# POLYMER AND COMPOSITE RHEOLOGY

### Second Edition, Revised and Expanded



### RAKESH K. GUPTA

## POLYMER AND COMPOSITE RHEOLOGY

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## POLYMER AND Composite Rheology

### Second Edition, Revised and Expanded

### RAKESH K. GUPTA

West Virginia University Morgantown, West Virginia



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Current printing (last digit): 10 9 8 7 6 5 4 3 2 To my wife, Gunjan

### BHARYA MOOLAM GRIHASTHASYA BHARYA MOOLAM SUKHASYA CHA BHARYA DHARMA FALA VAPTYAJ BHARYA SANTAN BRIDHYAYE

A wife is the quintessence of a home. She is the source of happiness and of everything that is good in life and the future of children.

Skanda Puran (Hindu scripture)



### Preface

Several outstanding books on rheology have appeared since *Polymer Rheology* was published in 1977. This book remains unique in the simple and straightforward manner in which it introduces the concepts of rheology and the observed flow behavior of polymers to the student as well as to the practicing engineer. The first edition emphasized general principles and their practical implications rather than theoretical constructs. This practical, industrial orientation has been maintained in the second edition, and the book has been updated to include developments of the past quarter century. The book has also been expanded to give essentially equal coverage to single-phase and multiphase systems. A knowledge of chemorheology is often essential for understanding the processing of (thermosetting) polymer-matrix composites; discussion of reactive polymers has been included for this reason. Few, if any, of the currently available rheology books treat as wide a range of topics as are covered in the second edition.

The specific aims of the second edition are: (i) to present the general behavior of polymer melts, polymer solutions, suspensions, emulsions, foams, granular powders, and polymer composites during flow, together with physical explanations of the observations; (ii) to provide information on the effects of the different factors that influence flow behavior, (iii) to describe and recommend methods of measuring, calculating, or theoretically estimating flow properties of polymers and polymeric composites; and (iv) to direct readers to the appropriate technical literature for further study and consideration of current research issues. All this is done using the minimum amount of mathematics—not an easy undertaking given the universally accepted complexity of the subject.

In pursuit of these goals and after an introductory chapter, standard techniques for making rheological measurements are presented in Chapter 2. Thereafter, each chapter begins with an explanation of the practical and theoretical importance of the topic being examined. This is followed by a presentation of typical data and how these data might be represented in graphical form and also by means of empirical equations. The body of each chapter considers the use of any specialized instruments, data reduction when employing the most relevant rheological techniques, and the influence of the various material, geometrical, and processing variables on the property of interest, and it provides physical explanations for the observations. There is discussion, with minimum mathematics, of available theoretical models and their ability to both predict observed behavior and quantitatively represent the data. Each chapter also elaborates on work in progress and research needs for the future. Finally, there is a listing of complete citations to the technical literature. The book concludes with a short chapter on the enigma of melt fracture, an annoving instability of rheological origin, that limits production rates during polymer processing operations.

This is a practical book aimed at both practicing engineers and graduate students. It is a storehouse of information but with an emphasis on science rather than on technology. No specific background has been assumed of the reader, and it is hoped that the book will be as useful to a chemist or an engineer who wants to learn about rheology owing to the requirements of a new assignment as it will be to a student engaged in advanced research. The choice of topics and the depth of coverage have been dictated as much by my own research interests as by my perception of the importance of the subject at hand. Time will tell whether these choices have been judicious ones or not.

I would like to thank Professor Hota V. S. GangaRao, my colleague at West Virginia University, for having introduced me to the fascinating field of polymer composites and also for involving me in research on a variety of topics related to the processing and use of composite materials. Professor Raj Chhabra of the Indian Institute of Technology at Kanpur read the entire manuscript, as did Dr. Deepak Doraiswamy of the DuPont Company (also an Adjunct Professor in the Department of Chemical Engineering at West Virginia University); both of them corrected errors, made suggestions for improvement, and directed me to appropriate work in the literature. Deepak, in addition, coauthored Chapter 10 on solid-in-liquid suspensions. I am grateful to them both for their constant help and encouragement. The book also benefited from the several suggestions of Professor Jan Mewis and Dr. Kurt Wissbrun, who helped with and read Chapter 8 on the rheology of liquid crystalline polymers. Parts of the book were written during 1998/99 while I was on sabbatical leave as a Visiting Research Scientist at DuPont's Washington Works in Parkersburg, West Virginia; I thank Dr. Robert Cook for making my stay there possible, and I thank all my DuPont associates for their hospitality. In the course of the three years that it took me to complete

### Preface

the writing of this book, I badgered innumerable friends and professional colleagues for reprints, preprints, and thesis copies. Their courtesy in acceding to my frantic requests made my work and the work of the ever-helpful interlibrary loan personnel in our Evansdale Library so much easier. I also wish to thank Ms. Linda Rogers, who typed all the equations for me and helped me incorporate all the revisions in the manuscript.

I did not know the late Larry Nielsen personally even though I worked briefly for the Monsanto Company. I feel honored to have been asked to revise and expand *Polymer Rheology*. I have made a sincere effort to maintain the character of the first edition, and I have attempted to retain as much as possible of the material that appeared in that edition. I hope that the readers will recognize this book to be as much Nielsen's as mine.

