Materials Rheology: An Overview

Stuart J. Kurtz, Guest Editor

My fellow authors and I have assembled a series of articles on using rheology to understand the structure and processing of a wide range of materials. We approach this task by presenting an introduction to the concepts of rheology and some illustrative applications, followed by a description of linear viscoelasticity and a description of the rheological behavior of elastic fluids. These concepts and related tools are then used to describe molten polymers, colloidal suspensions, latex systems, electrorheological fluids, and gels. In each of these areas, we show how rheology provides insights into the structure of materials and the type of information required to process them. We also show that the rheological approach spans macroscopic and microscopic domains. These aspects of rheology are of value to materials scientists and engineers. We hope these examples will clarify the relevance of rheology to materials.

If we are successful in this presentation, you will obtain a flavor of the process of rheological studies. While reading through these articles, look for the interplay of the concepts of molecular or domain structures and the flow and deformation of the bulk materials. These articles may even inspire you to examine the role that rheology may play in your own studies.

What is Rheology?

Rheology, derived from the Greek root *rhe* meaning flow, is the study of the deformation and flow of matter. This definition would seem to encompass quite a bit. Indeed, at its first meeting in 1929 the Society of Rheology adopted the motto, *Παντα ρει*, "everything flows" (from the words of the Greek philosopher, Heraclitus). Rheologists do, in fact, study the deformation and flow of all types of materials: polymer melts, composite materials, rubber, biological materials, solutions, suspensions, soils, foods, lubricants, glaciers, liquid crystals, and many others. What these materials have in common is the complexity of their rheological response to either flow or deformation. One might say that rheologists study rheologically interesting and sometimes useful materials.

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Examples of *interesting* rheological effects can be found with the toy, Silly Putty™, as described by A. Wineman. Placed on a table, Silly Putty will flow like a liquid under the force of gravity but will bounce like a rubber ball if thrown against a hard surface. A *useful* rheological effect comes with the addition of small amounts of a water-soluble polymer, polyethylene oxide, to water. The resulting "rapid water" has much higher rates of flow in fire hoses at the same pressure drop compared to water without the polymer. Rheological properties are also important for optimizing the drilling of muds in oil fields, obtaining consistent texture (or response to chewing) in food, and developing product formulations that allow rapid, stable fabrication and processing. In manufacturing paints, the control of rheology is important in the formulation of a dripless and spatterless product, the desirability of which can be attested to by weekend painters. The subsequent articles in this issue also note other important rheological effects.

There are several common approaches to studying the rheology of materials, and they can be divided into studies of averaged behavior (e.g., viscosity), correlations and computations with molecular and structural parameters, and models. Models can be further classified. Some models are derived from mathematical constructs alone, and some from a combination of mathematical and physical models. Important rheological parameters such as viscosity are used in many of these models to describe average behavior. These parameters are generally neither constant nor linearly related to independent variables such as shear rate or shear stress. The parameters are extremely useful in themselves and can be obtained from experiments without regard to the molecular structure of the materials. Even for complex rheological measurements such as the transient responses of materials, the underlying molecular structure is sometimes ignored. As we shall see, for the best understanding of materials, especially those that show complex nonlinear rheological relationships, it is important to include the molecular structure. Integrating knowledge of the molecular structure with the predictions of appropriate models helps relate rheological measurements to molecular structure.

Rheology is one of many ways to examine the structure of materials. Dynamic rheological tests (described in Wineman's article) are often used as a measure of the interactions among structures such as molecules or other associations. Like using electrical or electromagnetic fields, using mechanical stress or strain fields also probes the molecule itself and larger associated structures. Such probes are sometimes the only really useful methods for looking at molecular entanglements of very long molecules or extended structures, as well as for studying their interactions. Thus rheology examines averaged or lumped effects in some cases and probes the detailed structures in others.

