Application Note

Rheology of high-performance coatings

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Rheology is the branch of science involved in 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, as well as predicting product performance and consumer acceptance.

Importance of rheology for coatings

Rheological phenomena are found in every coatings operation. Coatings, which are complex structured fluids, need to be characterized by their structures and flow properties in order to be applied successfully. Rheology allows us to study the microscopic structure of colloidal systems by measuring their macroscopic flow behavior under shear stress, and thus is the ideal method for studying coatings. The study of flow behavior of concentrated suspensions like coatings has always been of great interest in rheology due to their unique rheological characteristics and required rheological application performance.

The general nature of coatings

The applications of rheology vary from one class of materials to another because the mechanical behavior during processing can be quite different. Both the behavior of the material in process and the method of processing are linked to the composition of the material, which in turn governs its final function as the product. Neither one can be altered independently since one determines the other. The change in rheological properties of a suspension is a manifestation of the type and magnitude of particle interactions of the sample. Therefore, a survey of the general composition and material characteristics of the product involved precedes the determination of the rheological techniques used in the coating industry.

Rheological instrumentation

The DYNALYSER (*Figure 1*) and STRESSTECH HR

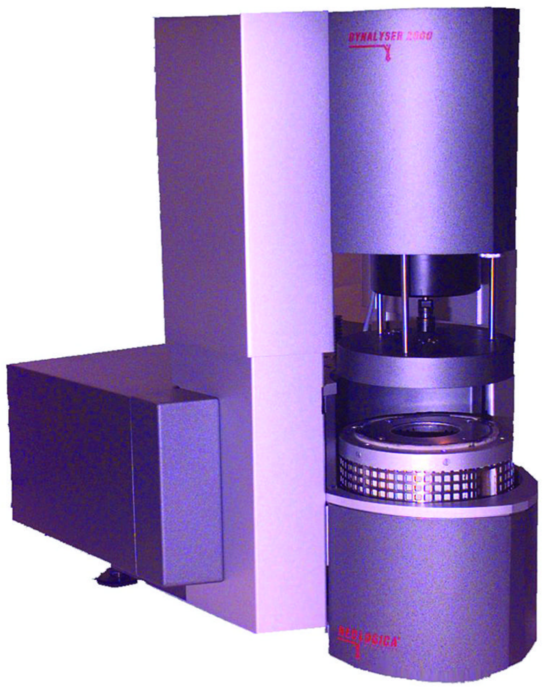

Figure 1 *DYNALYSER rheological characterization system.*

Figure 2 *STRESSTECH HR rheometer.*

(*Figure 2*) are research-grade analytical instruments (**REOLOGICA Instruments, Inc.,** Bordentown, NJ; **ATS RheoSystems,** Lund, Sweden) that are 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 spray and brush coatings, two-component curing systems, gels, and powder coatings through rigid, solid-state samples.

The rheometers feature an ac asynchronous motor drive system, universal temperature cells based on the Joule-Thomson effect, wide torque, shear stress, temperature, shear rate, frequency range, true Microsoft® Windows™-based operational software (**Microsoft Corp.,** Redmond, WA), patented Differential Pressure Quantitative Normal Force, 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 of the company's rheometers are designed on a modular platform to allow easy upgradability. A wide range of accessories satisfy the most demanding applications with ease of operation.

Storage stability

The stability of a coating can be established and controlled in a number of ways, including stabilization through steric and electrostatic forces. These forces must be large enough to overcome the forces of settling, mainly gravity and density differential between phases. The most problematic issues are sedimentation and syneresis, viscosity changes, and loss of curing capability.

The stability of colloidal particles is often produced by the adsorption of molecules onto the surface of the particles. Stabilizers are often ionic surface-active agents used to produce repulsive electrostatic forces between nonionic particles. In general, the stability of a suspension depends on the particle size and distribution, the density difference between particles and the continuous phase, particle concentration, and particle–particle interactions.

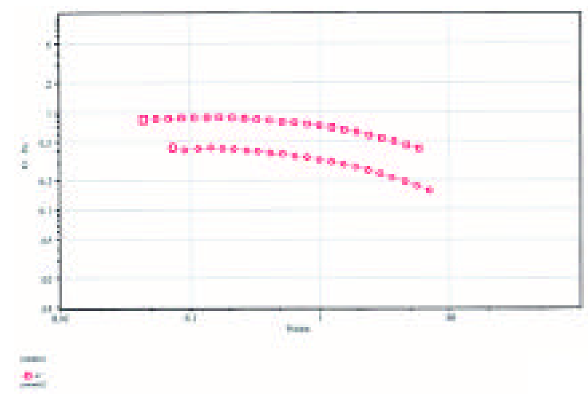

Figure 3 *Dynamic strain sweep of two dispersions, a method often utilized to analyze the stability of a material system.*

