Polymer Processing Instabilities

Control and Understanding



edited by Savvas G. Hatzikiriakos Kalman B. Migler

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Control and Understanding

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Marcel Dekker

New York

CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742

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International Standard Book Number-13: 978-1-4200-3068-6 (eBook - PDF)

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Preface

Polymer processing has grown in the past 50 years into a multi-billion dollar industry with production facilities and development labs all over the world. The primary reason for this phenomenal growth compared to other materials is the relative ease of manufacture and processing. Numerous methods have been developed to process polymeric materials at high volume and at relatively low temperatures.

But despite this success, manufacturing is limited by the occurrence of polymer processing instabilities. These limitations manifest themselves in two ways; first as the rate limiting step in the optimization of existing operations, and second in the introduction of new materials to the marketplace. For example, it is natural to ask what is the rate limiting step for processing operations; why not run a given operation 20% faster? Quite frequently, the answer to this question concerns flow instabilities. As the polymeric material is processed in the molten state; it retains characteristics of both liquids and solids. The faster one processes it, the more solid like its response becomes; seemingly simple processing operations become intractably difficult and the polymer flow becomes "chaotic" and uncontrollable.

A second problem concerns the development of new materials; this is particularly pressing because new materials with enhanced properties offer relief from the commodities nature of the polymer processing industry. But in order to gain market acceptance, they must also enjoy ease of processability and there are numerous examples of new materials which processed poorly and suffered in the market.

The past decade has seen great progress in our efforts to understand and control polymer processing instabilities; however much of the success is scattered throughout the scientific and technical literature. The intention of this book is to coherently collect these recent triumphs and present them to a wide audience. This book is intended for polymer rheologists, scientists, engineers, technologists and graduate students who are engaged in the field of polymer processing operations and need to understand the impact of flow instabilities. It is also intended for those who are already active in fields such as instabilities in polymer rheology and processing and wish to widen their knowledge and understanding further.

The chapters in this book seek to impart both fundamental and practical understanding on various flows that occur during processing. Processes where instabilities pose serious limitations in the rate of production include extrusion and co-extrusion, blow molding, film blowing, film casting, and injection molding. Methods to cure and eliminate such instabilities is also of concern in this book. For example, conventional polymer processing additives that eliminate flow instabilities such as sharkskin melt fracture, and nonconventional polymer processing additives that eliminate flow instabilities such as gross melt fracture are also integral parts of this book. Materials of interest that are covered in this book include most of the commodity polymers that are processed as melts at temperatures above their melting point (polyethylenes, polypropylenes, fluoropolymers, and others) or as concentrated solutions at lower temperatures.

Greater emphasis has been given to the flow instability of melt fracture since such phenomena have drawn the attention of many researchers in recent years. Moreover, these phenomena take place in a variety of processes such as film blowing, film casting, blow molding, extrusion and various coating flows. Equally important, however, instabilities take place in other processing operations such as draw resonance and the "dog-bone effect" in film casting, tiger-skin instabilities in injection molding, interfacial instabilities in co-extrusion and several secondary flows in various contraction flows. An overall overview of these instabilities can be found in the introduction (Chapter 1).

It is hoped that this book fills the gap in the polymer processing literature where polymer flow instabilities are not treated in-depth in any book. Research in this field, in particular over the last ten years, has produced a significant amount of data. An attempt is made to distil these data and to define the state-of-the art in the field. It is hoped that this will be useful to researchers active in the field as a starting point as well as a guide to obtain

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helpful direction in their research. It would be almost impossible to include all the knowledge generated over the past fifty-to-sixty years in a single book. As such, we would like to apologize for not citing several important reports and contributions to the field.

> Savvas G. Hatzikiriakos Kalman B. Migler

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1

Overview of Processing Instabilities

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1.1 POLYMER FLOW INSTABILITIES

Hydrodynamic stability is one of the central problems of fluid dynamics. It is concerned with the breakdown of laminar flow and its subsequent development and transition to turbulent flow (1). The flow of polymeric liquids differs significantly from that of their low-viscosity counterparts in several ways and, consequently, the nature of flow instabilities is completely different. Most notably, whereas for low-viscosity fluids it is the inertial forces on the fluid that cause turbulence (as measured by the *Reynolds number*), for highviscosity polymers, it is the elasticity of the fluid that causes a breakdown in laminar fluid flow (as measured by the *Weissenberg number*). Additionally, the

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high viscosity and the propensity for the molten fluid to slip against solid surfaces contribute to a rich and diverse set of phenomena, which this book aims to review.

In this introductory chapter, an overview of most flow instabilities that are discussed and examined in detail in this book is presented. Both experimental observations as well as modeling of flows with the purpose of predicting flow instabilities are of concern in subsequent chapters. In addition, ways of overcoming these instabilities with the aim of increasing the rate of production of polymer processes are also of central importance [e.g., use of processing aids to eliminate surface defects (*melt fracture*), adjustment of molecular parameters, and rational adjustment of operating procedures and geometries to obtain better flow properties].

1.2 PART A: THE NATURE OF POLYMERIC FLOW

Polymeric liquids exhibit many idiosyncracies that their Newtonian counterparts lack. Most notably are: 1) the normal stress and elasticity effects; 2) strong extensional viscosity effects; and 3) wall slip effects. These properties of polymeric liquids change dramatically the nature and structure of the flow compared to the corresponding flow of Newtonian liquids. Chapter 2 of Ref. 2 presents a comprehensive overview of such striking differences in Newtonian flow compared to their non-Newtonian counterparts. Part A of this book (Chapters 2–4) is thus devoted to the fundamental aspects of polymeric flow from the perspective of processing regime, where the above effects are most manifest.

Chapter 2 by Dealy introduces the reader to the concepts of polymer rheology that are most important to polymer processing and defines a large number of the terms needed to read the rest of the book. It describes how to relate the stress on a fluid to an imposed strain, first for the simple linear case and then for the cases more relevant to processing, such as nonlinear flows (such as shear thinning) and also extensional flows (which are prevalent in most processing operations.) It carefully defines the *Weissenberg* number, which characterizes the degree of nonlinearity or anisotropy exhibited by the fluid in a particular deformation, as well as the *Deborah* number, which is a measure of the degree to which a material exhibits elastic behavior. It cautions the reader that our knowledge and measurement ability in this area are still in their infancy.

Chapter 3 by Mitsoulis describes secondary flows in processing operations, in particular those in which vortices or helices appear. This is a classic case in which a flow phenomenon (vortices), which occurs for Newtonian flows, also occurs for polymeric flows, but the nature of the flow is quite distinct. For polymeric fluids, the transition to vortices is governed largely by

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the Deborah number. Depending on the response of the fluid to extensional flows, the occurrence and magnitude of the vortices can be quite different. This chapter describes the occurrence of these flows in a number of processing flows including extrusion, calendaring, roll/wire coating, and coextrusion.

Chapter 4 by Archer describes the phenomenon of wall slip, where the fluid velocity does not go to zero at a solid wall. Again, although this phenomenon has been reported for Newtonian fluids, it is relatively weak and difficult to observe. However, for polymeric liquids, wall slip can be quite large; it significantly impacts on the flow behavior (and necessary modeling) of processing operations. This chapter describes the significant advances made recently on the measurement of wall slip, on the molecular theory describing it, and on the relationship at the interface between a polymer and a solid substrate. Although wall slip has been studied extensively in regard to its effects on extrusion instabilities, it plays a critical role in other processing operations as well.

