POLYMER RHEOLOGY

Neither purely viscous nor perfectly elastic, polymeric fluids have a fading memory of their undeformed shape and display spectacular phenomena not seen in Newtonian fluids.

Daniel De Kee and Kurt F. Wissbrun

Polymers, foods, cosmetics, paints, pharmaceuticals—these are just a few of the many industries in which rheology research finds application. Rheology addresses the relationship between the stress on materials and the resulting deformation, and is therefore a part of continuum mechanics. Two laws dating back to the 17th century are very important in rheology. Hooke's law describes the behavior of an elastic solid, relating the stress to the deformation via a constant elastic modulus. And Newton's law describes the behavior of a linear viscous fluid, relating the shear stress to the rate of deformation via a constant viscosity coefficient. The aim of rheology today is to describe the more complex behavior of most real materials when they are examined over a wide range of stresses and deformations.

Historically, the pioneers of the field were interested in such problems as the non-Newtonian viscosity of paints and the time-dependent deformation of concrete beams under load. The greatest advances in understanding occurred, however, with the advent, starting in the 1930s, of technologies based on synthetic high-molecular-weight polymers. These materials display a wide variety of readily observed (see figure 1, for example) unusual rheological phenomena, which are of great importance to the synthesis, processing and end-use characteristics of the materials. As a result, probably a majority of rheological research in the past five decades has been devoted to the study of polymeric materials.

In recent years, many of the experimental techniques and theoretical and numerical approaches developed in the study of polymers have been adapted for application to many other materials—granular materials, colloidal and coarse suspensions, foams, micellar solutions and inhomogeneous solids, to name just a few. In this article, we limit ourselves to a few areas of polymer fluid rheology that are relatively new or that, even though studied for a long time, still present unresolved problems.

In all fluid mechanics problems, it is necessary to solve the momentum and energy conservation equations subject to boundary conditions that define the geometry of the problem and subject to a mathematical description of the fluid. That description is called a constitutive equation, a rheological equation of state that relates the time-dependent stresses and strains.

Most polymers (familiar as plastics, synthetic fibers and elastomers) have linear molecular backbones, with their flexibility attributable to rotation about the backbone bonds. Under the influence of Brownian motion, they assume the shape of a coil, which can be described as the result of a three-dimensional random walk. Distortion of the coil results in a stress that tends to restore the undeformed shape. This property is the basis for the classical entropic theory of rubber elasticity. The volume pervaded by a coil is much larger than the molecular volume; in other words, the density of a coil is much smaller than the measured macroscopic density. Therefore, in concentrated solutions or in melts of high-molecular-weight polymers, many coils from different molecules overlap in a given volume element, resulting in strong intermolecular interactions, which have often been called entanglements (figure 2). These entanglements are supposed to play a role similar to that of the chemical crosslinks in rubber elasticity theory, but they are not fixed and can respond to external stresses and to Brownian motion.

Daniel De Kee *is a professor of chemical engineering at Tulane University in New Orleans. He is president of the International Committee on Rheology.* **Kurt Wissbrun** *is retired from Hoechst-Celanese and is now a consultant and adjunct professor of chemical engineering at the University of Delaware in Newark. He is past president of the Society of Rheology.*

As a result the behavior of polymeric fluids falls somewhere between that of a purely viscous material and that of a perfectly elastic material. A volume element of an elastic material has a perfect memory of its undeformed shape; that of a viscous fluid has no memory at all. Polymer solutions and melts are viscoelastic; a volume element of such a material has a partial memory that fades with time after a deformation is imposed. The viscoelastic character of polymeric materials is responsible for a number of spectacular phenomena not observed with Newtonian fluids, as discussed in the box on page 28 and in figures 1, 3 and 4. Excellent presentations of non-Newtonian rheological phenomena can be found in references 1–3.

The examples in the box draw attention to the striking differences between the behaviors of Newtonian and non-Newtonian materials. Several other examples are described in references 1–3, and no doubt a variety of flow phenomena involving viscoelastic liquids still remain to be discovered and explained.

Here we briefly describe a few topics of interest to the rheological community involved with polymers. They include the development of appropriate equations of state, instabilities in melt flows and the very complex behavior of liquid crystals.