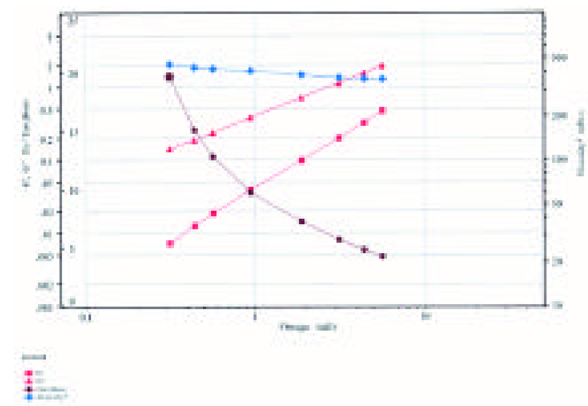

Figure 4 *Dynamic frequency sweep of suspension with nonassociated particles.*

An indispensable rheological technique for examining the stability of coatings is the oscillatory strain sweep measurement. In oscillatory shear measurements, or dynamic mechanical measurements, a sinusoidally varying shear forcing function is imposed on the material, and the amplitude and phase lag of the resulting shear function are measured. The test is said to be in the linear viscoelastic region (LVE) if the input and output functions are linearly proportional, and both functions are not distorted.

Figure 3 shows the results of strain sweeps of two commercial dispersion systems. The maximum strain up to which G′ remains constant is called the critical strain. The critical strain, which indicates the minimum energy needed to disrupt the structure, is dependent on the dispersion quality. Below the critical strain limit, the test conditions only perturb the structure slightly, but do not alter or destroy it. Therefore, if the difference in the critical strain of two systems is known, the comparative quality of the dispersions could be determined. For these two materials, samples 1 and 2, the critical strain is 0.20 and 0.15, respectively. As a rule of thumb, the higher the critical strain, the better the system is dispersed. For accurate determination of the LVE, the rheometer must have excellent low-angular-position resolution, in this example, 1e-05 rad.

Rheological experiments can also be used to predict the storage stability of suspensions. The test

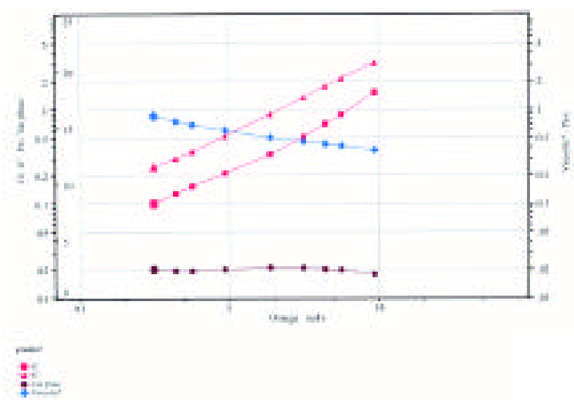

Figure 5 *Dynamic frequency sweep of suspension with weakly associated particles.*

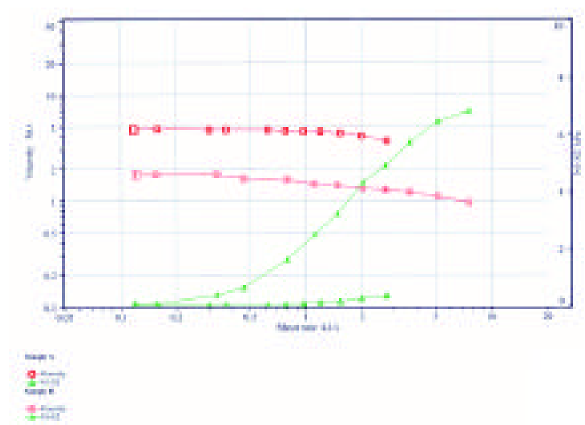

Figure 7 *Normal stress difference of coatings A and B measured using Differential Pressure Normal Force Sensor.*

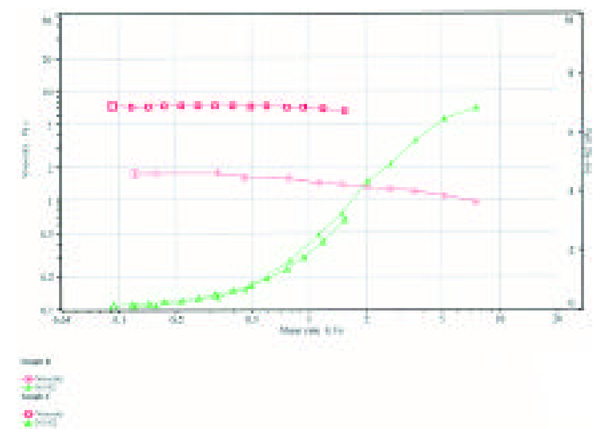

Figure 8 *Normal stress difference of coatings B and C measured using Differential Pressure Normal Force Sensor.*