Rakesh K. Gupta



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### Introduction to Polymer Rheology

### I. RHEOLOGY

Rheology can be defined as the science of the flow and deformation of matter. For low-molecular-weight fluids, the study of rheology involves the measurement of viscosity. For such fluids, the viscosity depends primarily upon the temperature and hydrostatic pressure. However, the rheology of high-molecular-weight liquids, whether neat or filled, is much more complex because polymeric fluids show nonideal behavior. In addition to having complex shear viscosity behavior, polymeric liquids show elastic properties, such as unequal normal stresses in shear and a prominent tensile viscosity in extension. All these rheological properties depend upon the rate of deformation, the molecular weight and structure of the polymer, and the concentration of various additives and fillers, as well as upon the temperature. In addition, even at a constant rate of deformation, stresses are found to depend on time.

The subject of rheology is very important for both polymers and polymeric composites. This is true for two reasons. Firstly, flow is involved in the processing and fabrication of such materials in order to make useful objects. Thus, fluid rheology is relevant to polymer processing and determines stress levels in operations such as extrusion, calendering, fiber spinning, and film blowing. Similarly, rheology influences residual stresses, cycle times, and void content in composite processing operations such as bag molding, compression molding, and injection molding. Clearly, a quantitative description of polymer processing operations; these models can be employed for process optimization and for predicting the onset of flow instabilities. In the use of polymers, though, it is generally the

mechanical properties that are important. Mechanical behavior, however, is influenced by rheological behavior, and this is the second important reason for studying polymer rheology. For example, molecular orientation has dramatic effects on the mechanical properties of molded objects, fibers, and films. For shortfiber composites, fiber orientation plays the role of molecular orientation in unfilled systems. The kind and degree of molecular or fiber orientation are largely determined by the rheological behavior of the polymer and the nature of the flow in the fabrication process.

Rheology is involved in many other aspects of polymer science. For example, many polymers are made from emulsions of monomers in stirred reaction vessels. The resulting latices flow through pipes and may end up as a paint that is applied to a surface by some process in which the rheological properties of the latex must be controlled carefully. Plastisols, which are a suspension of a polymer in a liquid, are fabricated into useful objects by processes such as rotational molding. Powdered polymers or granules must flow from bins and must perform properly in a fabrication process such as rotational molding and in powder coatings. The rheology of polymer powders is important also in the first sections of extruders and in injection molding machines before the polymer softens to a liquid. Note that at a less fundamental level, rheological measurements, both transient and steady state, can be employed for product characterization and quality control purposes. Such measurements are often also used for examining and understanding the interaction of the different constituents of a multicomponent or multiphase mixture and their influence on the flow and other properties of such materials.

### **II. MATERIAL FUNCTIONS IN VISCOMETRIC FLOWS**

The flow field that is generated in most standard instruments used to measure rheological properties is a particular kind of shear flow called *viscometric flow*. All the motion in a viscometric flow is along one coordinate direction, say,  $x_1$  in Figure 1.1, the velocity varies along a second coordinate direction, say,  $x_2$ , and the third direction is neutral. This is illustrated schematically in Figure 1.1, where a liquid is confined between two flat plates of area *A* separated by a distance *D*. When the upper plate is moved in the  $x_1$  direction relative to the lower plate, the liquid is sheared with the amount of shear strain  $\gamma$  being defined as

$$\gamma = \tan \theta = \frac{\text{Amount of shear displacement } S}{\text{Distance between shearing surfaces } D}$$
(1.1)

The rate of shear strain will then be

$$\dot{\gamma} = \frac{\text{Relative velocity}}{\text{Distance } D}$$
(1.2)



FIGURE 1.1 Schematic diagram for the measurement of shear viscosity.

which equals  $dv_1/dx_2$  for small values of *D*. The rate of shear strain is commonly referred to as the *velocity gradient* or more simply as just the *shear rate*. It is evident that the shear rate will be independent of time if the relative velocity is constant.

A constant force *F* is typically required to move the top plate in Figure 1.1 at a constant velocity relative to the lower plate. This is a shear force, and on dividing this quantity by the area *A* of the shear face one gets the shear stress  $\tau$ . For a Newtonian liquid, the shear stress is directly proportional to the shear rate, with the constant of proportionality being called the *dynamic viscosity*  $\eta$ . If the fluid is not Newtonian, a plot of the shear stress against the shear rate is not a straight line but a curve, such as the lower solid line shown in Figure 1.2. The liquid may be Newtonian at very low shear rates to give a limiting viscosity  $\eta_0$  from the initial slope of the  $\tau$ -versus- $\dot{\gamma}$  curve. When the  $\tau$ -versus- $\dot{\gamma}$  curve is nonlinear, the viscosity (the adjective *dynamic* is commonly omitted) is no longer a constant, and it becomes a function of the shear rate. It is now defined as the slope of the scant line from the origin to the shear stress at the given value of the shear rate; that is,

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{1.3}$$

Another kind of non-Newtonian behavior is Bingham plastic behavior. This is illustrated by the upper solid line in Figure 1.2. Here the  $\tau$ -versus- $\dot{\gamma}$  curve is linear, but it does not pass through the origin; the value of the intercept on the shear stress axis is called the *yield stress*. Note that the slope of the shear stress curve at the chosen value of the shear rate is known as the consistency  $\eta_{\rm s}$ .