Constitutive equations

To solve flow problems, one must introduce an equation of state that relates the stress tensor to various kinematic tensors. The development of appropriate constitutive equations to describe the stress state of viscoelastic liquids is an area of active research and controversy. No theory is yet available that adequately describes all of the observed phenomena in a variety of flows.[4]

Constitutive equations have been developed based on continuum mechanics or on the molecular structure of the

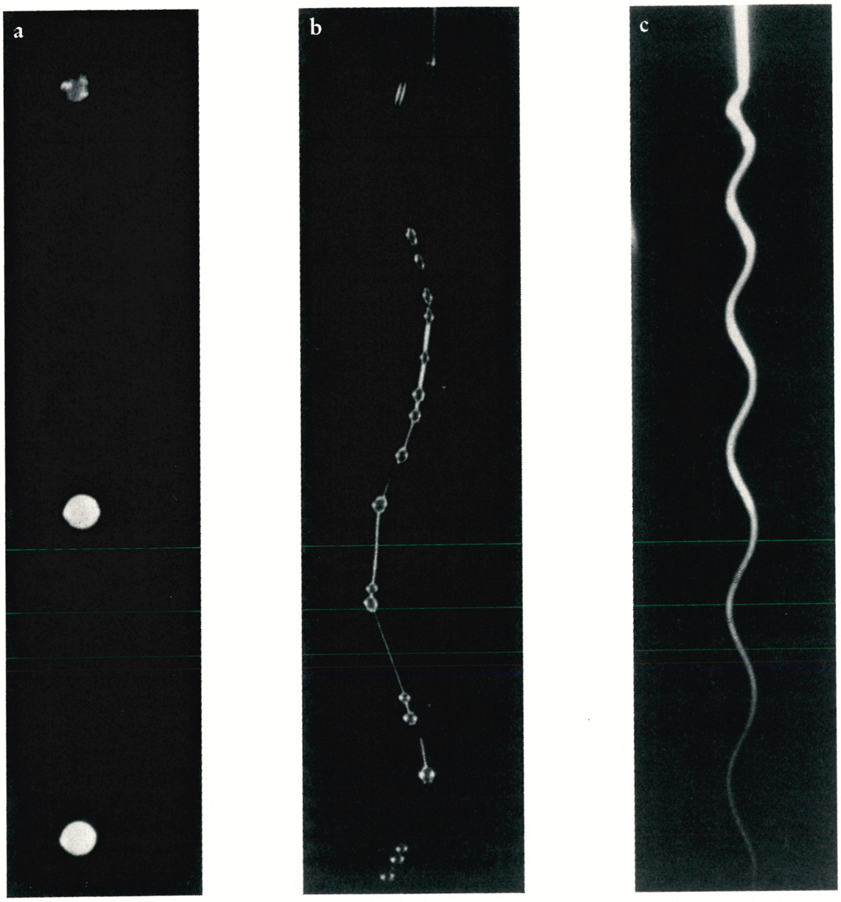

FIGURE 1. LIQUID EMERGING from a vibrating nozzle. **a:** Newtonian fluid. **b:** Dilute polymer solution. **c:** Concentrated polymer solution. The Newtonian fluid breaks into droplets. The concentrated polymer solution emerges as a structurally stable nonuniform wave. Dilute polymer solutions exhibit a behavior that is in between; that is, the droplets are connected by a thread. (From C. F. Chan Man Fong, D. De Kee, C. Gryte, J. Non-Newt. Fluid Mech. **46**, 111, 1993.)

fluids. In the continuum approach, no explicit consideration is given to the molecular structure of the material, and an appropriate relationship between suitable dynamic and kinematic variables is postulated.

In the molecular approach, the molecular structure of the fluid is taken into consideration. In modeling polymeric materials, one first represents the polymer molecules by mechanical models. One then introduces a probability distribution of the molecules. Finally, one calculates the average of all quantities so that a relationship between macroscopic quantities of interest can be obtained. Three models have been studied extensively by rheologists: the bead-rod-spring model, the reptation model and the transient network model.

