximum temperature rise due to viscous heating is given by

$$\Delta T_{\max} = \frac{\eta v_0^2}{8k} \quad (5.35)$$

where v_0 represents a characteristic velocity in the flow system, such as plate velocity in a simple shear flow, and k represents the thermal conductivity. To estimate the importance of viscous dissipation, the Brinkman number, Br , is often computed

$$Br = \frac{\eta v_0^2}{k(T_w - T_{g \text{ or } m})} \quad (5.36)$$

The Brinkman number is the ratio of the heat generated via viscous dissipation and the heat conducted out of the system via conduction. A Brinkman number > 1 implies that the temperature field will be affected by viscous dissipation. The choice of temperatures in the denominator of the equation depends on the type of material and problem being analyzed.

5.3.1 Simple Shear Flow

Simple shear flows, as represented in Fig. 5.19, are very common in polymer processing, such as inside extruders as well as in certain coating flows. The flow field in simple shear is the same for all fluids and is described by

$$v_z = v_0 \frac{y}{h} \quad (5.37)$$

for the velocity distribution and

$$Q = \frac{v_0 h W}{2} \quad (5.38)$$

for the volumetric throughput, where W represents the width of the plates.

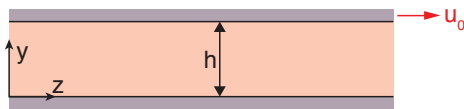


Figure 5.19 Schematic diagram of a simple shear flow

5.3.2 Pressure Flow Through a Slit

The pressure flow through a slit, as depicted in Fig. 5.20, is encountered in flows through extrusion dies or inside injection molds. The flow field for a Newtonian fluid is described by

$$v_z(y) = \left(\frac{h^2 \Delta p}{8\mu L} \right) \left[1 - \left(\frac{2y}{h} \right)^2 \right] \quad (5.39)$$

and

$$Q = \frac{Wh^3 \Delta p}{12\mu L} \quad (5.40)$$

for the net volumetric throughput. When using the power-law model, the flow field is described by

$$v_z(y) = \left(\frac{h}{2(s+1)} \right) \left(\frac{h \Delta p}{2\mu L} \right)^s \left[1 - \left(\frac{2y}{h} \right)^{s+1} \right] \quad (5.41)$$

and

$$Q = \frac{Wh^2}{2(s+2)} \left(\frac{h \Delta p}{2\mu L} \right)^s \quad (5.42)$$

for the throughput, where $s = 1/n$, and n the power-law index.

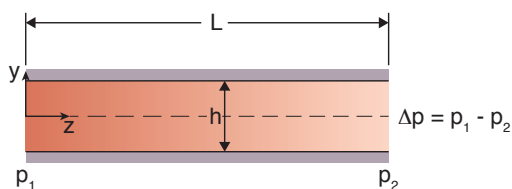


Figure 5.20 Schematic diagram of pressure flow through a slit

5.3.3 Pressure Flow through a Tube – Hagen-Poiseuille Flow

Pressure flow through a tube (Fig. 5.21), or Hagen-Poiseuille flow, is the type that exists inside the runner system in injection molds, as well as in extrusion dies and inside the capillary viscometer. For a Newtonian fluid, the flow field inside a tube is described by

$$v_z(r) = \frac{R^2 \Delta p}{4\mu L} \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (5.43)$$

and

$$Q = \frac{\pi R^4 \Delta p}{8\mu L} \quad (5.44)$$

for the throughput.

Using the power law model, the flow through a tube is described by

$$v_z(r) = \frac{R}{1+s} \left(\frac{R \Delta p}{2mL} \right)^s \left[1 - \left(\frac{r}{R} \right)^{s+1} \right] \quad (5.45)$$

and

$$Q = \left(\frac{\pi R^3}{s+3} \right) \left(\frac{R \Delta p}{2mL} \right)^s \quad (5.46)$$

for the throughput.

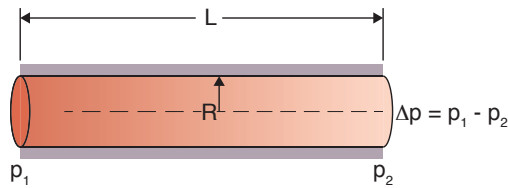


Figure 5.21 Schematic diagram of pressure flow through a tube

5.3.4 Couette Flow

The Couette device, as depicted in Fig. 5.22, is encountered in bearings and in certain types of rheometers. It is also used as a simplified flow model for mixers and extruders. The Newtonian flow field in a Couette device is described by

$$v_\theta(r) = \frac{\Omega}{\kappa^2 - 1} \left(\frac{R_0^2 - r^2}{r} \right) \quad (5.47)$$

where $\Omega = R_0 / R_i$. Using the power law model, the flow field inside a Couette device is described by

$$v_\theta(r) = \frac{\Omega}{\kappa^{2s} - 1} \left(\frac{R_0^{2s} - r^{2s}}{r^{2s-1}} \right) \quad (5.48)$$

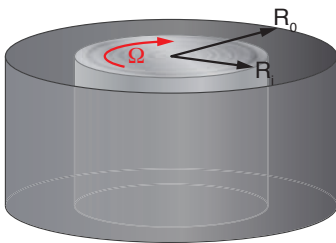


Figure 5.22 Schematic diagram of a Couette device

■ 5.4 Viscoelastic Flow Models

Viscoelasticity has already been introduced in Chapter 3, based on linear viscoelasticity. However, in polymer processing large deformations are imposed on the material, requiring the use of non-linear viscoelastic models. There are two types of general, non-linear viscoelastic flow models: the differential type and the integral type.

5.4.1 Differential Viscoelastic Models

Differential models have traditionally been the choice for describing the viscoelastic behavior of polymers when simulating complex flow systems. Many differential viscoelastic models can be described using the general form

$$Y\tau + \lambda_1 \tau_{(1)} + \lambda_2 \left(\dot{\gamma} \cdot \tau + \tau \cdot \dot{\gamma} \right) + \lambda_3 (\tau \cdot \tau) = \eta_0 \dot{\gamma} \quad (5.49)$$

where $\tau_{(1)}$ is the *first contravariant convected time derivative* of the deviatoric stress tensor and represents rates of change with respect to a convected coordinate system that moves and deforms with the fluid. The *convected derivative* of the deviatoric stress tensor is defined as

$$\tau_{(1)} = \frac{D\tau}{Dt} - (\nabla v^t \cdot \tau + \tau \cdot \nabla v) \quad (5.50)$$

The constants in Eq. 5.49 are defined in Table 5.3 for various viscoelastic models commonly used to simulate polymer flows. A review by Bird and Wiest [6] provides a more complete list of existing viscoelastic models, and Giacomini et al. renewed the interest in co-rotational models [35].

The *upper convective model* and the *White-Metzner model* are very similar, with the exception that the White-Metzner model incorporates the strain rate effects of the relaxation time and the viscosity. Both models provide a first order approximation to flows in which shear rate dependence and memory effects are important. However, both models predict zero second normal stress coefficients. The *Giesekus model* is molecular-based, non-linear in nature and describes the power law region for viscosity and both normal stress coefficients. The *Phan-Thien Tanner models* are based on network theory and give non-linear stresses. Both the Giesekus and Phan-Thien Tanner models have been successfully used to model complex flows.

Table 5.3 Definition of Constants in Eq. 5.49

Constitutive model	γ	λ_1	λ_2	λ_3
Generalized Newtonian	1	0	0	0
Upper convected Maxwell	1	λ_1	0	0
White-Metzner	1	$\lambda_1(\dot{\gamma})$	0	0
Phan-Thien Tanner-1	$e^{-\varepsilon(\lambda/\eta_0)tr\underline{\underline{\tau}}}$	λ_1	$\frac{1}{2}\xi\lambda$	0
Phan-Thien Tanner-2	$1-\varepsilon(\lambda/\eta_0)tr\underline{\underline{\tau}}$	λ	$\frac{1}{2}\xi\lambda$	0
Giesekus	1	λ_1	0	$-(\alpha\lambda_1/\eta_0)$

An overview of viscoelastic flow models with a literature review on the subject is given by Giacomini et al. [6] and Phan-Thien [36], and details on numerical implementation of viscoelastic models are given by Osswald and Hernández-Ortiz [37]. As an example of the application of differential models to predict flow of polymeric liquids, it is worth mentioning the work by Dietsche and Dooley [38], who evaluated the White-Metzner, the Phan-Thien Tanner-1, and the Giesekus models by comparing finite element⁹ and experimental results of the flow inside multi-layered coextrusion dies. Figure 5.23 [39] presents the progression of a matrix of colored circular polystyrene strands flowing in an identical polystyrene matrix down a channel with a square cross section of 0.95×0.95 cm. The cuts in the figure are shown at intervals of 7.6 cm.

The circulation pattern caused by the secondary normal stress differences inside non-circular dies were captured well by the Phan-Thien Tanner and Giesekus models but, as expected, not by the White-Metzner model. Figure 5.24 presents flow patterns predicted by the Phan-Thien Tanner model along with the experimental rearrangement of 165 initially horizontal layers of polystyrene in square, rectangular, and tear-drop shaped dies¹⁰. In all three cases, the shapes of the circulation patterns were predicted accurately. The flow simulation of the square die predicted a velocity on the order of 10^{-5} m/s along the diagonal of the cross section, which was in agreement with the experimental results. Holmes et al. [40] simulated the viscoelastic secondary flows in square ducts using a finite volume approach. Single mode and multimode Giesekus and Phan-Thien Tanner (PTT) models were implemented and were able to reproduce full three-dimensional (3D) flow through the square ducts. Results for low density polyethylene (LDPE), polystyrene, and polycarbonate were all in agreement with experiments [39] and FEM simulation [38].

⁹ They used the commercially available code POLYFLOW for their simulation.

¹⁰ These geometries are typical for distribution manifolds used in sheeting dies.

Also worth mentioning is work done by Baaijens [41], who evaluated the Phan-Thien Tanner models 1 and 2, and the Giesekus models. He compared finite element results to measured isochromatic birefringence patterns using complex experiments with polymer melts and solutions. His simulation results predicted the general shape of the measured birefringence patterns. He found that at high Deborah numbers, the Phan-Thien Tanner models converged much more easily than the Giesekus model.

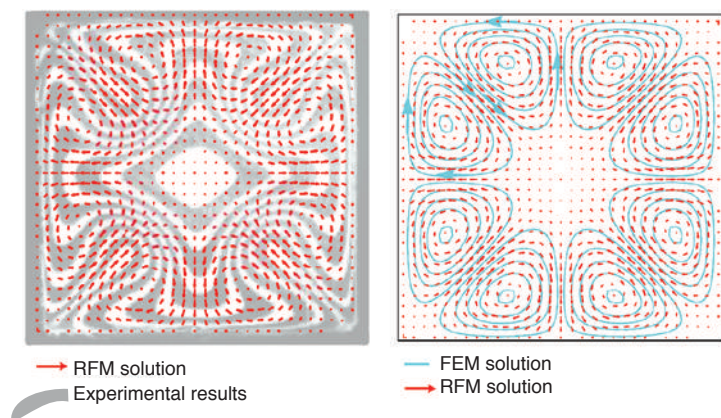


Figure 5.23

Polystyrene strand profile progression in a square die

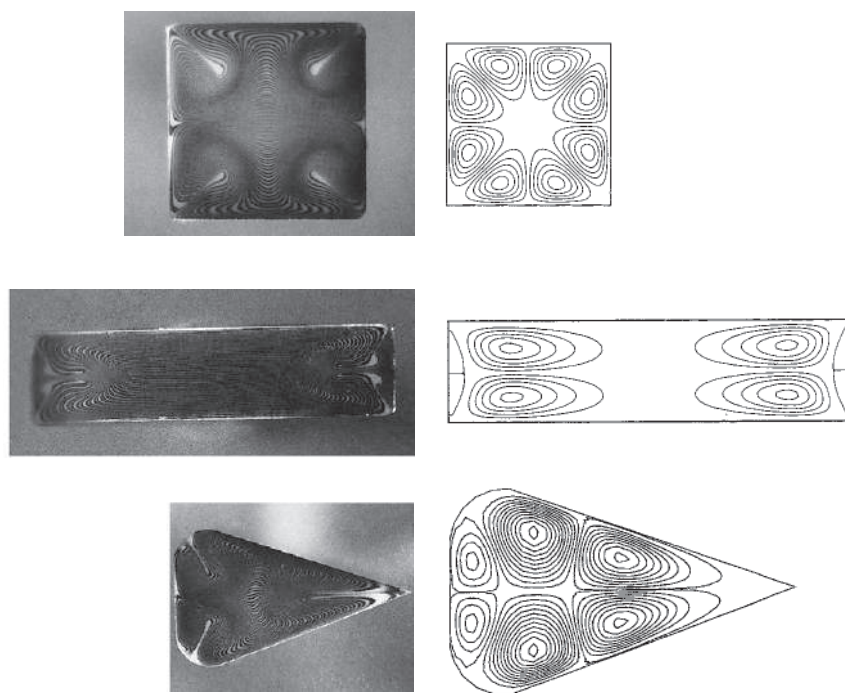


Figure 5.24 Comparison between experimental and predicted flow patterns of polystyrene in square, rectangular, and tear-drop shaped dies

5.4.2 Integral Viscoelastic Models

Integral models with a memory function have been widely used to describe the viscoelastic behavior of polymers and to interpret their rheological measurements [9, 42]. In general the single integral model can be described as

$$\underline{\underline{\tau}} = \int_{-\infty}^t M(t-t') \underline{\underline{S}}(t') dt' \quad (5.51)$$

where $M(t-t')$ is a memory function and $\underline{\underline{S}}(t')$ is a deformation dependent tensor defined by

$$\underline{\underline{S}}(t') = \phi_1(I_1, I_2) \underline{\underline{\gamma}}_{[0]} + \phi_2(I_1, I_2) \underline{\underline{\gamma}}_{[0]}^{[0]} \quad (5.52)$$

where I_1 and I_2 are the first invariant of the Cauchy and Finger strain tensors, respectively.

Table 5.4 [43–47] defines the constants ϕ_1 and ϕ_2 for various models. In Eq. 5.52, $\underline{\underline{\gamma}}_{[0]}$ and $\underline{\underline{\gamma}}_{[0]}^{[0]}$ are the *finite strain tensors* given by

$$\underline{\underline{\gamma}}_{[0]} = \underline{\underline{\Delta}}^t \cdot \underline{\underline{\Delta}} - \underline{\underline{\delta}} \quad \text{and} \quad (5.53)$$

$$\underline{\underline{\gamma}}_{[0]}^{[0]} = \underline{\underline{\delta}} - \underline{\underline{E}} \cdot \underline{\underline{E}}^t \quad (5.54)$$

Table 5.4 Definition of Constants in Eq. 5.52

Constitutive model	ϕ_1	ϕ_2
Lodge rubber-like liquid	1	0
K-BKZ*	$\frac{\partial W}{\partial I_1}$	$\frac{\partial W}{\partial I_2}$
Wagner**	$e^{-\beta \sqrt{\alpha I_1 + (1-\alpha) I_2 - 3}}$	0
Papanastasiou-Scriven-Macosko***	$\frac{\alpha}{(\alpha-3) + \beta I_1 + (1-\beta) I_2}$	0

* $W(I_1, I_2)$ represents a potential function which can be derived from empiricisms or molecular theory.

** Wagner's model is a special form of the K-BKZ model

*** The Papanastasiou-Scriven Macosko model is also a special form of the K-BKZ model.

The terms $\underline{\underline{\Delta}}$ and $\underline{\underline{E}}$ are displacement gradient tensors¹¹ defined by

$$\Delta_{ij} = \frac{\partial x'_i(x'_j, t')}{\partial x_j} \quad \text{and} \quad (5.55)$$

¹¹ Another combination of the displacement gradient tensors often used are the *Cauchy strain tensor* and the *Finger strain tensor* defined by $\underline{\underline{B}}^{-1} = \underline{\underline{\Delta}}^t \cdot \underline{\underline{\Delta}}$ and $\underline{\underline{B}} = \underline{\underline{E}} \cdot \underline{\underline{E}}^t$, respectively.

$$E_{ij} = \frac{\partial x_i(x', t', t)}{\partial x_j'} \quad (5.56)$$

where the components Δ_{ij} measure the displacement of a particle at past time t' relative to its position at present time t , and the terms E_{ij} measure the material displacements at time t relative to the positions at time t' .

A memory function $M(t-t')$ that is often applied and that leads to commonly used constitutive equations is written as

$$M(t-t') = \sum_{k=1}^n \frac{\eta_k}{\lambda_k^2} \exp\left(-\frac{t-t'}{\lambda_k}\right) \quad (5.57)$$

where λ_k and η_k are relaxation times and viscosity coefficients at the reference temperature T_{ref} , respectively.

Once a memory function has been specified one can calculate several material functions using [4]

$$\eta(\dot{\gamma}) = \int_0^\infty M(s) s (\phi_1 + \phi_2) ds \quad (5.58)$$

$$\psi_1(\dot{\gamma}) = \int_0^\infty M(s) s^2 (\phi_1 + \phi_2) ds \quad (5.59)$$

$$\psi_2(\dot{\gamma}) = \int_0^\infty M(s) s^2 (\phi_2) ds \quad (5.60)$$

For example, Figs. 5.25 and 5.26 present the measured [48] viscosity and first normal stress difference data, respectively, for three blow molding high density polyethylene grades along with a fit obtained from the Papanastasiou-Scriven-Macosko [47] form of the K-BKZ equation. A memory function with a relaxation

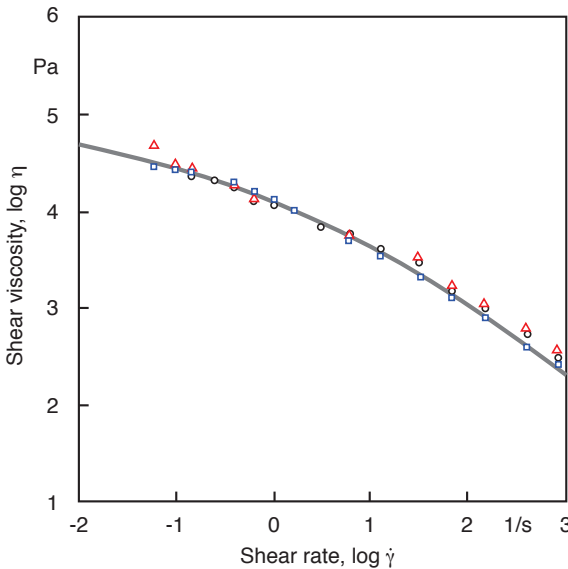


Figure 5.25 Measured and predicted shear viscosity for various high density polyethylene resins at 170 °C

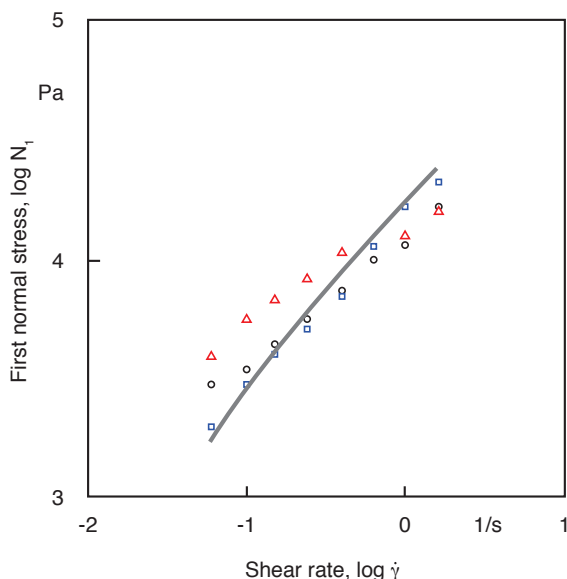


Figure 5.26 Measured and predicted first normal stress difference for various high density polyethylene resins at 170 °C

spectrum of 8 relaxation times was used. The coefficients used to fit the data are summarized in Table 5.5 [42]. The viscosity and first normal stress coefficient data presented in Figs. 5.4 and 5.5 where fitted with the Wagner [9] form of the K-BKZ equation [9]. Luo and Mitsoulis used the K-BKZ model with the data in Table 5.5 to simulate the flow of HDPE through annular dies. Figure 5.27 [42] shows simulation results for a converging, a straight, and a diverging die geometry. The results shown in Fig. 5.27 were in good agreement with experimental results¹².