The SI unit for viscosity is Pa-s, where Pa is the abbreviation for Pascal, which is Newtons per square meter. In the past, it was common to measure vis-



FIGURE 1.2 Measurement of viscosity from shear stress versus rate of shear curves.

cosity in the cgs unit of poise, which is the same as dyne second per  $cm^2$  or g/cm-s. The viscosity of water is about 1 m Pa-s, or 1 centipoise, since 1 Pa-s equals 10 poise. Typical polymer melts have viscosities generally of the order of  $10^2-10^3$  Pa-s.

In general, it is found that the shear viscosity of polymers decreases as the shear rate increases. This behavior is known as *shear thinning*, and an important consequence of this result is that the well-known Hagen–Poiseuille equation does not hold for the flow of polymers through a circular tube. In particular, one finds that on doubling the flow rate through the tube, the necessary pressure drop is less than doubled.

For a fluid at rest, it is easy to show [1] that all the surface stresses that are present within the fluid are normal stresses and that at any location, these are not only equal in magnitude but also independent of the orientation of the surface. This single normal stress is compressive in character, and it is commonly called the *pressure* and denoted by the symbol p. From the definition of a fluid, the absence of motion of course implies the absence of shear stresses. Conversely, for a fluid in motion, it must necessarily be true that either shear stresses are

#### Introduction to Polymer Rheology

present or the normal stresses are unequal. For the situation depicted in Figure 1.1, we have seen that flow arises due to the application of a shear stress. If the liquid being sheared is polymeric, one finds that the normal stresses along the three coordinate directions (see Fig. 1.3) become unequal; for Newtonian fluids, however, normal stresses remain equal to each other. Due to the fact that most liquids can be considered incompressible for all practical purposes, the application of equal normal stresses (or pressure) along the three coordinate directions does not lead to deformation or a change in volume; it is only unequal normal stresses that cause motion and deformation. As a consequence, one cannot determine the absolute value of the pressure from a measurement of fluid deformation, which is a measure of the change in distances between material points or material planes; one can only deduce normal stress differences.

It is common practice to define the first and second normal stress differences as follows:

First normal stress difference 
$$N_1 = \sigma_{11} - \sigma_{22}$$
 (1.4)

Second normal stress difference  $N_2 = \sigma_{22} - \sigma_{33}$  (1.5)



FIGURE 1.3 Schematic diagram showing the notation for normal stresses in a shear field.

While the first normal stress difference tends to force the shear plates in Figure 1.3 apart, the second normal stress difference tends to create bulges in the polymer at the edge of the plates either parallel or perpendicular to the direction of the applied force *F*. Indeed, it is the presence of the first normal stress difference in shear that is responsible for the swelling of an isothermal jet of polymer on emerging into air from a die or capillary. It is found that the normal stress differences are even functions of the shear rate, and it is customary to define the first and second normal stress coefficients,  $\psi_1$  and  $\psi_2$ , as ratios of the respective stress differences with the square of the shear rate. At low shear rates, both these coefficients tend to attain constant values.

In cases where the relative velocity of the shearing plates in Figure 1.3 is not constant but varies in a sinusoidal manner so that the shear strain and the rate of shear strain are both cyclic and have a small amplitude, the shear stress is also sinusoidal. In these dynamic mechanical experiments, the stress is out of phase with the rate of strain unless the fluid is Newtonian. In this situation, a complex viscosity  $\eta^*$  can be measured. In general, the complex viscosity contains an elastic component in addition to a term similar to the ordinary steady state viscosity. The complex viscosity is defined by:

$$\eta^* = \eta' - i\eta'' \tag{1.6}$$

The dynamic viscosity  $\eta'$  is related to the steady state viscosity and is the part of the complex viscosity that measures the rate of energy dissipation. Similarly, the imaginary viscosity  $\eta''$  measures the elasticity, or stored energy. These two viscosities are computed from the real and imaginary parts of the shear modulus using the following relations:

$$\eta'' = \frac{G'}{\omega} \tag{1.7}$$

$$\eta' = \frac{G''}{\omega} \tag{1.8}$$

where  $\omega$  is the frequency of the oscillations in radians per second. The storage modulus, or dynamic rigidity, G', is defined as the component of the stress in phase with the strain divided by the strain amplitude; the loss modulus, G'', is defined as the component of the stress out of phase with the strain divided by the strain amplitude. The ratio of the loss modulus to the storage modulus, G''/G', is known as tan  $\delta$  and is an alternate measure of energy dissipation in viscoelastic materials. Note that for a perfectly elastic material, G'' is zero, while for Newtonian liquids (that are perfectly viscous) G' is zero. In general, both G' and G'' are functions of frequency.

#### Introduction to Polymer Rheology

The variation, with the rate of deformation, temperature and other variables, of the different material functions defined in this section is discussed in detail in later chapters for a large variety of polymeric fluids.