The bead-rod-spring model has been proposed to describe dilute polymer solutions. The polymer molecules are idealized as dumbbells, consisting of two beads joined by a spring. Hydrodynamic, Brownian and intramolecular forces act on the beads. The polymer solution is modeled as these dumbbells suspended in a Newtonian fluid of constant viscosity. In the absence of external forces, neglecting inertia terms and considering the flow to be homogeneous, one can obtain a constitutive equation for a dilute polymer solution. More realistic models portray macromolecular chains as consisting of N beads connected by N–1 springs. Further improvements involve the consideration of non-Hookean springs and the inclusion of hydrodynamic interaction.

In concentrated solutions and in polymer melts, the motion of a chain is constrained by other chains, and this is taken into account in both the reptation model and in the network model.

In the reptation theory, the constraint that polymer chains cannot pass through each other is interpreted such that each chain is confined to move inside an imaginary tube.[5,6] A constitutive equation based on this concept can be written as

$$\boldsymbol{\sigma} = \int_{\infty}^{t} \{M_1[t-t', I_1(t,t'), I_2(t,t')]\, \mathbf{C}_t^{-1} + M_2[t-t', I_1, I_2\,](\mathbf{C}_t^{-1})^2\} \mathrm{d}t,$$

where $\boldsymbol{\sigma}$ is the extra stress tensor and I_1 and I_2 are invariants of the Finger deformation tensor $\mathbf{C}_t^{-1}$. The memory functions M_1 and M_2 can be written as products of functions of the past time $(t-t')$ and of deformation only. This equation is known in continuum mechanics as the Kaye–BKZ equation.

The transient network model is an adaptation of network theories of rubber elasticity.[7] In the case of polymer melts and concentrated polymer solutions, the network junctions are temporary, rather than permanent as in a chemically cross-linked rubber. That is, they can be destroyed and new junctions can be formed. The loss and creation of segments are analogous to the loss and creation of tubes in the reptation model.

The transient network model can describe many of the phenomena associated with linear (small deformation) viscoelasticity. It does not predict shear thinning of viscosity as observed in viscometric flows of polymeric fluids. One way of overcoming this shortcoming is to allow for the rates of creation and loss of segments to be functions of a macroscopic variable such as an invariant of the shear rate.

Such shear-rate-dependent models can satisfactorily predict the rheological properties of polymeric systems.[8] They have been objected to on the ground that they do not recover the linear viscoelastic behavior in small-

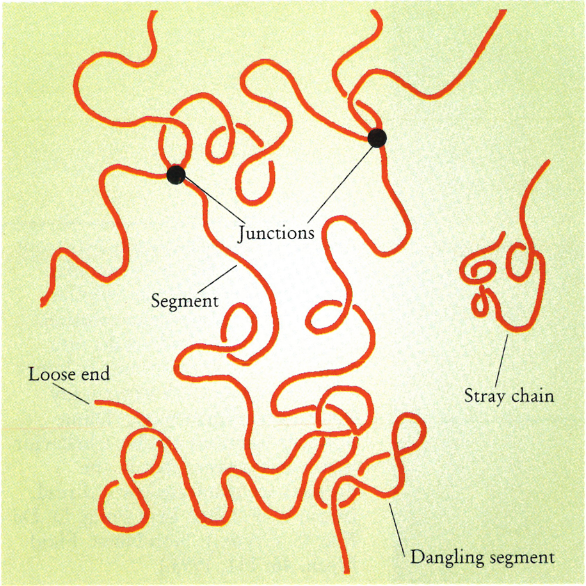

FIGURE 2. **POLYMER NETWORK.** The part of a molecule that joins two successive junctions is an active segment. A chain that is connected to only one junction is a dangling segment. A chain that is not attached to the network is a stray chain.

amplitude oscillatory flow. This objection can be refuted by noting that, in the case of small strains, the creation and loss of junctions are due to Brownian motion and are independent of the imposed flow, and so the model reduces to linear viscoelasticity in small-amplitude oscillatory flows. It also has been suggested that the stress generated is strain-rate dependent and not strain dependent.[3,9,10] At present, the model parameters of the network theory are not related to the molecular structure of the material, and future research should focus on seeking such a connection. Other successful models[11] have assumed the rates of loss and formation of junctions to be functions of the invariants of the stress tensor, and some researchers have proposed a strain-dependent model.[12] Such a model assumes the rates of creation to be constants and the rates of loss to depend on the trace of $\mathbf{C}_t$ as well as on the trace of $\mathbf{C}_t^{-1}$, resulting in a model that can be considered to be a special case of the reptation model or of the Kaye–BKZ model.