Unlike Newtonian fluids, polymer melts slip over solid surfaces when the wall shear stress exceeds a critical value. For example, Fig. 1.1 illustrates the well-known Haagen–Poiseuille steady-state flow of a Newtonian fluid (Fig. 1.1a) and two typical corresponding profiles for the case of a molten polymer (Fig. 1.1b and c), indicating a small deviation from the no-slip boundary condition and plug flow. Although the classical no-slip boundary condition applied in Newtonian fluid mechanics (perhaps with the exception of rarefied gas dynamics where the continuum hypothesis does not apply), wall slip is typical in the case of molten polymers.

For the case of a passive polymer–wall interface where there is no interaction between the polymer and the solid surface, de Gennes (4) proposed an interfacial rheological law suggesting that a melt would slip at all shear rates. This theory was extended by Brochard-Wyart and de Gennes (5) to distinguish the case of a passive interface (no polymer adsorption) from that of an adsorbing one. It has been predicted that there exists a critical wall



FIGURE 1.1 Typical velocity profiles of polymer melt flow in capillaries: (a) no-slip; (b) partial slip; and (c) plug flow.

shear stress value at which a transition from a weak to a strong slip takes place. These predictions have been suggested to be true through experimentation (6,7), and Chapter 4 contains a further enhancement of the theory by Archer. The various mechanisms of wall slip in the case of flow of molten polymers are still under debate and many observations need better and complete explanation.

1.3 PART B: MELT FRACTURE IN EXTRUSION

Part B is devoted to describing extrusion—one of the simpler processing operations but is critically important because it is ubiquitous in polymer manufacturing and exhibits a full range of instabilities (Chapters 5–9). Here the instabilities revolve around the phenomena of *melt fracture*, wall slip, and polymer elasticity. The phenomena of melt fracture and wall slip have been studied for the past 50 years but have not yet been explained (3). Not only are these phenomena of academic interest, but they are also industrially relevant as they may limit the rate of production in processing operations. For example, in the continuous extrusion of a typical linear polyethylene at some specific output rate, the extrudate starts losing its glossy appearance; instead, a matte surface finish is evident and, at slightly higher output rates, small-amplitude periodic distortions appear on its surface (see Fig. 1.2). This phenomenon, known as *sharkskin* or *surface melt fracture*, is described in Chapter 5 by Migler.

At higher values of the output rate, the flow ceases to be constant; instead, the pressure oscillates between two limiting values and the extrudate



FIGURE 1.2 Typical extrudates showing: (a) smooth surface; (b) shark skin melt fracture; (c) stick-slip melt fracture; and (d) gross melt fracture.

Overview of Processing Instabilities

surface alternates between relatively smooth and distorted portions (Fig. 1.2c). These phenomena are known as *oscillating*, *stick-stick*, or *cyclic melt fracture*, and are discussed in Chapter 6 by Georgiou. The chapter focuses on the critical stresses for the instability as well as the effects of operating conditions and molecular structure. A one-dimensional phenomenological model successfully describes much of the data.

At even higher values of the output rate, a new instability known as *gross melt fracture (GMF)* occurs, which is described in Chapter 7 by Dealy and Kim. Whereas sharkskin and stick–slip instability are associated with the capillary tube, GMF originates in the upstream region where the polymer is accelerated from a wide-diameter barrel to a narrow-diameter capillary or orifice. The extensional stress on the polymer associated with such a flow can rupture it, leading to a chaotic appearance when it finally emerges from the capillary. This chapter presents a number of observations and contains a critical review of our understanding of GMF from the perspective of our limited understanding of what causes the rupture of molten polymers.

To increase the rate of production by eliminating or postponing the melt fracture phenomena to higher shear rates, processing additives/aids must be used. These are mainly fluoropolymers and stearates, which are widely used in the processing of polyolefins such as high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE). They are added to the base polymer at low concentrations (approximately 0.1 %), and they effectively act as die lubricants, modifying the properties of the polymer–wall interface (increasing slip of the molten polymers). Chapter 8 by Kharchenko, Hatzikiriakos, and Migler discusses processing additives with particular emphasis on fluoropolymer additives. These fluoropolymer additives have been known for a long time, but until recently, one could only speculate as to precisely how they function. Recently, through visualization methods, the precise nature of the coating and how it is created through the flow have become clear. Although these fluoropolymer additives are effective for sharkskin and stick–slip instability, they remain ineffective for the case of GMF.

It has been recently discovered that compositions containing boron nitride can be successfully used as processing aids to not only eliminate surface melt fracture, but also to postpone gross melt fracture and thereby permit the use of significantly higher shear rates. These processing aids can be used for a variety of important extrusion processes, namely, tubing extrusion, film blowing, blow molding, and wire coating. The mechanisms by which boron nitride affects the processability of molten polymers and other important experimental observations related to the effects of boron nitride-based processing aids on the rheological behavior and processability of polymers can be found in Chapter 9 by Hatzikiriakos.

1.4 PART C: APPLICATIONS

1.4.1 Draw Resonance in Film Casting

In film casting as well as in extrusion coating of polymeric sheet, a polymeric melt curtain is extruded through a narrow die slot, across an air gap or a liquid bath, and then onto a pair of (or just a single) take-up or chill rolls (see Fig. 1.3). Efforts to increase production speed and/or reduce film thickness by going to higher draw ratio (take-up speed/extrudate speed) are hampered by *edge neck-in* and *bead formation*, but mainly by process instabilities (draw resonance and edge weave) (7), which give rise to spontaneous thickness and width oscillations (Fig. 1.4). Due to the high melt viscosity, the liquid curtain is usually pulled downstream by the drum, resulting in a long effective casting span. As a result, the curtain necks-in at the edges giving rise to a nonuniform gauge profile with a characteristic "dog bone" shape (Fig. 1.4). On the other hand, draw resonance is accompanied by spontaneous thickness and width oscillations—effects that are undesirable in film production.

Chapter 10 by Co summarizes experimental observations of such instabilities that might occur in film casting and extrusion coating of polymeric materials. In addition, modeling and stability analysis of draw resonance with the aim of predicting such instabilities are also thoroughly discussed. As will be seen in this chapter, computational fluid mechanics modeling can help predict such instabilities and extend the parameter range of stable and defect-free operation (so-called "process operability window").



FIGURE 1.3 Schematic of a typical film casting process.



FIGURE 1.4 Instabilities associated with the film casting process of polymers.

1.4.2 Fiber Spinning Instabilities

A simple schematic of the fiber spinning process is depicted in Fig. 1.5. The polymer melt is pumped by an extruder and flows through a plate containing many small holes—the spinneret. Fig. 1.5 shows the flow of the fiber through one such hole. The extruded filament is air-cooled by exposure to ambient air, and it is stretched by a rotating take-up roll at a point lower to its solidification point.

