

Keywords: structured fluids, sol gel transition, solution, yield stress, thixotropy, viscosity, mechanical stability, shelf life, flow curve, inks, cosmetics, dispersions, food

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## GENERAL CONSIDERATIONS

### Fluids: Simple or Structured

Fluid materials, by definition, are systems which flow when subjected to stress. How they respond to an input stress is the heart of rheological testing and may be a complex issue. There are many types of fluids: pure substances, mixtures, dispersions and solutions, falling into the categories of either simple or structured fluids. Each has its own unique behavior when subjected to stress. In general, when a material has a uniform phase, such as a solution or pure substance, it is referred to as a simple fluid. Materials which contain more than one phase, such as solid particles dispersed in a liquid, gas particles in foam or an emulsion of immiscible liquids are considered structured fluids since their rheological behavior is in general dominated by the interactions of the constituents.

### Structured fluids

Many of the materials we use each day are structured fluids. Most foods, cosmetics, pharmaceuticals and paints contain particles or droplets of an immiscible fluid suspended in a carrier liquid. A number of soft semisolid materials also fall under the category of structured fluids since they have a multiphase structure and exhibit complex flow behavior. Some examples would be cheeses, lipstick, caulk, and bread dough.

Many factors affect the stability of structured fluids. The viscosity of the liquid phase in dispersions usually plays an important role on the flow properties of the material. Dispersions have wide variations in performance depending on particle size, shape, concentration, and any attraction with the continuous phase in which they are suspended. When there is a repulsive electrostatic or steric force between particles they end not to settle rapidly, instead forming a network structure which will stabilize the suspension if undisturbed. Shearing or even Brownian motion can destroy this delicate structure and break down the fluids viscosity.

Structured fluids do not obey a simple linear relationship between applied stress and flow (Newtonian fluid behavior) as shown in Figure 1 for suspensions of latex particles with increasing volume fraction in water.

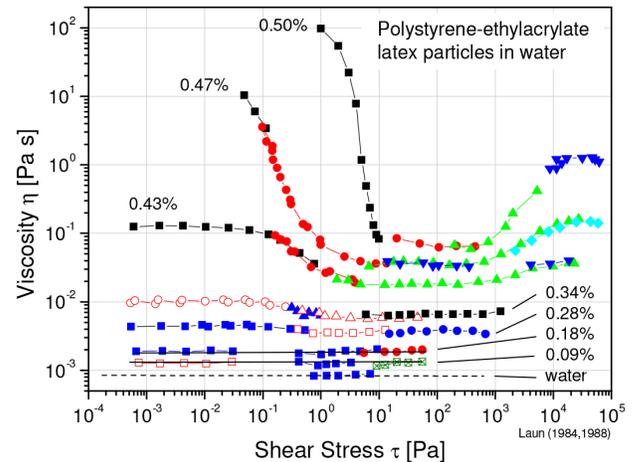


Figure 1: Viscosity of a structured fluid as a function of shear rate and particle concentration<sup>1</sup>

Nearly all these materials have a viscosity that drops at higher rates of shear velocity resp. stress. This is the phenomenon of shear thinning which becomes progressively larger as the volume concentration of solid particles increases. At high concentration of solid content, the low shear rate viscosity region disappears completely, the material is yielding. Some materials show after the shear thinning region with increasing rate or stress, an increase of the viscosity, usually due to structure rearrangements as a result of the applied shear. This is referred to as flow induced shear thickening.

### Characteristic flow parameters and functions

#### Bingham Flow

Eugene Bingham, a colloid chemist, first coined the term "Rheology." He also showed that for many real fluids a critical level of stress must be attained in order to initiate flow. Below this critical stress,  $\tau_y$ , the material behaves as a solid, absorbing the stress energy without flowing. Once the threshold of critical stress has been reached, the material yields to flow, hence the term, yield stress. The yield stress is the reason, why you need to shake or tap a bottle to make the ketchup flow. Materials which exhibit Newtonian flow beyond the yield bear the name Bingham Fluids.