Recent developments in the network theory deal with predictions of "stress jump" and shear thickening. Stress jump is defined as the instantaneous finite change in the stress due to a sudden finite change in the rate of deformation. Not all constitutive equations can predict a stress jump; it requires the introduction of a singularity in the memory function. In essence the memory function is represented in two parts. One is associated with a response due to the active network segments. The other accounts for the contributions of the solvent molecules, stray chains and dangling segments. The cause of shear thickening is the flow-induced complex arrangement of the material due to effects such as electrostatic interaction, hydrogen bonding and the trapping of dangling segments and stray chains by the active network. These effects lead to an increase in the number of junctions and hence an increase in viscosity.

Other recent developments include

▷ The introduction of the slip-link model. Slip-links are small rings through which the chain can pass freely. This idea can be combined with a network model so that one can consider a network of active Gaussian segments between slip-links.[13] Due to the possibility of slip, the number of monomers between two junctions can vary upon deformation and may lead to disentanglement. The constitutive equation now involves a slip function, as well as a disentanglement function.

▷ The introduction of constitutive equations based on structural kinetics—that is, based on a set of equations describing the degree of structural nonequilibrium.[3]

▷ The introduction of the double reptation model, where the reptation of a stress point (a junction) is considered in addition to the reptation inside the tube.[14] A combination of the reptation and network models may shed light on the process of loss and creation of junctions and on the deformation of segments.

Instabilities in melt flows

It has been known for more than 50 years that when molten polymers are extruded at a sufficiently high rate of flow, the extrudate becomes distorted and no longer has a cross-sectional shape resembling that of the die. Studies have identified a wide range of types of distortion, some of which are illustrated in figure 4. For historical reasons,

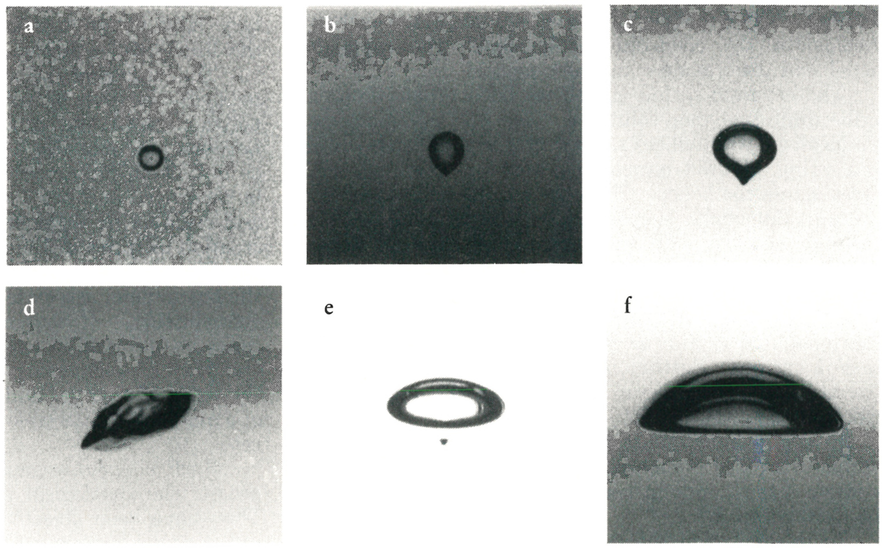

FIGURE 3. **SHAPES OF BUBBLES** in a 1% by mass polyacrylamide solution (prepared in a 50% mixture of glycerine and water) (**a**, **b**, **c**, **e** and **f**) and in a Newtonian 40% aqueous glycerine solution (**d**). Bubble volumes **a–f** are 0.01 ml, 0.1 ml, 1 ml, 1 ml, 2 ml and 10 ml, respectively. Smaller bubbles are shown at greater magnification. Note the striking difference in bubble shape between frames **c** and **d**. They both portray a 1 ml air bubble, but the one in frame **c** is rising in a viscoelastic solution whereas the one in frame **d** is rising in a Newtonian fluid.

