Rheological instrumentation for the characterization of polymers

BY STEVEN M. COLO, KAJ HEDMAN, AND BRUCE K.S. RUDOLPH

RHEOLOGICAL instruments and measurements find applications in any industry where the flow characteristic of a material determines its processibility, performance, and/or consumer acceptance. An understanding of the rheological properties of polymers in both the molten and solid states is extremely important to all sectors of the plastics industry.

Rheology is the branch of science dealing with the flow and deformation of materials. The materials under investigation can range from low-viscosity fluids, semisolids, and polymer melts to solid-state rigid samples. In the case of polymers, rheological behavior is controlled directly by molecular structure, crystallinity, cross-linking, and polydispersity. Whether involved in manufacturing the resin, producing the machinery used in resin production, or processing the resin into a final product, rheological measurements are of practical importance. These quantitative, objective measurements bridge the gap between molecular structure, processibility, and ultimate performance properties.

Traditional tests for polymers focus on the amount (mass) of material passing through a known diameter orifice in a given time frame, usually 10 min. This type of test, known as fluidity index or melt index (MI), provides a single point measurement of the flowability of a material. In this test, there is little control or knowledge of the test flow pattern, and thus the strain history is different for each material studied. This single point value is a composite of both the viscosity and elasticity in the sample. This empirical value is not defined in terms of a particular deformation, but rather in terms of a particular, arbitrary laboratory procedure. Due to the nature of the measurement, it is not possible to determine the effect of the viscosity contribution independent of the elasticity. Many times, samples with the same MI value process drastically different from each other.

*Mr. Colo is President, **ATS RheoSystems,** 195 Chesterfield-Jacobstown Rd., Wrightstown, NJ 08562, U.S.A.; tel.: 609-758-1750; fax: 609-758-3498; e-mail: atsrheosystems@internetmci.com. Dr. Hedman is with **REOLOGICA Instruments AB,** Lund, Sweden; tel. 011-4646-127760. Mr. Rudolph is National Sales Manager, **ATS RheoSystems,** 150 Divadale Dr., Toronto, Canada, M4G-2P6; tel.: 416-422-5474.*

Figure 1 *The STRESSTECH controlled stress/strain rheometer.*

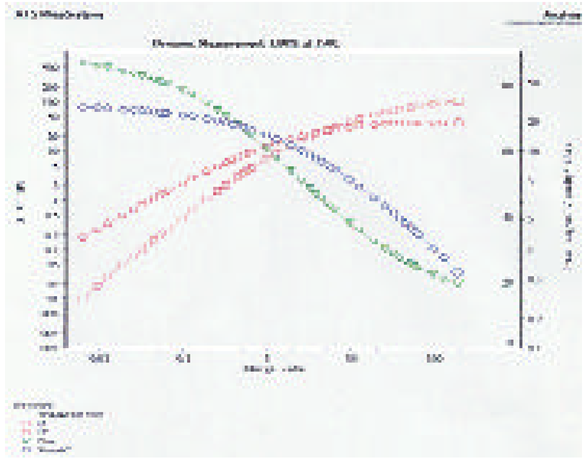

Figure 2 *Response of a low-density polyethylene sample at 150 °C.*

The measurement of well-defined rheological material properties provides a more reliable basis than empirical tests for characterizing and comparing materials. In addition, analyzing a process by use of fundamental physical principles is superior to empirical methods. In order to evaluate and understand the complex flow characteristics of polymers, it is necessary to characterize the flow properties over a wide range of deformation conditions, e.g., stress and/or rates of shear, and a means of deconvoluting how the viscosity and elasticity components contribute to the overall flow properties is required. This can be accomplished with the STRESSTECH controlled stress/strain rheometer (**ATS RheoSystems** [Wrightstown, NJ] and **REOLOGICA Instruments AB** [Lund, Sweden]) (*Figure 1*). The rheometer can accurately measure viscosity and elasticity by creep/recovery, forced dynamic oscillation in constant stress or strain, and/or constant shear rate with Quantitative Normal Stress (NI).

Viscosity, elasticity, and viscoelasticity

Industrial processes subject material to complex flow fields and varied temperature histories. The viscosity, along with the elastic component, of a sample has a controlling effect on the selection of a particular plastic for a certain application. Ideally, materials would behave either entirely elastic and obey Hooke's Law, which states the stress in the sample is a function of deformation only and not a function of time, or entirely viscous and obey Newton's Law of viscosity, which states the stress in the sample is a function of the rate of deformation. Although these basic concepts exist theoretically and in some very simple materials, such as steel and water, most important industrial materials like polymers do not behave entirely as one of these two ideal classes of materials. Polymers possess properties of both elastic and viscous materials, and the contribution of each component varies with time, temperature, deformation, and rate of deformation. Polymers fit into a broad class of complex fluids and are characterized by the term viscoelastic.

