

# Fast Oscillation Rheological Data Analysis for Real-Time Cure Profiling and Shrinkage Determination of Developing Network Systems

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

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 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.

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.

Today, rheological instrumentation and rheometry are accepted techniques 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 (TTIT) profile is the controlling rheological parameter. Following the work by Gillham 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,



Figure 1 DYNALYSER, The Complete Rheological Characterization System.

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, that 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



Figure 2 STRESSTECH rheometer.

repeat structure, those that join intermediate molecular weight polymers together (cross-linking), and condensation reactions.

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

## Rheological instrumentation

In principle, the curing process can be easily followed by using dynamic mechanical rheological measurements, since 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 experiment, and the instrument does the rest.

DNS 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. Often 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, their cost is high. Detailed knowledge and an objective, reproducible, multipoint measurement capable of decomposing the rheological behavior into individual components is necessary. Both DYNALYSER, The Complete Rheological Characterization System, and the STRESSTECH rheometer (ATS RheoSystems/REOLOGICA Instruments, Bordentown, NJ) used in this study provide all of the required instrument features and capabilities.

The DYNALYSER (Figure 1) and the STRESSTECH HR (Figure 2) are research-grade analytical instruments capable of measuring the 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 preregs through rigid, solid-state samples.

The rheometers incorporate the following patented features: wide torque, shear stress, temperature, shear rate, and frequency range; true Windows-based operational software; patented Differential Pressure Quantitative 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, allowing easy upgradability. A wide range of accessories are available to satisfy demanding applications with ease of operation.

The STRESSTECH HR rheometer equipped with optional UV cell and light source is shown in Figure 3. The rheometer and integrated light source allow for user-selectable illumination and exposure time and intensity. In

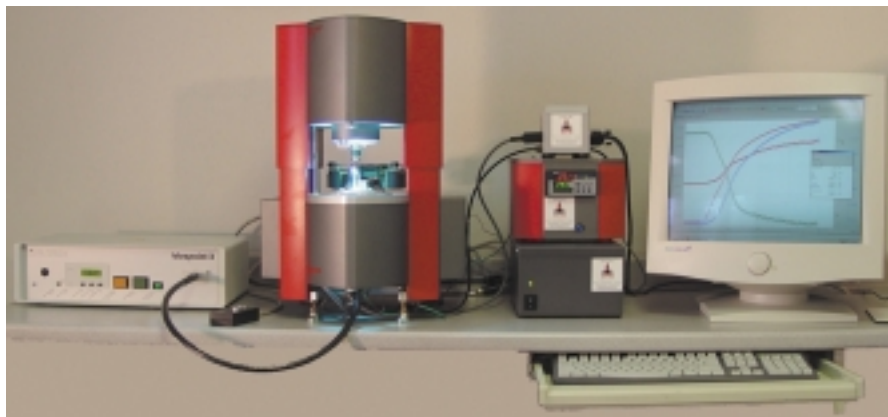


Figure 3 STRESSTECH HR with UV cure option.

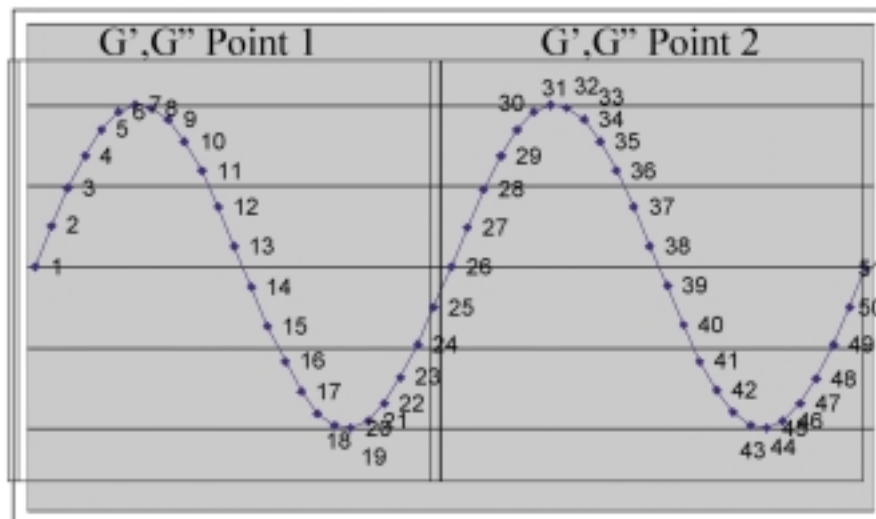


Figure 4 Standard oscillation result.