As in all other polymer processing operations discussed before, the rate of production is limited by the onset of instabilities, and these are discussed in Chapter 11 by Jung and Hyun. Three types of instability might occur in fiber spinning (8). The first instability is called *spinnability*, which is defined as the ability of the polymer melt to stretch without breaking (8). *Necking* might occur due to capillary waves or a *brittle* type of fracture due to crystallization induced by stretching. The second type of instability is referred to as *draw resonance*, which manifests itself as periodic fluctuation of the cross-sectional area in the take-up area. This latter instability is similar to draw resonance occurring in the film casting process of polymers (see Fig. 1.4). Finally, *melt fracture* phenomenon, as with other types of instabilities that may limit the



FIGURE 1.5 Schematic of a typical fiber spinning process.

rate of production such as fiber spinning, involves extrusion through dies at high shear rates.

Experimental observations in fiber spinning application for various resins are discussed in conjunction with modeling techniques of the process with a focus on draw resonance. Attempts to predict such instabilities with the aim of predicting operability windows for increasing the rate of production are also discussed. The rheological properties of the melts that play a role in stabilizing/destabilizing the process are also relevant in such discussions.

1.4.3 Film Blowing Instabilities

A simple schematic of the film blowing process is depicted in Fig. 1.6. An extruder melts the resin and forces it to flow through an annular die. The melt extruded in the form of a tube is stretched in the machine direction by means of nip roles above the die, as shown in Fig. 1.6. Air flows inside the film bubble to cool down the hot melt. Thus, a frost line is established. The ratio of the film velocity to the average velocity of the melt in the die is referred to as the *draw down ratio* (DDR).

The film blowing instabilities are discussed in great detail in Chapter 11 by Jung and Hyun. As in all polymer processes discussed so far, several

Overview of Processing Instabilities



FIGURE 1.6 Schematic of a typical film blowing process.

instabilities might result as the extrusion rate (production rate) and DDR are increased. First, as the extrusion rate is increased (shear rate in the die), melt fracture might result depending on the molecular characteristics of the resin. These are manifested as loss of gloss of the film, small-amplitude periodic distortions, or more severe form of gross distortions. These instabilities influence seriously the optical and mechanical properties of the final product. Melt fracture is discussed in detail in Chapters 5–7 (present volume). Ways of postponing these instabilities to higher shear rates by means of using processing aids are discussed in Chapters 8 and 9 (present volume).

Draw resonance also occurs in this process as the DDR ratio increases (9). In the present process, draw resonance appears as periodic fluctuations of the bubble diameter known also as bubble instability shapes (10). Another type of draw resonance that might occur in film blowing is in the form of film gauge (film thickness) nonuniformity. This typically occurs at high production rates when the cooling rate requirements are increased (11). Molecular orientation during stretching of the film and the extensional properties of the resin in the melt state are important factors influencing the quality of the final products (11).

1.4.4 Coextrusion and Interfacial Instabilities

Coextrusion instabilities are discussed in depth in Chapter 12 by Dooley. Coextrusion refers to the process when two or more polymer liquid layers are extruded from a die to produce either a multilayer film or a fiber. There are three main problems associated with coextrusion. First, depending on the materials to be processed, *melt fracture* phenomenon might appear. This has already been discussed as these phenomena occur in most polymer processes that produce extrudates at high production rates.

More importantly are the instabilities caused by differences in the viscous and elastic properties of the components (see Fig. 1.7). If there is a significant viscosity difference between two liquids (i.e., two-layer flow), then the fluid having the lower viscosity will tend to encapsulate the fluid having the higher viscosity (9). For this to occur, the length-to-gap ratios should be relatively high, which gives enough time for rearrangement. Finally, even in the absence of a viscosity mismatch, the interface can become wavy. These instabilities are collectively known in coextrusion as *convective interfacial instabilities*, or simply *interfacial instabilities*. These instabilities are demonstrated in Chapter 12 to be caused by viscoelastic mismatches between the fluids coextruded, together with the geometry used for the process (11–14). For example, the point of layer merging or the point on the interface at the exit might cause interfacial waviness. The phenomena are complicated and not completely well understood as there are multiple factors involved.

1.4.5 Injection Molding and Tiger Stripes Instability

In injection molding, the polymer melt is softened first in an extruder and pumped forward through a runner to fill in a mold that is in the shape of the product article. The challenge is to produce a product that is free of voids, has a smooth and glossy surface, exhibits no warpage, and has sufficient mechanical strength and stiffness for its end use. The latter is significantly influenced by residual stresses due to the viscoelastic nature of flow, as well as due to



FIGURE 1.7 Instabilities in coextrusion: (a) gradual encapsulation of a viscous fluid (2) by a less viscous fluid (1) as both flow in a circular tube; and (b) interfacial instability in the form of a wavy interface.



FIGURE 1.8 Instabilities in injection molding: (a) formation of a weld line; and (b) the phenomenon of jetting.

shrinkage during cooling of the mold. As in most polymer processing operations, several problems (instabilities) might appear.

First, if the cavity to be filled has an insert, then the melt flow splits and flows around the obstacle. Consequently, these moving fronts meet again to result a *weld line* or *knit line*. In other cases, multiple runners are used to fill in the mold and, therefore, multiple *weld lines* result (see Fig. 1.8a). Lack of sufficient reentanglement of molecules across this line would lead to poor mechanical strength of the final product.

Jetting is another problem that might occur in injection molding. When the size (gap or diameter) is much smaller than the mold gap, the melt does not properly wet the entrance to the mold in order to fill it gradually. Instead, it "snakes" its way into the gap. This is shown in Fig. 1.8b.

Flow instabilities during injection molding (mold filling) also result in surface defects on polymer parts. For example, in filled polypropylene systems, the regular dull part of finished parts is broken by periodic shiny bands perpendicular to the flow direction (15). The appearance of these striped surface defects is known as *tiger stripes*. At the leading edge of the flow during mold filling, the polymer undergoes what is known as "fountain flow." Great recent progress in this area is summarized in Chapter 13 by Bogaerds, Peters, and Baaijens, in which they demonstrate that there is a viscoelastic flow instability at this air–polymer–wall juncture that leads to the tiger stripe phenomenon.

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2

Elements of Rheology

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2.1 RHEOLOGICAL BEHAVIOR OF MOLTEN POLYMERS

Flow instabilities that occur in melt processing arise from a combination of polymer viscoelasticity and the large stresses that occur in large, rapid deformations. This is in contrast to flows of Newtonian fluids, where inertia and surface tension are usually the driving forces for flow instabilities. Both the elasticity and the high stresses that occur in the flow of molten polymers arise from their high molecular weight (i.e., from the enormous length of their molecules). The high stresses are associated with the high viscosity of molten commercial thermoplastics and elastomers. Typical values range from 10^3 to 10^6 Pa s, whereas the viscosity of water is about 10^{-3} Pa sec. An easily observed manifestation of melt elasticity is the large swell in cross section that occurs when a melt exits a die.

The way melts behave in very small or very slow deformations is described quite adequately by the theory of *linear viscoelasticity* (LVE), and one material function, the linear relaxation modulus G(t), is sufficient to describe the response of a viscoelastic material to any type of deformation history, as long as the deformation is very small or very slow. This information is useful in polymer characterization and determination of the relaxation spectrum. However, there is no general theoretical framework that describes

viscoelastic behavior in the large, rapid deformations that arise in polymer processing (i.e., there exists no general theory of *nonlinear viscoelasticity*). Nonlinear phenomena that arise in large, rapid flows include the strong dependence of viscosity on shear rate and the very large tensile stresses that arise when long-chain branched polymers are subjected to extensional deformations.

