

Rheology of developing network systems: New techniques, capabilities, and instruments

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Rheology is the branch of science that deals with the flow and deformation of materials. Rheological instrumentation and rheological measurements have become essential tools in the analytical laboratory for characterizing component materials and final products, monitoring process conditions, and predicting product performance and consumer acceptance.

Rheologically speaking, developing network systems (DNS) materials can range from low-viscosity radiation curable monomers to more viscous two-component and thermally curable fluids and gels to

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hard, vitrified materials. Knowledge of the rheological and mechanical properties of these varied systems is important in the design and optimization of flow processes for production and quality control, in predicting storage and stability conditions, and in understanding and designing the required materials mechanical properties.

Rheological behavior is associated directly with performance qualities such as comfort in the case of hydrogel contact lenses, cure time in the case of quick-set epoxy adhesives, and ultimate mechanical strength in the case of structural polymers.

Today, rheological instrumentation and rheometry are accepted techniques that are used to more fully characterize, understand, and control the production and use of DNS materials. The way in which a particular chemical structure is studied or analyzed, the techniques and instrumentation involved, and

the manner in which they may be used or modified to solve a problem are paramount.

Importance of rheology

In the case of photoinitiated DNS materials, the time-temperature-intensity transformation profile (TTIT) is the controlling rheological parameter. Following the work by Gilham and Enns in developing the use of the time-temperature-transition (TTT) diagrams, the TTIT profile accounts for photoinitiated reactions and, like TTT, is analogous to the phase diagrams used by metallurgists. The TTIT diagram is used to track the effect of temperature, time, and intensity on the physical state of a DNS material. Understanding and predicting the kinetics of these materials is of practical interest both in the manufacturing process and in end-product performance and reliability.

Although there have been many studies on kinetics of DNS materials, most have focused on the method of calorimetry, such as differential scanning calorimetry (DSC) or differential thermal analysis (DTA). In those studies, the definition of the state of cure is not directly correlated to the physical, mechanical, or rheological properties of the material. Conversely, kinetic methods from rheometry are able to predict properties, such as viscosity and dynamic modulus, which are used to determine manufacturing operations and end-product performance of DNS materials.

The kinetics are determined from time-dependent dynamic mechanical response using classical network elasticity theory to relate the measured viscoelastic properties to gelation and vitrification as a function of time, temperature, intensity, etc. DNS materials reactions can be classified into those that involve the loss of one molecular species, those that join monomers together without changes in the repeat structure, those that join intermediate molecular weight polymers together (crosslinking), and condensation reactions.

Rheological characterization of DNS materials requires several unique instrument capabilities: 1) wide torque, angular displacement, and temperature ranges; 2) data collection rates in excess of 10 sample data points/sec; 3) adjustment for sample volume changes during gelation; and 4) ability to monitor the properties of samples that start out as low-viscosity liquids and proceed to become hard solids.



Figure 1 DYNALYSER complete rheological characterization system.

Rheological instrumentation

In principle, the curing process can easily be followed by using dynamic mechanical rheological measurements as the buildup of a three-dimensional network is reflected in the change of viscoelastic properties. Today, rheological instrumentation is considered a required analytical tool by scientists and is used on a daily basis. These research-grade instruments are **Microsoft** (Redmond, WA) Windows™-based, and measurements are made quickly and easily with the use of straightforward, user-friendly software. The operator simply loads the sample into the instrument and selects the appropriate experimental conditions; the instrument does the rest.

DNS materials can be single-component or complex mixtures of different materials in which individual components are mixed together to produce a desired reaction profile and/or finished product. Many times, they are not homogeneous, and the properties vary throughout the sample. Traditionally, single-point viscosity tests have been performed using empirical techniques. These simple viscosity experiments compress the complex viscoelastic response of a sample into a single parameter, and are not adequate for characterizing or providing insight into the TTIT of DNS materials. The materials in use today are slated for high-performance applications and, as a result, the cost of these materials is high. Detailed knowledge and an objective, reproducible, multi-point measurement capable of decomposing the rheological behavior into individual components are necessary. Both the DYNALYSER complete rheological characterization system and the STRESSTECH rheometer (**ATS RheoSystems /REOLOGICA Instruments** [Bordentown, NJ, and North Hollywood, CA]) used in this study provide all of the required instrument features and capabilities.



Figure 2 STRESSTECH rheometer.