### **III. EXTENSIONAL FLOW**

Besides viscometric flow, the other major category of flow of practical interest that can be generated in the laboratory is extensional flow. In mathematical terms, extensional flow may be represented in a rectangular Cartesian coordinate system  $x_1$  by the following set of equations for the three components of the velocity vector:

$$v_1 = \dot{\varepsilon}_1 x_1 \tag{1.9}$$

$$v_2 = \dot{\varepsilon}_2 x_2 \tag{1.10}$$

$$\mathbf{v}_3 = \dot{\mathbf{\varepsilon}}_3 x_3 \tag{1.11}$$

which also defines the stretch rates  $\varepsilon_1$ . In uniaxial extension at constant stretch rate (see Fig. 1.4),  $\dot{\varepsilon}_1 = \dot{\varepsilon}$  and  $\dot{\varepsilon}_2 = \dot{\varepsilon}_3 = -\dot{\varepsilon}/2$ . The distance between material planes that are perpendicular to the flow direction increases with time in extensional flow. A material plane is a surface that always contains the same material points or particles. As material planes move apart, polymer molecules tend to



**FIGURE 1.4** Schematic diagram for the measurement of extensional, or tensile, viscosity.

uncoil, and ultimately one can even have stretching of chemical bonds which results in chain scission. Stresses in the flow direction can, therefore, reach fairly large values. By integrating Eq. (1.9), one finds that, at constant stretch rate, the length of a strip of material increases exponentially:

$$\ln \frac{L}{L_0} = \dot{\varepsilon}t \tag{1.12}$$

in which  $L_0$  is the initial length and L is the length at some later time t.

The only stress that one can measure experimentally in uniaxial extension is the tensile stress  $\sigma_E$ , which, with reference to Figure 1.4, is

$$\sigma_E = \frac{F}{A} \tag{1.13}$$

For constant-stretch-rate homogeneous deformation that begins from rest, one defines a tensile stress growth coefficient

$$\eta_{\vec{k}}(t,\dot{\epsilon}) = \frac{\sigma_{\vec{k}}}{\dot{\epsilon}}$$
(1.14)

which has the dimensions of viscosity. The limiting value of  $\eta_{\ell}$  as time approaches infinity is termed the *tensile* or *extensional* or *elongational viscosity*,  $\eta_{\ell}$ . In general,  $\eta_{\ell}$  is a function of the stretch rate, although in the limit of vanishingly low stretch rates [2]

$$\lim_{\varepsilon \to 0} \frac{\eta_E}{\eta_0} = 3 \tag{1.15}$$

where  $\eta_0$  is the zero shear rate viscosity.

For Newtonian liquids, the extensional viscosity is three times the shear viscosity; but for polymeric liquids, the tensile viscosity may exceed the zero shear viscosity by a couple of orders of magnitude. Extensional viscosity is of great practical importance when polymers flow through channels or tubes in which the cross-sectional area is decreasing. Examples include flow through porous media, the spinning of fibers, and the filling of molds in injection molding.

### IV. THE STRESS TENSOR

If one isolates a rectangular parallelepiped of material having infinitesimal dimensions such as shown in Figure 1.5, one finds that two kinds of forces act on the material element. These are body forces and surface forces. *Body forces* result from the action of external fields such as gravity; *surface forces* express the influence of material outside the parallelepiped but adjacent to a given surface.



FIGURE 1.5 Diagram showing the notation used for components of the stress tensor.

Dividing the surface force by the area on which it acts yields the *stress vector*. Since the parallelepiped has six surfaces, there are six stress vectors.

Because each of the stress vectors can be resolved into three components parallel to the three coordinate axes, one has a total of 18 components. These are labeled  $T_{ii}$  or  $\sigma_{ii}$ , where the two subscripts help to identify a specific component. The first subscript, *i*, identifies the surface on which the stress acts; the surface, in turn, is identified by the direction of the outward-drawn normal. The second subscript, *j*, identifies the direction in which the stress component acts. Nine of the 18 components can be represented using a 3 × 3 matrix, called the *stress tensor*:

$$\begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix}$$

 $T_{11}$ , for example, acts on a surface whose outward drawn normal points in the positive  $x_1$  direction; the stress component itself also acts in the same direction. The other nine components of the stress are the same as these nine, but they act on opposite faces.

By means of a torque balance on a cubic element, it can be shown (see Ref. 1, for example) that  $T_{ij}$  equals  $T_{ji}$ . Thus, the stress tensor is symmetrical and only six of the nine components are independent quantities. Further, by examining the equilibrium of the tetrahedron shown in Figure 1.6, it can be demonstrated [1] that if the normal to the inclined surface is  $\hat{n}$ , the components of the surface stress f acting on that surface,  $f_i$ , are (in matrix notation):

$$\begin{bmatrix} f_1 \\ f_2 \\ f_3 \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{12} & T_{22} & T_{23} \\ T_{13} & T_{23} & T_{33} \end{bmatrix} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix}$$
(1.16)

where  $n_i$  are the components of  $\hat{n}$ . Knowing the components of the stress tensor, therefore, allows one to obtain the stress vector acting on any plane described by the unit normal  $\hat{n}$ .

It is one of the major goals of rheologists to try to relate the stress tensor to the strain or the rate of strain. Recall that in Section II, it was shown that  $T_{12}$ is a unique function of the shear rate, while in Section III the net tensile stress was related to the stretch rate; the net tensile stress is nothing but  $T_{11} - T_{22}$ . These relationships between specific stress components and specific rate-of-strain components are known as *material functions*. The general equation relating the



FIGURE 1.6 Equilibrium of a tetrahedron.

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stress tensor to the three-dimensional strain or rate of strain tensor (the word *tensor* is simply another term for *matrix*) is known as a *constitutive equation*.