Flow instabilities nearly always occur in response to large, rapid deformations. This means that a flow simulation able to predict when a flow will become unstable must be based on a reliable model of nonlinear viscoelastic behavior. The lack of such a model at the present time greatly limits our ability to model instabilities. Also lacking are generally accepted, quantitative criteria for the occurrence of instabilities, for example, in terms of a dimensionless group.

Although there remain major difficulties in the modeling of melt flow instabilities, many experimental observations have been reported, and empirical correlations with various rheological properties have been proposed. In order to understand these, some knowledge of the rheological behavior of molten polymers is needed. It is the purpose of the present chapter to provide a brief overview to prepare the uninitiated reader to understand the later chapters of this book and the current stability literature.

2.2 VISCOELASTICITY – BASIC CONCEPTS

Molten polymers are elastic liquids, and it is their elasticity that is the root cause of most flow instabilities. Thus, these are usually *hydroelastic* rather than *hydrodynamic* instabilities. Melts of high polymers can store elastic energy and, as a result, they retract when a stress that has been applied to them is suddenly released. However, they do not recover all the strains undergone as a result of this stress, as they are liquids, and their deformation always entails some viscous dissipation. These materials are thus said to have a *fading memory*.

The elasticity of polymers is intimately associated with the tendency of their molecules to become oriented when subjected to large, rapid deformations. This molecular orientation gives rise to anisotropy in the bulk polymer, and manifestations of this anisotropy include flow birefringence and normal stress differences.

A variable of central importance in the rheological behavior of polymers is time. Any system whose response to a change in its boundary conditions involves both energy storage and energy dissipation must have at least one material property that has units of time. Examples of such systems are resistance–capacitance electrical circuits and the suspension systems of automobiles, which include springs (to store energy) and shock absorbers (to

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dissipate energy). A system often used to demonstrate this fact consists of a linear (Hookean) spring and a linear dashpot, connected in series as shown in Fig. 2.1. This system is called a *Maxwell element*, and we will see that its behavior has proven very useful in describing the viscoelastic behavior of polymers.

The force in the spring is proportional to the distance through which it is stretched ($F_s = K_e\Delta X_s$), and the force in the dashpot is proportional to the velocity with which its ends are separated [$F_d = K_v(dX_d/dt)$]. In the absence of inertia, the forces in the two elements are equal, and the displacement of one end relative to the other is $\Delta X = \Delta X_s + \Delta X_d$. From this, it is easy to demonstrate that if the assembly is subjected to sudden stretching in the amount of ΔX_0 , the force will rise instantaneously to $K_e\Delta X_0$ and then decay exponentially, as shown by Eq. (2.1):

$$F(t) = K_{\rm e}\Delta X_0 \exp\left[-t(K_{\rm e}/K_{\rm v})\right]$$
(2.1)

We see that the ratio (K_v/K_e) is a parameter of the system and has units of time. It is thus the *relaxation time* of the mechanical assembly.

2.3 LINEAR VISCOELASTICITY

Linear viscoelasticity is a type of rheological behavior exhibited by polymeric materials in the limit of very small or very slow deformations. Although not directly applicable to the deformations that give rise to gross melt fracture,



FIGURE 2.1 The simplest mechanical analog of a viscoelastic liquid; the single Maxwell element consisting of a linear spring in series with a linear dashpot.

LVE behavior is important for two reasons. First, information about linear viscoelastic behavior is very useful in the characterization of a polymer (i.e., in determining its molecular structure). Second, it provides information about the linear relaxation spectrum, which is an essential element of a model of nonlinear viscoelastic behavior. A comprehensive discussion of the linear viscoelastic properties of polymers can be found in the book by Ferry (1).

The most basic experiment in viscoelasticity is the measurement of the transient stress following a sudden "step" deformation. In the case of molten polymers, this is nearly always a shearing deformation, and the measured stress is reported in terms of the relaxation modulus G(t). This function of time is defined as the stress divided by the amount of shear strain γ imposed on the sample at t = 0:

$$G(t) \equiv \sigma(t) / \gamma \tag{2.2}$$

A function such as this, which is a characteristic of a particular material, is called a *material function*.

The basic axiom of linear viscoelasticity, the Boltzmann superposition principle, tells us that this function is independent of γ and contains all the information needed to predict how a viscoelastic material will respond to any type of deformation, as long as this deformation is very small or very slow. This principle can be stated in terms of an integral equation as follows for simple shear deformation:

$$\sigma(t) = \int_{t'=-\infty}^{t} G(t - t') d\gamma(t')$$
(2.3)

where σ is the shear stress at time *t*, and $d\gamma(t')$ is the shear strain that occurs during the time interval dt'. This can easily be generalized for any kinematics by use of the *extra stress tensor* and the *infinitesimal strain tensor*, whose components are represented by σ_{ij} and γ_{ij} , respectively:

$$\sigma_{ij}(t) = \int_{t'=-\infty}^{t} G(t - t') \mathrm{d}\gamma_{ij}(t')$$
(2.4)

and, in terms of the rate-of-strain tensor, this is:

$$\sigma_{ij}(t) = \int_{t'=-\infty}^{t} G(t - t') \dot{\gamma}_{ij}(t') dt'$$
(2.5)

The extra stress is that portion of the total stress that is related to deformation. We recall that for in an incompressible fluid, an isotropic stress (i.e., one that has no shear components and whose normal components are the same in all directions) does not generate any deformation. For example, the

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Earth's atmosphere at sea level, when completely still, is under a compressive stress of one atmosphere. Thus, there is an isotropic component of the total stress tensor that is not related to deformation in an incompressible fluid. And the infinitesimal strain tensor is a very simple measure of deformation that is valid only for very small deformations. The rate-of-deformation tensor is related to the velocity components by Eq. (2.6):

$$\dot{\gamma}_{ij} \equiv \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) \tag{2.6}$$

Eqs. (2.4) and (2.5) are alternative, concise statements of the Boltzmann superposition principle. A very simple model of linear viscoelastic behavior can be obtained by inserting into Eq. (2.5) the relaxation modulus that is analogous to a single Maxwell element (i.e., a single exponential):

$$G(t) = G \mathrm{e}^{-t/\tau_{\mathrm{r}}} \tag{2.7}$$

where G is the instantaneous modulus and τ_r is a *relaxation time*. This is called the *Maxwell model* for the relaxation modulus. Inserting this into Eq. (2.4), we obtain the simplest model for linear viscoelasticity:

$$\sigma_{ij}(t) = G \int_{t'=-\infty}^{t} \mathrm{e}^{-(t-t')/\tau_{\mathrm{r}}} \mathrm{d}\gamma_{ij}(t')$$
(2.8)

The stress relaxation in an actual polymer can only very rarely be approximated by a single exponential, and G(t) is usually represented either by a discrete or a continuous *relaxation spectrum*. In the case of a discrete spectrum, the relaxation modulus is represented as a sum of weighted exponentials, as shown by Eq. (2.9):

$$G(t) = \sum_{i=1}^{N} G_i e^{-t/\tau_i}$$
(2.9)

Comparing Eqs. (2.1) and (2.9), we see that this is analogous to the response of a mechanical assembly consisting of a series of Maxwell elements connected in parallel, so that the displacements of all the elements are the same, and the total force is the sum of the forces in all the elements. Thus, Eq. (2.9) is called the *generalized Maxwell model* for the relaxation modulus.