Not all materials have interesting rheological behavior under all conditions. It is necessary to specify the material's rheological parameters within the context of its thermodynamic state, the force and deformation fields on the material, and the rates and time scales of interest. Rates and time scales are often key. A measure of their importance is given by the Deborah number, N_{Deb}, a dimensionless number that relates a characteristic time for the material's response to a characteristic time scale for the process. The name Deborah comes from the reference to the observation that "even the mountains flow before the Lord" (Judges 5:5). Indeed, across the range of materials that rheologists study, interesting results are sometimes found at deformation rates from the extremely slow, at less than 10^{-8} s^{-1}, to greater than 10^{8} s^{-1}. Not only is this range of deformation rates large, but so is the total range of values for rheological measurements such as viscosity. Viscosity, the ratio of the shear stress to the deformation rate, may range over more than 20 orders of magnitude. Very few measured parameters have such a wide range of values. This in itself makes for interesting studies.

Applications of Rheology

Questions often arise as to when and how rheology is to be applied to a problem. Aside from asking a rheologist (who would most likely find a way to involve rheology in at least some aspect of any problem), one might rephrase the question as follows: To what extent does the complexity of the material's response influence the results of processing or product properties or provide a useful insight into the understanding of the material's structure? Simple models such as Newtonian fluids (described by a single constant viscosity) or Hookian solids (described by a single constant modulus) would be less likely to employ rheological tools and approaches than problems concerning materials whose structures change due to stress, time scale of deformation, or their history of deformation. These are the key parameters used to describe, model, and test the rheological behavior of materials.

Qualitative knowledge of the rheological behavior of materials is often useful in process design. For example, the phenomenon of extrudate swell, an increase in diameter of material exiting a die, may be very important in the extrusion of materials with viscoelastic response. If one is seeking a given rod diameter from a circular die, extrudate swell may cause problems in dimensional control. This is especially critical when the swell may be shear-rate dependent, as is very likely, and when subsequent post die drawing may be limited. Rheological studies of extrudate swell show the importance of stretching flows at the die entrance, die geometry such as the length-to-diameter ratio, and shear rate in the die. This example and many others like it demonstrate that rheology is a basic tool for polymer processing and other manufacturing operations, much as chemistry is a basic tool in reactor design.

Although rheology is often described in mathematical terms involving integral equations or complex differential equations, much can still be learned from the use of approximations employing non-Newtonian viscosity, elastic recovery, orientation functions and so on. Such approximations often yield the insights needed for process modeling, characterization of materials, product development, product quality control, and correlations. On the other hand, too great a simplification may remove some key phenomenon of interest. Rheological approaches to understanding materials and materials processing require a judgment concerning the best approach and are therefore more than just the process of finding and using the right equation. An appreciation of the actual structure of the material being studied is usually required. The articles in this issue bring out this approach very clearly.

The Articles

A. Wineman begins with an introduction to viscoelasticity. Such studies provide a foundation for formulating and solving many of the questions asked in rheology. He shows how the use of tests such as creep and stress relaxation can be interpreted in terms of molecular structure. Linear viscoelasticity continues today as an important tool used by rheologists, first because of the elegant mathematical structure of linear viscoelasticity, and second because the theoretical interrelations work so well for so many materials.

J.M. Dealy extends the application of linear viscoelasticity to polymeric liquids. He then focuses on the most widely studied nonlinear viscoelastic material, polymer melts, in large deformation flows. Again, the material structure, in this case the molecular parameters such as molecular weight distribution and long chain branching, strongly affect the flow and processing of these materials. Polymers within a given "class," such as polyethylene, are really made up of many different types or grades. Different polymer grades are preferred in specific processing operations such as blow molding, blown film, and injection molding because of particular rheological behavior and a final set of properties. The rheological concepts developed here are useful across many materials.

