Real Time UV-Cure Profiling, Shrinkage Determination, and Post Cure Dynamic Mechanical Analysis
of Developing Network Systems

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R heology is the branch of science dealing with the flow and deformation of materials. Rheological instrumentation and rheological measurements have become essential tools in the analytical laboratories for characterizing component materials and final products, monitoring process conditions, as well as predicting product performance and consumer acceptance.

Rheological behavior is directly associated with performance qualities such as comfort in the case of contact lenses, cure time in the case of fiber optic coatings and inks, and ultimate mechanical strength in the case of structural polymers.

Rheologically speaking, developing network systems (DNS) can range from low-viscosity, radiation-curable monomers to more viscous two-component and thermally curable fluids and gels, up to hard-vitrified materials. A 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 material mechanical properties.

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Today, rheological instrumentation and rheometry are accepted techniques used to more fully characterize, understand, and control the production and use of DNS materials. How a particular chemical structure is studied or analyzed, the techniques and instrumentation involved, and how these may be used or modified to solve a problem are paramount in understanding the material-structure-processing relationships.

Importance of Acceptable Rheology

In the case of photoinitiated DNS materials, the time-temperature-intensity transformation profile (TTIT) is the controlling rheological parameter. Following the work by Gillham and Enns[1] 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
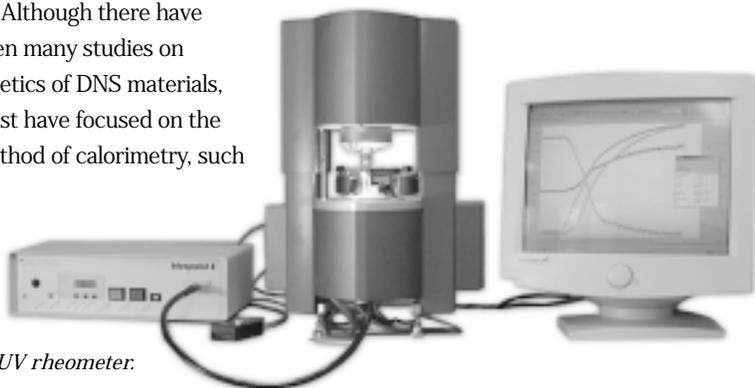
A UV rheometer.

as differential scanning (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 reactions can be classified into those that involve the loss of one molecular species, those that join "mers" together without change in the repeat structure, those that join intermediate molecular weight polymers together (crosslinking) and condensation reactions.

Rheological characterization of fast-cure DNS materials requires several unique instrument capabilities:
- Data collection rates in excess of 10 sample data points/s.
- Adjustment for sample volume changes during gelation.
- Wide torque, angular displacement, and temperature ranges.
- Ability to follow samples starting out as low-viscosity liquids and proceeding to hard solids.

Rheological Instrumentation

In principle, using dynamic mechanical rheological measurements can easily follow the curing process, as the build-up of a 3-D 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 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 experiment, and the instrument does the rest.

DNS can be single component or complex mixtures of different materials where 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 in characterizing and/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 for these materials is high. Detailed knowledge and an objective, reproducible, multi-point measurement capable of decomposing the rheological behavior into individual components is necessary.

A rheometer equipped with optional UV cell and source allows for user selectable illumination and exposure time and intensity. In addition, the environment around the sample and temperature can be controlled.

Fast Oscillation Data Analysis

Historically, rheological oscillation data acquisition consisted of sampling one or more periods and then deriving the real and complex components of the sample response from the measured waves utilizing an FFT. The minimum requirement of a single complete wave cycle has limited the utility of dynamic oscillation to capture very fast changes in material structure such as those that are encountered in UV curing, where the sample may change from a low-viscosity liquid to a solid in a few seconds. The fastest theoretical data rate in samples/ seconds (minimum time for each data point) would be equal to the frequency in Hz. For many DNS materials, especially radiation-curable DNSs where the events of interest occur within two seconds of illumination, this data collection rate is too slow to capture the TTIT transient cure profile.