Table 5.5 Material Parameter Values in Eq. 5.57 for Fitting Data of High Density Polyethylene Melts at 170 °C

k	λ_k (s)	η_k (Pa·s)
1	0.0001	52
2	0.001	148
3	0.01	916
4	0.1	4210
5	1.0	8800
6	10.0	21,200
7	100.0	21,000
8	1000.0	600

¹² The degree of the agreement between experiment and simulation varied between the resins.

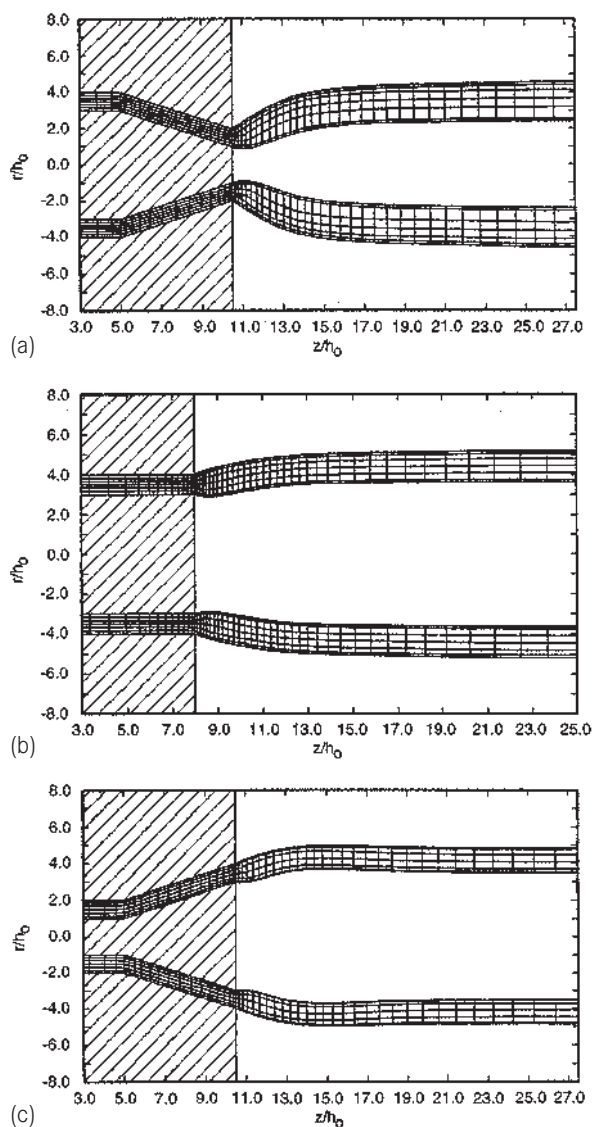


Figure 5.27 Predicted extrudate geometry for: (a) converging, (b) straight, and (c) diverging annular dies

■ 5.5 Rheometry

In industry there are various ways to qualify and quantify the properties of a polymer melt. The techniques range from simple analyses for checking the consistency of the material at certain conditions, to more complex measurements to evaluate viscosity and normal stress differences. This section includes three such techniques to give the reader a general idea of current measuring techniques.

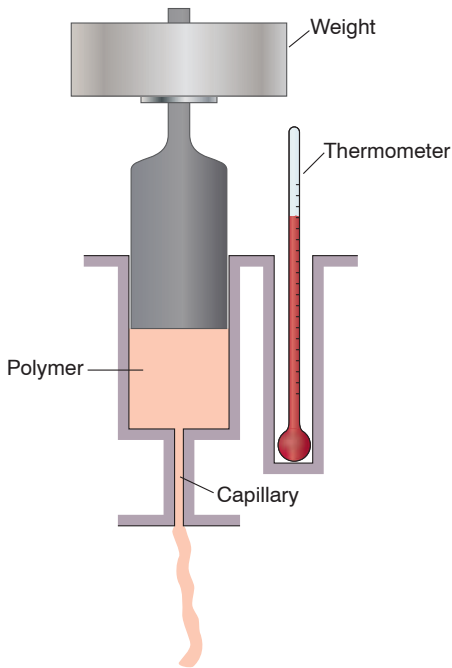


Figure 5.28 Schematic diagram of an extrusion plastometer used to measure melt flow index

5.5.1 The Melt Flow Indexer

The melt flow indexer is often used in industry to characterize a polymer melt and as a simple and quick means of quality control. It takes a single point measurement using standard testing conditions specific to each polymer class on a ram type extruder or extrusion plastometer, as shown in Fig. 5.28. The standard procedure for testing the flow rate of thermoplastics using an extrusion plastometer is described in the ASTM D1238 test [49]. During the test, a sample is heated in the barrel and extruded from a short cylindrical die using a piston actuated by a weight. The weight of the polymer in grams extruded during the 10-minute test is the melt flow index (MFI) of the polymer.

5.5.2 The Capillary Viscometer

The most common and simplest device for measuring viscosity is the capillary viscometer. Its main component is a straight tube or capillary, and it was first used to measure the viscosity of water by Hagen [50] and Poiseuille [51]. A capillary rheometer has a pressure driven flow for which the velocity gradient or strain rate and also the shear rate will be maximum at the wall and zero at the center of the flow, making it a non-homogeneous flow.

Since pressure driven viscometers employ non-homogeneous flows, they can only measure steady shear functions such as viscosity, $\eta(\dot{\gamma})$. However, they are widely used because they are relatively inexpensive to build and simple to operate. Despite their simplicity, long capillary viscometers provide the most accurate viscosity data available. Another major advantage is that the capillary rheometer has no free surfaces in the test region, unlike other types of rheometers, such as the cone and plate rheometers, which we will discuss in the next section. When the strain rate dependent viscosity of polymer melt is measured, capillary rheometers may be the only satisfactory method of obtaining such data at shear rates $> 10 \text{ s}^{-1}$. This is important for processes with higher rates of deformation, such as mixing, extrusion, and injection molding. Because its design is basic and it only needs a pressure head at its entrance, capillary rheometers can easily be attached to the end of a screw- or ram-type extruder for on-line measurements. This makes the capillary viscometer an efficient tool for industry.

The basic features of the capillary rheometer are shown in Fig. 5.29. A capillary tube of radius R and length L (Fig. 5.21) is connected to the bottom of a reservoir. Pressure drop and flow rate through this tube are used to determine the viscosity.

To derive the viscosity relation, the following assumptions are made:

- no velocity in the r and θ directions (Fig. 5.21),
- the polymer is incompressible, and
- fully developed, steady, isothermal, laminar flow.

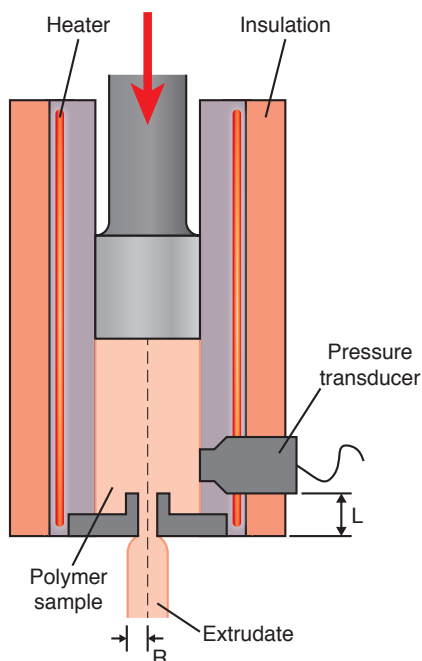


Figure 5.29 Schematic diagram of a capillary viscometer

The capillary viscometer can be modeled using the z-component of the equation of motion in terms of stress, τ , as

$$0 = \frac{dp}{dz} + \frac{1}{r} \frac{d}{dr} (r \tau_{rz}) \quad (5.61)$$

where,

$$\frac{dp}{dz} = \frac{p_0 - p_L}{L} \quad (5.62)$$

Integrating for the shear stress term gives:

$$\tau_{rz} = \frac{(p_0 - p_L)r}{2L} + \frac{C_1}{r} \quad (5.63)$$

The constant C_1 is taken to be zero because the stress cannot be infinite at the tube axis.

5.5.3 Computing Viscosity Using the Bagley and Weissenberg-Rabinowitsch Equations

At the wall the shear stress is:

$$\tau_{r=R} = \tau_w = \frac{R(p_0 - p_L)}{2L} = \frac{R \Delta p}{2L} \quad (5.64)$$

Equation 5.64 requires that the capillary be sufficiently long to assure a fully developed flow where end effects are insignificant. However, due to end effects the actual pressure profile along the length of the capillary exhibits a curvature. The effect is shown schematically in Fig. 5.30 [52] and was corrected by Bagley [53] using the end correction e as,

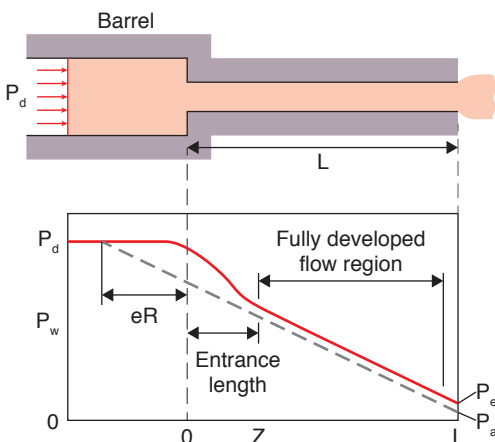


Figure 5.30 Entrance effects in a typical capillary viscometer

$$\tau_w = \frac{1}{2} \frac{(p_0 - p_L)}{\left(\frac{L}{R} + e\right)} \quad (5.65)$$

The correction factor e at a specific shear rate can be found by plotting pressure drop for various capillary L/D ratios as shown in Fig. 5.31 [52].

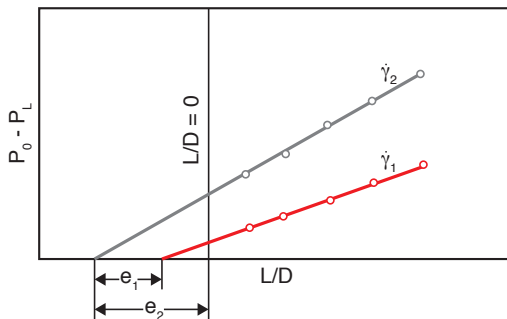


Figure 5.31 Bagley plots for two shear rates

The equation for shear stress can now be written as

$$\tau_{rz} = \frac{r}{R} \tau_w \quad (5.66)$$

To obtain the shear rate at the wall, $\frac{dv_z}{dr}$, the Weissenberg-Rabinowitsch [54] equation can be used

$$-\frac{dv_z}{dr} = \dot{\gamma}_w = \frac{1}{4} \dot{\gamma}_{aw} \left(3 + \frac{d(\ln Q)}{d(\ln \tau)} \right) \quad (5.67)$$

where, $\dot{\gamma}_{aw}$ is the apparent or Newtonian shear rate at the wall and is written as

$$\dot{\gamma}_{aw} = \frac{4Q}{\pi R^3} \quad (5.68)$$

The shear rate and shear stress at the wall are now known. Therefore, using the measured values of the flow rate, Q , and the pressure drop, $p_0 - p_L$, the viscosity can be calculated using

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \quad (5.69)$$

5.5.4 Viscosity Approximation Using the Representative Viscosity Method

A simplified method to compute viscosity, developed by Schümmer and Worthoff [55], takes advantage of the fact that Newtonian and shear thinning materials have a common streamline at which the strain rate is the same. This is schematically represented in Fig. 5.32, where the common streamline is located at r_s . The posi-

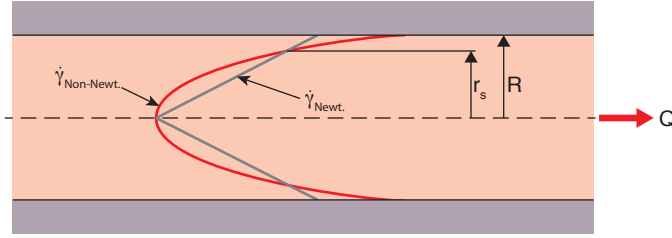


Figure 5.32 Strain rate distribution in Newtonian and non-Newtonian fluids flowing through a capillary

tion of that streamline is related to the power law index and varies between $0.7715 R$ and $0.8298 R$ for power law indices between 1.4 and 0.25. A close approximation is given by¹³

$$r_s \approx \frac{\pi}{4} R = 0.7854 R \quad (5.70)$$

and the strain rate at that point is given by

$$\bar{\dot{\gamma}} = \frac{4}{\pi} \frac{Q}{R^4} r_s \approx \frac{Q}{R^3} \quad (5.71)$$

The shear stress at the location r_s can be calculated using

$$\bar{\tau} = \left(\frac{p_0 - p_L}{L} \right) \frac{r_s}{2} \approx \frac{\pi}{8} R \left(\frac{p_0 - p_L}{L} \right) \quad (5.72)$$

5.5.5 The Cone-Plate Rheometer

The cone-plate rheometer is often used to measure the viscosity and the primary and secondary normal stress coefficient functions as functions of shear rate and temperature. The geometry of a cone-plate rheometer is shown in Fig. 5.33. Because the angle θ_0 is very small, typically $< 5^\circ$, the shear rate can be considered to be constant and is given by

$$\dot{\gamma}_{\theta\phi} = \frac{\Omega}{\theta_0} \quad (5.73)$$

where Ω is the angular velocity of the cone. The shear stress can also be considered constant and can be related to the measured torque, T ,

$$\tau_{\theta\phi} = \frac{3T}{2\pi R^3} \quad (5.74)$$

The viscosity function can now be obtained from

¹³ The value $\pi/4$ was not mathematically derived but offers a significant simplification to the equations with a final error in viscosity of less than 5%.

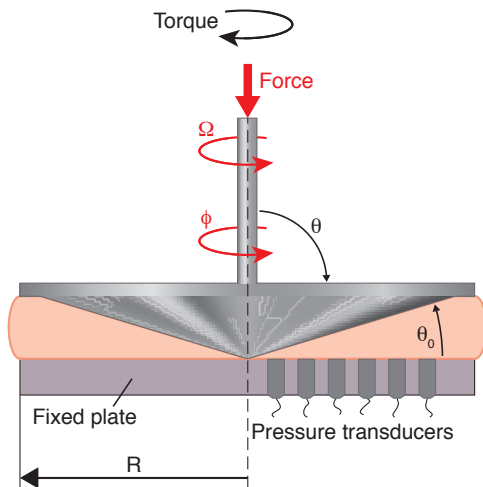


Figure 5.33 Schematic diagram of a cone-plate rheometer

$$\eta(\dot{\gamma}_{\theta\phi}) = \frac{\tau_{\theta\phi}}{\dot{\gamma}_{\theta\phi}} \quad (5.75)$$

The primary normal stress coefficient function, ψ_1 , can be calculated by measuring the force, F , required to maintain the cone in place and can be computed using

$$\psi_1 = \frac{2F}{\pi R^2 \dot{\gamma}^2} \quad (5.76)$$

Although it is also possible to determine the secondary stress coefficient function from the normal stress distribution across the plate, it is very difficult to get accurate data.

5.5.6 The Couette Rheometer

Another rheometer commonly used in industry is the concentric cylinder or Couette flow rheometer schematically depicted in Fig. 5.34. The torque, T , and rotational speed, Ω , can be easily measured. The torque is related to the shear stress that acts on the inner cylinder wall and can be computed as follows:

$$\tau_i = \frac{T}{2\pi r_i^2 L} \quad (5.77)$$

If we consider a power-law fluid confined between the outer and inner cylinder walls of a Couette device, the shear rate at the inner wall can be computed using

$$\dot{\gamma}_i = \frac{2\Omega}{n \left(1 - (r_i / r_o)^{2/n} \right)} \quad (5.78)$$

The power-law index can be determined with experimental data using

$$n = \frac{d \log \tau_i}{d \log \Omega} \quad (5.79)$$

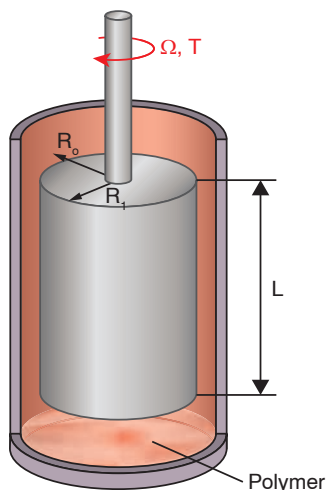


Figure 5.34 Schematic diagram of a Couette rheometer

Once the shear strain rate and stress are known, the viscosity can be computed using

$$\eta = \frac{\tau_i}{\dot{\gamma}} \quad (5.80)$$

The major sources of error in a concentric cylinder rheometer are the end-effects. One way of minimizing these effects is by providing a large gap between the inner cylinder end and the bottom of the closed end of the outer cylinder.

5.5.7 Extensional Rheometry

It should be emphasized that the shear behavior of polymers measured with the equipment described in the previous sections is by no means an indicator of the extensional behavior of polymer melts. Extensional rheometry is the least understood field of rheology. The simplest way to measure extensional viscosities is to stretch a polymer rod held at elevated temperatures at a speed that maintains a constant strain rate as the rod reduces its cross-sectional area. The viscosity can easily be computed as the ratio of instantaneous axial stress to elongational strain rate. The biggest problem when trying to perform this measurement is to hold the rod at its ends as it is pulled apart. The most common way to grab the specimen is with toothed rotary clamps to maintain a constant specimen length [56]. A schematic of Meissner's extensional rheometer incorporating rotary clamps is shown in Fig. 5.35 [56].

Another set-up that can be used to measure extensional properties avoiding clamping problems and without generating orientation during the measurement is the lubricating squeezing flow [57], which generates an equibiaxial deformation. A schematic of this apparatus is shown in Fig. 5.36.