The continuous spectrum $F(\tau)$ is defined in terms of a continuous series of exponential decays, as shown by Eq. (2.10):

$$G(t) = \int_0^\infty F(\tau) \mathrm{e}^{-t/\tau} \mathrm{d}\tau$$
(2.10)

It turns out to be more convenient to work with the time-weighted spectrum function $H(\tau)$, which is defined as $\tau F(\tau)$, as shown by Eq. (2.11):

$$G(t) = \int_{-\infty}^{\infty} H(\tau) \mathrm{e}^{-t/\tau} \mathrm{d} \, \ln \tau$$
(2.11)

It has been found that frequency (oscillatory shear) domain experiments are much easier to perform than time domain (step strain) experiments, and these provide an alternative means of establishing the linear behavior of a polymer. In oscillatory shear, the input strain is sinusoidal in time:

$$\gamma(t) = \gamma_{o} \, \sin(\omega t) \tag{2.12}$$

As long as the response is linear (i.e., if γ_0 is sufficiently small), the shear stress is also sinusoidal, but with a phase shift δ , as shown by Eq. (2.13):

$$\sigma(t) = \sigma_{\rm o} \, \sin(\omega t + \delta) \tag{2.13}$$

The response could be characterized by the amplitude ratio (σ_0/γ_0) and the phase shift δ as functions of frequency, but it is more informative to represent the response in terms of frequency-dependent in-phase (*G*') and out-of-phase (*G*) components, as shown by Eq. (2.14):

$$\sigma(t) = \sigma_{\rm o}(G' \sin \omega t + G'' \cos \omega t) \tag{2.14}$$

The two material functions of this relationship are $G'(\omega)$, the *storage modulus*, and $G''(\omega)$, the *loss modulus*. The most common way of reporting linear viscoelastic behavior is to show plots of these two functions. Ferry (1) provides formulas for converting one LVE material function into another.

An alternative approach to viscoelastic characterization is to impose a prescribed stress on the sample and monitor the strain. If a stress σ_0 is imposed instantaneously at time zero, and the resulting shear strain is divided by this stress, the resulting ratio is the creep compliance J(t):

 $J(t) \equiv \gamma(t) / \sigma_{\rm o} \tag{2.15}$

If the imposed stress is sufficiently small, the result will be governed by the Boltzmann superposition principle, and the creep compliance can, in principle, be calculated if the relaxation modulus G(t) is known.

One can also impose a sinusoidal stress and monitor the time-dependent deformation as an alternative technique to determine the storage and loss moduli.

2.4 VISCOSITY

Viscosity is defined as the steady-state shear stress divided by the shear rate in a steady simple shear experiment. For a Newtonian fluid, the viscosity is independent of shear rate, and this is also the prediction of the theory of linear

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viscoelasticity. This means that a molten polymer will exhibit a shear rateindependent viscosity at a sufficiently small shear rate, although such a lowshear rate may be difficult to access experimentally, especially in the case of polymers with broad molecular weight distribution or long-chain branching. Outside this range, the viscosity is a strong function of shear rate, and the dependency of viscosity on shear rate $\eta(\dot{\gamma})$ is an example of a nonlinear material function.

2.4.1 Dependence of Viscosity on Shear Rate, Temperature, and Pressure

At sufficiently high-shear rates, the viscosity often approaches a power-law relationship with the shear rate. Figure. 2.2 is a plot of viscosity vs. shear rate for a molten polymer, and it shows both a low-shear rate Newtonian region and a high-shear rate power-law region. These data were reported by Meissner (2) some years ago and represent the ultimate in rheometrical technique. The variation of η with $\dot{\gamma}$ implies the existence of at least one material property with units of time. For example, the reciprocal of the shear rate at which the extrapolation of the power-law line reaches the value of η_0 is a characteristic time that is related to the departure of the viscosity from its zero-shear value. Let us call such a nonlinearity parameter τ_n .

The viscosity falls sharply as the temperature increases, as shown in Fig. 2.2. Two models are widely used to describe this dependency: the Arrhenius



FIGURE 2.2 Viscosity vs. shear rate at several temperatures for a low-density polyethylene. (From Ref. 2.)

equation and the Williams-Landel-Ferry (WLF) equation. These are given in standard rheology references (1,3,4).

2.4.2 Dependence on Molecular Structure

The limiting low-shear-rate viscosity η_0 , the zero-shear viscosity, increases linearly with weight-average molecular weight when this is below an entanglement molecular weight M_C , whereas above this value, the viscosity increases in proportion to $(M_w)^{\alpha}$, where α is usually around 3.5. This is one of several dramatic rheological manifestations of the phenomenon called entanglement coupling, which has a very strong effect on the flow of high-molecular-weight polymers. Although it was once thought that these effects were caused by actual physical entanglements between molecules, it is now recognized that they are not the result of localized restraints at specific points along the chain. Instead, it is understood that they result from the severe impediment to lateral motion that is imposed on a long molecule by all the neighboring molecules, although the term entanglement continues to be used to describe this effect. At higher shear rates, the effect of molecular weight on viscosity decreases, so it is the zero-shear value η_0 that is most sensitive to molecular weight.

2.5 NORMAL STRESS DIFFERENCES

The shear rate-dependent viscosity is one manifestation of nonlinear viscoelasticity, and there are two additional steady-state material functions associated with steady simple shear when the shear rate is not close to zero. These are the *first and second normal stress differences* $N_1(\dot{\gamma})$ and $N_2(\dot{\gamma})$. The three material functions of steady simple shear $\eta(\dot{\gamma})$, $N_1(\dot{\gamma})$, and $N_2(\dot{\gamma})$ are known collectively as the viscometric functions.

These are defined using the standard frame of reference for simple shear shown in Fig. 2.3. The shear stress σ is σ_{21} (equal to σ_{12}), and the three normal stresses are: σ_{11} , in the direction of flow (x_1) ; σ_{22} , in the direction of the gradient (x_2) ; and σ_{33} , in the *neutral* (x_3) direction. As this is, by definition, a



FIGURE 2.3 Standard coordinate definitions for simple shear.

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two-dimensional flow, there is no velocity and no velocity gradient in the x_3 direction.

In an incompressible material, normal stresses are themselves of no rheological significance because as long as they are equal in all directions, they cause no deformation. However, differences between normal stress components are significant, because they do cause deformation. For steady simple shear, the two rheologically significant differences are defined by Eq. (2.16a,b):

$$N_1(\dot{\gamma}) = \sigma_{11} - \sigma_{22} \tag{2.16a}$$

$$N_2(\dot{\gamma}) \equiv \sigma_{22} - \sigma_{33} \tag{2.16b}$$

In the limit of zero-shear rate (i.e., for linear viscoelastic behavior), these two material functions approach zero, and as the shear rate increases, they are at first proportional to the square of the shear rate. Thus, although the shear stress becomes linear with shear rate as the shear rate approaches zero, N_1 and N_2 are second order in $\dot{\gamma}$ in this limit. This dependency inspired the definition of the two alternative material functions defined by Eq. (2.17a,b):

$$\Psi_1(\dot{\gamma}) \equiv N_1/\dot{\gamma}^2 \tag{2.17a}$$

$$\Psi_2(\dot{\gamma}) \equiv N_2/\dot{\gamma}^2 \tag{2.17b}$$

In other chapters of this book, it will be shown that these functions are related to several types of flow instability that occur in flows of viscoelastic melts.