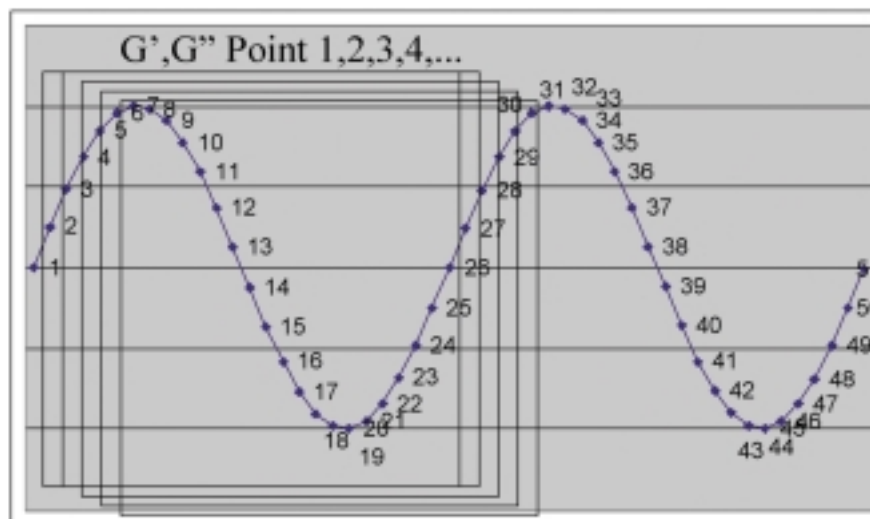


Figure 5 Fast Oscillation result.

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 a Fast Fourier Transform (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, in which the sample may change from a low-viscosity liquid to a solid in a few seconds. The fastest theoretical data rate in samples/sec (minimum time for each data point) would be equal to

the frequency in hertz. For many DNS materials, especially radiation-curable DNSs where the events of interest occur within 2 sec of illumination, this data collection rate is too slow to capture the TTIT transient cure profile.

Figure 4 shows a conventional oscillation data sampling sequence for a time sweep at 1.0 Hz (1 cycle/sec). Points 1–25 will be acquired in 1 sec from the start of the experiment and then processed to provide the first data point. Points 26–50 will be acquired and processed to provide the second data point, etc.

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

In recent years, new techniques have been developed to obtain dynamic moduli (or compliance) using quarter- or half-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. The techniques still do not provide the data sampling rate adequate for capturing the transient cure profile for rapid DNS materials. A technique called Fast Oscillation (REOLOGICA Instruments) 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, in which a sinusoidally varying forcing function is applied to the sample and the equally varying sample response is measured. Dynamic oscillatory data at constant frequency are collected as a single continuous stream of waves, then analyzed via FFT using a moving average (Figure 5).  $G'$  and  $G''$  are determined at the raw sampling rate of the analogue 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/sec.

Figure 5 shows a Fast Oscillation data sampling sequence for a time sweep at 1.0 Hz (1 cycle/

sec). Points 1–25 will be acquired in 1 sec from the start of the experiment and then processed to provide the first data point. Points 2–26 will be acquired and processed to provide the second data point, etc.

- Points 1–25 acquired in 1.0 sec and sent to FFT to generate first data point (same as standard oscillation program)
- Points 2–26 acquired in an additional 0.04 sec and sent to FFT to generate second data point
- Points 3–27 acquired in an additional 0.08 sec and sent to FFT to generate third data point
- The time between data points is  $\frac{1}{25} = 0.040$  sec
- 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 select to employ autotension to account for sample consolidation as a result of cross-linking.

### 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. The rheometer and software have been developed to handle this by allowing 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 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 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 6. A typical fiber-optic primary coating with photoinitiator is cured photochemically between the 25-mm-diam plates of the rheometer equipped with the UV cell. Initially, the gap is set at 0.2 mm. The dynamic shear moduli ( $G'$  and  $G''$ ) rise rapidly after the shutter is opened, while  $\tan \delta$