Due to fluid incompressibility, though, one cannot relate  $T_{ij}$  to deformation. This is because no amount of pushing, i.e., the application of hydrostatic pressure, can cause a change in volume. It is only when pressures are unequal that a strain, which can be understood as a change in the distance between neighboring particles, takes place. It is for this reason that it is usual to separate the stress tensor into two parts:

$$\begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{12} & T_{22} & T_{23} \\ T_{13} & T_{23} & T_{33} \end{bmatrix} = \begin{bmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{bmatrix} + \begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{12} & \tau_{22} & \tau_{23} \\ \tau_{13} & \tau_{23} & \tau_{33} \end{bmatrix}$$
(1.17)

where *p* is the hydrostatic pressure whose presence causes no strain for incompressible materials and the  $\tau_{ij}$  are components of the extra stress tensor whose presence causes strain to take place. Strain, therefore, is related to the extra stress  $\tau$  rather than to the total stress T.

### V. THE RATE OF STRAIN TENSOR

The shear rate defined in Eq. (1.2) can be generalized to three dimensions by defining the rate-of-strain tensor  $\dot{\gamma}$  as

$$\dot{\gamma}_{ii} = \left(\frac{\partial v_i}{\partial x_i} + \frac{\partial v_i}{\partial x_i}\right) \tag{1.18}$$

and it is evident that for the flow situation in Figure 1.1, the shear rate is simply the 1.2 component of  $\dot{\gamma}$ . Furthermore, for a Newtonian liquid,

$$T_{\eta} = \tau_{\eta} = \eta \dot{\gamma}_{\eta} \tag{1.19}$$

provided  $i \neq j$ , and

$$T_u = -p + \eta \dot{\gamma}_u \tag{1.20}$$

in which both *i* and *j* can be 1, 2, or 3.

Everything that we have defined so far has been with reference to a rectangular Cartesian coordinate system. In numerous practical situations, though, it is more appropriate to work in curvilinear coordinates. This parallel treatment may be found in more advanced books on rheology (see Ref. 3, for example).

Finally, we remark that the development of constitutive equations or, equivalently, the formulation of expressions similar to Eqs. (1.19) and (1.20) but applicable to polymeric fluids is merely a means to an end. In modeling polymer processing operations, one needs to solve boundary value problems involving the flow of polymeric fluids. The solution procedure involves inserting the constitutive equation into the momentum and energy balance equations and solving the resulting coupled differential equations subject to appropriate boundary conditions. In this regard, the no-slip boundary condition, which states that at a fluid– solid boundary the velocity of the fluid is the same as that of the solid, has been an article of faith for an extremely long time. Recent evidence [4], though, suggests that this boundary condition may not be universally valid. Indeed, slip at the solid–liquid boundary has been hypothesized to be the cause of polymer processing instabilities such as melt fracture; these instabilities tend to limit the rate of production during processes such as extrusion, fiber spinning, and film blowing [5].

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## 2

### Instruments for Shear Rheology

### I. INTRODUCTION

A great variety of instruments have been used to measure the rheological properties of polymer solutions and polymer melts when these are subjected to shear deformation |1-3|. These instruments range in sophistication from simple melt indexers employed for quality control purposes to very complicated, researchgrade rheometers capable of measuring, as a function of temperature and rate of deformation, both steady-state and transient values of the various material functions defined in the previous chapter. As might be expected, these instruments span a wide price range [2,3], depending on the capability of the viscometer, and they are manufactured and marketed by a large number of manufacturers all over the world. In this chapter, we consider general-purpose, shear instruments that one might expect to find in any laboratory devoted to rheological work; these include capillary viscometers as well as rotational viscometers. We describe the essential features of each type of instrument, present the basic equations used for data analysis, and discuss equipment limitations and sources of error. A consideration of actual data, their possible molecular interpretation, and representation using constitutive equations is deferred to later chapters. Extensional viscometers are examined in Chapter 7, while specialized instruments are introduced throughout this book as appropriate.

Since shear viscosity has been measured for a very long time, we might expect shear rheometry to be a mature field. However, new instruments are continually being introduced. Some, such as the sliding-plate rheometer, involve new concepts; others improve on existing instruments as far as the ease of measurement and data analysis or the range of measurement is concerned. Yet others allow us to make measurements on complex materials or materials that might be reactive or temperature sensitive.

### **II. CAPILLARY VISCOMETERS**

The standard instrument for the measurement of the steady shear viscosity of polymeric fluids at shear rates witnessed in typical polymer processing operations is the capillary viscometer, shown schematically in Figure 2.1. In this device, the polymer sample is forced by a piston or by pressure from a reservoir through a capillary; to obtain consistent results, the ratio of the reservoir diameter to the capillary diameter has to exceed 12. In commercial instruments, the capillary is usually vertical, and it can be detached from the viscometer so that we may make measurements with other capillaries having different entrance angles or different



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FIGURE 2.1 Schematic diagrams of three types of viscometers.

#### Instruments for Shear Rheology

values of length L or diameter D. In actual use, we fill the cold reservoir, called the *barrel*, with a polymer solution or with pellets of the neat or filled polymer and then heat the system to the test temperature. Once thermal equilibrium is attained, extrusion is begun, and the volumetric flow rate Q of polymer coming from the capillary at a given pressure drop is recorded. If the plunger speed can be specified, as is commonly the case, it is not necessary actually to collect the extrudate. A load cell is employed to measure the force of extrusion.