#### Plastic Flow

Most materials do not exhibit Newtonian flow after the yield, but have a viscosity that decreases (shear thinning) until a plateau is reached. Lipsticks, drilling muds and toothpaste are good examples of shear thinning non-Newtonian materials

with a yield stress.

### Pseudoplasticity

Some materials do not have a yield stress, nevertheless they behave nonlinear. These are considered pseudoplastic. They flow instantaneously upon application of stress but also display shear thinning behavior. Polymer solutions exhibit pseudoplastic flow as does bread dough and many paints and cosmetics. A plot of viscosity versus shear rate for different types of materials is shown in Figure 2.

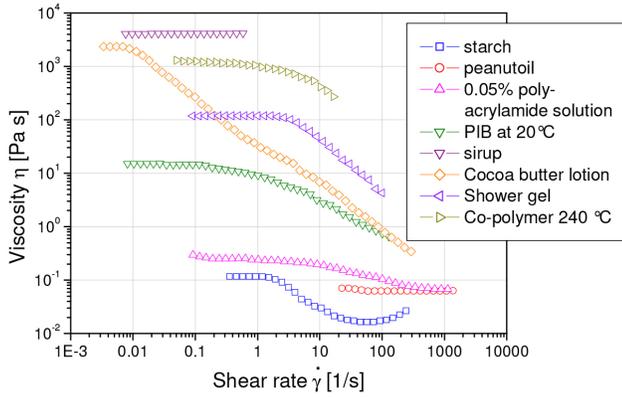


Figure 2: Viscosity versus shear rate for different types of material

### Dilatancy

Dilatancy, also known as shear thickening, is an unusual phenomenon whereby materials actually increase their viscosity upon stirring or shearing. In some cases these are dense suspensions of solid particles in a fluid medium, which develop greater spacing between particles during agitation. This behavior is infamous in quicksand, moist beach sand and certain pharmaceuticals such as a suspension of penicillin. Shear thickening often results from material instability and structure rearrangements or phase separation.

### Thixotropy

For many fluid materials, viscosity is mostly independent of time, and is only a function of the shear rate and temperature. For concentrated dispersions their viscosity does not reach a steady value for some time upon application of stress, or shear rate. This steady state is dependent on the stabilization of internal network structures that can be broken down by shearing, and require time to rebuild. A steady state plateau in viscosity is reached if an equilibrium has been established between structure breakdown and rebuilding. Upon ceasing the shear rate which caused the breakdown, the material reforms its internal network, and the viscosity recovers (Figure 3). The term used to describe this phenomenon is Thixotropy. In studying such materials it can be beneficial to destroy the network structure entirely by shearing the material, giving a clean-slate for examination of the path by which the viscosity rebuilds.

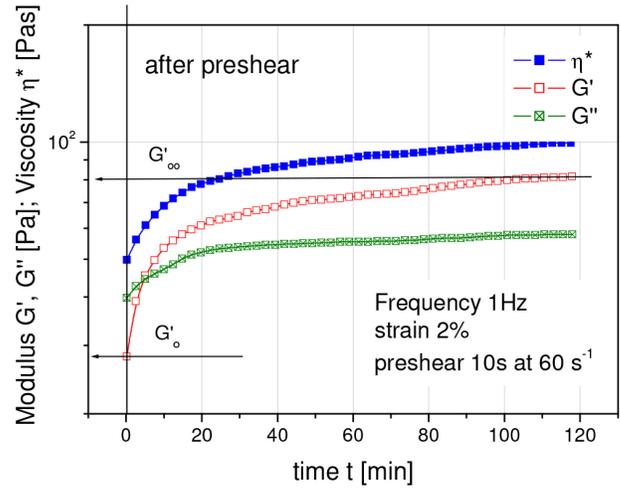


Figure 3: Structure build up after previous shear monitored with small strain amplitude oscillatory testing

The viscosity of thixotropic materials does not follow the same path on structure breakdown and recovery. In most cases, when the shear rate is slowed, the stress path lags forming a hysteresis loop, which then returns to a point lower than the initial critical shear stress. The area within the hysteresis loop represents the energy consumed in structure breakdown (Figure 4).