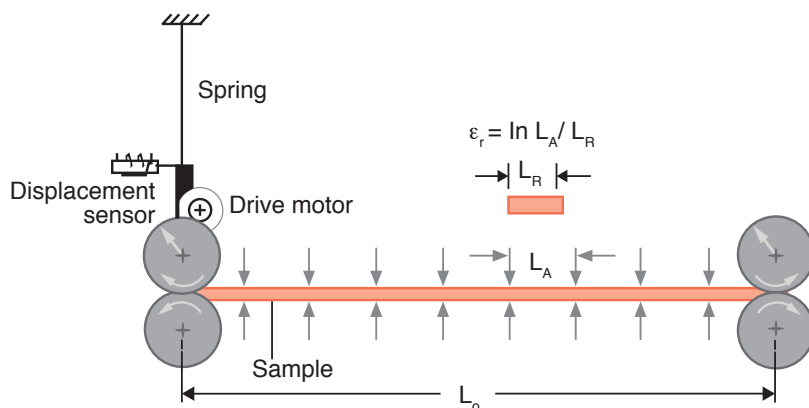


Figure 5.35 Schematic diagram of an extensional rheometer

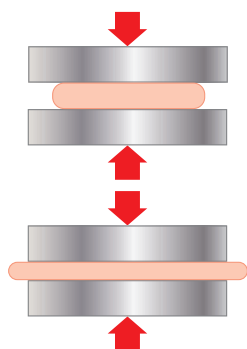


Figure 5.36 Schematic diagram of squeezing flow

It is clear from the apparatus description on Fig. 5.35 that carrying out tests to measure extensional rheometry is a very difficult task. One of the major problems arises because of the fact that, unlike with shear tests, it is not possible to achieve steady state condition with elongational rheometry tests. The reason is that the cross-sectional area of the test specimen is constantly diminishing. Figure 5.37 [56] shows this effect by comparing shear and elongational rheometry data for polyethylene.

Finally, another equibiaxial deformation test is carried out by blowing a bubble and measuring the pressure required and the size of the bubble during the test. This test has been successfully used to measure extensional properties of polymer membranes for blow molding and thermoforming applications. Here, a sheet is clamped between two plates with circular holes and a pressure differential is introduced to deform it. The pressure applied and the resulting deformation of the sheet are monitored with time and related to extensional properties of the material. Assuming an incompressible material, the instantaneous thickness of the sheet can be computed using the notation shown in Fig. 5.38:

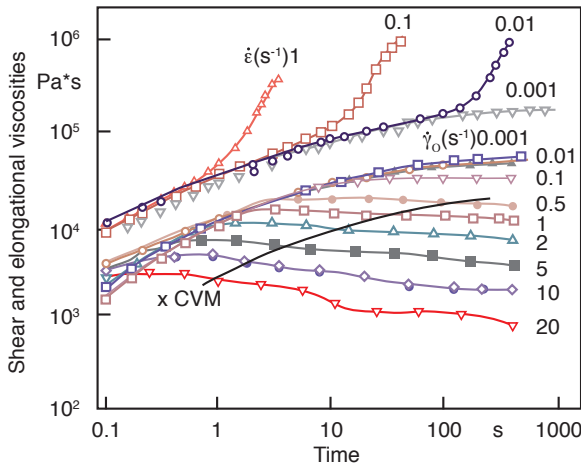


Figure 5.37 Development of elongational and shear viscosities during deformation for polyethylene samples

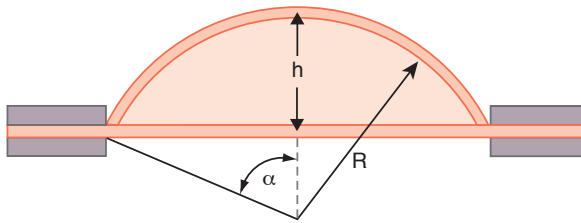


Figure 5.38 Schematic diagram of sheet inflation

$$t = t_0 \left(\frac{D^2}{8Rh} \right) \quad (5.81)$$

The instantaneous radius of curvature of the sheet is related to bubble height by

$$R = \frac{D^2}{8h} + \frac{h}{2} \quad (5.82)$$

The biaxial strain can be computed using

$$\varepsilon_b = \ln \left(\frac{2\alpha R}{D} \right) \quad (5.83)$$

and the biaxial stress can be calculated using

$$\sigma_b = \frac{R\Delta P}{2t} \quad (5.84)$$

For more detail on extensional rheometry, beyond the scope of this book, the reader should refer to the literature [58].

■ 5.6 Surface Tension

Although surface tension is generally not included in rheology chapters, it does play a significant role in the deformation of polymers during flow, especially during dispersive mixing of polymer blends. Surface tension, σ_s , between two materials appears as a result of different intermolecular interactions. In a liquid-liquid system, surface tension manifests itself as a force that tends to maintain the surface between the two materials to a minimum. Thus, the equilibrium shape of a droplet inside a matrix that is at rest is a sphere. When three phases touch, such as liquid, gas, and solid, they result in different contact angles depending on the surface tension between the three phases. Figure 5.39 schematically depicts three different cases. In case 1, the liquid perfectly wets the surface with a continuous spread, leading to a wetting angle of zero. Case 2, with moderate surface tension effects, shows a liquid that has a tendency to flow over the surface with a contact angle between zero and $\pi/2$. In case 3, with a high surface tension effect, the liquid does not wet the surface, which results in a contact angle greater than $\pi/2$. In Fig. 5.39, σ_s denotes the surface tension between the gas and the solid, σ_l the surface tension between the liquid and the gas, and σ_{sl} the surface tension between the solid and liquid. Using geometry one can write

$$\cos \theta = \frac{\sigma_s - \sigma_{sl}}{\sigma_l} \quad (5.85)$$

The wetting angle can be measured using simple techniques such as a projector, as shown schematically in Fig. 5.40. This technique, originally developed by Zisman [59], can be used in the ASTM D2578 [60] standard test. Here, droplets of known surface tension, σ_l , are applied to a film. The measured values of $\cos \phi$ are plotted as a function of surface tension, σ_l , as shown in Fig. 5.41, and extrapolated to find the *critical surface tension*, σ_c , required for wetting.

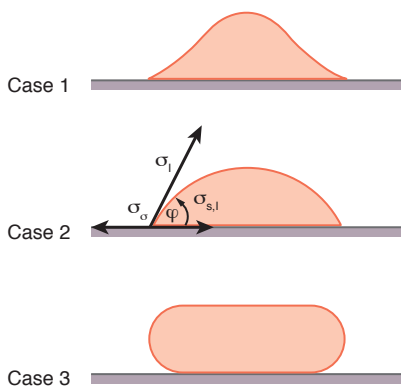


Figure 5.39 Schematic diagram of contact between liquids and solids with various surface tension effects

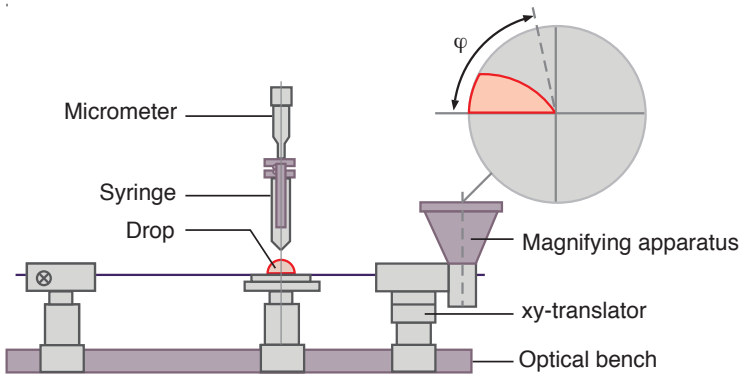


Figure 5.40 Schematic diagram of apparatus to measure contact angle between liquids and solids

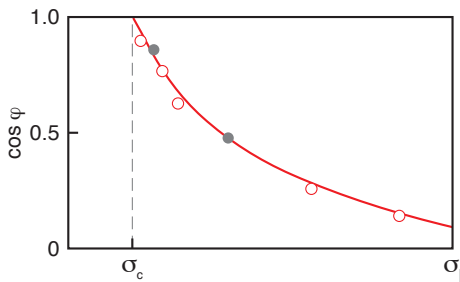


Figure 5.41 Contact angle as a function of surface tension

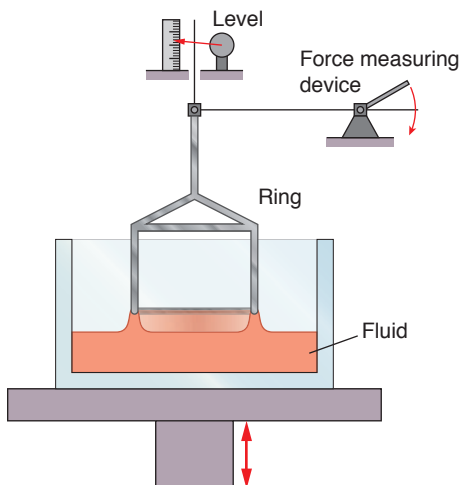


Figure 5.42 Schematic diagram of a tensiometer used to measure surface tension of liquids

For liquids of low viscosity, a useful measurement technique is the tensiometer, schematically represented in Fig. 5.42. Here, the surface tension is related to the force it takes to pull a platinum ring from a solution. Surface tension values for

selected polymers are listed in Table 5.6 [61], for some solvents in Table 5.7 [62], and surface tension values between polymer-polymer systems in Table 5.8 [61].

Furthermore, Hildebrand and Scott [63] found a relationship between the solubility parameter¹⁴, δ , and surface tension, σ_s for polar and non-polar liquids. Their relationship can be written as [64]

$$\sigma_s = 0.24\delta^{2.33}V^{0.33} \tag{5.86}$$

where V is the molar volume of the material. The molar volume is defined by

$$V = \frac{M}{\rho} \tag{5.87}$$

where M is the molar weight. It should be noted that the values in Eqs. 5.86 and 5.87 must be expressed in cgs (centimeter-gram-second) units.

There are many areas in polymer processing and in engineering design with polymers in which surface tension plays a significant role; they include mixing of polymer blends, which is discussed in detail in Chapter 6 of this book, adhesion, treatment of surfaces to make them non-adhesive, and sintering.

During manufacturing it is often necessary to coat and crosslink a surface with a liquid adhesive or bonding material. To enhance adhesion it is often necessary to raise surface tension by oxidizing the surface, by creating COOH groups, using flames, etching or releasing electrical discharges. These approaches are also used when enhancing the adhesion properties of a surface before painting.

On the other hand it is often necessary to reduce adhesiveness of a surface, e.g., when releasing a product from the mold cavity or when coating a pan to give it nonstick properties. A material that is often used for this purpose is polytetrafluoroethylene (PTFE), mostly known by its trade name of teflon.

Table 5.6 Typical Surface Tension Values of Selected Polymers at 180 °C

Polymer	σ_s (N/m)	$\partial\sigma_s/\partial T$ (N/m/°C)
Polyamide resins (290 °C)	0.0290	–
Polyethylene (linear)	0.0265	-5.7×10^{-5}
Polyethylene terephthalate (290 °C)	0.027	–
Polyisobutylene	0.0234	-6.6×10^{-5}
Polymethyl methacrylate	0.0289	-7.6×10^{-5}
Polypropylene	0.0208	-5.8×10^{-5}
Polystyrene	0.0292	-7.2×10^{-5}
Polytetrafluoroethylene	0.0094	-6.2×10^{-5}
Polyvinyl acetate	0.0259	-6.6×10^{-5}

¹⁴ Solubility parameter is defined in Chapter 6.

Table 5.7 Surface Tension for Several Solvents

Solvent	σ_s (N/m)
n-Hexane	0.0184
Formamide	0.0582
Glycerin	0.0634
Water	0.0728

Table 5.8 Surface Tension between Polymers

Polymer	σ_s (N/m)	$\partial\sigma_s/\partial T$ (N/m/°C)	T (°C)
PE-PP	1.1×10^{-3}	–	140
PE-PS	5.1×10^{-3}	2.0×10^{-5}	180
PE-PMMA	9.0×10^{-3}	1.8×10^{-5}	180
PP-PS	5.1×10^{-3}	–	140
PS-PMMA	1.6×10^{-3}	1.3×10^{-5}	140

Finally, during the sintering process, surface tension plays a key role, especially when bringing together pairs of particles at high temperatures without applying pressure. Using the notation for the sintering process presented in Fig. 5.43, Menges and Reichstein [65] developed the relation

$$x^2 \approx \frac{\sigma_s D t}{\eta} \tag{5.88}$$

where, σ_s is the surface tension, t is time, and η the viscosity.

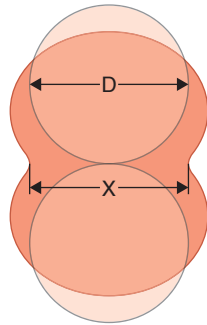


Figure 5.43 Schematic of the sintering process

Examples

1. Derive the equation that describes the pressure driven velocity field inside a tube of constant diameter (Eq. 5.43).

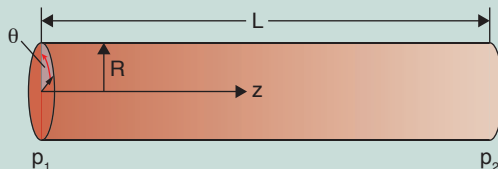


Figure 5.44 Tube geometry and coordinate system

In our solution scheme, we must first choose a coordinate system:

Next we must state our assumptions:

- no variations in the θ direction: $\frac{\partial}{\partial \theta} = u_\theta = 0$,
- steady state: $\frac{\partial}{\partial t} = 0$,
- no velocity in the radial direction: $u_r = 0$.

The continuity equation (Appendix I) reduces to

$$\frac{\partial u_z}{\partial z} = 0$$

Using the reduced continuity equation and the above assumptions, only the z -component of the equation of motion (Appendix I) is needed

$$0 = -\frac{\partial p}{\partial z} + \mu \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u_z}{\partial r} \right) \right]$$

Letting $\frac{\partial p}{\partial z} = \frac{\Delta p}{L}$ and integrating gives

$$r \frac{\partial u_z}{\partial r} = \frac{r^2}{2\mu} \left(\frac{\Delta p}{L} \right) + C_1$$

Since $\frac{\partial u_z}{\partial r} = 0$ at $r = 0$, $C_1 = 0$. Integrating again, we get

$$u_z = \frac{r^2}{4\mu} \left(\frac{\Delta p}{L} \right) + C_2$$

Since $u_z = 0$ at $r = R$, the above equation becomes

$$u = \frac{R^2 \Delta p}{4\mu L} \left[1 - \left(\frac{r}{R} \right)^2 \right]$$

2. Derive the equation that describes the annular flow in a wire coating process. The wire travels through the annulus at a speed, U , and we assume that the pressure inside the die equals atmospheric pressure. Use the notation presented in Fig. 5.45. Assume a power law viscosity.

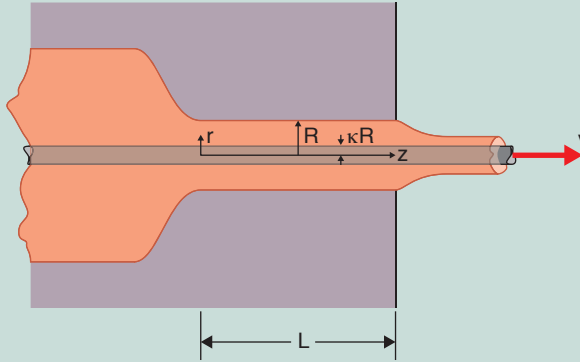


Figure 5.45 Wire coating process geometry and coordinate system

When solving this problem, we make similar assumptions as in Example 1.

This results in $\frac{\partial}{\partial \theta} = u_\theta = 0$, $\frac{\partial}{\partial t} = 0$ and $u_r = 0$. Here too, the continuity equation reduces to

$$\frac{\partial u_z}{\partial z} = 0$$

However, the pressure gradient, $\frac{\partial p}{\partial z}$, can be neglected. Because this problem is non-Newtonian, we need to use the general equation of motion (Appendix 1). The z-component reduces to

$$\frac{\partial}{\partial r}(r\tau_{rz}) = 0$$

Next, we define the deviatoric stress as a function of rate of deformation using

$$\tau_{rz} = \eta(T, \dot{\gamma}) \dot{\gamma}_{rz} = m_0 \dot{\gamma}^{n-1} \dot{\gamma}_{rz}$$

Since the only deformation that occurs is the shear deformation in the rz -plane, the magnitude of the rate of deformation tensor is given by

$$\dot{\gamma} = \dot{\gamma}_{rz} = \frac{\partial u_z}{\partial r}$$

The equation of motion, can now be written as

$$\frac{\partial}{\partial r} \left(r m_0 \left[\frac{\partial u_z}{\partial r} \right]^n \right) = 0$$

Integrating this equation twice, and applying two boundary conditions, $v_z = V$ at $r = \kappa R$, and $v_z = 0$ at $r = R$ we get

$$u_z = U \frac{\left[\left(\frac{r}{R} \right)^{\frac{1}{n}} - 1 \right]}{\kappa^{\frac{1}{n}} - 1}$$

3. Formulate a design equation for the end-fed sheeting die shown in Fig. 5.46 so that the extruded sheet is of uniform thickness. Your job is to specify the length of the approach zone or die land as a function of the manifold direction to achieve uniform flow. The manifold diameter is constant and the flow can be assumed isothermal with a Newtonian viscosity of η .