Dynamic measurements

Dynamic measurements, where a sample is subjected to a periodic deformation of stress or strain, are particularly well suited for viscoelastic materials like polymers because of their ability to rigorously determine both the elastic and viscous response of a sample in one experiment. The applied periodic deformation causes a periodic response in the sample. This response may be lag or lead the deformation, and this phase lag (delta, tan delta) is a direct measurement of the ratio of the viscous to elastic contribution to the overall response in the sample. Using the phase lag and the magnitude of the sample's response, the signal can be decomposed into the in phase and 90° out of phase components, the in phase representing the elastic response and the 90° out of phase the viscous response. From the in phase information, the storage modulus (G', E') is determined. The storage modulus is a measure of a sample's ability to store energy, and is called the elastic modulus. From the 90° out of phase information, the loss modulus (G", E") can be determined. The loss modulus is a measure of a sample's ability to dissipate energy. The ratio of the loss modulus to the storage modulus is called tan delta, and represents the damping properties of the sample. The response of a low density polyethylene (LDPE) sample at 150 °C is shown in *Figure 2*. A single value of MI cannot accurately describe the viscosity profile of this LDPE sample.

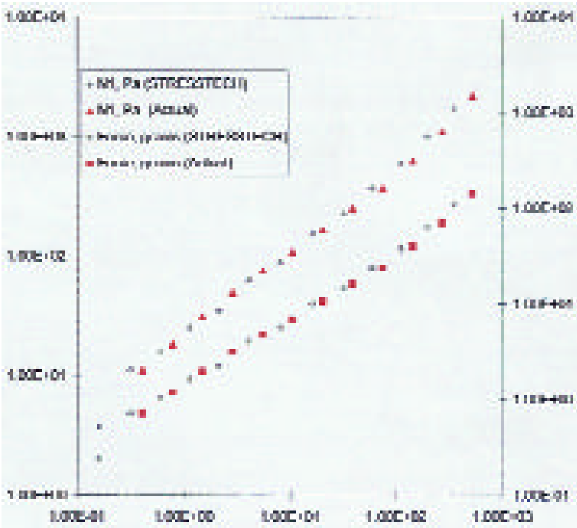

Figure 3 *Data on a normal stress standard of 2% polyisobutylene in cis- and trans-decaline.*

Influence of elasticity

Elasticity in polymers is controlled by molecular structure, most notably molecular weight, molecular weight distribution, and cross-linking/branching. This elastic contribution is most often manifested in melt fracture or shark skin on an extruded part. Many times, two materials with the same MI will process differently due to variations in the viscous and elastic nature of the sample. Since plastic materials have a fading memory, the processing conditions will impart shear history to the sample and, depending on the time scale of the process versus the relaxation time in the sample, this history can result in a nonuniform product. In order to fully understand the properties of a given polymer, accurate measurement of elasticity is required. This can be accomplished with a variety of experiments, most notably 1st Normal Stress measurements, where a sample is sheared between an upper cone and a lower flat plate of known dimensions. This shearing force results in an inward flow in the sample, causing a force perpendicular to the flow field to develop. A quantitative measure of this perpendicular or normal force gives a direct measure of the elastic component of the sample. Data on a normal stress standard (2% polyisobutylene in cis- and trans-decaline) are shown in *Figure 3*.

Solid-state mechanical properties

Proper selection of a plastic for a desired part is a basic requirement. Unfortunately, the final product may not possess the properties the plastic is expected to impart to the product. Variations due to molding conditions, mold design, temperature, and pressure have a dramatic influence on the properties of the final product. Impact properties, dimensional stability, and surface properties are most often effected.