W.B. Russel next introduces the concepts of colloids and suspensions. We get to see how macrostructure (larger than the molecular level) may be strongly influenced by the fields present during close interactions. A rheological description of the interactions along with dimensional analysis and statistical mechanics adds another dimension to understanding the structure and processing of such locally heterogeneous systems. This nicely introduces the fascinating work done by R.L. Hoffman on latex systems. Hoffman shows how changes in macrostructure, as measured by light diffraction, can be used to establish the cause of rheological yielding, shear thinning, and dilatancy in suspension systems. Another type of field interaction concerns the unusual case of electrorheological fluids.

T.C. Jordan and M.T. Shaw show how electric fields can be used to rapidly change a special material mixture from a fluid to a solid. The behavior is complex, requiring the use of rheological tools such as dynamic testing to elucidate the process. Such materials are interesting because of their current and potential applications in clutches, copying machines, valves, and other devices.

Another macroscopic structure occurring in polymers is a "gel." Here, primary chemical bonding called crosslinking extends the molecular structure (single molecules) to occupy a visibly large space. The structures are physically different from separate molecules and result in unique rheological behavior. H.H. Winter describes some of the rheological techniques used to study this interesting structure.

For the reader interested in a more detailed presentation of rheology, though still appropriate as an introductory text, I recommend the book by Barnes et al[1]. For those interested in specific applications of rheology to polymer melts, I have found J.A. Brydson's[2] text particularly user friendly. The articles in this issue contain additional references.

References

1. H.A. Barnes, J.F. Hutton, and K. Walters, *An Introduction to Rheology* (Elsevier Science Publishers, 1989).
2. J.A. Brydson, *Flow Properties of Polymer Melts*, 2nd ed. (George Godwin Limited, 1981). □

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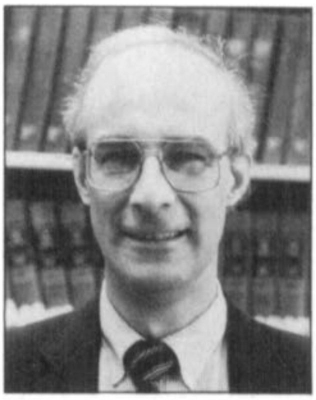
John M. Dealy



Richard L. Hoffman

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Stuart J. Kurtz, Guest Editor for this issue of the *MRS Bulletin,* is technology manager in the Center for Polymer Processing and Rheology, Union Carbide Chemicals and Plastics Company, Bound Brook, New Jersey. He received an MSE degree in polymer materials and an MA and PhD in chemical engineering from Princeton University. He held academic positions in polymer engineering at Rensselaer Polytechnique Institute and the Federal University of SãoCarlos, Brazil, before joining Union Carbide in 1974. At Union Carbide he has been involved in rheology, polymer processing, compounding, on-line quality control, product development, and product support, and has publications and patents in these areas. He was appointed a research associate in 1990 and is currently responsible for rheology studies and polymer processing development.

John M. Dealy obtained his doctorate at the University of Michigan in 1965 and is now professor of chemical engineering at McGill University, Montreal, Quebec. Dealy has developed several new techniques for the rheological characterization of molten plastics, including a sliding plate rheometer suitable for studying nonlinear viscoelasticity and an in-line rheometer that can be used as a process control sensor. His research in polymer processing has covered studies of film blowing, blow molding, and pipe extrusion. Dealy is the author of *Melt Rheology and Its Role in Plastics Processing* (1990) and *Rheometers for Molten Plastics* (1982), and has written chapters on rheology in other books. Past president of the Society of Rheology, he recently organized a Rheology Group within the Society of Plastics Engineers.

Richard L. Hoffman is a senior fellow at Monsanto Company, Indian Orchard, Massachusetts. His published research has focused on the rheology of concentrated suspensions, mechanisms by which particles generate roughness at interfaces undergoing extensional flow, characterization of the advancing front between a liquid and a gas, and improved techniques for particle size measurement. Hoffman received an MA and PhD in chemical engineering from Princeton University and a BChE and MS from Ohio State University. He is associated with the Society of Rheology, where he serves as a member of the Bingham Awards Committee.