2.6 TRANSIENT SHEAR FLOWS USED TO STUDY NONLINEAR VISCOELASTICITY

The response of a molten polymer to any transient shear flow that involves a large or rapid deformation is a manifestation of nonlinear viscoelasticity. Some examples of flows used to characterize nonlinear melt behavior are described in this section.

For large-step stress relaxation, the relaxation modulus is a function of the imposed strain as well as time: $G(t,\gamma)$. Except at very short times, the nonlinear relaxation modulus is often found to exhibit *time-strain separability*, which means that it can be represented as the product of the linear relaxation modulus and a function of strain $h(\gamma)$ called the *damping function*, as shown by Eq. (2.18):

$$G(t,\gamma) = G(t)h(\gamma) \tag{2.18}$$

The damping function is thus a material function that is wholly related to nonlinearity in a step strain test. As the strain approaches zero, $h(\gamma)$ obviously approaches one, and as the strain increases, it decreases.

The damping effect can be understood in terms of the *tube model* of the dynamics of polymeric molecules. In this model, the constraints imposed on a given polymer chain by the surrounding molecules and that give rise to entanglement effects are modeled as a tube. In response to a sudden deformation, the tube is deformed, and the relaxation of the molecule of interest is constrained by its containment in its tube. When the imposed deformation is very small, two mechanisms of relaxation occur: equilibration and *reptation*. Equilibration involves the redistribution of stress along the chain within the tube. Further relaxation can only occur as a result of the molecule escaping the constraints of the tube, and this requires it to slither along or *reptate* out the tube. This is a much delayed mechanism, and this is the cause of the plateau in the relaxation modulus for polymers with narrow molecular weight distributions. If the molecular weight is not narrow, the shorter molecules making up the tube will be able to relax fast enough to cause a blurring of the tube. This phenomenon is called *constraint release* and speeds up the relaxation of a long molecule in its tube.

The relaxation processes described above apply to linear viscoelastic behavior. If the deformation is not small, there is an additional relaxation mechanism—*retraction within the tube*. This is a fast relaxation, and once it is completed, the remainder of the relaxation process occurs as in the case of a linear response. It thus results in a relaxation modulus curve that has an early, rapid decrease due to retraction, followed by a curve that has the same shape as that for linear behavior. Thus, except for the very short-term relaxation, the relaxation modulus can be described as the linear modulus multiplied by a factor that accounts for the relaxation by retraction. This factor is the damping function.

In *start-up of steady simple shear*, the measured stress is divided by the imposed constant shear rate to obtain the *shear stress growth coefficient*, which is defined as follows:

$$\eta^+(t) \equiv \sigma(t)/\dot{\gamma} \tag{2.19}$$

And the similarly defined *shear stress decay coefficient* $\eta^{-}(t)$ describes stress relaxation following the cessation of steady simple shear.

2.7 EXTENSIONAL FLOWS

Most experimental studies of melt behavior involve shearing flows, but we know that no matter how many material functions we determine in shear, outside the regime of linear viscoelasticity, they cannot be used to predict the behavior of a melt in any other type of flow (i.e., for any other flow kinematics). A type of flow that is of particular interest in commercial processing and the instabilities that arise therein is extensional flow. In this

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type of flow, material points are stretched very rapidly along streamlines. An important example is the flow of a melt from a large tube into a much smaller one. In order to satisfy mass continuity, the velocity of a fluid element must increase markedly as it flows into the smaller tube, and this implies rapid stretching along streamlines. This is shown schematically in Fig. 2.4.

Although entrance flow subjects some fluid elements to large rates of elongation, the rate of elongation is not uniform in space, so this flow field is not useful in determining a well-defined material function that describes the response of a material to extensional flow. It turns out to be quite difficult to subject a melt to a uniform stretching deformation, and this is why reports of such measurements are much rarer than those of shear flow studies.

The experiment usually carried out to study the response of a melt to uniaxial extension is start-up of steady simple extension at a constant *Hencky strain rate* \dot{k} . The Hencky strain rate is defined as follows, in terms of the length L of a sample:

$$\dot{\varepsilon} = \mathrm{d} \, \ln \, L/\mathrm{d}t \tag{2.20}$$

Note that the length of a sample subjected to a constant Hencky strain rate increases exponentially with time. This strain rate is a measure of the speed with which material particles are separated from each other. The nonlinear material function most often reported is the *tensile stress growth coefficient*, which is defined as the ratio of the tensile stress to the strain rate, as shown by Eq. (2.21):

$$\eta_{\rm E}^+(t,\dot{\varepsilon}) \equiv \sigma_{\rm E}(t,\dot{\varepsilon})/\dot{\varepsilon} \tag{2.21}$$



FIGURE 2.4 Sketch of entrance flow showing stretching along streamlines: (a) without corner vortex; (b) with corner vortex.

2.8 DIMENSIONLESS GROUPS GOVERNING THE BEHAVIOR OF VISCOELASTIC FLUIDS

When making a general statement about the flow behavior of polymers, it is useful to represent the results of theoretical treatments and experiments in terms of dimensionless variables. Two dimensionless groups are often used to describe the rate or duration of an experiment. One of these, the Weissenberg number (Wi), is a measure of the degree of nonlinearity or anisotropy exhibited by the fluid in a particular deformation, and the second, the Deborah number (De), is a measure of the degree to which a material exhibits elastic behavior. We will see in later chapters that these groups are useful for describing flow instabilities.

The *Deborah number* (*De*) is a measure of the degree to which the fluid will exhibit elasticity in a given type of deformation. More specifically, it reflects the degree to which stored elastic energy either increases or decreases during a flow. In steady simple shear, at steady state, when all stresses are constant with time, the amount of stored elastic energy is constant with time, so the Deborah number is zero. Thus, it is only in transient flows that the Deborah number has a nonzero value. Here "transient" means that the state of stress in a fluid element changes with time. This can arise as a result of a time-varying boundary condition, in a rheometer, or of the flow from one channel into a smaller one so that acceleration is involved. This dimensionless group is the ratio of a time arising from the fluid's viscoelasticity (i.e., its relaxation time) to a time that is a measure of the duration of the deformation.

For example, consider the response of a fluid to the start-up of steady simple shear in which a shear rate of $\dot{\gamma}$ is applied to a fluid initially in its rest state. In the initial stages of the deformation, the shear stress will increase with time and will eventually reach a steady value. At times *t* after the shearing is begun, the stress will continue to change with time until *t* is long compared to the relaxation time of the fluid. Thus, the Deborah number for this deformation is τ_r/t ; when this ratio is large (short times), the amount of stored elastic energy is increasing, but when it is small (long times), it becomes steady, and *De* approaches zero. In this example, the Deborah number varies with time.