The capillary rheometer has a number of advantages. First, the instrument is relatively easy to fill. This is an important consideration, since most polymer melts are too viscous to pour readily even at high temperatures. The test temperature and rate of shear are varied readily. The shear rates and flow geometry are similar to the conditions actually found in extrusion and in injection molding. In addition to the viscosity, some indication of polymer elasticity is found from the die swell of the extrudate. Finally, factors affecting the surface texture of the extrudate and the phenomenon of melt fracture can be studied. However, there are disadvantages too. The principal disadvantage is that the rate of shear is not constant but varies with radial position within the capillary. Another disadvantage is the necessity of making a number of corrections in order to get accurate viscosity values, especially with low-viscosity materials or when short capillaries are used.

In general, the velocity profile in the capillary is fully developed only in the region away from the inlet and the exit. At the capillary ends, there must be velocity rearrangements, and the pressure gradient varies with axial position and is larger than that in the fully developed region. If, however, the ratio of the capillary length to the capillary diameter is large, say, 50 or more, we may neglect end effects and assume that the pressure gradient in the entire capillary is  $(p_1 - p_2)/L$ , the difference between the inlet and exit pressures divided by the capillary length. By means of a force balance, then, the magnitude of the shear stress at the capillary wall,  $\tau_w$ , is:

$$\tau_{w} = (p_{1} - p_{2})\frac{R}{2L}$$
(2.1)

where *R* is the capillary radius. To determine the shear viscosity, we need to divide the wall shear stress by the shear rate at the wall,  $\dot{\gamma}_{\mu}$ . For any non-Newtonian fluid, the expression for the wall shear rate is given as [4]:

$$\dot{\gamma}_{w} = \frac{4Q}{\pi R^{3}} \left( \frac{3}{4} + \frac{1 \ d \ln Q}{4 \ d \ln \tau_{w}} \right)$$
(2.2)

To measure the viscosity as a function of shear rate, the flow rate is determined as a function of the pressure drop. This can be converted to flow rate as a function of the wall shear stress using Eq. (2.1), which then allows us to compute the derivative appearing in Eq. (2.2) at any given value of the wall shear stress. The ratio of this wall shear stress to the corresponding wall shear rate calculated from Eq. (2.2) gives the shear viscosity at one shear rate—the one corresponding to the chosen value of the shear stress at the wall. By repeating this process at other values of the wall shear stress, we can trace out the entire  $\eta$ -versus- $\dot{\gamma}$  curve or the flow curve.

If the non-Newtonian fluid obeys the power law, in which the shear stress depends upon the shear rate to the *n*th power, Eq. (2.2) takes the form:

$$\dot{\gamma}_{n} = \frac{4Q}{\pi R^{3}} \left( \frac{3n+1}{4n} \right)$$
(2.3)

where

$$n = \frac{d \log \tau}{d \log \dot{\gamma}}$$
(2.4)

In the special case of a Newtonian liquid, *n* equals unity and the wall shear rate is simply  $4Q/\pi R^3$ . It is, therefore, seen that the quantity in brackets in Eq. (2.2) corrects the rate of shear for non-Newtonian liquids [5]; this is known as the *Rabinowitsch correction* and  $4Q/\pi R^3$  is called the *apparent wall shear rate*. Clearly, for a Newtonian liquid, the shear viscosity is:

$$\eta = \frac{\pi R^{a} (p_{\perp} - p_{2})}{8LQ}$$
(2.5)

The use of Eq. (2.5), which is the well-known Hagen-Poiseuille equation, allows us to use Newtonian liquids to calibrate the viscometer and to check that the experimental procedure is satisfactory. Note that the shear rate is always a maximum at the wall but that the velocity is zero at the wall. The characteristics of capillary flow are shown in the bottom section of Fig. 2.2. The solid lines are for Newtonian liquids; the dashed lines are typical of polymeric non-Newtonian fluids. Under conditions in which Q is the same for both Newtonian and non-Newtonian fluids, the area under the velocity distribution curves should be the same rather than as shown in Fig. 2.2. where conditions have been adjusted to match the velocities at the center of the capillary.

A small-diameter capillary is preferred in order that one may make measurements using small-sized samples (working volumes of 25 ml are common). Even for neat polymer melts, the practical lower limit is about 0.025 cm; otherwise, blockage can occur due to the presence of impurities in the polymer. Furthermore, the use of capillaries having large L/D values is desirable for theoretical reasons. However, this is possible only for low-viscosity liquids for which the pressure drop would otherwise be small. When working with molten polymers, long capillaries cannot be used due to thermal degradation problems and because



FIGURE 2.2 Characteristics of the three viscometers shown in Fig. 2.1. Solid lines refer to Newtonian fluids; broken lines are typical of non-Newtonian polymer melts.

the pressure drops are excessive; the latter fact causes problems with data analysis, since the viscosity can depend on pressure at high pressures.

If short capillaries are used, the variation in the pressure gradient along the tube axis cannot be neglected, and the effective length of the capillary becomes greater than the true length. This is taken into account through the Bagley [6,7] correction. The shear stress at the wall of Eq. (2.1) becomes

$$\tau_{v} = \frac{R(p_1 - p_2)}{2(L + eR)} = \frac{p_1 - p_2}{2(L/R + e)} = \frac{(p_1 - p_2) - p_0}{2L/R}$$
(2.6)

The Bagley correction factor e should be independent of capillary length, but in general it does vary somewhat with L/R because of the elasticity of polymer melts. The Bagley correction is determined by measuring the pressure drop at constant rate of shear for several capillary lengths and extrapolating to zero pres-

sure drop, as shown in Figure 2.3. In Eq. (2.6),  $p_0$  is the pressure drop corresponding to a capillary of zero length for a given rate of shear.