Therese Jordan, received a BS in chemical engineering in 1985 from Tufts University, and completed studies in polymer science in 1989 at the University of Connecticut. Her graduate research focused on elucidating fundamental mechanisms of the electrorheological response in polymer suspensions. She is currently a member of the research staff at GE Corporate Research and Development, Schenectady, New York. Her current research concerns miscibility in polymer blends, the effects of molecular architecture on the rheology of polymer melts, and structure-property relationships in suspensions of fumed silica. She is a member of the Society of Rheology, American Chemical Society, Tau Beta Pi and Sigma Si.

William B. Russel, professor of chemical engineering and faculty associate of the Materials Institute at Princeton University, received BA and MChE degrees from Rice University in 1969 and a PhD in chemical engineering from Stanford University in 1973. He has been a NATO Postdoctoral Fellow in applied mathematics and theoretical physics at Cambridge University, a Visiting Fellow in applied mathematics at the Australian National University, Hougen Visiting Professor in chemical engineering at the University of Wisconsin, and the Unilever Visiting Professor in physical chemistry at Bristol University. His research interests center on colloidal dispersions, particularly understanding and controlling their phase behavior and rheology in order to formulate and process materials. He is author of a monograph, *The Dynamics of Colloidal Systems* (1987) and co-author of a graduate text, *Colloidal Dispersions* (1989).

Montgomery T. Shaw completed BChE and MS degrees in chemical engineering at Cornell University, then moved to Princeton University, where he studied under Prof. Tobolsky, obtaining his PhD in 1970. For the next six years, he was associated with the R&D department of Union Carbide Corporation, Bound Brook, New Jersey. In 1977, Shaw joined the faculty of the Chemical Engineering

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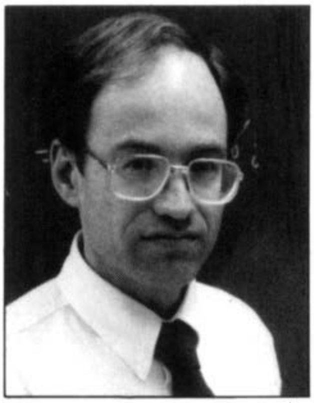
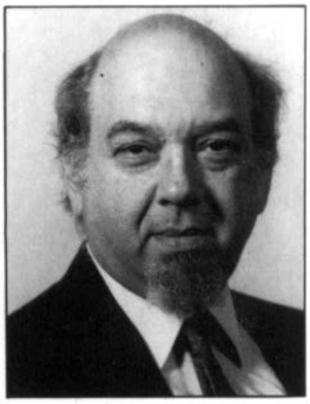
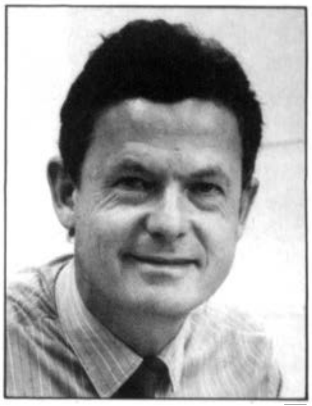


Montgomery T. Shaw



Alan S. Wineman



Horst Henning Winter

Alan S. Wineman received a PhD in applied mathematics from Brown University in 1964. He is currently a professor in the department of mechanical engineering and applied mechanics at the University of Michigan. His research activities deal with mathematical models for large deformations of polymeric materials, including development of constitutive equations, simulation of manufacturing processes, interaction of deformation and diffusion, and microstructural changes.

Horst Henning Winter is a professor of chemical engineering and of polymer science and engineering at the University of Massachusetts at Amherst. He completed his PhD in chemical engineering at the University of Stuttgart (1973) and also his Habilitation (1976). Since 1989, he has been editor of *Rheologica Acta*. Winter's current research spans rheology and material structure (gels, block copolymers, blends, and liquid crystalline polymers), modeling of processing flows, and development of rheometrical methods. ☐

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