The DYNALYSER (Figure 1) and STRESSTECH (Figure 2) are research-grade analytical instruments capable of measuring viscous, elastic, and viscoelastic properties of liquids, gels, and solids. Both instruments were developed for use by the serious rheologist, and provide a very broad measurement range, spanning low-viscosity samples such as UV curable monomers to more viscous products such as two-component epoxy systems, gels, and prepreps through rigid, solid-state samples.

The rheometers incorporate the following features: wide torque, shear stress, temperature, shear rate, and frequency ranges; true Windows-based operational software; patented Differential Pressure Normal Force Sensor; patented Sealed Cell measuring system for testing samples above their boiling point; automatic gap setting; remote diagnostics capability via modem; and automatic inertia compensation. In addition, all **ATS RheoSystems** rheometers are designed on a modular platform to allow easy upgradeability. A wide range of accessories satisfy the most demanding applications with ease of operation.

Temperature control and profiling

Temperature is one of the critical, controlling parameters for DNS materials. The study of DNS materials requires precise control of sample temperature and/or sample temperature profiling. Research rheometers utilize various temperature control systems in order to achieve the desired stability, range, and transient rates. **ATS RheoSystems/REOLOGICA Instruments** developed the Joule-Thomson Effect principle for their Extended Temperature Cells (ETC). This approach was selected over other typical designs such as the thermoelectric (Peltier) approach and forced-air convection furnace method employed by other commercial rheometers for several important reasons: 1) wide, continuous temperature range; 2) high transient rates without the use of LN₂ or an external circulator; and 3) minimal temperature gradients in the sample.

Figure 3 shows typical heating and cooling profiles for the ETC system in the temperature range 25–150 °C. The maximum system transient rate is better than 20 °C/min for both heating and cooling.

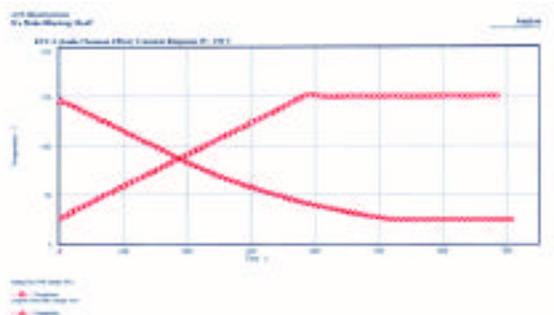


Figure 3 ETC-3 temperature cell transient response.

Normally, when studying DNS materials, transient rates in excess of 5 °C/min are not employed due to sample thermal inertia. However, fast transient rates are useful for preconditioning the sample and for faster test setup and cleanup.

Figure 3 shows that the ETC control loop is critically damped, producing minimum overshoot, while maintaining stability of ± 0.1 °C. In addition, with the use of the upper, independently heated and controlled clamshell furnace, sample temperature gradients are better than ± 0.1 °C.

Fast oscillation data analysis

Traditionally, when performing viscoelastic measurements, proper data analysis would require the rheometer to collect data over at least one complete period of oscillation. Therefore, the fastest theoretical data rate in samples/sec (minimum time for each data point) would be equal to the frequency in Hz. However, sampling and calculation delays limit the practical data rate to a much lower value. For many DNS materials, especially radiation curable DNS materials where the events of interest occur with 10 sec of illumination, this data collection rate is too slow to capture the TTIT cure profile. For this reason, a data collection and analysis package called Fast Oscillation (ATS RheoSystems/REOLOGICA Instruments) was developed.

The Fast Oscillation program is used to measure rapid, transient changes in a material. Based on the oscillation program, it works under the same principle where a sinusoidally varying forcing function is applied to the sample and the equally varying sample response is measured. The measured values are evaluated by one of several sampling methods selected by the user. The number of measurement points to be measured and presented can be set by the user, allowing data collection rates greater than 50 points/sec.

The program also includes the ability to control the shutter of a remote light source. The Relay Setting allows the user to set the intervals during which the light source shutter is turned on and off.

User-selectable and quantitative, controlled axial normal force control

The cure of DNS materials typically results in shrinkage of as much as 10–15%. If the measure-

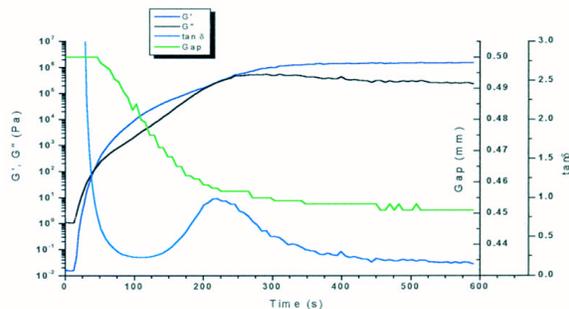


Figure 4 UV cure profile utilizing Expert Condition Normal Force gap compensation.