After assigning a coordinate system and assuming the notation presented in Fig. 5.47, the flow of the manifold can be represented using the Hagen-Poiseuille equation as

$$Q = \frac{\pi R^4}{8\eta} \left(-\frac{dp}{dz} \right)$$

and the flow in the die land (per unit width) using slit flow

$$q = \frac{h^3}{12\eta} \left(-\frac{dp}{dl} \right) = \frac{h^3}{12\eta} \left(\frac{p}{L_L} \right)$$

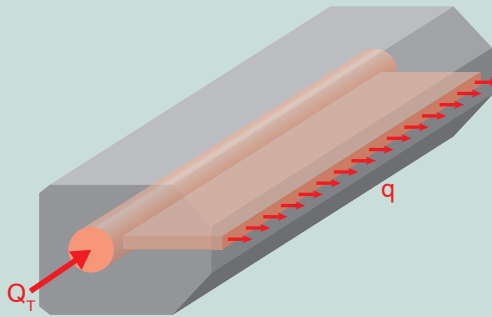


Figure 5.46 Schematic of an end-fed sheeting die

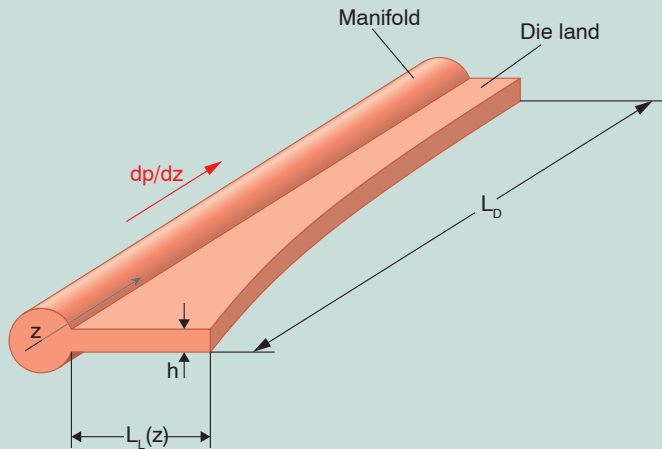


Figure 5.47 End-fed sheeting die coordinates and dimensions

A manifold that leads to a uniform sheet must deliver a constant throughput along the die land. Performing a flow balance within the differential element shown in Fig. 5.48 results in

$$Q(z + \Delta z) - Q(z) - q(z) \Delta z = 0$$

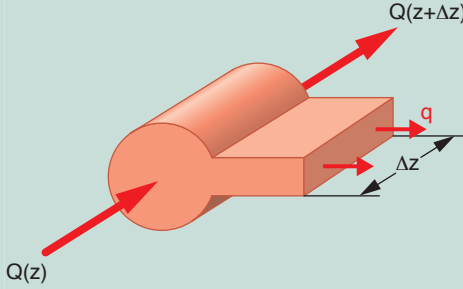


Figure 5.48 Differential element of an end-fed sheeting die

and letting $\Delta z \rightarrow 0$ results in

$$\frac{dQ}{dz} = -q = \text{constant}$$

If we integrate and let $Q = Q_r$ at $z = 0$ and $Q = 0$ at $z = L_d$ we get

$$Q(z) = Q_r \left(1 - \frac{z}{L_d} \right)$$

Hence,

$$\frac{dQ}{dz} = -\frac{Q_r}{L_d} = -\frac{h^3}{12\eta} \frac{\rho(z)}{L_l(z)}$$

which results in

$$L_l(z) = \frac{h^3}{12\eta} \frac{L_d}{Q_r} \rho(z)$$

where $\rho(z)$ is unknown. We can now rewrite the manifold equation as

$$\frac{d\rho}{dz} = -\frac{8\eta}{\pi R^4} Q_r \left(1 - \frac{z}{L_d} \right)$$

and then, letting $\rho = \rho_0$ at $z = 0$, we get

$$\rho = \rho_0 - \frac{8\eta Q_r L_d}{\pi R^4} \left[\left(\frac{z}{L_d} \right) - \frac{1}{2} \left(\frac{z}{L_d} \right)^2 \right]$$

which leads to a land length of

$$L_l = \frac{h^3 L_d \rho_0}{12\eta Q_r} - \frac{2h^3 L_d^2}{3\pi R^4} \left[\left(\frac{z}{L_d} \right) - \frac{1}{2} \left(\frac{z}{L_d} \right)^2 \right]$$

Problems

1. During the filling stage of the injection molding cycle, would the pressure requirements for a PP with a MFI = 10 be larger or smaller, relative to a PP with a MFI = 4? Why?
2. Model the viscosity of the PE-LD shown in Fig. 5.4 using the power law model and the Bird-Carreau model.
3. Derive the equation that predicts the volumetric throughput during pressure flow through a slit, assuming a Newtonian viscosity (Eq. 5.40).
4. Derive the Hagen-Poiseuille equation for a power law fluid (Eq. 5.46).
5. You are to extrude a polystyrene sheet through a die with a land length of 0.1 m. What is the maximum speed you can extrude the sheet if you are extruding polystyrene with the viscoelastic properties presented in Fig. 3.44 of Chapter 3.
6. The metering section of a single screw extruder can be modeled using a combination of shear flow and pressure flow between parallel plates. Derive the relation between volumetric throughput versus pressure build-up, Δp , in a melt extruder of a Newtonian fluid. Hint: Use the notation given in Chapter 6.
7. In Example 5.2, obtain an expression for the flow rate, coating thickness, and the axial force required to pull the wire through the die.
8. Formulate the design equation for an end-fed sheeting die such as the one in Example 3. Unlike the example, the new die should have a variable radius manifold as in Fig. 5.48. In this case, the axial distance from the manifold center to the die exit must be constant.

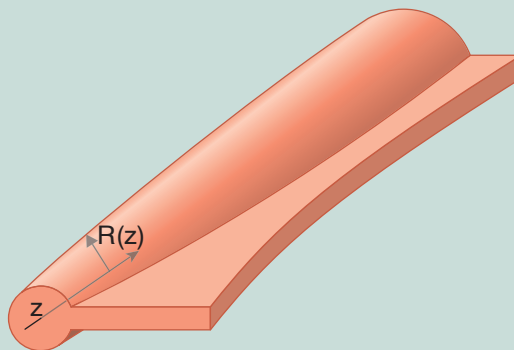


Figure 5.49 End-fed, variable diameter manifold sheeting die coordinates and dimensions

9. State the differences between a shear flow and an extensional flow.

10. The design department of an injection molding company has decided to increase the thickness of your product by a factor of 2. How does this modification affect the cooling time?
11. What assumptions must be made in order to use Eq. 5.40 to model the pressure flow through an annular die?
12. The tube in Example 1 is now set up vertically. How does this change the velocity profile if gravity is considered?

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Appendix

■ Appendix I

Table I Guide Values of the Physical Properties of Plastics

Polymer	Abbreviation	Density		Mechanical properties	
		g/cm ³	lb/in ³	Tensile strength	
				N/mm ²	psi
Low density polyethylene	PE-LD	0.914/0.928	0.0329–0.0330	8/23	1140/3270
High density polyethylene	PE-HD	0.94/0.96	0.0338–0.0345	18/35	2560/4980
EVA	EVA	0.92/0.95	0.0331–0.0341	10/20	1420/2840
Polypropylene	PP	0.90/0.907	0.0324–0.0327	21/37	2990/5260
Polybutene-1	PB	0.905/0.920	0.0325–0.0331	30/38	4270/5400
Polyisobutylene	PIB	0.91/0.93	0.0327–0.0334	2/6	284/853
Poly-4-methylpent-1-ene	PMP	0.83	0.0298	23/28	3560/3980
Ionomers	–	0.94	0.0338	21/35	2990/4980
Rigid PVC	PVC-U	1.38/1.55	0.0496–0.0557	50/75	7110/10670
Plasticized PVC	PVC-P	1.16/1.35	0.0417–0.0486	10/25	1420/3560
Polystyrene	PS	1.05	0.0378	45/65	6400/9240
Styrene/acrylonitrile copolymer	SAN	1.08	0.0392	75	10670
Styrene/polybutadiene graft polymer	SB	1.05	0.0378	26/38	3700/5400
Acrylonitrile/polybut./styrene graft polymer	ABS	1.04/1.06	0.0374–0.0381	32/45	4550/6400
AN/AN elastomers/styrene graft polymer	ASA	1.04	0.0374	32	4550
Polymethylmethacrylate	PMMA	1.17/1.20	0.0421–0.0431	50/77	7110/10950
Polyvinylcarbazole	PVK	1.19	0.0428	20/30	2840/4270
Polyacetal	POM	1.41/1.42	0.0507–0.0511	62/70	8820/9960
Polytetrafluoroethylene	PTFE	2.15/2.20	0.0774–0.0791	25/36	3560/5120
Tetrafluoroethylene/hexafluoropropylene copolymer	FEP	2.12/2.17	0.0763–0.0781	22/28	3130/3980
Polytrifluorochloroethylene	PCTFE	2.10/2.12	0.0755–0.0762	32/40	4550/5690
Ethylene/tetrafluoroethylene	E/TFE	1.7	0.0611	35/54	4980/7680
Polyamide 6	PA 6	1.13	0.0406	70/85	9960/12090
Polyamide 66	PA 66	1.14	0.0410	77/84	10950/11950
Polyamide 11	PA 11	1.04	0.0374	56	7960
Polyamide 12	PA 12	1.02	0.0367	56/65	7960/9240
Polyamide 6-3-T	PA-6-3-T	1.12	0.0403	70/84	9960/11950
Polycarbonate	PC	1.2	0.0432	56/67	7960/9530
Polyethyleneterephthalate	PET	1.37	0.0492	47	6680
Polybutyleneterephthalate	PBT	1.31	0.0471	40	5690
Polyphenyleneether modified	PPE	1.06	0.0381	55/68	7820/9670
Polysulfone	PSU	1.24	0.0446	50/100	7110/14200
Polyphenylenesulfide	PPS	1.34	0.0483	75	10670
Polyarylsulfone	PAS	1.36	0.0490	90	12800
Polyethersulfone	PES	1.37	0.0492	85	12090
Polyarylether	PAE	1.14	0.0411	53	7540
Phenol/formaldehyde, grade 31	PF	1.4	0.0504	25	3560
Urea/formaldehyde, grade 131	UF	1.5	0.0540	30	4270
Melamine/formaldehyde, grade 152	MF	1.5	0.0540	30	4270
Unsaturated polyester resin, grade 802	UP	2.0	0.0720	30	4270
Polydiallylphthalate (GF) molding compound	PDAP	1.51/1.78	0.0543–0.0640	40/75	5690/10670
Silicone resin molding compound	SI	1.8/1.9	0.0648–0.0684	28/46	3980/6540
Polyimide molding	PI	1.43	0.0515	75/100	10570/14200
Epoxy resin, grade 891	EP	1.9	0.0683	30/40	4270/5690
Polyurethane casting resin	PU	1.05	0.0378	70/80	9960/11380
Thermoplastic PU-elastomers	PU	1.20	0.0432	30/40	4270/5690
Linear polyurethane (U ₅₀)	PU	1.21	0.0435	30 (σ ₁)	4270 (σ ₁)
Vulcanized fiber	VF	1.1/1.45	0.0396–0.0522	85/100	12090/14200
Celluloseacetate, grade 432	CA	1.30	0.0468	38 (σ ₁)	5400 (σ ₁)
Cellulosepropionate	CP	1.19/1.23	0.0429–0.0452	14/55	7990/7820
Celluloseacetobutyrate, grade 413	CAB	1.18	0.0425	26 (σ ₁)	3600 (σ ₁)

Elongation at break %	Tensile modulus of elasticity		Ball indentation hardness		Impact strength kJ/m ²	Notched impact strength	
	N/mm ²	kpsi	10-s-value	10-s-value psi		kJ/m ²	ft lb/ in of notch
300/1000 100/1000 600/900 20/800 250/280 > 1000 13/22 250/500	200/500 700/1400 7/120 11000/1300 250/350 — 1100/1500 180/210	28.4/71.1 99.6/199 0.99/17.1 156/185 35.6/49.8 — 156/213 25.6/29.9	13/20 40/65 — 36/70 30/38 — — —	1850/2840 5690/9240 — 5120/9960 4270/5400 — — —	no break no break no break no break no break no break — —	no break no break no break 3/17 4/no break no break — —	— — no break 0.5/20 no break no break 0.4/0.6 6/15
10/50 170/400	1000/3500 —	142/498 —	75/155 —	10670/22000 —	no break / > 20 no break	2/50 no break	0.4/20 —
3/4 5 25/60 15/30 40	3200/3250 3600 1800/2500 1900/2700 1800	455/462 512 256/356 270/384 256	120/130 130/140 80/130 80/120 75	17100/18500 18500/19900 11380/18500 11380/17100 10670	5/20 8/20 10/80 70/no break no break	2/2.5 2/3 5/13 7/20 18	0.25/0.6 0.35/0.5 no break 2.5/12 6/8
2/10 — 25/70	2700/3200 3500 2800/3200	384/455 498 398/455	180/200 200 150/170	25600/28400 28400 21300/24200	18 5 100	2 2 8	0.3/0.5 — 1/2.3
350/550 250/330 120/175 400/500	410 350 1050/2100 1100	58.3 49.8 149/299 156	27/35 30/32 65/70 65	3840/4980 4270/4550 9240/9960 9240	no break — no break —	13/15 — 8/10	3.0 no break 2.5/2.8 no break
200/300 150/300 500 300 70/150	1400 2090 1000 1600 2090	199 284 142 228 284	75 100 75 75 160	10670 14200 10670 10670 22800	no break no break no break no break no break	no break 15/20 30/40 10/20 13	3.0 2.1 1.8 2/5.5 —
100/130 50/300 15 50/60	2100/2400 3100 2000 2500	299/341 441 284 356	110 200 180 —	15600 28400 25600 —	no break no break no break no break	20/30 4 4 —	12/18 0.8/1.0 0.8/1.0 4
25/30 3 13 30/80 25/90	2600/2750 3400 2600 2450 2250	370/391 484 370 348 320	— — — — —	— — — — —	— — — — —	— — — — —	1.3 0.3 1/2 1.6 8.0
0.4/0.8 0.5/1.0 0.6/0.9 0.6/1.2 — — 4/9	5600/12000 7000/10500 4900/9100 14000/20000 9800/15500 6000/12000 23000/28000	796/1710 996/1490 697/1294 1990/2840 1394/2200 853/1710 3270/3980	250/320 260/350 260/410 240 — — —	35600/45500 39000/49800 37000/58300 34100 — — —	> 6 > 6.5 > 7.0 > 4.5 — — —	> 1.5 > 2.5 > 1.5 > 3.0 — — —	0.2/0.6 0.5/0.4 0.2/0.3 0.5/16 0.4/15 0.3/0.8 0.5/1.0
4 3/6 400/450 35 (ε _u)	21500 4000 700 1000	3060 569 99.6 140	— — — —	— — — —	> 8 — no break no break	> 3 — no break 3	2/30 0.4 no break —
— 3 (ε _u) 30/100 4 (ε _u)	— 2200 420/1500 1600	— 313 59.7/213 228	80/140 50 47/79 35/43	11380/19900 7110 6680/11240 4980/6120	20/120 65 no break no break	— 15 6/20 30/35	— 2.5 1.5 4/5

(continued on next page.)

Table I Guide Values of the Physical Properties of Plastics (cont.)

Polymer	Abbreviation	Density	
		g/cm ³	lb/in ³
Low density polyethylene	PE-LD	0.914/0.928	0.0329–0.0330
High density polyethylene	PE-HD	0.94/0.96	0.0338–0.0345
EVA	EVA	0.92/0.95	0.0331–0.0341
Polypropylene	PP	0.90/0.907	0.0324–0.0327
Polybutene-1	PB	0.905/0.920	0.0325–0.0331
Polyisobutylene	PIB	0.91/0.93	0.0327–0.0334
Poly-4-methylpent-1-ene	PMP	0.83	0.0298
Ionomers	–	0.94	0.0338
Rigid PVC	PVC-U	1.38/1.55	0.0496–0.0557
Plasticized PVC	PVC-P	1.16/1.35	0.0417–0.0486
Polystyrene	PS	1.05	0.0378
Styrene/acrylonitrile copolymer	SAN	1.08	0.0392
Styrene/polybutadiene graft polymer	SB	1.05	0.0378
Acrylonitrile/polybut/styrene graft polymer	ABS	1.04/1.06	0.0374–0.0381
AN/AN elastomers/styrene graft polymer	ASA	1.04	0.0374
Polymethylmethacrylate	PMMA	1.17/1.20	0.0421–0.0431
Polyvinylcarbazole	PVK	1.19	0.0428
Polyacetal	POM	1.41/1.42	0.0507–0.0511
Polytetrafluoroethylene	PTFE	2.15/2.20	0.0774–0.0791
Tetrafluoroethylene/hexafluoropropylene copolymer	FEP	2.12/2.17	0.0763–0.0781
Polytrifluorochloroethylene	PCTFE	2.10/2.12	0.0755–0.0762
Ethylene/tetrafluoroethylene	E/TFE	1.7	0.0611
Polyamide 6	PA 6	1.13	0.0406
Polyamide 66	PA 66	1.14	0.0410
Polyamide 11	PA 11	1.04	0.0374
Polyamide 12	PA 12	1.02	0.0367
Polyamide 6-3-T	PA-6-3-T	1.12	0.0403
Polycarbonate	PC	1.2	0.0432
Polyethyleneterephthalate	PET	1.37	0.0492
Polybutyleneterephthalate	PBT	1.31	0.0471
Polyphenyleneether modified	PPE	1.06	0.0381
Polysulfone	PSU	1.24	0.0446
Polyphenylenesulfide	PPS	1.34	0.0483
Polyarylsulfone	PAS	1.36	0.0490
Polyethersulfone	PES	1.37	0.0492
Polyarylether	PAE	1.14	0.0411
Phenol/formaldehyde, grade 31	PF	1.4	0.0504
Urea/formaldehyde, grade 131	UF	1.5	0.0540
Melamine/formaldehyde, grade 152	MF	1.5	0.0540
Unsaturated polyester resin, grade 802	UP	2.0	0.0720
Polydiallylphthalate (GF) molding compound	PDAP	1.51/1.78	0.0543–0.0640
Silicone resin molding compound	SI	1.8/1.9	0.0648–0.0684
Polyimide molding	PI	1.43	0.0515
Epoxy resin, grade 891	EP	1.9	0.0683
Polyurethane casting resin	PU	1.05	0.0378
Thermoplastic PU-elastomers	PU	1.20	0.0432
Linear polyurethane (U ₅₀)	PU	1.21	0.0435
Vulcanized fiber	VF	1.1/1.45	0.0396–0.0522
Celluloseacetate, grade 432	CA	1.30	0.0468
Cellulosepropionate	CP	1.19/1.23	0.0429–0.0452
Celluloseacetobutyrate, grade 413	CAB	1.18	0.0425

Optical properties		Water absorption	
Refractive index n_D^{20}	Transparency	mg (4d)	% (24 h)
1.51	transparent	<0.01	<0.01
1.53	opaque	<0.01	<0.01
—	transparent/opaque	—	0.05/0.13
1.49	transparent/opaque	<0.01	0.01/0.03
—	opaque	<0.01	<0.02
—	opaque	<0.01	<0.01
1.46	opaque	—	0.01
1.51	transparent	—	0.1/1.4
1.52/1.55	transparent/opaque	3/18	0.04/0.4
—	transparent/opaque	6/30	0.15/0.75
1.59	transparent	—	0.03/0.1
1.57	transparent	—	0.2/0.3
—	opaque	—	0.05/0.6
—	opaque	—	0.2/0.45
—	translucent/opaque	—	—
1.49	transparent	35/45	0.1/0.4
—	opaque	0.5	0.1/0.2
1.48	opaque	20/30	0.22/0.25
1.35	opaque	—	0
1.34	transparent/translucent	—	<0.1
1.43	translucent/opaque	—	0
1.40	transparent/opaque	—	0.03
1.53	translucent/opaque	—	1.3/1.9
1.53	translucent/opaque	—	1.5
1.52	translucent/opaque	—	0.3
—	translucent/opaque	—	0.25
1.53	transparent	—	0.4
1.58	transparent	10	0.16
—	transparent/opaque	18/20	0.30
—	opaque	—	0.08
—	opaque	—	0.06
1.63	transparent/opaque	—	0.02
—	opaque	—	0.02
1.67	opaque	—	1.8
1.65	transparent	—	0.43
—	translucent/opaque	—	0.25
—	opaque	<150	0.3/1.2
—	opaque	<300	0.4/0.8
—	opaque	<250	0.1/0.6
—	opaque	<45	0.03/0.5
—	opaque	—	0.12/0.35
—	opaque	—	0.2
—	opaque	—	0.32
—	opaque	<30	0.05/0.2
—	transparent	—	0.1/0.2
—	translucent/opaque	—	0.7/0.9
—	translucent/opaque	130	—
—	opaque	—	7/9
1.50	transparent	130	6
1.47	transparent	40/60	1.2/2.8
1.47	transparent	40/60	0.9/3.2

(continued on next page)

Table I Guide Values of the Physical Properties of Plastics (cont.)