The Deborah number is only zero in deformations with constant stretch history (steady from the point of view of a material element). It is difficult to write a concise definition of a time constant that governs the rate at which stored elastic energy changes in a given deformation without reference to a specific rheological model, and we therefore give a definition of the Deborah number in general terms:

$$De = \frac{\tau_{\rm r}}{\text{characteristic time of transient deformation}}$$
(2.22)

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Turning to the Weissenberg number, its use can be demonstrated by reference to steady simple shear flow. We have seen that any fluid that has a shear rate-dependent viscosity or is viscoelastic must have at least one material constant that has units of time and is characteristic of rheological nonlinearity, and we have called this time τ_n . Furthermore, the type of behavior exhibited by a particular material depends on how this time constant compares with the reciprocal of the rate of the deformation. For example, let us say that a non-Newtonian fluid has a nonlinearity time constant τ_n of 1 sec. This implies that if the shear rate $\dot{\gamma}$ in steady simple shear is much smaller than the reciprocal of this time, its viscosity will be independent of shear rate. This suggests the definition of the Weissenberg number (Wi) as follows:

$$Wi \equiv \dot{\gamma}\tau_{\rm n} \tag{2.23}$$

(The symbols *We* and *Ws* are also used for the Weissenberg number.) Thus, this dimensionless group is a measure of the degree to which the behavior of a fluid deviates from Newtonian behavior. For single-phase, low-molecular-weight fluids, the time constant of the material is extremely short, so that the Weissenberg number is always very small for the flows that occur under normal circumstances. But for molten, high-molecular-weight polymers, τ_n can be quite large. For polymeric liquids, the Weissenberg number also indicates the degree of anisotropy generated by the deformation. And in the case of steady simple shear, the normal stress differences are manifestations of anisotropy and thus of nonlinear viscoelasticity. Therefore, the Weissenberg number also governs the degree to which the normal stress differences will differ from zero.

To summarize, when the Weissenberg number is very small in a simple shear flow, the viscosity will be independent of shear rate, and the normal stress differences will be negligible. These phenomena reflect the fact that in the limit of vanishing shear rate, the shear stress is first order in the shear rate, whereas the normal stress differences increase with the square of the shear rate. The Weissenberg number is easily defined for any flow with constant stretch history. For example, for steady uniaxial extension, we need only replace the shear rate by the Hencky strain rate $\dot{\epsilon}$.

In general, the degree to which behavior is nonlinear depends on the Weissenberg number. At very small deformation rates, Wi is much less than one, and the stress is governed by the Boltzmann superposition principle. At higher deformation rates, Wi increases and nonlinearity appears, as reflected, for example, in the dependence of viscosity on shear rate and the appearance of normal stress differences. The two characteristic times defined above (τ_n and τ_r) are closely related, and in recognition of this, the subscripts will be dropped in the rest of this discussion.

There are several pitfalls in the use of the two dimensionless groups defined above to characterize the response of a material to a given type of deformation. First, there are hardly any materials whose viscoelastic behavior can be described using a single relaxation time. More typically, a spectrum of times is required, and this causes difficulty in the choice of a time for use in defining the Deborah number. The "longest relaxation time" is often identified as the appropriate one for defining these groups, but for highly polydispersed or branched polymers, it may be impossible to identify a "longest time."

Another problem in the use of dimensionless groups to characterize deformations is that for a melt consisting of a single polymer, in several flows of practical interest, *Wi* and *De* are directly related to each other. This causes confusion, as authors of books and research papers tend to use the two groups interchangeably in all circumstances. Some examples will help to illustrate the correct use of the Weissenberg and Deborah numbers.

A flow that has been of great interest to both experimental and theoretical polymer scientists is the entrance flow from a circular reservoir into a much smaller tube or capillary. A Weissenberg number can readily be defined for this flow as the product of the characteristic time of the fluid and the shear rate at the wall of the capillary. However, entrance flow is clearly not a flow with constant stretch history, and the Deborah number is thus nonzero as well. Furthermore, as demonstrated by Rothstein and McKinley (5), in such flows, the two groups are directly related. This can lead to confusion when experimental data and flow simulation results are compared (6). Note that for fully developed capillary flow, De = 0.

On the other hand, a flow in which the two numbers can be varied independently is oscillatory shear. As used for the determination of the linear viscoelastic behavior of polymers, this deformation is carried out at very small strain amplitudes, so that the Weissenberg number will be much less than one. As the frequency is increased from zero, the Deborah number, defined here as $\omega \tau$, is at first very small, and the response is purely viscous. Because *Wi* is also very small, the melt behaves like a Newtonian fluid. If now the frequency is increased, the Deborah number increases and the importance of elasticity grows, and at very high *De*, the behavior becomes almost purely elastic.

If, however, the strain amplitude γ_0 is increased, then the strain rate amplitude $\dot{\gamma}_0 \equiv \omega \gamma_0$, and the Weissenberg number, which is equal to $\dot{\gamma}_0 \tau$, also increases. By changing the frequency or the amplitude, *Wi* and *De* can be varied independently. A convenient way of representing the parameter space of large-amplitude oscillatory shear is a Pipkin diagram, which is a graph of Weissenberg number vs. Deborah number (4,7). In such a diagram, the behavior in the lower left-hand corner (*Wi* \ll 1; *De* \ll 1) is that of a Newtonian fluid. Near the vertical axis (*De* \ll 1), the behavior is nonlinear but inelastic and is governed by the viscometric functions. Near the hori-

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zontal axis ($Wi \ll 1$), linear viscoelastic behavior is expected, and far to the right ($De \gg 1$), the behavior becomes indistinguishable from that of an elastic solid.

2.9 EXPERIMENTAL METHODS IN RHEOLOGY – RHEOMETRY

The objective of rheometry is to make measurements whose data can be interpreted in terms of well-defined material functions, without making any assumptions about the rheological behavior of the material. Examples of material functions are the viscosity as a function of shear rate and the relaxation modulus as a function of time. These functions are physical properties of a material, and the detailed method by which they are determined need not be reported in order for them to be properly interpreted. In contrast to this type of measurement are empirical industry tests that yield numbers that can be used to compare materials but are not directly related to any one physical property. Such test data are widely used as specifications for commercial products and for quality control. An important example that involves the flow of molten plastics is the *melt flow rate*, often called the *melt index* (8).

In an experiment designed to determine a material function, it is necessary to generate a deformation in which the streamlines are known a priori (i.e., that are independent of the rheological properties of the material). Such a deformation is called a *controllable* flow, and the number of such deformations is very limited. In fact, the only practically realizable controllable flows are simple shear, simple (uniaxial) extension, biaxial extension, and planar extension. And the last two of these are sufficiently difficult to generate that they are rarely used. Additional limitations on our ability to determine rheological material functions in the laboratory are imposed by various instabilities that occur even in these very simple flows.

There are two ways of generating a shear deformation in a rheometer: drag flow and pressure flow. In drag flow, one surface in contact with the sample moves relative to another to generate shearing. In pressure flow, pressure is used to force the fluid to flow through a straight channel, which may be a capillary or a slit. Drag flow can be used to determine a variety of material functions, including the storage and loss moduli as functions of frequency, the creep compliance as a function of time, the viscosity and normal stress differences as functions of shear rate, and various nonlinear transient material functions. Pressure-driven rheometers are useful primarily for the measurement of viscosity at high-shear rates.