ments are made with the gap at a constant setting, the shrinkage of the materials results in large internal stresses during the cure after gelation. The software that handles this situation allows the operator to change from a controlled gap setting mode to autotension mode (in which the axial normal force is controlled) at a user-selectable point or event. For measurements in the liquid state, the gap setting needs to be set at a constant value, but by the time the gel point is reached, the shear modulus has increased sufficiently for the sample to maintain its shape. Although shrinkage occurs throughout the chemical reaction, internal stresses will develop only after gelation occurs. As soon as the gel point is reached (i.e., $\tan \delta = 1$), the instrument changes to autotension mode and maintains the normal force at zero during the remainder of the cure cycle. The shrinkage can be monitored quantitatively using the gap measurements.

An example of an experiment run under these conditions is shown in Figure 4. A mixture consisting of 2-hydroxyethyl methacrylate, a small amount of ethylene glycol dimethacrylate crosslinker, and a photoinitiator in an inert solvent is cured photochemically between the 25-mm-diam plates of the rheometer equipped with the UV cell. Initially, the gap is set at 0.5 mm. The viscosity (η^*) and the moduli (G' and G''), measured at a frequency of 2 Hz and an oscillatory stress that was preprogrammed to increase from 25 to 2000 Pa during the experiment, rise rapidly after the shutter is opened, while $\tan \delta (= G''/G')$ drops from infinity ($G' = 0$ in the initial liquid state). When $\tan \delta$ drops below 1, the autotension mode is employed, and the reduction in the gap can be monitored during the remainder of the cure.

Without this adjustment to reduce the internal stresses, the measurement of the rheological properties in the solid state may be compromised by artifacts due to the delamination of the sample from the plate or the formation of voids in the sample.

Two-component epoxy system

Two-component epoxies find utility in a wide variety of applications. Normally, these DNS materials are crosslinked by adding equal amounts of resin and hardener. Of interest is the gelation time or workable time of the material. Introducing heat into this system acceler-

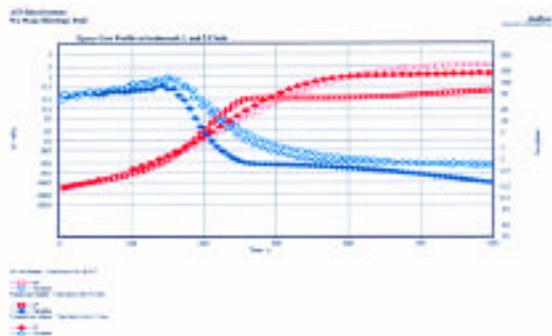


Figure 5 Two-component epoxy cure profiles as a function of heating rate.

ates the reaction, decreasing the workable time, thus speeding up the set time. Viscoelastic kinetic properties are monitored as a function of isothermal and nonisothermal cure conditions. The rheological properties measured are G , the shear modulus; η , the shear viscosity; and phase lag, $\tan \delta$ (G''/G').

Typical results for a commercial two-component, quick-set epoxy system are shown in *Figure 5*, where G^* is plotted versus cure time for both isothermal (25 °C) and nonisothermal conditions of 1 and 5 °C/min. The results were run at a frequency of 2 Hz and a command oscillatory stress of 1000 Pa. At a frequency of 2 Hz, the fastest theoretical data rate would be 2 points/sec, although the actual sampling rate is slower due to data collection and calculation time lags.

The data show the shear storage modulus (G^*) and $\tan \delta$ as a function of time (sec). G^* displays the typical S-shaped curve, while $\tan \delta$ goes through a maximum and then decreases to a small constant value. Initially, the sample is a low viscosity liquid of low mechanical stiffness, having little or no elasticity. The onset of crosslinking is reflected by the increase in G^* and decrease in $\tan \delta$. The initial increase in $\tan \delta$ is attributed to loosening of the sample's preliminary network from internal heat buildup. For stoichiometrically balanced DNS materials, $\tan \delta = 1$ coincides with the gel point (GP) measured with the traditional hotplate test.

This result indicates that the cure time decreases as a function of heating rate. Since nonisothermal cure is of practical importance in cure control, the nonisothermal cure curves can be obtained by programming heating at different heating rates. As the curing reaction reaches completion, the storage modulus approaches a constant value.