Depending on the viscoelastic properties of the polymer, the final product may be heterogeneous in terms of mechanical strain within the sample. These strained domains will change with time and cause additional variations in the part. Dynamic mechanical analysis

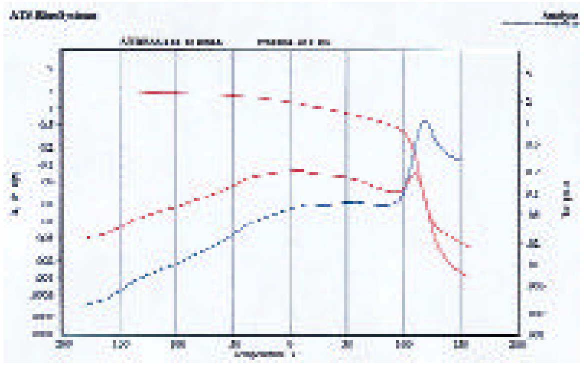

Figure 4 *Data on PMMA.*

(DMA) made over a wide range of time and temperature can provide a fingerprint of the molecular relaxations and ultimate properties in the part. Data on polymethymethacrylate (PMMA) are shown in *Figure 4*. The sample was evaluated over the temperature range –180 to 200 °C, and the resulting shear modulus (G', G") and damping (tan delta) are plotted versus temperature at a frequency of 1 Hz. PMMA shows two pronounced transitions, the first at 0 °C and the second at 100 °C. The latter is the glass transition temperature (Tg), where the material undergoes large-scale, main-chain motion. Below Tg, main-chain motion is frozen out and only side-chain motion and main-chain vibration are possible.

PMMA is known as a plastic with excellent impact resistance. This physical property is due to the material's ability to absorb and dissipate impact energy. PMMA has a well-defined secondary transition (beta relaxation mechanism), as evidenced by the maximum in G" at 0 °C. The value of G" is a measure of the energy-absorbing capability in the sample. Materials with large secondary transitions located at temperatures below the end-use temperature will possess superior impact energy to those without such a relaxation mechanism. Many times, a second component, an impact modifier, is added to a polymer to enhance the impact properties. This impact modifier has a transition below the end-use temperature of the material and provides the desired impact properties.

System setup

STRESSTECH is a modular product with a range of measuring systems and accessories. Measuring systems are available as concentric cylinders, cone/plate, parallel plate, double concentric cylinders, closed/pressure cells, and DMA. Special measuring systems for low-volume, high shear rates, and high sensitivity are also available. The measuring geometries can be made in stainless steel, titanium, polycarbonate, or any user-defined material. The instrument comes standard with a patented Differential Pressure Quantitative Normal Force sensor for reproducible sample-loading history, thermal expansion measurements, and Quantitative Normal Stress measurements. The diffusion air bearing has a low inertia with high axial and radial mechanical stiffness. STRESSTECH HR, a high-resolution version of the instrument, allows measurements at nanoradian displacement and nano Newton meter applied torques.

Electronic unit

The instrument's electronics are contained within the mechanical unit, and the instrument is built around a dedicated, high-speed 32-bit central processing unit (CPU). This consolidation enhances performance and versatility due to electrical connections using a high-speed bus rather than through cables to a separate electronics cabinet. In addition, bench space is kept to a minimum. The motor control is based on digital, rather than analog, drive technology. The unit comes with a built-in diagnostic system and quick diagnostic service port for service engineers. Also included is a modem port for remote control operation and fault diagnostics for service. The power supply is designed to operate on a line voltage from 180 to 260 V or 90 to 140 V and an operating frequency between 47 and 63 Hz.

Software package

The standard software package is a Microsoft® Windows™ (**Microsoft Corp.,** Bellevue, WA) based rheological software. The computer is not dedicated only to running the instrument, but is available for use when making measurements. It can be used for printing previous results, writing a report, or performing measurements with another instrument. The software runs under both Windows 3.1 and Windows 95 (**Microsoft Corp.**).

The standard package offers measuring programs designed to be user friendly with few subdialogue levels and a recognizable design. Experiment method and analysis are available in the following test modes: viscometry, yield stress, constant rate, oscillation, oscillation stress sweep, oscillation strain control, creep/recovery, compare, analyze, time-temperature superposition, and spectrum transformation.

The software can link to user-designed methods including instrument setup and zero gapping using the Windows Recorder (**Microsoft Corp.**) icon and STRESSTECH's Project Software. The dialogue windows have many storable, editable functions for testing requirements, and can be reset to default values using default buttons. An example is the Oscillation Frequency Step measuring program, where stresses, delay times, integration periods, and sample sizes can be set individually for all frequencies. Another example is the zooming function, which is presented both in the Viscometry Stress step and Oscillation Frequency step allowing any number of steps and increments to be selected. The instrument also performs controlled strain and constant shear-rate measurements, and comes with automatic gap adjustments and compensation using the Normal Force sensor. The system enhances measurement reproducibility since the sample loading history is reproduced identically each time using a constant-loading force.