Polymer	Abbreviation	Density		Thermal properties			
		g/cm ³	lb/in ³	Service temperature			
				max./short time		max./continuous	
				°C	°F	°C	°F
Low density polyethylene	PE-LD	0.914/0.928	0.0329–0.0330	80/90	176/194	60/75	140/167
High density polyethylene	PE-HD	0.94/0.96	0.0338–0.0345	90/120	194/248	70/80	158/176
EVA	EVA	0.92/0.95	0.0331–0.0341	65	149	55	131
Polypropylene	PP	0.90/0.907	0.0324–0.0327	140	284	100	212
Polybutene-1	PB	0.905/0.920	0.0325–0.0331	130	266	90	194
Polyisobutylene	PIB	0.91/0.93	0.0327–0.0334	80	176	65	149
Poly-4-methylpent-1-ene	PMP	0.83	0.0298	180	356	120	248
Ionomers	–	0.94	0.0338	120	248	100	212
Rigid PVC	PVC-U	1.38/1.55	0.0496–0.0557	75/100	167/212	65/85	149/185
Plasticized PVC	PVC-P	1.16/1.35	0.0417–0.0486	55/65	131/149	50/55	122/131
Polystyrene	PS	1.05	0.0378	60/80	140/176	50/70	122/158
Styrene/acrylonitrile copolymer	SAN	1.08	0.0392	95	203	85	185
Styrene/polybutadiene graft	SB	1.05	0.0378	60/80	140/176	50/70	122/158
Acrylonitrile/polybut./styrene graft polymer	ABS	1.04/1.06	0.0374–0.0381	85/100	188/212	75/85	167/185
AN/AN elastomers/styrene graft polymer	ASA	1.04	0.0374	85/90	188/194	70/75	158/167
Polymethylmethacrylate	PMMA	1.17/1.20	0.0421–0.0431	85/100	188/212	65/90	149/194
Polyvinylcarbazole	PVK	1.19	0.0428	170	338	160	320
Polyacetal	POM	1.41/1.42	0.0507–0.0511	110/140	230	90/110	194/230
Polytetrafluoroethylene	PTFE	2.15/2.20	0.0774–0.0791	300	572	250	482
Tetrafluoroethylene	FEP	2.12/2.17	0.0763–0.0781	250	482	205	401
hexafluoropropylene copolymer	PCTFE	2.10/2.12	0.0755–0.0762	180	356	150	302
Polytrifluorochloroethylene	E/TFE	1.7	0.0611	220	428	150	302
Ethylene tetrafluoroethylene							
Polyamide 6	PA 6	1.13	0.0406	140/180	284/356	80/100	176/212
Polyamide 66	PA 66	1.14	0.0410	170/200	338/392	80/120	176/248
Polyamide 11	PA 11	1.04	0.0374	140/150	284/302	70/80	158/176
Polyamide 12	PA 12	1.02	0.0367	140/150	284/302	70/80	158/176
Polyamide 6-3-T	PA-6-3-T	1.12	0.0403	130/140	266/284	80/100	176/212
Polycarbonate	PC	1.2	0.0432	160	320	135	275
Polyethyleneterephthalate	PET	1.37	0.0492	200	392	100	212
Polybutyleneterephthalate	PBT	1.31	0.0471	165	329	100	212
Polyphenyleneether modified	PPE	1.06	0.0381	150	302	80	176
Polysulfone	PSU	1.24	0.0446	200	392	150	302
Polyphenylsulfide	PPS	1.34	0.0483	300	572	200	392
Polyarylsulfone	PAS	1.36	0.0490	300	572	260	500
Polyethersulfone	PES	1.37	0.0492	260	500	200	392
Polyarylether	PAE	1.14	0.0411	160	320	120	248
Phenol/formaldehyde, grade 31	PF	1.4	0.0504	140	284	110	230
Urea/formaldehyde, grade 131	UF	1.5	0.0540	100	212	70	158
Melamine/formaldehyde, grade 152	MF	1.5	0.0540	120	248	80	176
Unsaturated polyester resin, grade 802	UP	2.0	0.0720	200	392	150	302
Polydiallylphthalate (GF)	PDAP	1.51/1.78	0.0543–0.0640	190/250	374/482	150/180	302/356
molding compound							
Silicone resin molding compound	SI	1.8/1.9	0.0648–0.0684	250	482	170/180	338/356
Polyimide molding	PI	1.43	0.0515	400	752	260	500
Epoxy resin, grade 891	EP	1.9	0.0683	180	356	130	266
Polyurethane casting resin	PU	1.05	0.0378	100	212	80	176
Thermoplastic PU-elastomers	PU	1.20	0.0432	110	230	80	176
Linear polyurethane (U ₅₀)	PU	1.21	0.0435	80	176	60	140
Vulcanized fiber	VF	1.1/1.45	0.0396–0.0522	180	356	105	221
Celluloseacetate, grade 432	CA	1.30	0.0468	80	176	70	158
Cellulosepropionate	CP	1.19/1.23	0.0429–0.0452	80/120	176/248	60/115	140/239
Celluloseacetobutyrate, grade 413	CAB	1.18	0.0425	80/120	176/248	60/115	140/239

min./continuous		Heat deflection temperature				Coefficient of linear expansion		Thermal conductivity		Specific heat	
		°C	°F								
		VSP (Vicat 5 kg)	1.86/0.45 N/mm ²	VSP (Vicat lb)	264/66 psi	K ⁻¹ · 10 ⁶	in/in/°F · 10 ⁻⁶	W/mK	BTU in/ft ² h°F	kJ/kgK	BTU/lb°F
°C	°F										
-50	-58	-	35	-	95	250	140	0.32/0.40	2.2/2.8	2.1/2.5	8.8/10.5
-50	-58	60/70	50	140/158	122	200	110	0.38/0.51	2.6/3.5	2.1/2.7	8.8/11.5
-60	-76	-	34/62	-	93/144	160/200	90/110	0.35	2.4	2.3	9.5
0/-30	32/-22	85/100	45/120	185/212	113/248	150	83	0.17/0.22	1.2/1.5	2.0	8.3
0	32	70	60/110	158	140/230	150	83	0.20	1.4	1.8	7.5
-50	-58	-	-	-	-	120	67	0.12/0.20	0.8/1.4	-	-
0	32	-	-	-	-	117	65	0.17	1.2	2.18	9.1
-50	-58	-	38/45	-	100/113	120	67	0.24	1.7	2.20	9.2
-5	21	75/110	60/82	167/230	140/180	70/80	39/45	0.14/0.17	1.0/1.2	0.85/0.9	3.55/3.75
0/-20	32/-4	40	-	104	-	150/210	83/110	0.15	1.05	0.9/1.8	3.75/7.5
-10	14	78/99	110/80	172/210	230/176	70	39	0.18	1.25	1.3	5.4
-20	-4	-	104/90	-	219/194	80	45	0.18	1.25	1.3	5.4
-20	-4	77/95	104/82	171/203	219/180	70	39	0.18	1.25	1.3	5.4
-40	-40	95/110	80/120	203/230	176/248	60/110	33/61	0.18	1.25	1.3	5.4
-40	-40	92	100/110	198	212/230	80/110	44/61	0.18	1.25	1.3	5.4
-40	-40	70/100	60/100	158/212	140/212	70	39	0.18	1.25	1.47	6.15
-100	-148	180	-	356	-	-	-	0.29	2.0	-	-
-60	-76	160/173	110/170	320/344	230/338	90/110	50/61	0.25/0.30	1.7/2.1	1.46	6.1
-200	-328	-	-121	-	-250	100	56	0.25	1.7	1.0	4.20
-100	-148	-	-70	-	-158	80	45	0.25	1.7	1.12	4.65
-40	-40	-	-126	-	-259	60	33	0.22	1.5	0.9	3.75
-190	-310	-	71/104	-	160/219	40	22	0.23	1.6	0.9	3.75
-30	-22	180	80/190	356	176/374	80	44	0.29	2.0	1.7	7.1
-30	-22	200	105/200	392	221/392	80	44	0.23	1.6	1.7	7.1
-70	-94	175	150/130	347	302/266	130	72	0.23	1.6	1.26	5.25
-70	-94	165	140/150	329	284/302	150	83	0.23	1.6	1.26	5.25
-70	-94	145	140/80	293	284/176	80	45	0.23	1.6	1.6	6.70
-100	-148	138	130/145	280	266/293	60/70	33/39	0.21	1.45	1.17	4.90
-20	-4	188	-	280	-	70	39	0.24	1.65	1.05	4.40
-30	-22	178	50/190	352	122/374	60	33	0.21	1.45	1.30	5.40
-30	-22	148	100/140	298	212/284	60	33	0.23	1.60	1.40	5.85
-100	-148	-	175/180	-	347/356	54	30	0.28	1.95	1.30	5.40
-	-	-	137/-	-	277/-	55	31	0.25	1.70	-	-
-	-	-	-	-	-	47	26	0.16	1.10	-	-
-	-	-	-	-	-	55	31	0.18	1.25	1.10	4.6
-	-	-	150/160	-	302/320	65	36	0.26	1.80	1.46	6.1
-	-	-	150/190	-	302/374	30/50	17/28	0.35	2.40	1.30	5.40
-	-	-	130/-	-	266/-	50/60	28/33	0.40	2.75	1.20	5.0
-	-	-	180/-	-	356/-	50/60	28/33	0.50	3.45	1.20	5.0
-	-	-	230/-	-	446/-	20/40	11/22	0.70	4.85	1.20	5.0
-50	-58	-	220/-	-	428/-	10/35	55/19	0.60	4.15	-	5.0
-50	-58	-	480/-	-	896/-	20/50	11/28	0.3/0.4	2.05/2.75	0.8/0.9	3.35/3.75
-200	-239	-	240/-	-	464/-	50/63	28/35	0.6/0.65	4.15/4.50	-	-
-	-	-	200/-	-	392/-	11/35	6.1/19	0.88	6.1	0.8	3.35
-	-	-	90/-	-	194/-	10/20	5.5/11	0.58	4.0	1.76	7.30
-40	-40	-	-	-	-	150	83	1.7	1.15	0.5	2.10
-15	3	100	-	212	-	210	12	1.8	1.25	0.4	1.65
-30	-22	-	-	-	-	-	-	-	-	-	-
-40	-40	50/63	90/-	122/144	194/-	120	67	0.22	1.50	1.6	6.7
-40	-40	100	73/98	212	163/208	110/130	61/72	0.21	1.45	1.7	7.1
-40	-40	60/75	62/71	140/167	144/160	120	67	0.21	1.45	1.6	6.7

(continued on next page)

Table I Guide Values of the Physical Properties of Plastics (cont.)

Polymer	DIN 7728 Bl. I	Density		Electrical properties	
		g/cm ³	lb/in ³	Volume resistivity Ω cm	Surface resistance Ω
Low density polyethylene	PE-LD	0.914/0.928	0.0329–0.0330	$> 10^{17}$	10^{14}
High density polyethylene	PE-HD	0.94/0.96	0.0338–0.0345	$> 10^{17}$	10^{14}
EVA	EVA	0.92/0.95	0.0331–0.0341	$< 10^{15}$	10^{13}
Polypropylene	PP	0.90/0.907	0.0324–0.0327	$> 10^{17}$	10^{13}
Polybutene-1	PB	0.905/0.920	0.0325–0.0331	$> 10^{17}$	10^{13}
Polyisobutylene	PIB	0.91/0.93	0.0327–0.0334	$> 10^{15}$	10^{13}
Poly-4-methylpent-1-ene	PMP	0.83	0.0298	$> 10^{16}$	10^{13}
Ionomers	—	0.94	0.0338	$> 10^{16}$	10^{13}
Rigid PVC	PVC-U	1.38/1.55	0.0496–0.0557	$> 10^{15}$	10^{13}
Plasticized PVC	PVC-P	1.16/1.35	0.0417–0.0486	$> 10^{11}$	10^{11}
Polystyrene	PS	1.05	0.0378	$> 10^{16}$	$> 10^{13}$
Styrene/acrylonitrile copolymer	SAN	1.08	0.0392	$> 10^{16}$	$> 10^{13}$
Styrene/polybutadiene graft polymer	SB	1.05	0.0378	$> 10^{16}$	$> 10^{13}$
Acrylonitrile/polybut./styrene graft polymer	ABS	1.04/1.06	0.0374–0.0381	$> 10^{15}$	$> 10^{13}$
AN/AN elastomers/styrene graft polymer	ASA	1.04	0.0374	$> 10^{15}$	$> 10^{13}$
Polymethylmethacrylate	PMMA	1.17/1.20	0.0421–0.0431	$> 10^{15}$	10^{15}
Polyvinylcarbazole	PVK	1.19	0.0428	$> 10^{16}$	10^{14}
Polyacetal	POM	1.41/1.42	0.0507–0.0511	$> 10^{15}$	10^{13}
Polytetrafluoroethylene	PTFE	2.15/2.20	0.0774–0.0791	$> 10^{18}$	10^{17}
Tetrafluoroethylene/hexafluoropropylene copolymer	FEP	2.12/2.17	0.0763–0.0781	$> 10^{18}$	10^{16}
Polytrifluorochloroethylene	PCTFE	2.10/2.12	0.0755–0.0762	$> 10^{18}$	10^{16}
Ethylene/tetrafluoroethylene	E/TFE	1.7	0.0611	$> 10^{16}$	10^{13}
Polyamide 6	PA 6	1.13	0.0406	10^{12}	10^{10}
Polyamide 66	PA 66	1.14	0.0410	10^{12}	10^{10}
Polyamide 11	PA 11	1.04	0.0374	10^{13}	10^{11}
Polyamide 12	PA 12	1.02	0.0367	10^{13}	10^{11}
Polyamide 6-3-T	PA-6-3-T	1.12	0.0403	10^{11}	10^{10}
Polycarbonate	PC	1.2	0.0432	$> 10^{17}$	$> 10^{15}$
Polyethyleneterephthalate	PET	1.37	0.0492	10^{16}	10^{16}
Polybutyleneterephthalate	PBT	1.31	0.0471	10^{16}	10^{13}
Polyphenyleneether modified	PPE	1.06	0.0381	10^{16}	10^{14}
Polysulfone	PSU	1.24	0.0446	$> 10^{16}$	—
Polyphenylenesulfide	PPS	1.34	0.0483	$> 10^{16}$	—
Polyarylsulfone	PAS	1.36	0.0490	$> 10^{16}$	—
Polyethersulfone	PES	1.37	0.0492	10^{17}	—
Polyarylether	PAE	1.14	0.0411	$> 10^{10}$	—
Phenol/formaldehyde, grade 31	PF	1.4	0.0504	10^{11}	$> 10^8$
Urea/formaldehyde, grade 131	UF	1.5	0.0540	10^{11}	$> 10^{10}$
Melamine/formaldehyde, grade 152	MF	1.5	0.0540	11^{11}	$> 10^8$
Unsaturated polyester resin, grade 802	UP	2.0	0.0720	$> 10^{12}$	$> 10^{10}$
Polydiallylphthalate (GF) molding compound	PDAP	1.51/1.78	0.0543–0.0640	$10^{13}/10^{16}$	10^{13}
Silicone resin molding compound	SI	1.8/1.9	0.0648–0.0684	10^{14}	10^{12}
Polyimide molding	PI	1.43	0.0515	$> 10^{16}$	$> 10^{15}$
Epoxy resin, grade 891	EP	1.9	0.0683	$> 10^{14}$	$> 10^{12}$
Polyurethane casting resin	PU	1.05	0.0378	10^{16}	10^{14}
Thermoplastic PU-elastomers	PU	1.20	0.0432	10^{12}	10^{11}
Linear polyurethane (U ₅₀)	PU	1.21	0.0435	10^{13}	10^{12}
Vulcanized fiber	VF	1.1/1.45	0.0396–0.0522	10^{10}	10^8
Celluloseacetate, grade 432	CA	1.30	0.0468	10^{13}	10^{12}
Cellulosepropionate	CP	1.19/1.23	0.0429–0.0452	10^{16}	10^{14}
Celluloseacetobutyrate, grade 413	CAB	1.18	0.0425	10^{16}	10^{14}

Dielectric constant		Dissipation (power) factor $\tan \delta$		Dielectric strength		Tracking resistance		
50 Hz	10 ⁶ Hz	50 Hz	10 ⁶ Hz	kV/25 μ m	kV/cm	KA	KB	KC
2.29	2.28	$1.5 \cdot 10^{-4}$	$0.8 \cdot 10^{-4}$	> 700	—	3b	> 600	> 600
2.35	2.34	$2.4 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	> 700	—	3c	> 600	> 600
2.5/3.2	2.6/3.2	0.003/0.02	0.03/0.05	—	620/780	—	—	—
2.27	2.25	$< 4 \cdot 10^{-4}$	$< 5 \cdot 10^{-4}$	800	500/650	3c	> 600	> 600
2.5	2.2	$7 \cdot 10^{-4}$	$6 \cdot 10^{-4}$	700	—	3c	> 600	> 600
2.3	—	0.0004	—	230	—	3c	> 600	> 600
2.12	2.12	$7 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	280	700	3c	> 600	> 600
3.5	3.0	0.011	0.015	200/400	350/500	2/3b	600	600
4/8	4/4.5	0.08	0.12	150/300	300/400	—	—	—
2.5	2.5	$1/4 \cdot 10^{-4}$	$0.5/4 \cdot 10^{-4}$	500	300/700	1/2	140	150/250
2.6/3.4	2.6/3.1	$6/8 \cdot 10^{-3}$	$7/10 \cdot 10^{-3}$	500	400/500	1/2	160	150/260
2.4/4.7	2.4/3.8	$4/20 \cdot 10^{-4}$	$4/20 \cdot 10^{-4}$	500	300/600	2	> 600	> 600
2.4/5	2.4/3.8	$3/8 \cdot 10^{-3}$	$2/15 \cdot 10^{-3}$	400	350/500	3a	> 600	> 600
3/4	3/3.5	0.02/0.05	0.02/0.03	350	360/400	3a	> 600	> 600
3.3/3.9	2.2/3.2	0.04/0.06	0.004/0.04	300	400/500	3c	> 600	> 600
—	3	$6/10 \cdot 10^{-4}$	$6/10 \cdot 10^{-4}$	500	—	3b	> 600	> 600
3.7	3.7	0.005	0.005	700	380/500	3b	> 600	> 600
< 2.1	< 2.1	$< 2 \cdot 10^{-4}$	$< 2 \cdot 10^{-4}$	500	480	3c	> 600	> 600
2.1	2.1	$< 2 \cdot 10^{-4}$	$< 7 \cdot 10^{-4}$	500	550	3c	> 600	> 600
2.3/2.8	2.3/2.5	$1 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	500	550	3c	> 600	> 600
2.6	2.6	$8 \cdot 10^{-4}$	$5 \cdot 10^{-3}$	380	400	3c	> 600	> 600
3.8	3.4	0.01	0.03	350	400	3b	> 600	> 600
8.0	4.0	0.14	0.08	400	600	3b	> 600	> 600
3.7	3.5	0.06	0.04	300	425	3b	> 600	> 600
4.2	3.1	0.04	0.03	300	450	3b	> 600	> 600
4.0	3.0	0.03	0.04	250	350	3b	> 600	> 600
3.0	2.9	$7 \cdot 10^{-4}$	$1 \cdot 10^{-2}$	350	380	1	120/160	260/300
4.0	4.0	$2 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	500	420	2	—	—
3.0	3.0	$2 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	500	420	3b	420	380
2.6	2.6	$4 \cdot 10^{-4}$	$9 \cdot 10^{-4}$	500	450	1	300	300
3.1	3.0	$8 \cdot 10^{-4}$	$3 \cdot 10^{-3}$	—	425	1	175	175
3.1	3.2	$4 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	—	595	—	—	—
3.9	3.7	$3 \cdot 10^{-3}$	$13 \cdot 10^{-3}$	—	350	—	—	—
3.5	3.5	$1 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	—	400	—	—	—
3.14	3.10	$6 \cdot 10^{-3}$	$7 \cdot 10^{-3}$	—	430	—	—	—
6	4.5	0.1	0.03	50/100	300/400	1	140/180	125/175
8	7	0.04	0.3	80/150	300/400	3a	> 400	> 600
9	8	0.06	0.03	80/150	290/300	3b	> 500	> 600
6	5	0.04	0.02	120	250/530	3c	> 600	> 600
5.2	4	0.04	0.03	—	400	3c	> 600	> 600
4	3.5	0.03	0.02	—	200/400	3c	> 600	> 600
3.5	3.4	$2 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	—	560	1	> 300	> 380
3.5/5	3.5/5	0.001	0.01	—	300/400	3c	> 300	200/600
3.6	3.4	0.05	0.05	—	240	3c	—	—
6.5	5.6	0.03	0.06	—	300/600	3a	> 600	> 600
5.8	4.0	0.12	0.07	330	—	—	—	—
—	—	0.08	—	70/180	—	—	—	—
5.8	4.6	0.02	0.03	320	400	3a	> 600	> 600
4.2	3.7	0.01	0.03	350	400	3a	> 600	> 600
3.7	3.5	0.006	0.021	380	400	3a	> 600	> 600