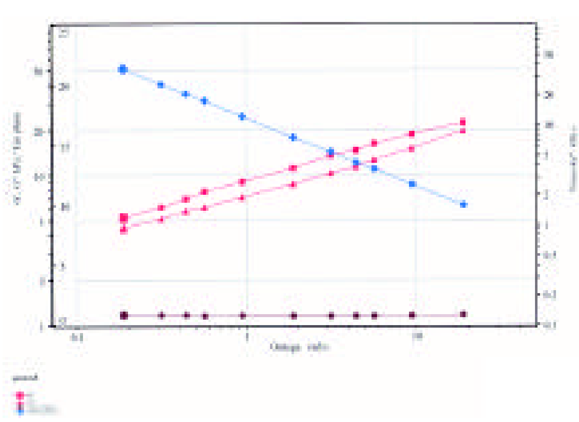

Figure 6 *Dynamic frequency sweep of suspension with strongly associated particles.*

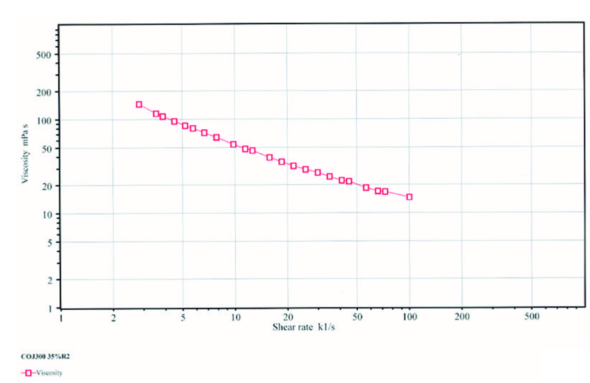

Figure 9 *Shear rate sweep of coating material exhibiting shear thinning.*

must be measured within the LVE. This necessitates using low-deformation oscillatory measurements as noted above, and, in addition, low drive frequencies. The data obtained hold valuable information about the particle–particle interactions. *Figures 4–6* show the frequency dependence (rad/sec) of the viscoelastic parameters, G′, G″, tan delta, and eta* for nonassociated, weakly associated, and strongly associated dispersed particles, respectively. A high tan δ, i.e., tan δ > 3, for a given concentration of particles, is indicative of an unassociated system. If the system exhibits tan δ in the midrange, i.e., 1 < tan δ < 3, then they are weakly associated; where tan δ < 1, the particles are highly associated.[1] Thus, a relatively quick and simple rheological experiment can be used to determine the degree of association. It has been documented in the literature that the degree of association correlates well to product syneresis and shelf-life stability of disperse systems.

Steady shear viscometry measurement

The concept of viscosity has a unique meaning in steady-state flow where the deformation is large scale and the sample's internal structure may be irrecoverable after cessation of shear. Also, the existence of nonzero diagonal components of the stress tensor in the simple shear flow of a liquid leads to a spectacular manifestation. This specific feature of elastic liquids is termed the Weissenberg effect.

The viscosity of high solids content coatings, i.e., resins and varnishes, is normally independent of shear rate; however, their inherent elasticity is an essential component in processing because the coating film thickness is highly dependent on it. The viscosity and elasticity of coating materials are affected by the following parameters: polymer molecular weight and structure, latex type and size distribution, pigment volume concentration, and surfactant concentration. Concentrated Newtonian suspensions are difficult to characterize from an experimental point of view, since viscoelastic measurements cannot be obtained at high enough deformation rates. Normal stress measurements are an alternative to viscoelastic measurements. Unfortunately, until recently it was very difficult to obtain reliable experimental data on low-viscosity samples, since the shear rates required are very high and the resulting normal stresses are very small. With the development of a high angular velocity induction position sensor and patented Differential Pressure Normal Force Sensor, reliable normal stress measurements can be obtained at shear rates above 100,000 s-1 at an axial load of 0.002 N with the STRESSTECH rheometer.

If the liquid is sheared between a cone and plate or parallel plate measuring system relative to the common axis, a normal force will develop on the surface of the plates. *Figure 7* shows the steady shear viscosity (Pa s) and first normal stress (Pa) difference as a function of shear rate (s-1) for two coating materials, one exhibiting unacceptable leveling performance in a high-speed coating operation. The two samples have nearly Newtonian flow behavior, although different by a factor of 3. From these results, one might conclude that the sample with the higher viscosity was the poor performer; however, this is not the case. Examining the normal stress results shows that the two samples exhibit dramatically different elasticity at shear rates above 1000 s-1. The elasticity results indicate that the normal stress difference of sample A is much smaller than sample B. For this process, the elasticity, not the viscosity, is the controller parameter. Making simple viscometric measurements on these samples, and for many other commercial coating materials, would not correlate with true processing performance.