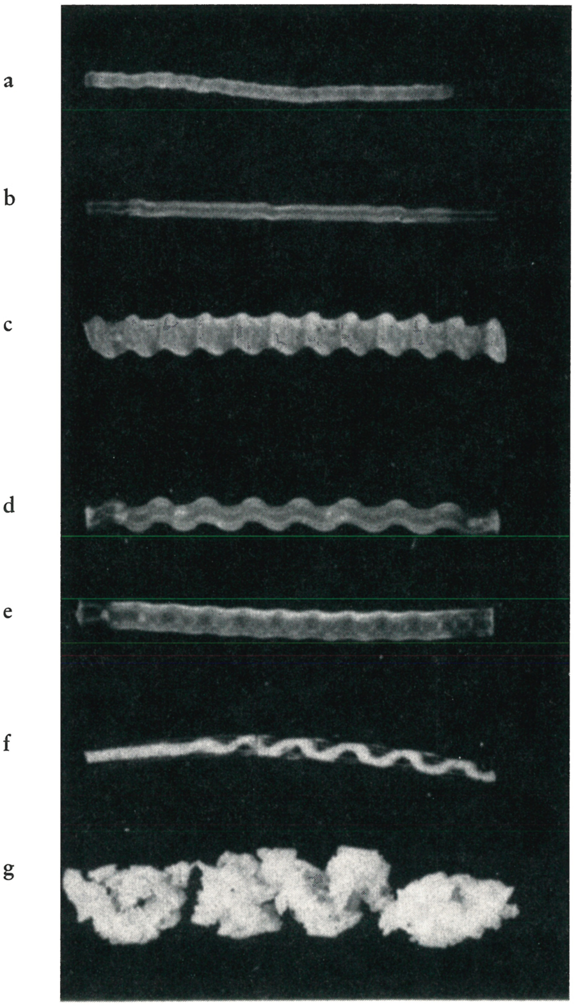

FIGURE 4. TYPICAL DISTORTED EXTRUDATES, illustrating some of the many varieties of melt fracture. **a:** Rigid polyvinyl chloride showing surface fracture. **b:** Polyethylene showing bamboo fracture. **c, d, e:** Polypropylene viewed from various angles, showing spiral melt fracture. **f:** Polymethylmethacrylate showing spiral fracture. **g:** Polytetrafluorethylene showing gross melt fracture. (From C. J. S. Petrie, M. M. Denn, Am. Inst. Chem. Engng. J. **22**, 209, 1976.)

the occurrence of these distortions is generally, but confusingly, referred to as melt fracture.

Two of these manifestations of instability have been studied in great detail by many investigators. One is the formation of surface roughness, which leads to a lack of gloss and clarity of the extruded film. The other is an apparent discontinuity, sometimes called spurt flow, of the flow curve (that is, shear stress versus shear rate), which causes distortion of the extrudate from a controlled pressure device. Both of these phenomena are of technological interest. The formation of surface roughness is a limiting factor on the rate at which acceptable film can be produced. The occurrence of spurt flow is beneficial in some processes, permitting extrusion to be done at a lower pressure or higher rate than if it did not occur.

Edward Bagley and his coworkers at Canadian Industries Ltd first observed spurt flow in the then newly introduced high-density polyethylene. This polymer is nearly linear, in contrast to the earlier "conventional" (low-density) polyethylene, which has many side branches emanating from the polymer backbone and is long enough to entangle. These long branches have profound effects on rheological behavior, including the suppression of the flow discontinuity. This phenomenon is illustrated in figure 5. Ascending the left branch of the flow curve, point A represents the conditions of pressure or flow rate when the flow jumps to point B on the right branch.

The rheometers most commonly used today are speed controlled. If a speed is selected at some point within the transition, the pressure and instantaneous flow rate oscillate, and the appearance of the extrudate changes periodically, giving rise to what is sometimes called bamboo fracture. This spurt effect can be attributed to loss of adhesion to the die wall due to a transition of the melt to a rubbery state under conditions of high shear stress. The jump in flow rate, therefore, is caused by massive slippage of the material near the wall. However, there are schools of thought that attribute the spurt effect to the bulk properties of the polymer itself, rather than to slip.