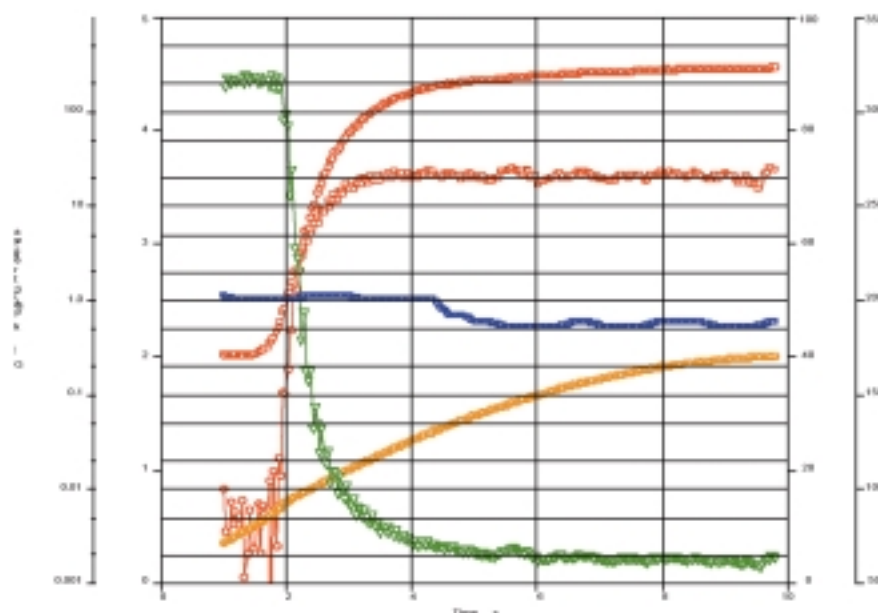


Figure 6 UV cure profile of fiber-optic coating using Fast Oscillation.

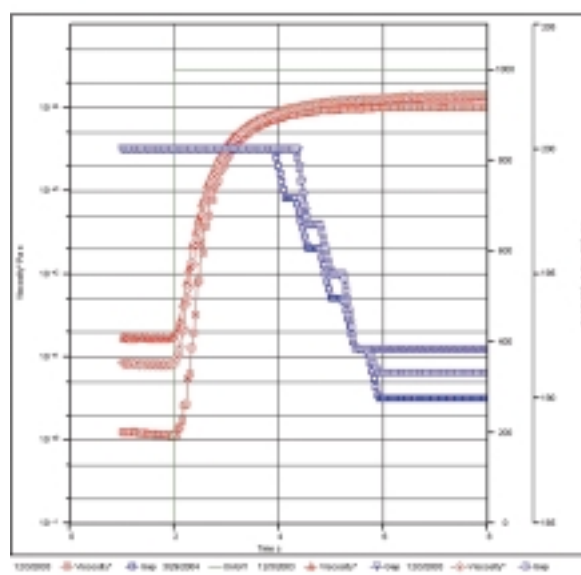


Figure 7 Comparison of three coatings.

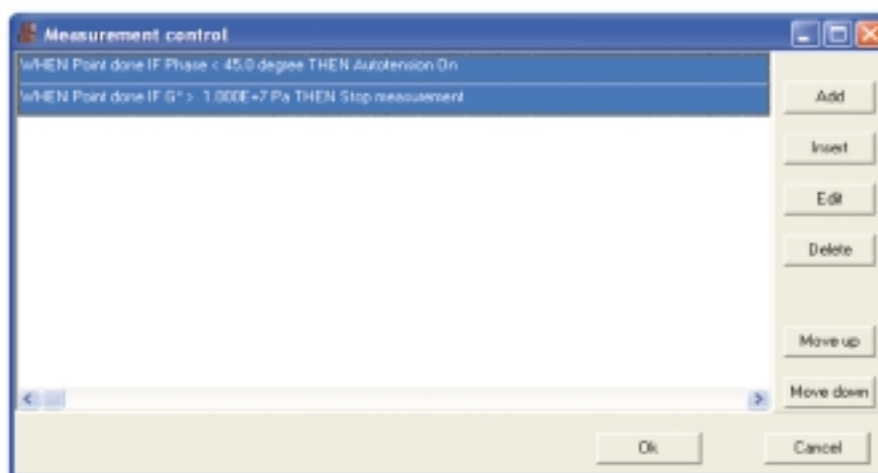


Figure 8 Expert Condition dialog box.

( $=G''/G'$ ) 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 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.

A comparison of three typical fiber-optic coatings at different monomer concentrations is shown in Figure 7. Initially, the samples show a difference in precure viscosity, trending inversely with monomer concentration. On exposure, all three samples exhibit the traditional UV cure profile with similar induction times. However, due to the large differences in precure 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 cross-link density is similar. The shrinkage trends with precure viscosity (i.e., the lowest-viscosity sample with the highest monomer concentration exhibits the most shrinkage).

An example of the Expert Condition dialog test parameter setup is shown in Figure 8. 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.

Another important requirement for a fast curing system is the ability to maintain the appropriate strain throughout the cure profile. The rheometer software has the ability to model the cure profile by employing either a constant, sigmoidal, or polynomial forcing function (Figure 9). This feature is essential in measuring materials that undergo several orders of magnitude change in modulus during cure. By utilizing these different stress profiles, the sample can be tracked from a low-viscosity fluid to a hard, vitrified solid regardless of its beginning, intermediate, and ending viscosity/modulus values.