Figure 1 shows a conventional oscillation data sampling sequence for a time sweep at 1.0 Hz (1 cycle/s). Points 1-25 will be acquired in one second from the start of the experiment and then processed to provide the first

FIGURE 1

Conventional oscillation data sampling
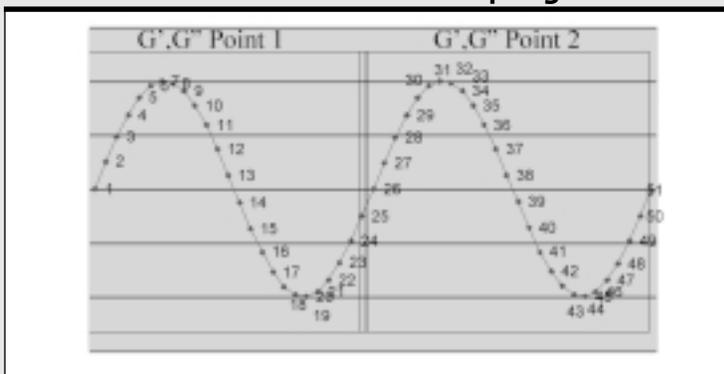
data point. Points 26-50 will be acquired and processed to provide the second data point, etc.

- Points 1-25 are sent to the CPU for FFT calculation requiring ~0.1 second.
- The actual FFT calculation takes between 1-4 seconds (actual time depends on number of points collected, 128 to 2048).
- The time between each data point result will be from 2-5 seconds.
- This data rate is exclusive of any other delay times, multiple iterations employed to reach a target strain for iterative strain control or auto-ranging.

In recent years, new techniques have been derived to obtain dynamic moduli (or compliance) using 1/4 or 1/2 wave analysis, with the benefit of faster data acquisition, albeit at some compromise in phase angle resolution. These partial wave techniques can improve the data rate by a factor of 2-4, but still suffer from the limitations listed above. These techniques still do not provide the data-sampling rate adequate for capturing the transient cure profile for rapid DNS materials. A new technique, called fast oscillation, has been developed for data acquisition that enables the user to acquire oscillation data at intervals as small as 1/100th of a period, with no loss in phase resolution.

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. Dynamic oscillatory data at constant frequency is collected as a single continuous stream of waves, then analyzed via FFT using a moving average (Figure 2). G' and G" are determined at the raw sampling rate of the analog wave, instead of the period of the oscillation. 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 100 points/seconds.

Figure 2 shows a fast oscillation data sampling sequence for a time sweep at 1.0 Hz (1 cycle/seconds).

- Points 1-25 acquired in one second and sent to FFT to generate first data point (same as standard oscillation program).
- Points 2-26 acquired in an additional 0.04 second and sent to FFT to generate second data point.
- Points 3-27 acquired in an additional 0.08 second and sent to FFT to generate third data point.
- The time between data points is 1/25=0.040 second.
- The data acquisition rate is 25 times faster than a standard oscillation program run at the same frequency.