Extensional rheometers are most often designed to generate uniaxial (tensile) extension in which either the tensile stress or the strain rate is maintained constant.

Below are presented brief overviews of the way melt rheometers are used. More detailed information about experimental rheology can be found in various rheology books (3,4).

2.9.1 Rotational Rheometers

Rotational rheometers can be classified according to the type of fixture used and by the variable that is controlled (i.e., the independent variable). Two types of fixture are commonly used with molten polymers: cone-plate and plate-plate. The flow between a cone and a plate, one of which is rotating with respect to the other at an angular velocity Ω , closely approximates uniform simple shear, as the shear rate at a radius *r* is the local rotational speed Ωr of the rotating fixture at *r*, divided by the gap between the fixtures at this value of *r*, which we call *h*. In the cone and plate geometry, this distance is linear with *r*, with the result that $r\Omega/h$ (i.e., the local shear rate) is uniform. This feature of cone-plate flow makes it useful for studies of nonlinear viscoelasticity. Coneplate fixtures are used to determine the viscosity and first normal stress difference as functions of shear rate at low-shear rates, as well as the response of the shear and normal stresses to various transient shearing deformations.

The equations for calculating the strain rate and stresses of interest are as follows for the case of a small cone angle Θ_0 :

$$\dot{\gamma} = \Omega/\Theta_{\rm o} \tag{2.24}$$

$$\sigma = 3M/2\pi R^3 \tag{2.25a}$$

$$N_1 = 2F/\pi R^2 \tag{2.26}$$

where Ω is the angular velocity of the rotating fixture; σ is the shear stress; M is the torque measured on either the rotating or the stationary shaft; F is the total normal thrust on the fixtures; and R is the radius of the fixtures.

Uniform simple shear is very well approximated by the flow between a cone and a plate; if the cone angle is small, and the shear rate is not very high. Starting at moderate shear rates, however, various types of instability render the flow unsuitable for rheological measurements. Thus, cone-plate fixtures are useful for determining moderate departures from linear viscoelasticity. The major concerns in using this technique are calibrating the sensors, avoiding degradation of the sample, and recognizing when an instability has occurred.

Although cone-plate fixtures can be used to determine the material functions of linear viscoelasticity, it is more convenient to use plate-plate fixtures for this application because the preparation and loading of samples, as well as the setting of the gap between the two fixtures, are much simplified. Although the local shear strain between the parallel plates varies linearly with

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radius, as long as the viscoelastic behavior is linear, the local stress is proportional to the strain, and the variation poses no problem in the interpretation of the data. The equations for calculating the storage and loss moduli are as follows:

$$G' = \frac{2M_{\rm o}h\cos\delta}{\pi R^4\phi_{\rm o}} \tag{2.25b}$$

$$G'' = \frac{2M_{\rm o}h\sin\delta}{\pi R^4\phi_{\rm o}} \tag{2.25c}$$

where M_o is the amplitude of the torque signal; ϕ_o is the amplitude of the angular displacement of the oscillating shaft; and δ is the phase angle between the angular displacement and the measured torque.

The primary concerns in making reliable measurements are calibrating the sensors, avoiding thermo-oxidative degradation of the sample, and ensuring that the amplitude selected for the deformation or torque does not take the sample out of its linear range of response.

Rotational rheometers can also be classified according to which variable is controlled. Thus, there are controlled strain (actually controlled angular motion) and controlled stress (actually controlled torque) instruments. Both can be used to determine linear viscoelastic properties, although controlled stress instruments give better results at low frequencies, whereas controlled strain instruments are preferred at high frequencies. Thus, the two types of rheometer provide information that is, to some degree, complementary.

2.9.2 Sliding Plate Rheometers

Sliding plate melt rheometers were developed to make measurements of nonlinear viscoelastic behavior under conditions under which cone-plate flow is unstable (i.e., in large, rapid deformations) (9). The sample is placed between two rectangular plates, one of which translates relative to the other, generating, in principle, an ideal rectilinear simple shear deformation. There are significant edge effects at large strains, and to minimize the effect of these on the measurement, the stress should not be inferred from the total force on one of the plates but measured directly in the center of the sample by a shear stress response to large, transient deformations (9,10). In addition, they have been used to determine the effect of pressure on the viscosity and nonlinear behavior of melts (11,12). Their advantage over capillary instruments for high-pressure measurements is that the pressure and shear rate in the sample are uniform.

Phenomena that limit their use are slip, cavitation, and rupture, which interrupt experiments at sufficiently high strains and strain rates. At the same time, however, sliding plate rheometers have been found to be useful tools for the study of melt slip (13).

2.9.3 Capillary and Slit Rheometers

Pressure-driven rheometers, particularly capillary instruments, are the work horses of plastics rheology, as they are relatively simple and easy to use. In most capillary rheometers, the flow is generated by a piston moving in a round reservoir to drive the melt through a small capillary, which often has a diameter of about 1 mm. After a short entrance length, the flow becomes fully developed (i.e., the velocity profile and shear stress become independent of distance from the entrance). For a Newtonian fluid, the fully developed velocity distribution is parabolic, and the wall shear rate can be calculated by knowing only the volumetric flow rate Q and the radius of the capillary R. However, in the case of a non-Newtonian fluid, the velocity distribution depends on the viscosity function, which is initially unknown. It has proven useful in polymer characterization, however, to use the formula for Newtonian fluids to define an *apparent wall shear rate* $\dot{\gamma}_A$. The wall shear rate $(\partial v/\partial v)$ ∂r)_{r = R} is actually negative because the velocity is zero at the wall and positive at the center, but it is the magnitude of this quantity that is universally used in discussing capillary and slip flow. Thus, the apparent wall shear rate is the positive quantity defined as follows:

$$\dot{\gamma}_{\rm A} \equiv \frac{4Q}{\pi R^3} \tag{2.27a}$$

Techniques for determining the true wall shear rate $\dot{\gamma}_w$ can be found in various rheology books (3,4).

If the pressure gradient in the region of fully developed flow is known, the wall shear stress can be readily calculated. It is possible to make such a measurement in a slit rheometer by mounting two or more pressure transducers in the wall of the slit. But in a capillary, this is not practical, and it is only the driving pressure $P_{\rm d}$ that is known, either from the force required to drive the piston, or from a pressure transducer mounted in the reservoir. The pressure at the exit of the capillary (1 atm) is practically negligible for highviscosity melts, so the driving pressure is essentially equal to the overall pressure drop. However, in addition to the pressure drop resulting from flow in the region of fully developed flow, $P_{\rm d}$ also includes a substantial *entrance* pressure drop. Two methods have been developed to determine the portion of the pressure drop due to entrance flow so that the magnitude of the true wall shear stress $\sigma_{\rm w}$ can be determined. These are the Bagley plot method and the orifice method (4). Once the wall shear stress has been calculated, it can be divided by the wall shear rate to yield the viscosity. Because the shear rate is not uniform along or across a capillary or slit, these flows are not useful for the