One idea that has been revived and elaborated is that the spurt effect is the result of a constitutive instability. Some constitutive equations predict that the flow curve will be double valued for some ranges of stress, accounting for the two branches of the flow curve. Supporting these theories are the experimental data for polymers whose molecules all have the same molecular weight (monodisperse systems). The data can be fitted with reasonable values of a characteristic elastic modulus, and for a range of molecular weights. Arguments against these theories are that they do not account for the lack of spurt flow for most polymers, that the molecular theory would not be expected to predict its existence for the high-density polyethylenes of broad molecular-weight distribution, and the failure so far to determine the theoretical parameters quantitatively by independent measurements.

A second theoretical suggestion that has been discussed, but that apparently has not been developed to the point of quantitative prediction, attributes the spurt effect (and manifestations of extrudate distortion) to a change in the type of applicable hydrodynamic equations. This change occurs when a critical velocity is reached in the viscoelastic constitutive equations that permit instantaneous elastic response. Materials obeying these constitutive equations permit the propagation of shear waves.[15] However, it has been pointed out that the very condition necessary for this picture, a zero "retardation time," is exactly contrary to that required for the constitutive instability models to have multivalued flow curves.[4] This paradox is as yet unresolved.

Another surface defect is the so-called sharkskin effect, a small-scale periodic roughness.[16] For a number of years, its origin had been thought to be an exit fracture phenomenon, resulting from the high acceleration of the surface elements of the extrudate that is required to equalize the axial velocities of the melt once free of the die wall. In the 1980s, however, Stuart Kurtz at the Union Carbide Corp pointed to an apparent coincidence of the onset of sharkskin with a change in the slope of the flow curve. Motivated by the effectiveness of certain additives in suppressing or minimizing sharkskin, by observations of the influence of the die's composition and by the attribution of the slope change to slip, A. V. Ramamurthy, also at Union Carbide, proceeded to make measurements of the slip velocity. He used the Mooney method, in which the slip velocity, assumed to depend only on the shear stress, is inferred from the apparent diameter dependence of the viscosity. And, indeed, Ramamurthy found

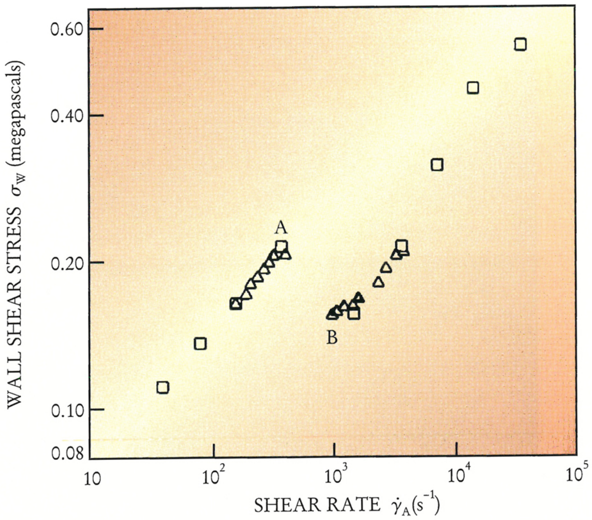

FIGURE 5. APPARENT FLOW CURVE of a resin showing two distinct branches. No steady flow is possible for apparent shear rates between those corresponding to points A and B. Triangles represent oscillating flow; squares, steady flow. (Adapted from S. G. Hatzikiriakos, J. M. Dealy, J. Rheol. **36**, 845, 1992.)

a coincidence of a "critical" stress for the onset of sharkskin. These findings have triggered an avalanche of studies of the slip phenomenon—and a concomitant amount of controversy.

Is slip the result of loss of adhesion of the melt to the wall, or of disentanglement of the bulk material from a highly adsorbed layer at the wall? Does it depend upon hydrostatic pressure, and if so, how? What is the dependence of slip velocity on molecular weight and on chemical structure, which affects entanglement density? Can the constitutive and hydrodynamic instabilities be differentiated from slip? Can slip be due to the existence of a highly mobile layer in the high-stress region near the wall? An ordered "nematic" state, a stress-induced migration of low-molecular-weight species to the wall and a disentangled melt have all been proposed as candidates, with some experimental support for each. It should be noted that the measurement of slip is subject to many experimental difficulties. It may be advantageous to consider direct optical measurements of velocity profiles rather than inference from macroscopic measurements.