The fast oscillation program also includes the ability to control the shutter of a remote light source. The "relay setting" dialog box allows the user to set the intervals during which the light source shutter is turned on and off. In addition, the user can elect to employ auto-tension to account for sample consolidation as a result of crosslinking.
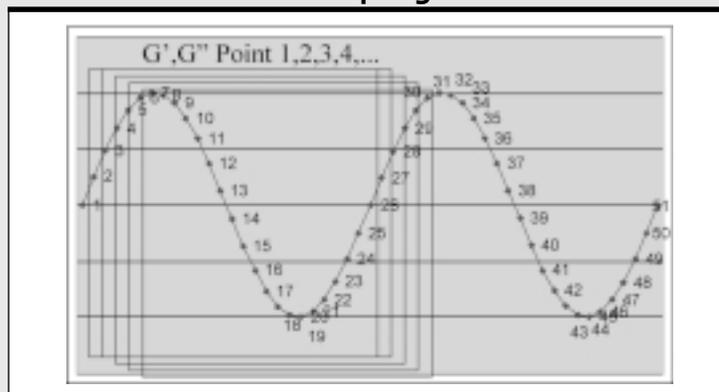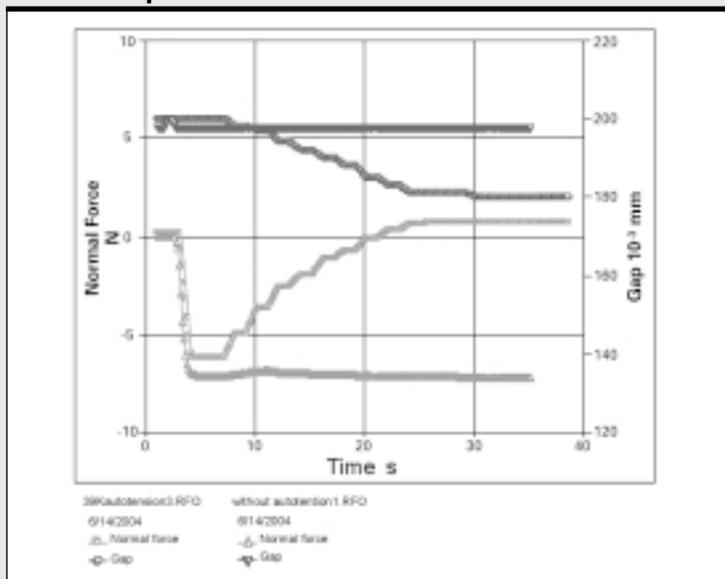
FIGURE 2

Fast oscillation data sampling

FIGURE 3

Fiber optic primary coating with photoinitiator cured photochemically between the 25-mm diameter plates of the rheometer

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Typical Fast Cure Profile of DNS Material

The cure of DNS materials typically results in shrinkage of 10-15%. If the measurements are made with the gap at a constant setting, the shrinkage of the materials will result in large internal stresses during the cure after gelation.

A rheometer and software have been developed to handle this shrinkage by allowing the operator to change from a controlled gap-setting mode to auto tension 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 must 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. Utilizing the

"expert condition" dialog selection, as soon as the gel point is reached (i.e., tan delta =1), the instrument changes to auto-tension mode and maintains the normal force at a user defined value

during the remainder of the cure cycle. The shrinkage can be monitored quantitatively using the gap measurements. The user can select the point at which to start controlling the applied "normal force" on the sample and, in addition, the point to terminate the experiment once the sample achieves full-cure based on its measured viscoelastic properties.

Shown in Figure 3 are data of a typical fiber optic primary coating with photoinitiator cured photochemically between the 25-mm diameter plates of the rheometer equipped with the UV cell run at a fixed gap of 0.2-mm compared to results with active normal force gap control set to value of 1.0 N. The data shows a significant buildup of tensile normal force (in excess of -7 N after UV exposure at two seconds). Active normal force gap control reduces the tensile normal force and equilibrates at the desired 1.0 N compressive normal force value.

An example of a real time UV-cure profile experiment run under these conditions is shown in Figure 4. Initially the gap is set at 0.2-mm.