The upper limit on the shear rate in capillary viscometers is about  $10^5-10^6$  sec<sup>-1</sup>. This comes about for a variety of reasons. As mentioned earlier, these instruments come in two basic designs, which differ in the method of melt extrusion. In the pressure-driven instrument, an inert gas is used to pump the liquid out of the reservoir, and we measure the volumetric flow rate corresponding to the applied pressure drop. For a capillary of given length and diameter, the maximum shear rate is set by the maximum pressure, but it can be increased further by increasing the capillary diameter. Increasing the diameter, though, causes a rather disproportionate increase in the volumetric flow rate, which can also lead to nonisothermal conditions due to viscous heating [8]. In a plunger-driven instrument, the extrusion velocity is fixed and the corresponding pressure drop is mea-



FIGURE 2.3 Bagley correction for capillary rheometers.

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sured. Now the maximum shear rate is decided by the maximum speed of the plunger, but it can be increased further by reducing the capillary diameter. However, we cannot exceed the upper limit of the force transducer; for instruments designed to work with filled polymers, this force limit may be as high as 100 kN. In addition, data cannot be trusted once instabilities such as melt fracture set in. The lower limit of operation of capillary viscometers is about 1-10 sec<sup>-1</sup>. This is determined by the occurrence of drips in a pressure-driven instrument, while for a plunger-type viscometer the lower limit is set by the amount of friction between the plunger and the barrel. As the plunger speed decreases, friction can become a significant part of the total pressure drop and make the viscosity measurements unreliable. More details about capillary viscometry are available in References 1-4 and 9. The development of a capillary viscometer capable of operating at ambient pressures substantially above atmospheric has been described by Galvin et al. [10]. Commercial instruments are also available. For example, Polymer Laboratories (now part of Rheometrics Scientific) markets instruments that can make measurements at pressures as high as 200 Mpa.

Almost all present-day commercial instruments are plunger driven and are quite versatile. Some, such as the Rosand RH7 series viscometer, can operate at temperatures upto 500 C, can have twin capillaries that allow two simultaneous experiments, and have the facility of a nitrogen purge for work with materials that are sensitive to moisture and oxygen. In addition, some viscometers have pressure transducers mounted near the capillary entrance. This allows us to obtain a more accurate estimate of the pressure drop, since we do not have to account for pressure losses in the barrel. Often these viscometers are used as extruders in laboratory experiments, and it is common to employ them for spinning fibers and for determining the melt strength of polymers.

Although it is a fairly routine matter to use a capillary viscometer to measure the rheological properties of polymer solutions and polymer melts, suspensions and emulsions have to be treated with care. For both suspensions and emulsions, data analysis can be complicated due to (1) structural changes that occur during the process of measurement, and (2) apparent slip at the viscometer wall due to depletion of the dispersed phase in the vicinity of a solid surface. These effects are considered in later chapters. A note of caution also needs to be sounded on the practical side. Highly loaded suspensions are known to be shear thickening, and the sudden increase in the shear stress can make the viscometer seize, resulting in physical harm to the instrument and the investigator.

In closing this section, we note that the theory of Poiseuille flow through slits is similar to that for circular tubes [4], and slit rheometers are also commercially available [2,3]. An advantage of slit rheometry is that shear rates greater than  $10^6 \text{ sec}^{-1}$  can be attained and isothermal conditions still maintained. As shown by Lodge in Collyer and Clegg [3], this feature can be used to measure

normal stress differences at shear rates higher than those accessible with rotational instruments. We discuss normal stress differences in detail in Chapter 5.

### III. COAXIAL CYLINDER VISCOMETERS

The coaxial cylinder, or concentric cylinder, or Couette viscometer, is frequently used for measuring the steady shear viscosity and dynamic mechanical properties of low-viscosity liquids, polymer solutions, solid-in-liquid suspensions, and emulsions. However, it is used only occasionally at high temperatures or for high-viscosity melts. In this instrument, as shown in Figure 2.1, the fluid sample is placed in the annular space between two concentric cylinders. In one version of the apparatus, in order to measure the liquid viscosity, either one of the two cylinders is rotated at a constant speed while the torque acting on the other (stationary) cylinder is measured. In another version of the viscometer, one cylinder is held stationary while the other one is rotated under the influence of a constant torque; the speed of rotation is measured by some kind of a tachometer device. When it is desired to measure dynamic properties, the constant speed of rotation is replaced by oscillation at a fixed frequency and small amplitude.

A major advantage of the coaxial cylinder viscometer is the nearly constant shear rate throughout the entire volume of fluid being measured if the space between cylinders is small; this criterion is satisfied by ensuring that the ratio of the diameter of the inner cylinder to the diameter of the outer cylinder exceeds 0.97. This is an important factor with non-Newtonian polymeric fluids, in which the viscosity may be strongly dependent upon the rate of shear. Coaxial cylinder instruments are simple to use and are calibrated easily, and the corrections can be small. Most of these instruments are able to go to very low deformation rates, which is an advantage when working with blood and biological fluids, where one does not want structure alteration during the process of measurement. A major disadvantage of these instruments is the difficulty in filling them with a very viscous polymer melt. A less important, but annoying, disadvantage is the creeping of the polymer up the shaft of the inner cylinder because of normal stresses developed in the polymer by the rotation of the cylinder.