In another example, *Figure 8* shows another high-speed coating sample. This time the viscosity of sample C is higher than sample B by a factor of 3, but the normal stress difference of the two samples is similar quantitatively and qualitatively. These two materials were found to produce acceptable coating performance under the same conditions as described above.

In general, a sample's rheological response and processing characteristics are highly dependent on the molecular weight distribution and/or volume fraction of the dispersed phase. These structural factors contribute more significantly to the development of normal stresses than to the viscosity. Although the normal stress effect is specific to the shear flow of a liquid, the physical causes of this phenomenon are attributed to the viscoelasticity of the material.

In the case of the nonlinearity of concentrated suspensions, shear thinning flow and thixotropy are commonly observed. When a network matrix is formed in the system, resistance to flow is built up in the system as the continuous phase becomes entrained in the network lattice, effectively increasing the volume fraction. Shear thinning is common in pigment pastes and trade sales coatings. Gel-coated systems of this type become thinner when stirred because the structure is broken down and the disperse phase is released from the network. *Figure 9* shows a typical shearing thinning coating where viscosity (Pa s) is plotted versus shear rate (s-1). The shear rate range of interest for this particular application was 5000–100,000 s-1.

Most samples show an increase in viscosity when held idle because the structure is reestablished. Thixotropy is often confused with pseudoplasticity. It should be remembered that the former is time-dependent changes, and the latter shear-dependent changes. A combination of thixotropic and pseudoplastic behavior is formulated into trade sales paints, gel coats, and certain other coatings to give low viscosity at the high shear rates of processing and application, followed by a viscosity recovery when the shearing stops. This recovery should be slow enough to allow flow and leveling, but fast enough to prevent noticeable sagging even where film thickness is fairly high.

Rheometer system setup

The DYNALYSER and STRESSTECH are designed for testing any rheological significant material, i.e., thermoplastics, thermosets, elastomers, semisolids, and/or fluids systems. The instruments combine versatility and accuracy with high value.

The modular research rheometers provide 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 offered. The measuring geometries can be made in stainless steel, titanium, polycarbonate, or any user-defined material. The instruments come standard with a Differential Pressure Normal Force Sensor for reproducible sample loading history, thermal expansion measurements, and quantitative normal stress measurements. The diffusion air bearing had 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, a high-resolution 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.

Universal temperature control cells are available using circulating fluid, Joule-Thomson effect, and cryogenics 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. The Sealed Cell for viscoelastic measurements above the sample's boiling point, and several high-pressure cells with an upper range of 5800 psig, are also 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 electronic cabinet. In addition, valuable bench space is kept to a minimum. The ac asynchronous motor drive system's control is based on digital rather than analog technology. The unit is provided 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 (**REOLOGICA Instruments/A TS RheoSystems**) is based on the Windows' operating platform and runs under Windows 2000, NT, or XP (**Microsoft**). The standard software package is a true multitasking interface with selectable user levels, thus providing many advantages to the researcher. 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 use 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 permit the operator 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 and project (multiexperiment linking); and time-temperature superposition and spectrum visualization and 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 makes it possible 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. Another example is the zooming function, which is present in both the Viscometry Stress Step and Oscillation Frequency Step, and allows any number of steps and increments to be selected. The instrument has automatic gap adjustments and thermal expansion compensation using the Differential Pressure Normal Force Sensor. The system enhances measurement reproducibility since the sample loading history is reproduced identically each time.

Figure 10 *VISCOTECH rheometer.*

Rheometers for any user level, application, and budget

The VISCOANALYSER (**REOLOGICA Instruments/ATS RheoSystems**) is an expandable capability, research-level rheometer system specifically designed with a clear upgrade path to a STRESSTECH unit as the user's needs and requirements dictate. VISCOTECH, an entry-level rheometer (**REOLOGICA Instruments/ATS RheoSystems**), provides research-level rheometer performance on a QC rheometer budget (*Figure 10*).

All rheometers are produced according to ISO 9001 standards 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

Important rheological characteristics have been reviewed, and results generated with a DYNALYSER and STRESSTECH rheometer on several different coating materials have been presented. In addition, a detailed interpretation of data and correlation of the rheological response with the physical/chemical properties of different coating materials was given. The rheological characterization of coating materials provides important information for engineers and scientists to improve and optimize their products and manufacturing processes. Most researchers and manufacturers depend on rheological measurements to develop products with a competitive edge in the marketplace. A reliable, high-performance, research-level rheometer and a thorough understanding of rheological measurements are necessary for success in today's marketplace.

Reference

1. Rohn CL. Analytical polymer rheology. Cincinnati, OH: Hanser Publishers, 1995: 203.

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