FIGURE 4

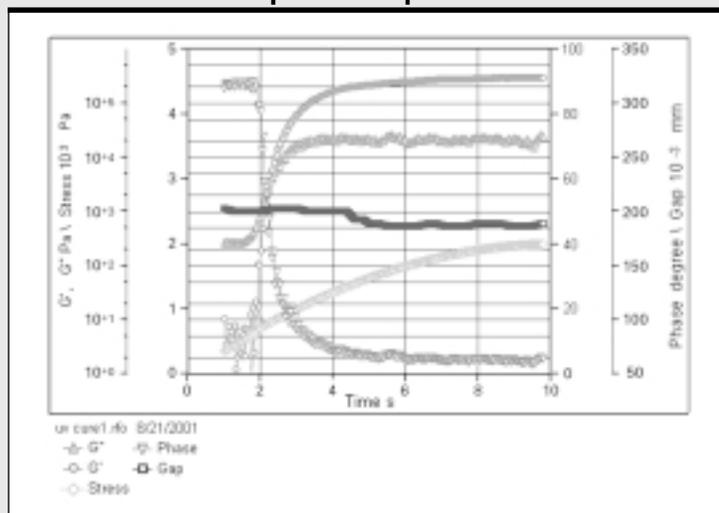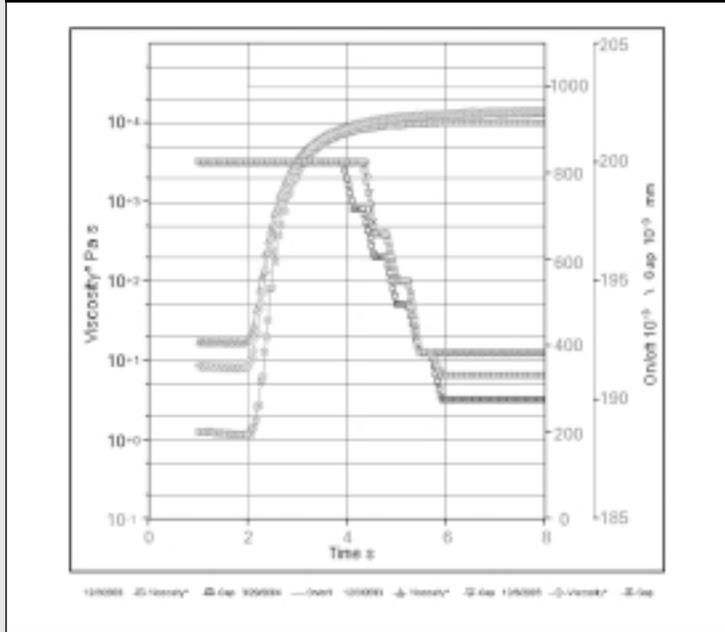**Real time UV-cure profile experiment**

FIGURE 5

Comparison of three typical fiber optic coatings with different monomer/oligomer concentrations

The dynamic shear moduli (G' and G") 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 one, the auto-tension mode is employed, and the reduction in the gap can be monitored during the remainder of the cure.

Without the 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.

Comparisons of three typical fiber optic coatings with different monomer/ oligomer concentrations are shown in Figure 5. Initially, the samples show a difference in pre-cure viscosity trending inversely with monomer concentration. On exposure, all three samples exhibit the traditional UV-cure profile with similar reactivity induction times. However, due to the large

differences in pre-cure viscosity, the time to reach a similar value of viscosity is dramatically different, and this would directly relate to differences in processing characteristics. After exposure, all three samples attain a similar plateau modulus indicating the crosslink density is similar. The shrinkage trends with pre-cure viscosity, i.e. the lowest viscosity sample with the highest monomer concentration exhibits the most shrinkage.

For many UV coatings the shrinkage due to crosslinking is the key parameter for end-use performance acceptance. As examples, organic dental fillings need to have the shrinkage optimized or the filling will delaminate from the tooth cavity wall. For common vinyl flooring, too much shrinkage will cause the tile to bend in a concave fashion after exposure. Figure 6 shows shrinkage data for a typical UV coating being measured by the normal force gap regulator at a frequency of 60Hz. Due to the speed of the UV reaction,