## DYNALYSER and STRESSTECH rheometer system setup

The DYNALYSER and STRESSTECH instruments are designed for testing any rheologically significant material: 1) thermoplastics, 2) thermosets, 3) elastomers, 4) semisolids, and/or 5) fluids systems. They combine versatility and accuracy with high value for the user.

The modular research rheometers are offered with a wide range of measuring systems and accessories. Measuring systems are available as concentric cylinders; cone/plates; parallel plates; 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 come 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.

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

STRESSTECH HR is the high-resolution version of the STRESSTECH rheometer, allowing measurements at microradian displacement and extremely low applied torque. The STRESSTECH HR increases the performance specifications to the DYNALYSER level.

Temperature control cells are available using circulating fluid, Joule-Thomson effect, and cryogenic LN<sub>2</sub> covering the range -180 to 550 °C. All measuring geometries are supported (i.e., cone/plate/parallel plate, concentric cylinder, and solids in torsion and tension). A patented Sealed Cell for measurements under moderate pressure with full dynamic and steady shear capabilities along with several high-pressure cells with an upper range of 5800 psig are available.

### 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 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, the use of valuable bench space is kept to a minimum. The motor control is based on digital rather than analogue 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 is based on the Windows operating platform and runs under Windows 2000 or XP. The standard software package is a true multitasking interface with selectable user levels, thus providing many advantages to the food scientist. It is designed to provide flexibility for configuring and using the **ATS RheoSystems/REOLOGICA Instruments** rheology system. The computer is not dedicated to simply running the instrument and is available for other use while 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 collect and analyze the resulting data. Viscometry, oscillation under stress and

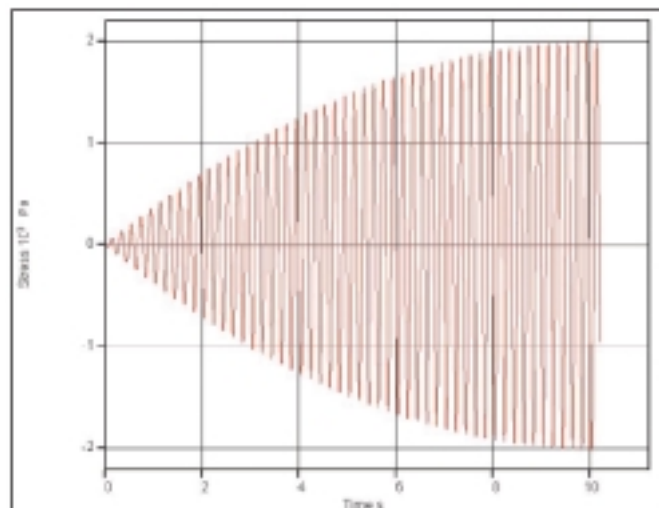


Figure 9 Polynomial amplitude function.

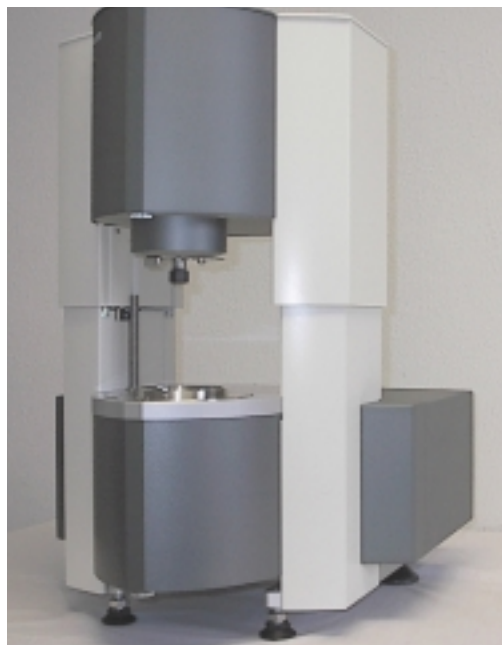


Figure 10 VISCOTECH rheometer.

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 are available, allowing 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.

RheoExplorer 5.0 includes the ability 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, where stresses, delay times, integration periods, and sample sizes may be set individually for all frequencies. The zooming function, which is present in both the viscometry stress step and oscillation frequency step, allows 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 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

The VISCOANALYSER is a modular research rheometer system fully upgradable to a STRESSTECH unit as the user's needs and requirements dictate. The VISCOTECH (Figure 10) is a cost-effective, entry-level research rheometer designed to be applications specific for routine viscoelastic measurements.

All **ATS RheoSystems/REOLOGICA Instruments** 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

This article reviews the important rheological characteristics for real-time light-curable materials and presents results generated with the STRESSTECH HR rheometer on UV-curable fiber-optic coatings. 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 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 today's marketplace.

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