Liquid crystal polymer rheology

Liquid crystals have long-range order of molecular orientation, which results in crystal-like anisotropy of properties such as optical birefringence and viscosity. However, liquid crystal molecules do not have long-range order of position, and therefore can flow. The study of liquid crystal polymers was limited to a small number of experimental and theoretical papers until the introduction of Kevlar in the early 1970s by E. I. duPont de Nemours & Co. The relatively linear and rigid molecular structure of this material is responsible not only for its remarkable mechanical properties, but also for the liquid crystalline behavior of the solutions from which Kevlar aramid fibers are formed. Further, the unique rheological behavior of these solutions, especially the remarkable decrease of viscosity (figure 6) compared to that of an isotropic solution, is essential for producing the fiber by an economically acceptable process.

The aromatic polyamides are lyotropic liquid crystal polymers—that is, they are transformed from the solid state to the liquid crystalline state by being dissolved in a suitable solvent. This limits their application to processes, such as fiber spinning, in which solvent removal is feasible. Solvent removal also has an economic cost. These disadvantages inspired research that led, in the 1980s, to the development of thermotropic polymers, which become liquid crystalline just by being heated, and are thus amenable to conventional plastics processing as well as fiber spinning. These materials are principally aromatic ester copolymers. At about the same time it was discovered that various cellulose-based polymers (especially hydroxypropylcellulose), which had long been articles of commerce, would also form lyotropic and thermotropic liquid crystal polymers.

The theoretical framework for the study of the rheology of liquid crystal polymers is based on the molecular theory of solutions of rigid rods, which predicts the dramatic decrease of viscosity illustrated in figure 6 and its scaling with the polymer's molecular weight.

Of the many unusual rheological phenomena exhibited by liquid crystal polymers, one of the most crucial for

Nature of Viscoelastic Materials

Polymers in concentrated solutions or melts can be pictured as forming a network of temporary junctions, as illustrated in figure 2. These fluids generally exhibit a viscosity that decreases with increasing rate of deformation. Moreover, they are viscoelastic in character. A classical manifestation of this property is the Weissenberg effect, in which the fluid climbs an immersed rotating rod, inverting the vortex that is observed when a rod is rotated in a Newtonian fluid.

When a polymer network is deformed by the action of a moving surface, the effect of Brownian motion to restore the isotropic network generates tensions in the flow direction and in the normal (perpendicular) direction. These tensions, the "normal stresses," are very important in the quantitative description of viscoelastic effects. An example of such an effect is the swelling of a material being extruded from a capillary. This phenomenon is obviously important to consider in industrial processes such as fiber spinning and film extrusion. (See PHYSICS TODAY, April, page 9.)

Less frequently discussed effects that illustrate differences between the behavior of Newtonian and non-Newtonian fluids are shown in figures 1 and 3. Bubble shapes (figure 3), except for very-small-volume bubbles, are not stable in Newtonian fluids. That is, several snapshots of the same-volume bubble would result in very different pictures. In viscoelastic fluids, however, the shapes are stable and vary with increasing volume, from a spherical shape to a prolate teardrop shape to an oblate cusped shape and finally to a spherical cap shape. Studies of bubble dynamics are quite important, as a variety of industrial phenomena rely on mass transfer, resulting from gas–liquid contact. Some processes, such as fermentation, require a large area for mass transfer, from a large number of small bubbles. Separation processes, on the other hand, are facilitated by coalescence of fast-rising large bubbles.