■ Appendix II

Table II Permeability of Films Made from Various Polymers

Polymer	Temperature	Film thickness	Water vapor	N ₂	Air	O ₂	CO ₂	H ₂	Ar	He
	SI									
	°C									
		μm ¹⁾	g/cm ² day	cm ³ /m ² day bar						
PE-LD	23	100	1	700	1100	2000	10000	8000	—	—
PE-HD (ρ=0.95 g/cm ³ , unstretched)	25	40	0.9	525	754	1890	7150	6000	—	—
	30	40	1.7	720	960	2270	8600	7600	—	—
	40	40	3.5	1220	1660	3560	13100	11400	—	—
	50	40	8.1	2140	2650	5650	19500	16800	—	—
PE-HD (ρ=0.95 g/cm ³ , stretched)	25	40	1.0	430	680	1210	5900	5000	—	—
	30	40	1.6	560	830	1530	7200	6000	—	—
	40	40	4.3	1050	1490	2650	11200	9400	—	—
	50	40	10.5	1870	2670	4650	18100	14800	—	—
E/VA copolymer, VAC 20%	23	100	455	1400	—	4000	17000	—	—	—
Polypropylene (unstretched)	25	40	2.1	430	700	1900	6100	17700	1480	19200
	30	40	3.2	600	960	2500	8400	18200	2100	21700
	40	40	7.4	1280	1820	5100	14800	28100	4100	29800
	50	40	19.0	2800	3600	9200	27300	46600	8000	43500
Polypropylene (stretched)	25	40	0.81	200	350	1000	3300	6700	—	7300
	30	40	1.2	260	480	1200	3900	8200	—	8500
	40	40	3.3	560	940	2300	7050	12300	—	12100
	50	40	8.4	1200	1850	4150	13200	19800	—	17800
PVC-U (unstretched)	20	40	7.6	12	28	87	200	—	—	—
PVC-U (stretched)	20	40	4.4	13	13	43	110	—	—	—
PVC-P	20	40	20	350	550	1500	8500	—	—	—
Polyvinylidenechloride	25	25	0.1/0.2	1.8/2.3	5/10	1.7/11	60/700	630/1400	—	—
Polystyrene (stretched)	25	50	14.0	27	80	235	800	1260	—	—
Polyacetal	20	40	2.5	10	16	50	96	420	—	—
PFEP copolymers	40	25	2.0	375	—	3000	6500	2000	—	—
	40	25	0.38/0.85	39	—	110/230	250/620	3400/5200	—	—
E/TFE copolymers	23	25	0.6	470	—	1560	3800	—	—	—
E/CTFE copolymers	23	25	9.0	150	—	39.0	1700	—	—	—
PVF	23	25	50.0	3.8	—	4.7	170	900	—	—
Polyamide 6	25	25	80/110	14	—	40	200	1500	—	—
Polyamide 66	25	25	15/30	11	—	80	140	—	—	—
Polyamide 11	25	25	1.5/4.0	50	—	540	2400	5000	—	—
Polyamide 12	25	25	0.35	200/280	—	800/1400	2600/5300	—	—	—
Polycarbonate	23	25	4	680	—	4000	14500	22000	—	—
Polyethyleneterephthalate (stretched)	23	25	0.6	9/15	—	80/110	200/340	1500	—	—
Polysulfone	23	25	6	630	—	3600	15000	28000	—	—
PU elastomers	23	25	13/25	550/1600	—	1000/4500	6000/22000	—	—	—
Polyimide	23	25	25	94	—	390	700	3800	—	—
Celluloseacetate	25	25	150/600	470/630	—	1800/2300	13000/15000	14000	—	—
Celluloseacetobutyrate	25	25	460/600	3800	—	15000	94000	—	—	—

¹⁾ 1 $\mu\text{m} = 0.0394 \text{ mil}$.

Appendix III

Table III General Properties of Selected Polymeric Materials

ABS — Acrylonitrile-Butadiene-Styrene Copolymer

Type: amorphous, blend

Characteristics: glossiness, high stiffness, impact resistance, scratch resistance, high dimensional stability, ability to be galvanized, poor environmental resistance

Identified by: opaqueness, sweet smell during burn test, yellow flame with soot

$\rho = 1.03 - 1.07 \text{ g/cm}^3$

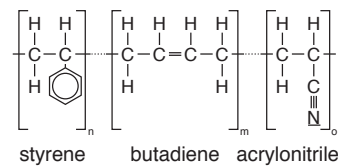
$c_p = 1470 \text{ J/(kg}\cdot\text{K)}$

$k = 0.3 \text{ W/(m}\cdot\text{K)}$

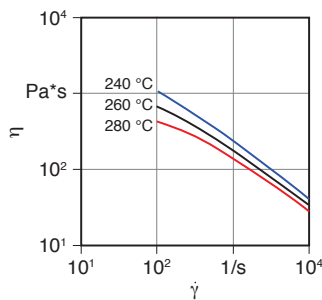
$E = 2200 - 3000 \text{ MPa}$

$T_{\text{max}}^{\text{short term}} = 80 - 95 \text{ }^\circ\text{C}$

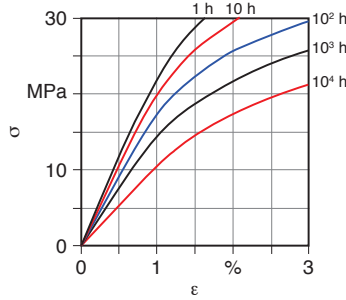
$T_{\text{max}}^{\text{long term}} = 75 - 85 \text{ }^\circ\text{C}$



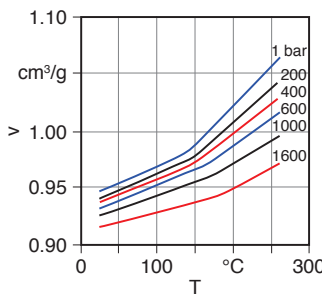
Viscosity:



Isochronous stress-strain:



pVT:



Modulus:

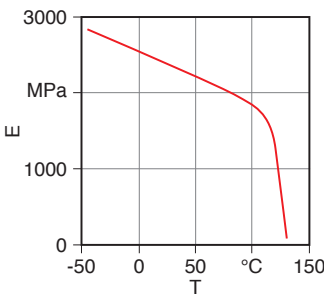


Table III General Properties of Selected Polymeric Materials (*cont.*)

ASA — Acrylonitrile-Styrene-Acrylester Copolymer

Type: amorphous

Characteristics: toughness, stiffness, shiny surface, higher environmental and chemical resistance than ABS

Identified by: opaqueness, sweet smell (styrene) when burned, bright flame, soot forming

$\rho = 1.04 - 1.07 \text{ g/cm}^3$

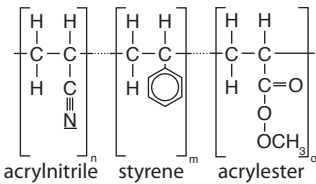
$c_p = 1300 \text{ J/(kg}\cdot\text{K)}$

$k = 0.18 \text{ W/(m}\cdot\text{K)}$

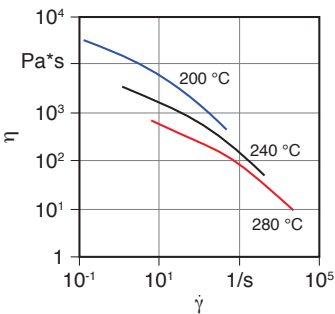
$E = 2300 - 2900 \text{ MPa}$

$T_{\text{max}}^{\text{short term}} = 85 - 95 \text{ }^\circ\text{C}$

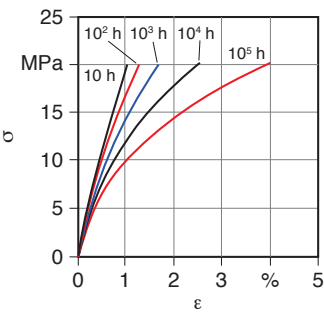
$T_{\text{max}}^{\text{long term}} = 75 - 85 \text{ }^\circ\text{C}$



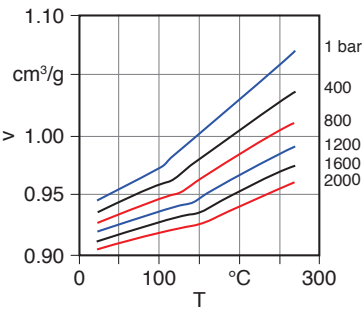
Viscosity:



Isochronous stress-strain:



p_vT:



Modulus:

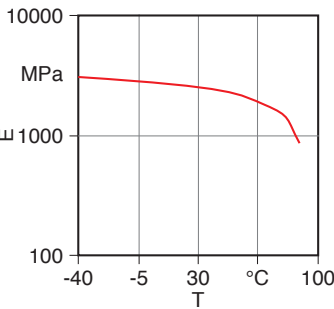


Table III General Properties of Selected Polymeric Materials (cont.)

PA6 — Polyamide 6

Type: semi-crystalline (30 – 40 %); (dry/std. hum./saturated)

Characteristics: abrasion resistance, impact resistance, absorption of water up to 9.5 %; often found as a fiber or filament, often found reinforced

Identified by: opaqueness, cream color, smell of burnt hair during burn test, yellow flame with blue halo

$\rho = 1.12 - 1.15 \text{ g/cm}^3$

$c_p = 1670 \text{ J/(kg}\cdot\text{K)}$

$k = 0.24 \text{ W/(m}\cdot\text{K)}$

$E = 600 - 2800 \text{ MPa}$

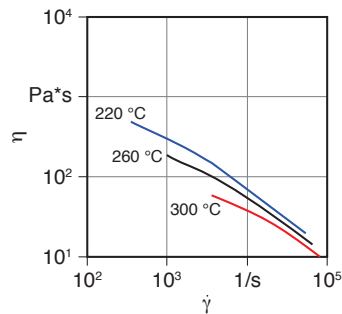
$T_{\text{short term max}} = 140 - 160 \text{ }^\circ\text{C}$

$T_{\text{long term max}} = 80 - 100 \text{ }^\circ\text{C}$

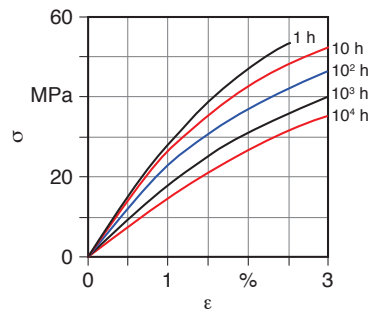


ε-caprolactam

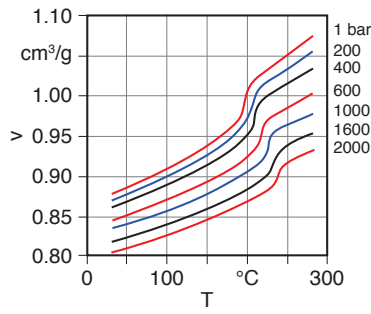
Viscosity:



Isochronous stress-strain:



p_vT:



Modulus:

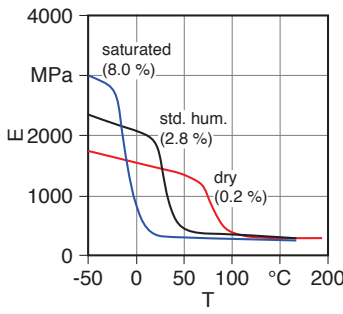


Table III General Properties of Selected Polymeric Materials (*cont.*)

PA12 — Polyamide 12

Type: semi-crystalline (35 – 45 %); (dry/std. hum./saturated)

Characteristics: low density, resistance to stress cracking, low water absorption (standard 0.7 %, saturated 1.5 %)

Identified by: milky white-yellow color, smell of burnt hair during burn test, yellow flame with blue halo; can be formed into a filament, melt drips

$\rho = 1.01 - 1.04 \text{ g/cm}^3$

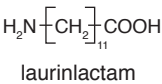
$c_p = 1260 \text{ J/(kg}\cdot\text{K)}$

$k = 0.23 \text{ W/(m}\cdot\text{K)}$

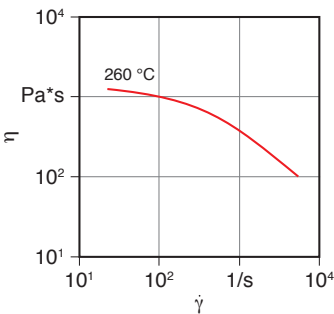
$E = 570 - 1400 \text{ MPa}$

$T_{\text{max}}^{\text{short term}} = 140 \text{ }^{\circ}\text{C}$

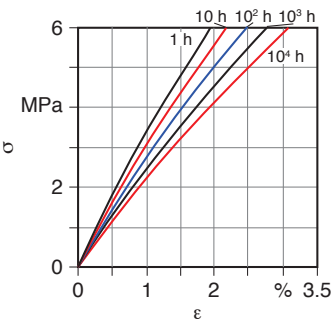
$T_{\text{max}}^{\text{long term}} = 70 - 80 \text{ }^{\circ}\text{C}$



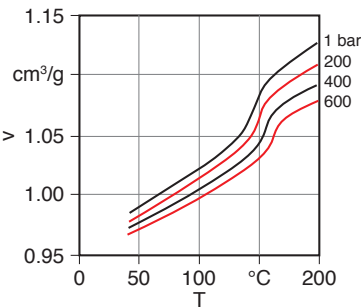
Viscosity:



Isochronous stress-strain:



pvT:



Modulus:

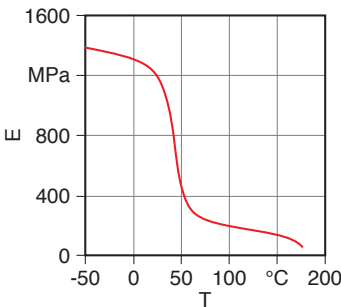


Table III General Properties of Selected Polymeric Materials (cont.)

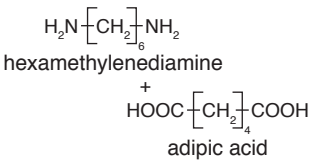
PA66 — Polyamide 66

Type: semi-crystalline (35 – 45 %); (dry/std. hum./saturated)

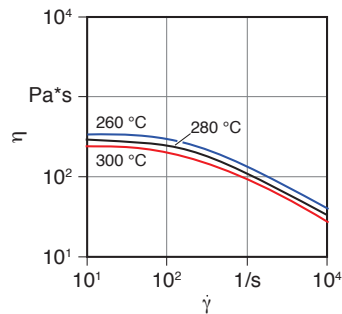
Characteristics: abrasion resistance, impact resistance, aging and heat resistance, absorption of water up to 8.5 %; often found as a fiber or filament, often found reinforced

Identified by: opaqueness, cream color, smell of burnt hair during burn test, yellow flame with blue halo

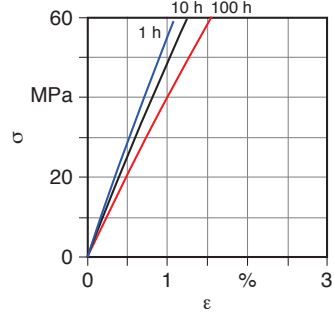
$\rho = 1.13 - 1.16 \text{ g/cm}^3$
 $c_p = 1670 \text{ J/(kg}\cdot\text{K)}$
 $k = 0.24 \text{ W/(m}\cdot\text{K)}$
 $E = 800 - 3000 \text{ MPa}$
 $T_{\text{max}}^{\text{short term}} = 140 - 170 \text{ }^\circ\text{C}$
 $T_{\text{max}}^{\text{long term}} = 80 - 100 \text{ }^\circ\text{C}$



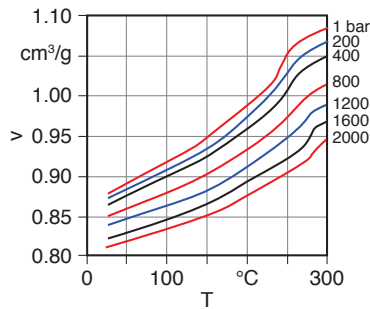
Viscosity:



Isochronous stress-strain:



p_vT:



Modulus:

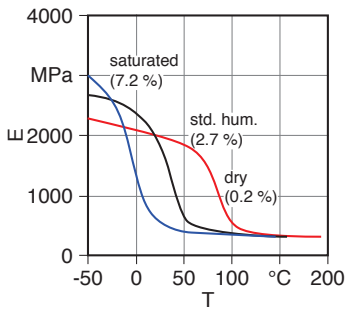


Table III General Properties of Selected Polymeric Materials (*cont.*)

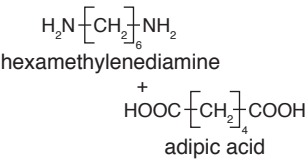
PA66 GF30 — Polyamide 66, 30 % Glass Reinforced

Type: semi-crystalline

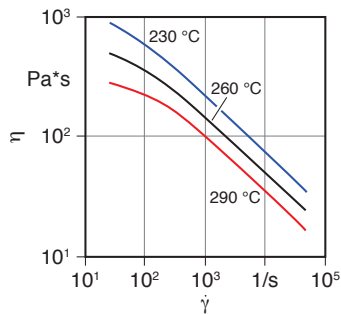
Characteristics: abrasion resistance, high stiffness, impact resistance, aging and heat resistance

Identified by: opaqueness, cream color, smell of burnt hari during burn test, yellow flame with blue halo

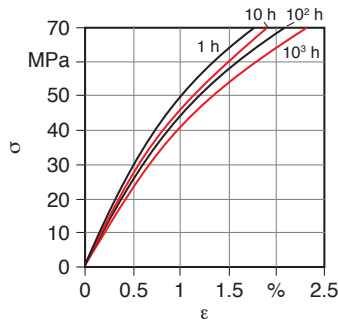
$\rho = 1.38 \text{ g/cm}^3$
 $c_p = 1260 \text{ J/(kg}\cdot\text{K)}$
 $k = 0.52 \text{ W/(m}\cdot\text{K)}$
 $E = x - x \text{ MPa}$
 $T_{\text{max}}^{\text{short term}} = 140 - 170 \text{ }^\circ\text{C}$
 $T_{\text{max}}^{\text{long term}} = 80 - 100 \text{ }^\circ\text{C}$



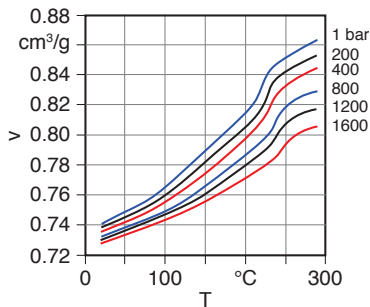
Viscosity:



Isochronous stress-strain:



pvT:



Modulus:

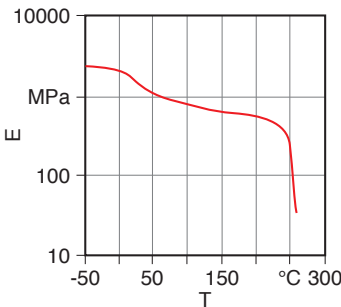


Table III General Properties of Selected Polymeric Materials (cont.)