For Newtonian liquids, the important equations for coaxial cylinder viscometers (neglecting end corrections) are [11]:

$$\tau(r) = \frac{M}{2\pi r^2 h}; \quad R_1 \le r \le R_2 \tag{2.7}$$

$$\dot{\gamma}(r) = \frac{2\omega R_1^2 R_2^2}{r^2 (R_2^2 - R_1^2)}$$
(2.8)

A torque *M* is produced by the rate of angular rotation  $\omega$  in radians per second. As shown in Figure 2.1, the radii of the inner and outer cylinders are  $R_1$  and  $R_2$ ,

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respectively. The immersed length of cylinder is h, and r is any arbitrary radius between  $R_1$  and  $R_2$ . The top part of Figure 2.2 illustrates the characteristics of coaxial cylinder instruments. The solid curves are for Newtonian liquids; the dashed line is typical of a non-Newtonian liquid. Note that Eq. (2.7), the relationship between the shear stress and the torque, is independent of the constitutive nature of the fluid. If the annular spacing is small compared to the diameter of the cylinders, the shear rate is nearly constant across the annular gap for all fluids; this shear rate is given by:

$$\dot{\gamma} = \frac{\omega R_1}{R_2 - R_1} \tag{2.9}$$

The main correction that must be applied to data in order to get the correct viscosity is an end correction for a coaxial cylinder viscometer. The liquid at the bottom of the inner cylinder creates additional drag and gives rise to a torque in addition to the torque due to the liquid in the annular gap. Thus, the measured torque is equivalent to that of an inner cylinder with an apparent length greater than its true length. The simplest way to account for this additional length is to calibrate the viscometer with a liquid of known viscosity and to use the following equation:

$$\eta = \frac{kM}{\omega} \tag{2.10}$$

The form of Eq. (2.10) follows from the fact that viscosity is the ratio of the shear stress to the shear rate, and these two quantities are given, respectively, by the right-hand sides of Eqs. (2.7) and (2.9). The instrument constant *k* takes into account any corrections as long as the volume of liquid in the viscometer is held constant. Of course, the end correction is negligible if the immersed length is a couple of orders of magnitude larger than the annular gap. The correction can also be minimized by shaping the bottom of the inner cylinder to resemble an inverted cone.

The maximum value of the shear rate achievable with coaxial cylinder viscometers is usually not an instrument limitation but depends on the nature of the fluid sample. For high viscosity liquids, viscous heating may become a problem; for low-viscosity liquids, the upper limit may be set by the occurrence of secondary flows or the transition to turbulent flow. Usually, though, we can make measurements at shear rates up to about 100 sec<sup>-1</sup>. At the other end of the scale, one can often go down to shear rates as low as  $10^{-2} \sec^{-1}$ , especially with high viscosity liquids; the limiting factor here is the sensitivity of the torque transducer or the torsion bar or spring employed to measure the torque. The Contraves lowshear instruments, for example, are able to measure torque values as low as  $10^{-9}$ Nm by replacing the torsion bar with a light-deflection compensating system. Here, the outer cylinder or cup is driven by a motor and the angular deflection of the stationary inner cylinder or bob is detected by a light beam reflected from a mirror attached to the bob axis and monitored by a photocell. In most coaxial cylinder viscometers, the sample size is about 1 ml and the maximum temperature is less than  $80^{\circ}$ C.

When the coaxial cylinder viscometer is used in the oscillatory mode, one cylinder is rigidly supported while the other one is given a small-amplitude angular dispacement of the form:

$$\phi = \phi_0 \sin(\omega t) \tag{2.11}$$

Now the torque becomes time dependent, but the shear stress (and this is sinusoidal) is still related to the torque by Eq. (2.7). The sinusoidal strain is easily determined from the geometry and is given by:

$$\gamma(t) = \frac{R_2 \phi}{R_2 - R_1} \tag{2.12}$$

A knowledge of the stress and strain as a function of time allows us to calculate the complex viscosity with the help of Eqs. (1.6-1.8) If, however, one of the cylinders is not rigidly held but is suspended from a torsion wire so that it too can oscillate, the theoretical analysis is somewhat involved, and the relevant results may be found in Walters [4].

A variation of the coaxial cylinder viscometer is the "Brookfield" viscometer—a cylindrical spindle rotating in a 600-ml container of fluid. While the Brookfield Company makes a variety of rotational viscometers, it is this simple, inexpensive device, commonly used for quality control purposes, that has become synonymous with the name of the company. The spindle is driven by a synchronous motor through a calibrated spring; the deflection of the spring is indicated by a pointer that displays a "dial" viscosity. When measurements are made on suspensions and pastes, the cylindrical spindle often cuts a hole in the material and the dial reading falls progressively. To prevent fluid channeling, we replace the cylindrical spindle with a T bar that is continuously raised and lowered in the fluid container. Again, the measured viscosity is not a fundamental quantity, but an empirical measure of the resistance to deformation of the fluid.

### IV. CONE-AND-PLATE VISCOMETERS

The geometrical characteristics of a cone-and-plate rheometer are shown in the bottom section of Figure 2.1. A flat, circular plate and a linearly concentric cone are rotated relative to each other. The cone is normally truncated so that there is no physical contact between the two members. The liquid is in the space between the plate and cone. The plate radius R is typically a couple of centimeters, whereas the cone angle  $\alpha$  is usually a few degrees. Either of the two members can be rotated or oscillated, and we measure the torque *M* needed to keep the