FIGURE 6

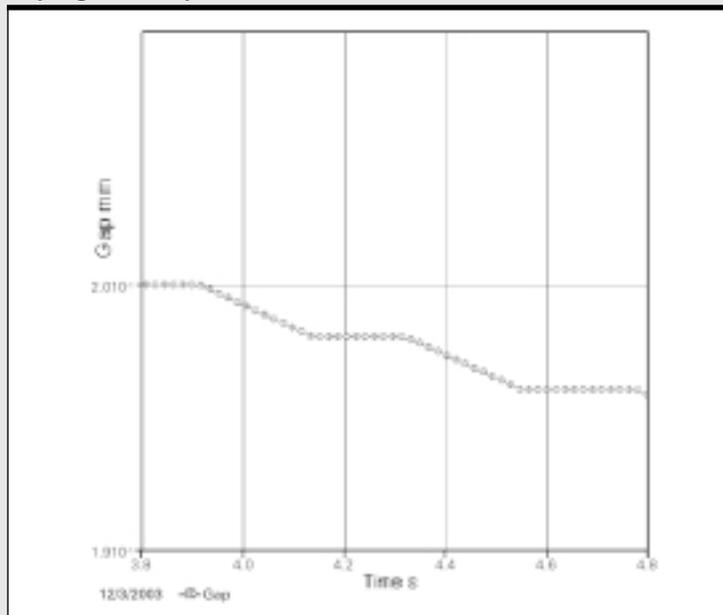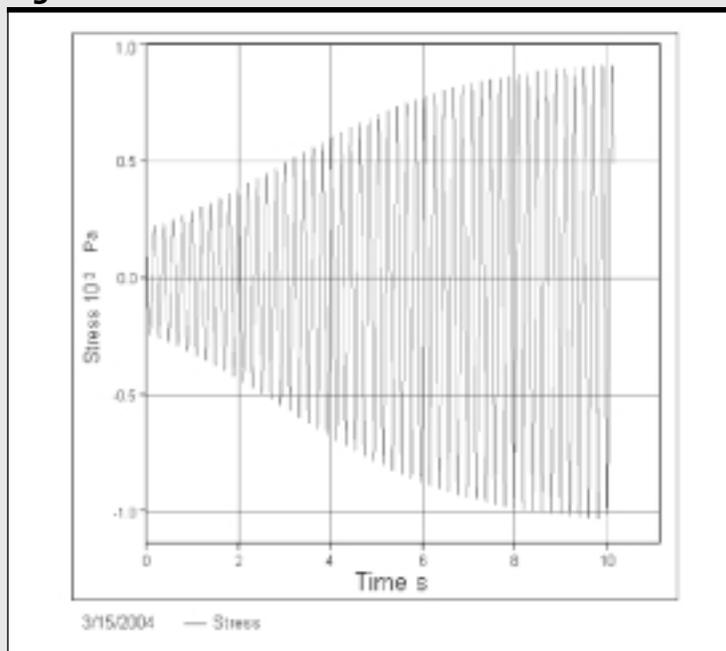### Shrinkage data for a typical UV coating
Gap regulation speed = 60 Hz

FIGURE 7

Sigmoidal waveform

3/15/2004 — Stress

profiles show a strong dependence on the temperature and the surrounding environment. Data run on a UV coating run at temperatures of 25°C and 85°C under a nitrogen blanket is shown in Figure 8 where viscosity is plotted vs. time. Illumination was turned on at 4.0 seconds. Following an Arrhenius relationship, the 85°C data shows approximately one decade lower pre-cure viscosity, 600 vs. 6,000 cps and the reaction kinetics are accelerated as is evident by the shortened induction time. The final value of viscosity is slightly higher for the 85°C sample, indicating an enhancement in the crosslink mechanism.

Exposure to oxygen during the curing process inhibits the generation of free radicals and results in a delayed cure profile. Many processes and thus the corresponding cure profile experiments are run under a purge gas blanket of nitrogen and this same

adjustment of the gap at this bandwidth is required for accurate cure profile and shrinkage determination.