PBT — Polybutylene Terephthalate

Type: semi-crystalline (40 – 50 %)

Characteristics: good dimensional stability, sensitivity to processing, favorable sliding and wear characteristics, good insulating properties; often reinforced

Identified by: orange colored sooty flame, sweet smell during burn test, melt drips

$\rho = 1.30 - 1.32 \text{ g/cm}^3$

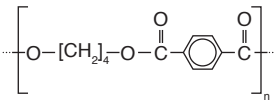
$c_p = 1300 \text{ J/(kg}\cdot\text{K)}$

$k = 0.21 \text{ W/(m}\cdot\text{K)}$

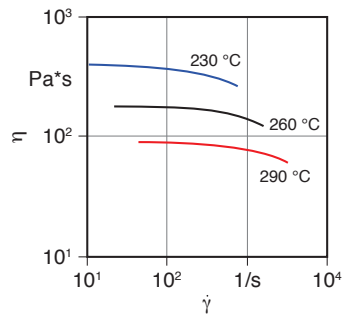
$E = 2500 - 2800 \text{ MPa}$

$T_{\text{max}}^{\text{short term}} = 160 \text{ }^\circ\text{C}$

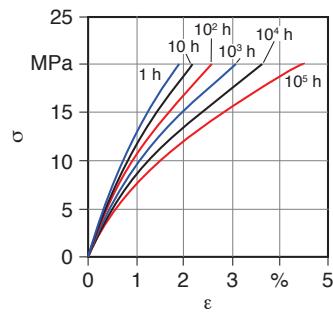
$T_{\text{max}}^{\text{long term}} = 100 \text{ }^\circ\text{C}$



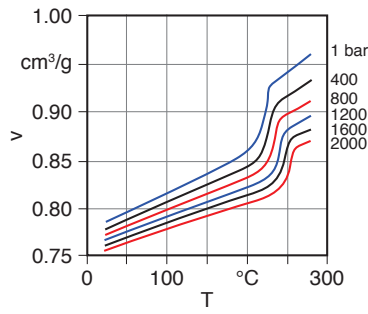
Viscosity:



Isochronous stress-strain:



pVT:



Modulus:

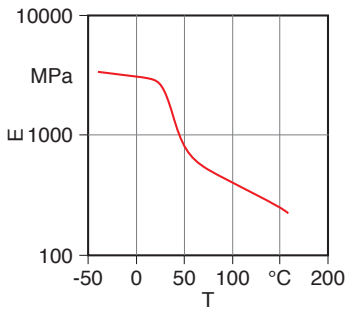


Table III General Properties of Selected Polymeric Materials (*cont.*)

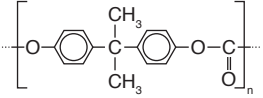
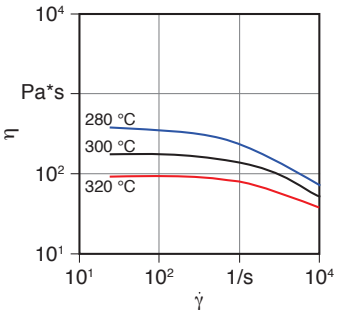
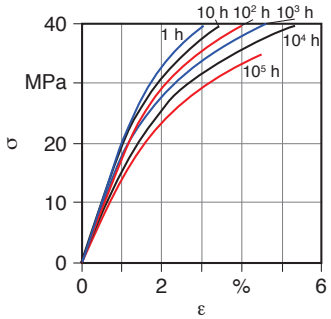
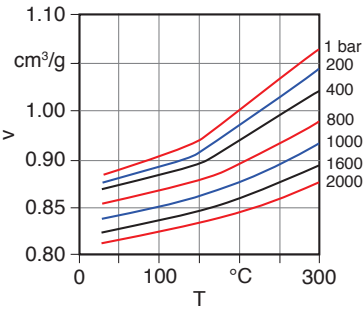
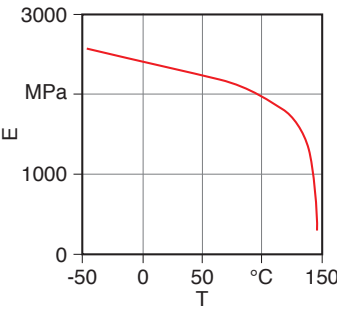
PC — Polycarbonate	
Type: amorphous Characteristics: glossiness, high optical properties, high dimensional stability, impact resistance, high thermal stability Identified by: transparency, dark yellow flame during burn test, soot forming, self extinguishment	$\rho = 1.20 - 1.24 \text{ g/cm}^3$ $c_p = 1260 \text{ J/(kg}\cdot\text{K)}$ $k = 0.2 \text{ W/(m}\cdot\text{K)}$ $E = 2200 - 2400 \text{ MPa}$ $T_{\text{max}}^{\text{short term}} = 135 \text{ }^\circ\text{C}$ $T_{\text{max}}^{\text{long term}} = 100 \text{ }^\circ\text{C}$ 
Viscosity: 	Isochronous stress-strain: 
p/T: 	Modulus: 

Table III General Properties of Selected Polymeric Materials (cont.)

PE-HD — High Density Polyethylene

Type: semi-crystalline (60 – 80 %)

Characteristics: low density, low strength and stiffness, low dimensional stability, high chemical resistance, high degree of crystallinity (60 – 80 %); inexpensive

Identified by: milky color, smell of paraffin during burn test, yellow flame, drips

$\rho = 0.94 - 0.96 \text{ g/cm}^3$

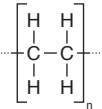
$c_p = 2300 \text{ J/(kg}\cdot\text{K)}$

$k = 0.63 \text{ W/(m}\cdot\text{K)}$

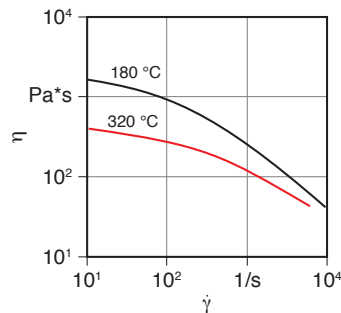
$E = 600 - 1400 \text{ MPa}$

$T_{\text{max}}^{\text{short term}} = 80 - 110 \text{ }^\circ\text{C}$

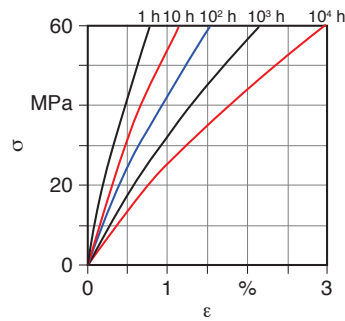
$T_{\text{max}}^{\text{long term}} = 60 - 80 \text{ }^\circ\text{C}$



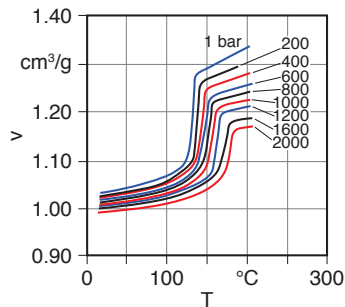
Viscosity:



Isochronous stress-strain:



p_vT:



Modulus:

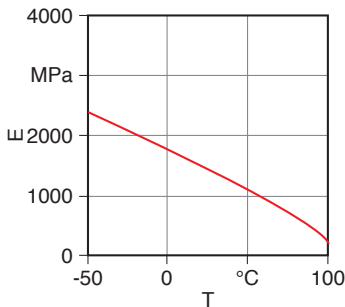


Table III General Properties of Selected Polymeric Materials (*cont.*)

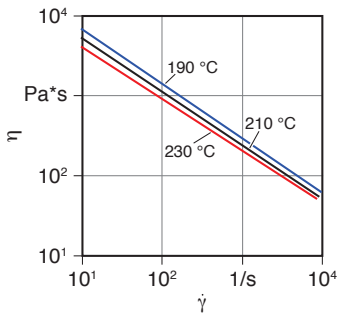
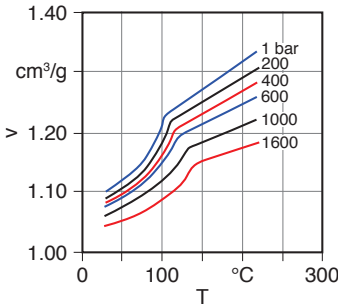
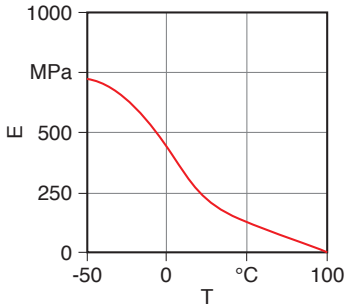
PE-LD — Low Density Polyethylene	
Type: semi-crystalline (40 – 55 %) Characteristics: low density, easy procession for several methods, good flow properties, low dimensional stability; inexpensive Identified by: translucence, smell of paraffin when burned, yellow flame, melt drips, floats in water	$\rho = 0.914 - 0.928 \text{ g/cm}^3$ $c_p = 2300 \text{ J/(kg}\cdot\text{K)}$ $k = 0.33 \text{ W/(m}\cdot\text{K)}$ $E = 200 - 400 \text{ MPa}$ $T_{\text{max}}^{\text{short term}} = 80 - 90 \text{ }^\circ\text{C}$ $T_{\text{max}}^{\text{long term}} = 60 - 70 \text{ }^\circ\text{C}$ $\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{---C} & \text{---C---} \\ & \\ \text{H} & \text{H} \end{array} \right]_n$
Viscosity: 	Isochronous stress-strain:
p_vT: 	Modulus: 

Table III General Properties of Selected Polymeric Materials (cont.)

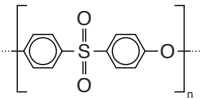
PES — Polyethersulfone

Type: amorphous

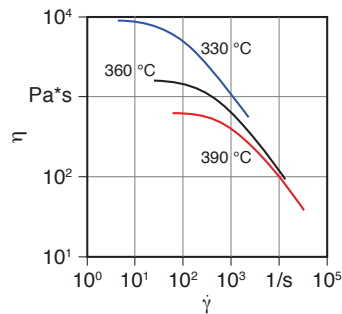
Characteristics: high thermal stbility, good chemical resistance, susceptibility to crack formation, water absorption

Identified by: transparency, light yellow color, difficult to ignite

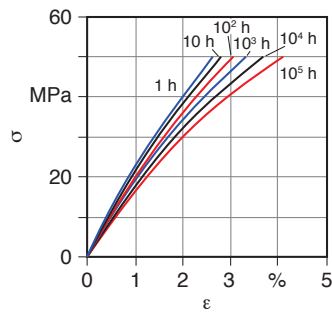
$\rho = 1.37 \text{ g/cm}^3$
 $c_p = 1100 \text{ J/(kg}^\circ\text{K)}$
 $k = 0.18 \text{ W/(m}^\circ\text{K)}$
 $E = 80 - 90 \text{ MPa}$
 $T_{\text{max}}^{\text{short term}} = 210 \text{ }^\circ\text{C}$
 $T_{\text{max}}^{\text{long term}} = 180 \text{ }^\circ\text{C}$



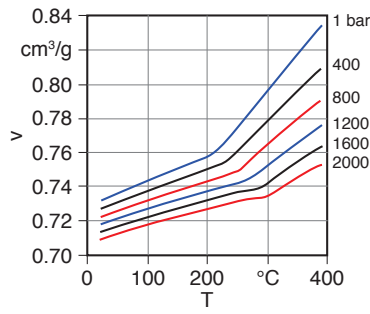
Viscosity:



Isochronous stress-strain:



p_vT:



Modulus:

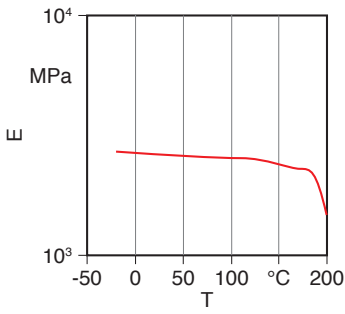


Table III General Properties of Selected Polymeric Materials (cont.)

PMMA — Polymethylmethacrylate

Type: amorphous

Characteristics: scratch resistance, stiffness, brittleness, good chemical and environmental stability, susceptibility to stress cracking

Identified by: transparency, flammability, blue flame during burn test, fruity and sweet smell during burn test

$\rho = 1.15 - 1.19 \text{ g/cm}^3$

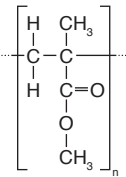
$c_p = 1470 \text{ J/(kg}\cdot\text{K)}$

$k = 0.2 \text{ W/(m}\cdot\text{K)}$

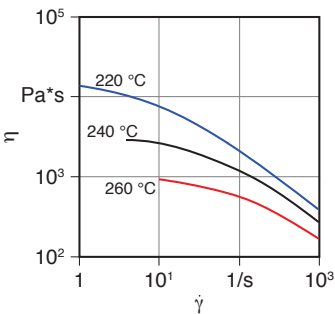
$E = 3100 - 3300 \text{ MPa}$

$T_{\text{max}}^{\text{short term}} = 85 - 95 \text{ }^\circ\text{C}$

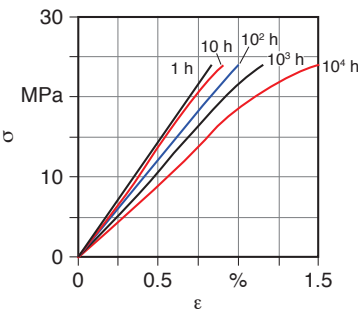
$T_{\text{max}}^{\text{long term}} = 65 - 80 \text{ }^\circ\text{C}$



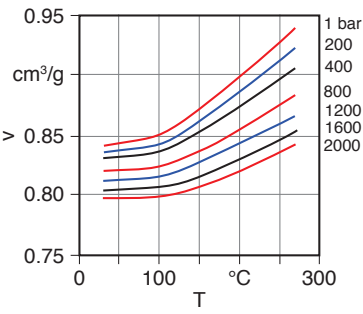
Viscosity:



Isochronous stress-strain:



p_vT:



Modulus:

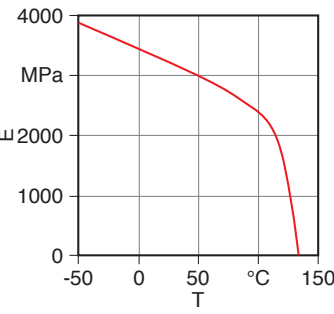


Table III General Properties of Selected Polymeric Materials (cont.)

POM — Polyoxymethylene

Type: semi-crystalline (70 – 80 %)

Characteristics: high strength and stiffness, high flexibility, low friction coefficient, high dimensional stability, low susceptibility to stress cracking, sensitivity to UV light

Identified by: opaqueness, white color, smell of formaldehyde during burn test, blue flame during burn test

$\rho = 1.41 - 1.43 \text{ g/cm}^3$

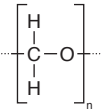
$c_p = 1470 \text{ J/(kg}^\circ\text{K)}$

$k = 0.2 \text{ W/(m}^\circ\text{K)}$

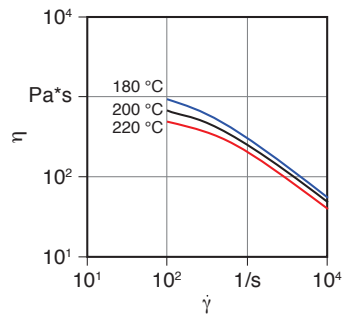
$E = 3000 - 3200 \text{ MPa}$

$T_{\text{short term max}} = 110 - 140 \text{ }^\circ\text{C}$

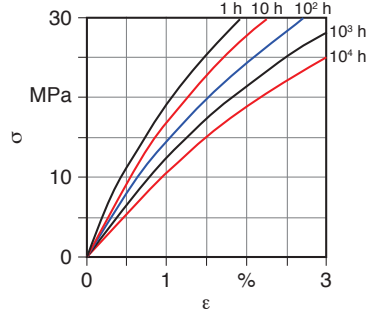
$T_{\text{long term max}} = 90 - 100 \text{ }^\circ\text{C}$



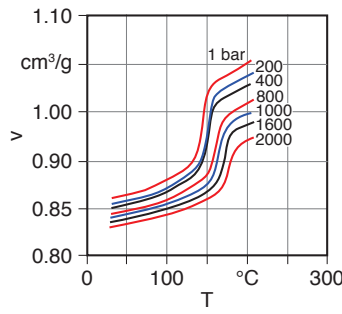
Viscosity:



Isochronous stress-strain:



pvT:



Modulus:

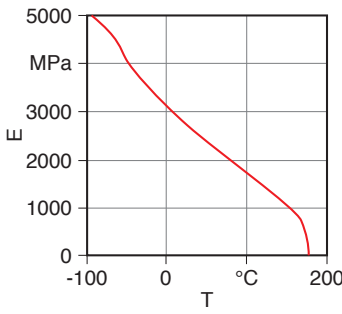


Table III General Properties of Selected Polymeric Materials (*cont.*)

PP — Polypropylene

Type: semi-crystalline

Characteristics: low strength and stiffness, low dimensional stability, low stress cracking, chemical resistance, copolymerization with ethylene reduces glass transition temperature; often filled and reinforced, homopolymer brittle at low temperatures, inexpensive

Identified by: translucence, smell of parafin during burn test, bright blue flame during burn test

$\rho = 0.90 - 0.91 \text{ g/cm}^3$

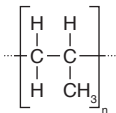
$c_p = 1930 \text{ J/(kg}\cdot\text{K)}$

$k = 0.24 \text{ W/(m}\cdot\text{K)}$

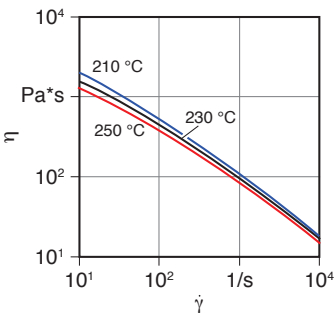
$E = 1300 - 1800 \text{ MPa}$

$T_{\text{max}}^{\text{short term}} = 130 \text{ }^\circ\text{C}$

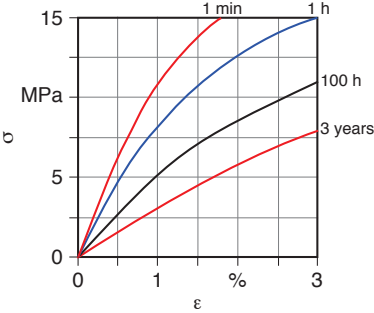
$T_{\text{max}}^{\text{long term}} = 90 \text{ }^\circ\text{C}$



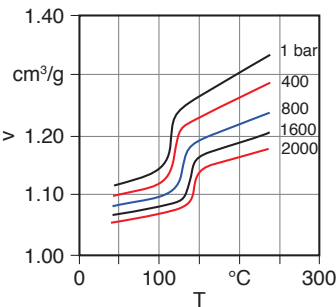
Viscosity:



Isochronous stress-strain:



pvT:



Modulus:

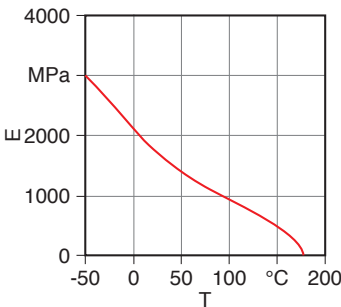


Table III General Properties of Selected Polymeric Materials (cont.)