Another common use of rheometry for DNS materials is the study of the mechanical properties after cure. Dynamic mechanical analysis (DMA) in both torsion and tension modes provides the user information on the thermally induced relaxation transitions and corresponding mechanical stiffness of a DNS material. Experimentally, the challenges rheologically speaking are temperature accuracy and thermal control, the compensation for thermal expansion of the sample, and the alleviation of any molded-in stresses in the test specimen. The DYNALYSER and STRESSTECH rheometers, utilizing the Dif-

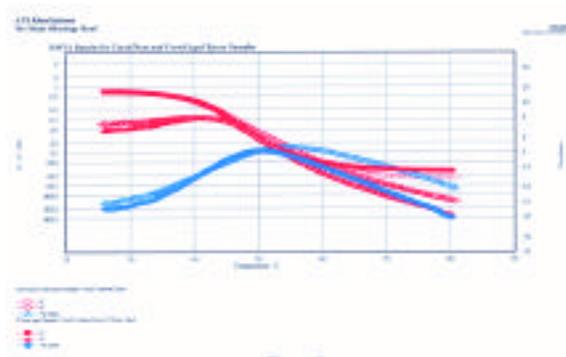


Figure 6 Mechanical properties of neat and annealed cured epoxy sample.

ferential Pressure Quantitative Normal Force Sensor, allow for continuous monitoring and adjustment of the sample's thermal expansion.

Figure 6 illustrates a typical plot of the storage modulus (G'), the loss modulus (G''), and $\tan \delta$ versus temperature for a neat and aged isothermal cured epoxy material. The aged epoxy material was conditioned at 100 °C for 24 hr. The samples for DMA torsional analysis are rectangular with dimensions of 25 mm length, 10 mm width, and 2 mm thickness.

The results show a peak in $\tan \delta$ around 55 °C, which indicates the glass transition, T_g . The transition of the neat material is broader than the aged material. Conditioning of the sample at 100 °C for 24 hr allows the curing reaction to continue slowly, narrowing the distribution of chain length between crosslinks, reducing the free volume between monomer units, and relieving molded-in stresses. As a result, the transition peak is sharper. Below T_g , the values of G' are similar, as expected. Most materials possess stiffness of 1 GPa in the glassy region. Above T_g , the aged material shows a lower value of G' , as a result of less internal stress in the sample. The value of G' in this rubbery region can be directly related to crosslink density.

Glass transitions have been studied by other analytical techniques such as DSC and thermal mechanical analysis (TMA). However, many times the transitions of interest are much less pronounced. Particularly, T_g of crosslinked and semicrystalline materials is often difficult to measure by DSC or TMA.

Thermally reversible DNS materials

The gelation behavior of an aqueous system has been studied using the Sealed Cell measuring system. First, a dynamic oscillatory temperature scan was performed from 30 to 120 °C at a heating rate of 5 °C/min and a frequency of 0.2 Hz (*Figure 7*). The results indicate that the sample possesses a low viscosity of 70 mPa sec at room temperature, and gelation starts at a temperature around 63 °C, as shown by the increase in viscoelastic properties. The reaction continues as a function of temperature and time, and the end result is a thick, gel-like consistency sample at a temperature of 120 °C. Of particular interest are the results above 100 °C, where the data indicate that the properties of

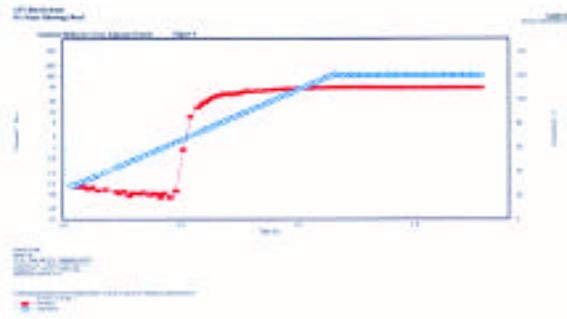


Figure 7 Cure behavior of an aqueous system at 120 °C with the Sealed Cell.

the gelled system are stable. The integrity of the data is maintained well above the boiling point of water.

The Sealed Cell measuring system (*Figure 8*) was designed to be application-specific for the measurement of viscoelastic rheological properties (G' , G'' , $\tan \delta$) of solutions above their boiling point. This measuring system, used in conjunction with either the DYNALYSER or STRESSTECH, allows measurements under pressure with full dynamic oscillation and viscometric capability. The cell employs a noncontacting, air-bearing seal rather than standard O-rings. The air-bearing seal is effectively frictionless, and permits dynamic oscillatory testing throughout the frequency range of the instrument. Aqueous samples and solvent-based systems can be measured above their boiling point. No other device can obtain dynamic oscillatory results, especially on low-viscosity samples, above the sample's boiling point, due to the mechanical friction limitation of the cell's seals and bearings.