Another important requirement for a fast-curing system is the ability to maintain the appropriate command strain throughout the cure profile. The rheometer software has the ability to model the cure profile by employing a constant, sigmodial or polynomial amplitude coefficient (Figure 7). This feature is essential in measuring materials that undergo several orders of magnitude change in modulus during cure. By utilizing these different amplitude profiles, the sample can be tracked from a low-viscosity fluid to hard-vitrified solid regardless of its beginning, intermediate and ending viscosity/modulus values.

Effect of Environment and Temperature on UV-Cure Profile

As with thermally cured DNS materials, UV DNS materials cure

FIGURE 8

Data on a UV coating run at temperatures of 25°C and 85°C under a nitrogen blanket

4/1/0002 .o. Viscosity'   4/1/0002 -o- Viscosity'
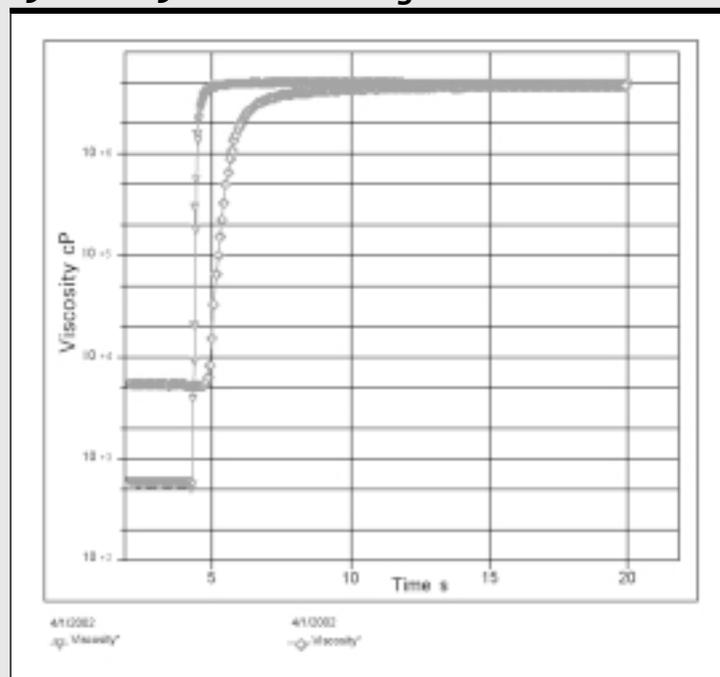
TABLE 1

Curable adhesive properties

Adhesive	Viscosity (cps @ 25°C)	Relative Hydrophobicity	Cured Tg (°C)
51325	355	1	21.5
51335	473	2	22.4
51345	593	3	27.6
51355	852	4	29.2

environment can be employed for the rheological cure analysis.[2]

Post-Cure Dynamical Mechanical Thermal Analysis

The dynamic mechanical properties of four laminating adhesives were determined using samples spiked with 1.0% photoinitiator. The samples were UV cured isothermally at room temperature with a constant frequency of 5 Hz. The cured samples were then characterized by Dynamic Mechanical Thermal Analysis (DMTA) as a function of temperature from 120°C to -10°C. Both UV-cure profile and DMTA experiments were performed on a STRESSTECH HR rheometer system.

The compositions of the adhesives were varied to include a range of hydrophobic and dynamic mechanical (DMTA) properties (Table 1).

Following UV curing, the DMTA properties of the adhesives were characterized as a function of temperature. A representative DMTA plot for the cured 51335 adhesive is shown in Figure 9. The glass transition tempera-ture (Tg) of the cured adhesives can be determined from the ratio (tan delta) of the loss (G") to storage (G') modulus. The tan delta curve for all four adhesives is shown in Figure 10. The peaks values (Tg) taken from the data are shown in Table 1.

### Real Time Rheological vs. IR Cure Profile Methods

Historically, real time IR has been employed to follow the cure of UV DNS materials. The IR technique follows the disappearance of double bonds in the sample and attempts to relate that to the build up of viscosity/modulus. This technique suffers from the fact that one is measuring a chemical response and trying to relate that to the sample's physical property response. It has been found that a significant percentage of double bonds are reacted before any change in viscosity is noted and typical time lags on the order of a few seconds are common.[3] If the control-ling process variable is the viscosity/modulus value, the time delay from the IR measurement is unacceptable in tuning the process control variables.