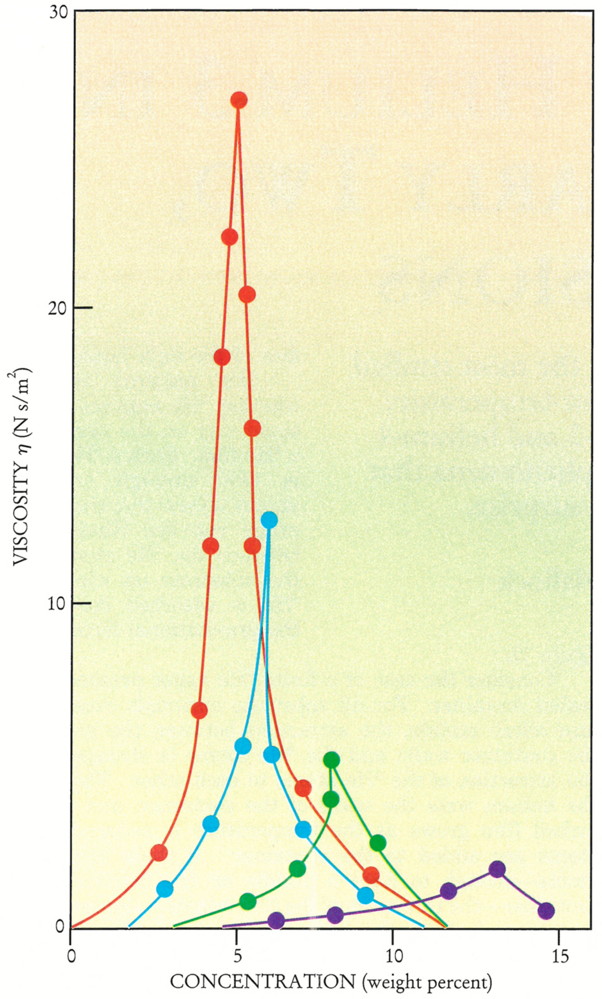

FIGURE 6. CONCENTRATION DEPENDENCE of the viscosity of solutions of polyparabenzamide. The four curves correspond to solutions of polyparabenzamide of decreasing (from left to right) molecular masses in dimethylacetamide/lithium chloride. Each curve shows a decrease of viscosity upon transformation to the liquid crystal phase. (Adapted from ref. 17, chap. 1.)

arriving at the present level of understanding was the observation of a negative primary normal stress difference in steady shear flow.[17] This property contrasts with the behavior of almost all other materials in the absence of an inertial effect. It is manifested by a tendency to pull together, rather than to push apart, the fixtures of a cone-and-plate viscometer, in which the test sample is confined between one fixture that is rotated while the other is held stationary. The explanation of this phenomenon was found to rest on the fact, originally unexpected, that liquid crystal polymers tend to "tumble" in a shear flow, rather than to align at a small angle to the flow direction, which is the most commonly observed situation with low-molecular-weight liquid crystals.[18] Clarification of this question has led to a clearer understanding of many other observations, including the occurrence of a very large number of defects (disclinations) in the orientational order of liquid crystal polymers.

The persistence and the high density of these defects, which are particularly pronounced in the thermotropic polymers, are believed to be responsible for the as-yet-unexplained rheological phenomena of liquid crystal polymers. The outstanding problem is the existence of so-called "region I" behavior, characterized by shear-thinning viscosity at very low shear rates. Associated with this behavior is a change of defect texture with shear rate and, conversely, an effect of the texture on the viscosity. Complex effects of shear history, nonlinear pressure gradients in flow through a tube or slot and the occurrence of a contraction of the thickness of an extrudate (in contrast to the usual expansion) are all believed to be the result of this interaction between defect texture and rheology.

Not discussed at all in this brief exposition is the growing interest in "side chain" liquid crystal polymers, whose liquid crystal molecular subgroups are pendant from the polymer backbone, rather than forming the backbone as in the polymers discussed above.

Future developments

Although prediction of the direction of scientific advance is notoriously hazardous, three specific trends in rheological research can be discerned at this time. First, the study of materials, such as dendrimers, which are more complex than the homogeneous linear polymers that have been the subject of so much research in recent decades, will become increasingly important. Second, observation of the structure of materials while they are being deformed is becoming an essential tool for rheology. In part this trend is motivated by the need to understand the coupling of structure and deformation of complex substrates, and in part by the increasing ability to apply tools such as nuclear magnetic resonance imaging and high-intensity x-ray diffraction. And third, as in all fields of science, numerical simulation on all scales, from molecular to macroscopic, is an increasingly valuable adjunct to classical theoretical and experimental studies.

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