Rheometer system setup

The DYNALYSER and STRESSTECH rheometers are designed for testing any rheological significant material: thermoplastics, thermosets, elastomers, semi-solids, and fluids systems. The modular research rheometers have a wide range of measuring systems and accessories. Measuring systems are available as concentric cylinders, cone/plate, parallel plate, double concentric cylinders, sealed/pressure cells, and dynamic mechanical analysis (DMA) of rods, bars, fibers, and films. 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 instruments are supplied standard with the 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.

The rheometers operate with a separate power supply unit that should be left on continuously. This reduces startup time and makes it possible for the instrument processor to maintain values for gap and other user-defined settings.



Figure 8 Sealed Cell measuring system.

STRESSTECH HR, a high-resolution (HR) version of the STRESSTECH rheometer, allows measurements at microradian displacement and extremely low applied torque. The STRESSTECH rheometer equipped with HR increases the performance specifications to the DYNALYSER level.

Temperature control cells are available using circulating fluid, Joule-Thomson Effect, and cryogenic covering the range -180 to 500 °C. All measuring geometries are supported, i.e., cone/plate/parallel plate, concentric cylinder, and solids in torsion and tension. Several high-pressure cells with an upper range of 5800 psig are offered.

Rheometer electronic unit

The rheometer's electronic components 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 on the motherboard bus rather than through cables to a separate electronics cabinet. In addition, valuable 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 electronics power supply is designed to operate on a line voltage between 180 and 260 V or 90 and 140 V, and an operating frequency between 47 and 63 Hz.

Software package

RheoExplorer 5.0 software (**ATS Rheosystems**) is based on the Windows operating platform and runs under Windows NT, 98, or 2000. The standard software package is a true multitasking interface with selectable user levels, thus providing many advantages to the scientist. It is designed to provide flexibility for configuring and using the rheology system. The computer is not dedicated to simply running the instrument, and is available for other uses when making measurements. The computer can be used for printing

previous results, writing a report, or performing measurements with another instrument.

The software enables a normal PC to be used as the interface to allow the user to control the instrument and then collect and analyze the resulting data. Viscometry, oscillation under stress and strain control, stress relaxation, creep and recovery, constant rate, yield stress, fast oscillation, process control, project (multiexperiment linking), time-temperature superposition, and spectrum transformation packages allow the sample to be analyzed via different rheological procedures. Powerful data analysis capability allows model fitting, graph and table customization, and cut/paste operation to all other Windows-based software.

The software includes possibilities to link user-designed methods, including instrument setup and zero gapping using the project software. The dialogue windows have many storable, editable functions for unique testing requirements, and can be reset to default values using default buttons. An example is the Oscillation Frequency Step measuring program, in which stresses, delay times, integration periods, and sample sizes may be set individually for all frequencies. Another example is the zooming function, which is present in both 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 is supplied with automatic gap adjustments and thermal expansion compensation using the Differential Pressure Quantitative Normal Force Sensor. The system enhances measurement reproducibility since the sample loading history is reproduced identically each time.

Rheometers for any user level, application, and budget

VISCOANALYSER (ATS RheoSystems/REOLOG - ICA Instruments), an entry-level research rheometer system, is fully upgradeable to a STRESSTECH unit as the user's needs and requirements dictate. DSR QC (ATS RheoSystems/REOLOGICA Instruments) (Figure 9) is an economical dynamic shear rheometer (DSR) designed to be applications-specific for routine viscoelastic measurements in the QC laboratory.

The rheometers are produced according to ISO 9001 and are tested to operate according to the electromagnetic compatibility rules within the European Community. The instruments are tested to be labeled with the CE-mark.

Conclusion

The important rheological characteristics and results generated with both a DYNALYSER and STRESSTECH rheometer on several different DNS materials have been presented. A detailed interpretation of data and correla-



Figure 9 DSR QC dynamic shear rheometer.

tion of the rheological response with the physical/chemical properties of different DNS materials was given. The rheological characterization of DNS materials provides important information for engineers and scientists to improve and optimize their products and manufacturing processes. Today, most researchers and manufacturers rely on rheological measurements to develop customer-favored products with a competitive edge in the marketplace. A reliable research-level rheometer and a thorough understanding of rheological measurements is now a necessity for success in the marketplace.

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