Conclusion

This article reviews the important rheological characteristics for real time light-curable materials and presents results generated with a rheometer on UV-curable fiber optic coatings and adhesives. In addition, a detailed interpretation of data and correlation of the rheological response with the physical/chemical properties of different DNS materials has been presented. 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 count on rheological measurements to predict/control process variables and develop

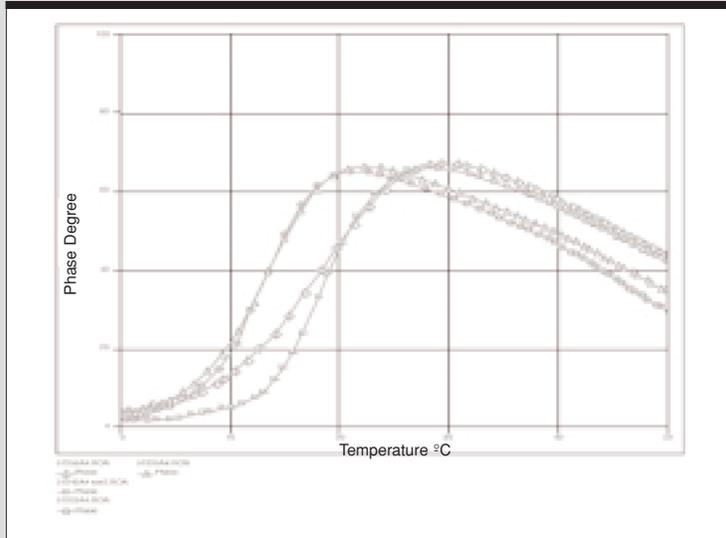## FIGURE 9

DMTA plot for cured 51335 adhesive
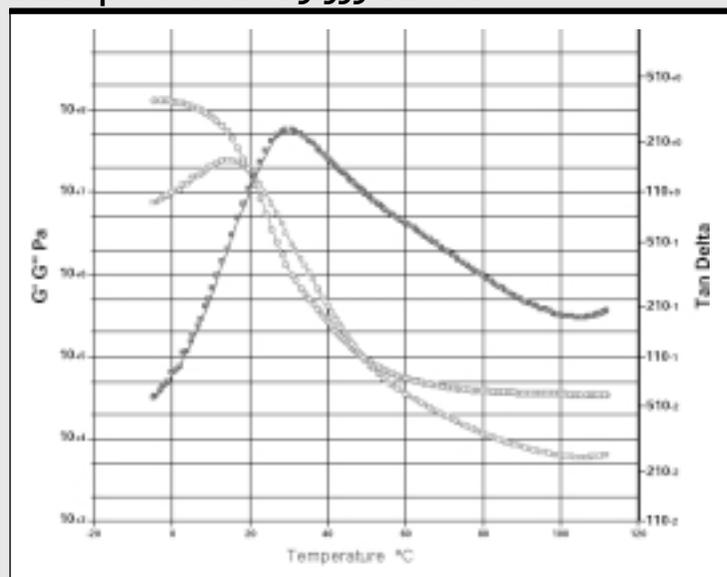
customer-favored products with a competitive edge. A reliable research level rheometer and a thorough understanding of rheological measurements is now a necessity for success in today's marketplace. ▶

FIGURE 10

Tan delta curve

References

1. J.K. Gillham and J.B. Enns, On the Cure and Properties of Thermosetting Polymers using TBA, TRIP Vol. 2, No. 12, Dec. 1994.

2. Personal discussions with Dr. Robert Johnson, DSM, May 2004.

3. K. Dake, How Fast Do Acrylates Cure, Adhesive Age, May 2002.