PPE — Polyethyleneether

Type: amorphous

Characteristics:

Identified by: opaqueness

$\rho = 1.06 \text{ g/cm}^3$

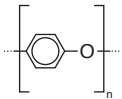
$c_p = 1400 \text{ J/(kg}^\circ\text{K)}$

$k = 0.23 \text{ W/(m}^\circ\text{K)}$

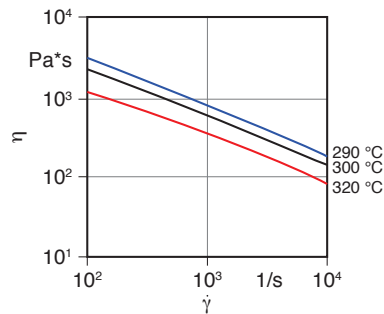
$E = 2000 \text{ MPa}$

$T_{\text{max}}^{\text{short term}} = 150 \text{ }^\circ\text{C}$

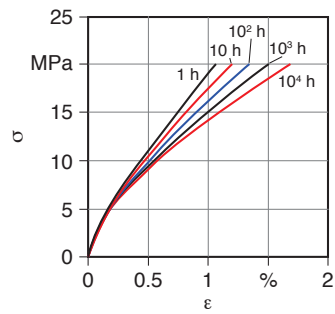
$T_{\text{max}}^{\text{long term}} = 80 \text{ }^\circ\text{C}$



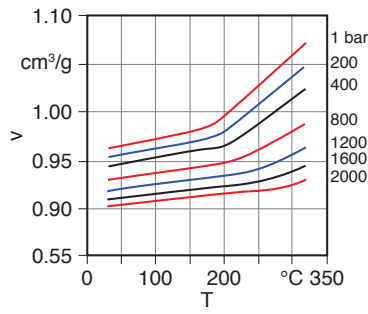
Viscosity:



Isochronous stress-strain:



pvT:



Modulus:

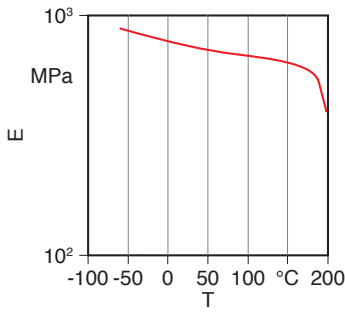


Table III General Properties of Selected Polymeric Materials (*cont.*)

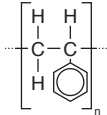
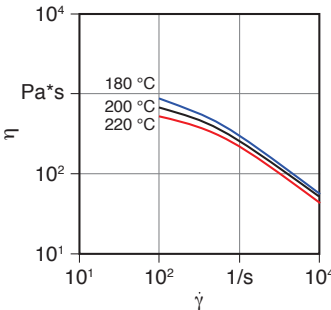
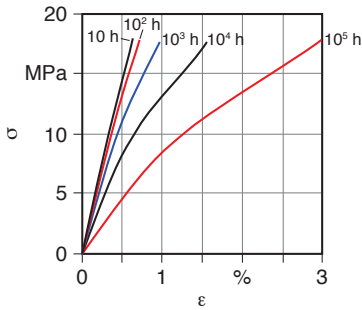
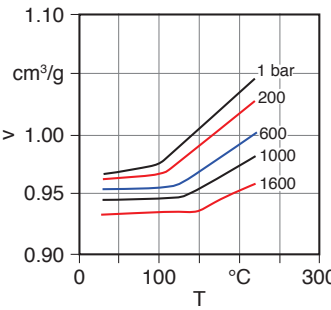
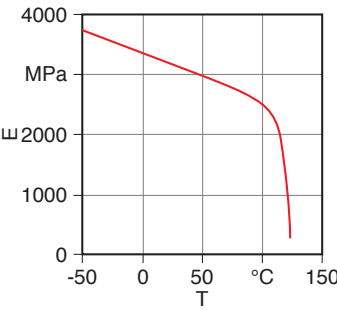
PS — Polystyrene	
Type: amorphous Characteristics: high stiffness, brittleness, glassy smooth surface, good dimensional stability, susceptibility to stress cracking, limited chemical stability Identified by: transparency, sweet smell (styrene) during burn test, yellow flame and soot during burn test	$\rho = 1.05 \text{ g/cm}^3$ $c_p = 1340 \text{ J/(kg}\cdot\text{K)}$ $k = 0.15 \text{ W/(m}\cdot\text{K)}$ $E = 1100 - 2800 \text{ MPa}$ $T_{\text{max}}^{\text{short term}} = 90 \text{ }^\circ\text{C}$ $T_{\text{max}}^{\text{long term}} = 80 \text{ }^\circ\text{C}$ 
Viscosity: 	Isochronous stress-strain: 
p_vT: 	Modulus: 

Table III General Properties of Selected Polymeric Materials (cont.)

PVC-R — Rigid Polyvinylchloride

Type: amorphous

Characteristics: low toughness at low temperature, good dimensional stability, good environmental resistance, large variability in properties when plasticized; inexpensive

Identified by: transparency to opaqueness, poisonous fumes during burn test, release of hydrochloric acid during burn test, self extinguishment

$\rho = 1.38 - 1.55 \text{ g/cm}^3$

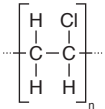
$c_p = 1000 \text{ J/(kg}\cdot\text{K)}$

$k = 0.16 \text{ W/(m}\cdot\text{K)}$

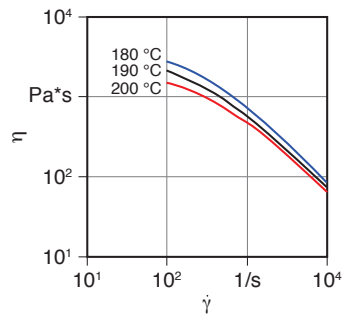
$E = 2700 - 3000 \text{ MPa}$

$T_{\text{max}}^{\text{short term}} = 70 \text{ }^\circ\text{C}$

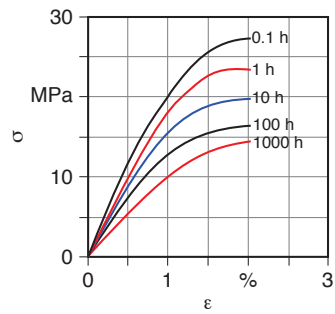
$T_{\text{max}}^{\text{long term}} = 60 \text{ }^\circ\text{C}$



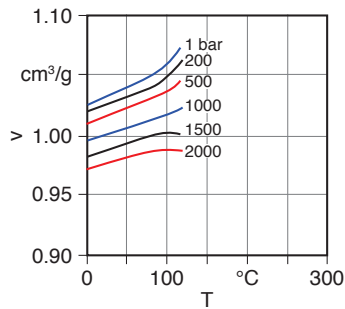
Viscosity:



Isochronous stress-strain:



p_vT:



Modulus:

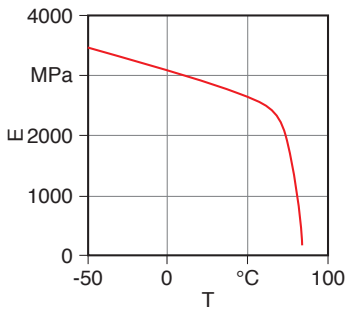


Table III General Properties of Selected Polymeric Materials (cont.)

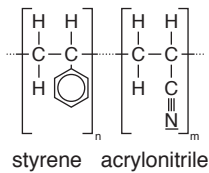
SAN — Styrene-Acrylonitrile Copolymer

Type: amorphous

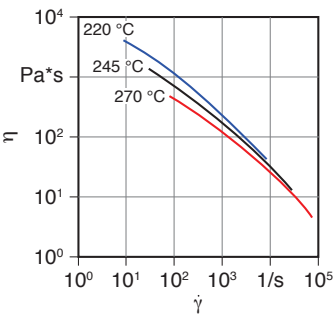
Characteristics: high strength and stiffness, good dimensional stbility, good chemical resistance, lower resistance against stress cracking than PS

Identified by: yellowish color, transparency, smell of styrene during burn test, bright flame, soot forming

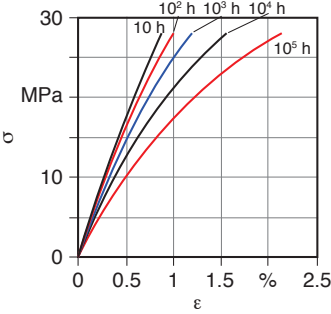
$\rho = 1.08 \text{ g/cm}^3$
 $c_p = 1300 \text{ J/(kg}\cdot\text{K)}$
 $k = 0.18 \text{ W/(m}\cdot\text{K)}$
 $E = 3500 - 3700 \text{ MPa}$
 $T_{\text{max}}^{\text{short term}} = 95 \text{ }^\circ\text{C}$
 $T_{\text{max}}^{\text{long term}} = 85 \text{ }^\circ\text{C}$



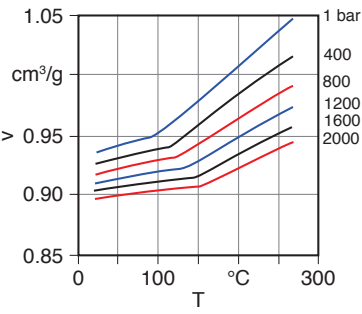
Viscosity:



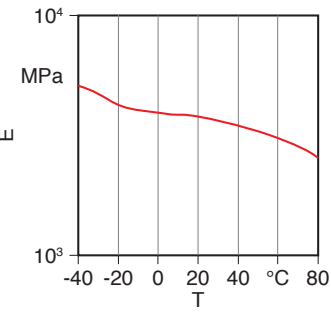
Isochronous stress-strain:



p_vT:



Modulus:



■ Appendix IV – Balance Equations

Continuity Equation

Cartesian Coordinates (x, y, z)

$$\frac{\partial}{\partial x}(\rho u_x) + \frac{\partial}{\partial y}(\rho u_y) + \frac{\partial}{\partial z}(\rho u_z) = 0$$

Cylindrical Coordinates (r, θ, z):

$$\frac{1}{r} \frac{\partial}{\partial r}(\rho r u_r) + \frac{1}{r} \frac{\partial}{\partial \theta}(\rho u_\theta) + \frac{\partial}{\partial z}(\rho u_z) = 0$$

Energy Equation for a Newtonian Fluid

Cartesian Coordinates (x, y, z)

$$\begin{aligned} & \rho C_v \left(\frac{\partial T}{\partial t} + u_x \frac{\partial T}{\partial x} + u_y \frac{\partial T}{\partial y} + u_z \frac{\partial T}{\partial z} \right) \\ &= K \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + 2\mu \left(\left(\frac{\partial u_x}{\partial x} \right)^2 + \left(\frac{\partial u_y}{\partial y} \right)^2 + \left(\frac{\partial u_z}{\partial z} \right)^2 \right) \\ &+ \mu \left(\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right)^2 + \left(\frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \right)^2 + \left(\frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y} \right)^2 \right) + \dot{Q} \end{aligned}$$

Cylindrical Coordinates (r, θ, z):

$$\begin{aligned} & \rho C_v \left(\frac{\partial T}{\partial t} + u_r \frac{\partial T}{\partial r} + \frac{u_\theta}{r} \frac{\partial T}{\partial \theta} + u_z \frac{\partial T}{\partial z} \right) \\ &= K \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right) + 2\mu \left(\left(\frac{\partial v_r}{\partial r} \right)^2 + \left(\frac{1}{r} \left(\frac{\partial v_\theta}{\partial \theta} + v_r \right) \right)^2 + \left(\frac{\partial v_z}{\partial z} \right)^2 \right) \\ &+ \mu \left(\left(\frac{\partial v_\theta}{\partial z} + \frac{1}{r} \frac{\partial v_z}{\partial \theta} \right)^2 + \left(\frac{\partial v_r}{\partial r} + \frac{\partial v_r}{\partial z} \right)^2 + \left(\frac{1}{r} \frac{\partial v_r}{\partial \theta} + r \frac{\partial}{\partial r} \left(\frac{v_\theta}{r} \right) \right)^2 \right) + \dot{Q} \end{aligned}$$

Momentum Balance

Momentum Equation in Terms of τ

Cartesian Coordinates (x, y, z)

$$\begin{aligned}\rho \left(\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right) &= -\frac{\partial p}{\partial x} \left(\frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z} \right) + \rho g_x \\ \rho \left(\frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \right) &= -\frac{\partial p}{\partial y} \left(\frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} + \frac{\partial \tau_{zy}}{\partial z} \right) + \rho g_y \\ \rho \left(\frac{\partial v_z}{\partial t} + v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \right) &= -\frac{\partial p}{\partial z} \left(\frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{yz}}{\partial y} + \frac{\partial \tau_{zz}}{\partial z} \right) + \rho g_z\end{aligned}$$

Cylindrical Coordinates (r, θ, z):

$$\begin{aligned}\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta^2}{r} + v_z \frac{\partial v_r}{\partial z} \right) \\ = -\frac{\partial p}{\partial r} + \left(\frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rr}) + \frac{1}{r} \frac{\partial \tau_{r\theta}}{\partial \theta} - \frac{\tau_{\theta\theta}}{r} + \frac{\partial \tau_{rz}}{\partial z} \right) + \rho g_r \\ \rho \left(\frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r v_\theta}{r} + v_z \frac{\partial v_\theta}{\partial z} \right) \\ = -\frac{1}{r} \frac{\partial p}{\partial \theta} + \left(\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{r\theta}) + \frac{1}{r} \frac{\partial \tau_{\theta\theta}}{\partial \theta} + \frac{\partial \tau_{\theta z}}{\partial z} \right) + \rho g_\theta \\ \rho \left(\frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_z}{\partial \theta} + v_z \frac{\partial v_z}{\partial z} \right) \\ = -\frac{\partial p}{\partial z} + \left(\frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) + \frac{1}{r} \frac{\partial \tau_{\theta z}}{\partial \theta} + \frac{\partial \tau_{zz}}{\partial z} \right) + \rho g_z\end{aligned}$$

Navier-Stokes Equation

Cartesian Coordinates (x, y, z)

$$\begin{aligned}\rho \left(\frac{\partial u_x}{\partial t} + u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} + u_z \frac{\partial u_x}{\partial z} \right) &= -\frac{\partial p}{\partial x} + \mu \left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2} \right) + \rho g_x \\ \rho \left(\frac{\partial u_y}{\partial t} + u_x \frac{\partial u_y}{\partial x} + u_y \frac{\partial u_y}{\partial y} + u_z \frac{\partial u_y}{\partial z} \right) &= -\frac{\partial p}{\partial y} + \mu \left(\frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} + \frac{\partial^2 u_y}{\partial z^2} \right) + \rho g_y \\ \rho \left(\frac{\partial u_z}{\partial t} + u_x \frac{\partial u_z}{\partial x} + u_y \frac{\partial u_z}{\partial y} + u_z \frac{\partial u_z}{\partial z} \right) &= -\frac{\partial p}{\partial z} + \mu \left(\frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} + \frac{\partial^2 u_z}{\partial z^2} \right) + \rho g_z\end{aligned}$$

Cylindrical Coordinates (r, θ, z):

$$\begin{aligned}
 & \rho \left(\frac{\partial u_r}{\partial t} + u_r \frac{\partial u_r}{\partial r} + \frac{u_\theta}{r} \frac{\partial u_r}{\partial \theta} - \frac{u_\theta^2}{r} + u_z \frac{\partial u_r}{\partial z} \right) \\
 &= -\frac{\partial p}{\partial r} + \mu \left(\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r u_r) \right) + \frac{1}{r^2} \frac{\partial^2 u_r}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial u_\theta}{\partial \theta} + \frac{\partial^2 u_r}{\partial z^2} \right) + \rho g_r \\
 \\
 & \rho \left(\frac{\partial u_\theta}{\partial t} + u_r \frac{\partial u_\theta}{\partial r} + \frac{u_\theta}{r} \frac{\partial u_\theta}{\partial \theta} + \frac{u_r u_\theta}{r} + u_z \frac{\partial u_\theta}{\partial z} \right) \\
 &= -\frac{1}{r} \frac{\partial p}{\partial \theta} + \mu \left(\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r u_\theta) \right) + \frac{1}{r^2} \frac{\partial^2 u_\theta}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial u_r}{\partial \theta} + \frac{\partial^2 u_\theta}{\partial z^2} \right) + \rho g_\theta \\
 \\
 & \rho \left(\frac{\partial u_z}{\partial t} + u_r \frac{\partial u_z}{\partial r} + \frac{u_\theta}{r} \frac{\partial u_z}{\partial \theta} + u_z \frac{\partial u_z}{\partial z} \right) \\
 &= -\frac{\partial p}{\partial z} + \mu \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u_z}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 u_z}{\partial \theta^2} + \frac{\partial^2 u_z}{\partial z^2} \right) + \rho g_z
 \end{aligned}$$