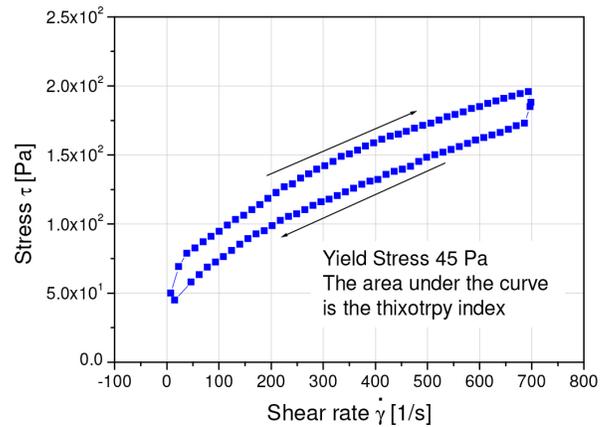


Figure 4: Hysteresis loop of a thixotropic material

### Rheopexy

Whereas a thixotropic fluid's viscosity decreases over time under an imposed constant shear rate, a rheopectic fluid's viscosity increases under an imposed shearing action. A rheopectic fluid such as a dense suspension of latex particles or plastisols will gel when agitated. If allowed to rest, a rheopectic fluid will return to its original lower viscosity. The viscosity-shear rate curve forms a hysteresis loop and the hysteresis can be repeated indefinitely. This is a way to distinguish between true and apparent rheopectic behavior - fluids that change physically or chemically (gelling, solvent evaporation) while a shear is imposed also experience a viscosity increase. These changes, however, will not be

reversible and therefore do not represent true rheopexy.

*Time Dependency- Creep and Creep Recovery*

The stress and strain rate dependent behavior of a material may be only part of the picture. In many cases time dependency has to be considered also. Materials are also time dependent. Hookean and Newtonian materials respond immediately upon an input stress or strain rate. When a stress is imposed on a so-called viscoelastic material, it does not immediately respond with constant flow, even though the stress may be sufficiently above the critical stress or yield point. Upon removal of the stress, these types of materials recover to their original state, but slowly, and usually incompletely. This behavior is referred to as creep. Creep studies can also be used to determine the yield stress of materials (see Figure 5). A series of creep and recovery (application of a constant stress followed by a period of zero stress) can be performed in incrementally higher and higher stress levels.

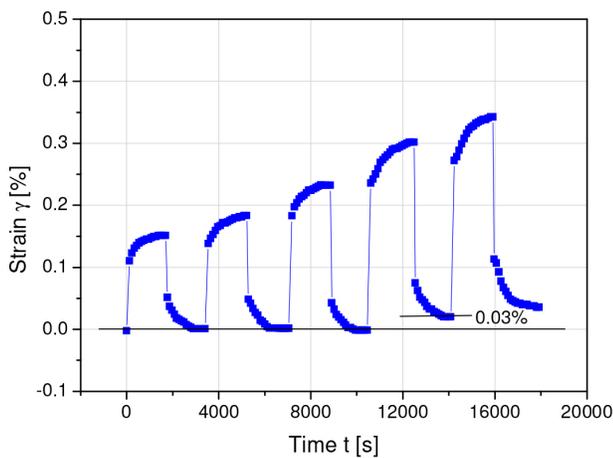


Figure 5: Series of creep tests to determine the yield point

Below the yield stress the material behaves as a solid, with complete recovery. When the material fails to recover completely, it has reached its yield stress.

**EXAMPLES OF RHEOLOGICAL TEST METHODS**

**Yield stress and stress ramp**

Structured fluids often will not flow unless they have reached a critical stress level called the yield stress, below which a material is "fully" elastic and above which the structure of the material breaks and it flows. The Yield stress is an important parameter in product delivery and use such as the ease with which a shampoo can be dispensed from a bottle, or the consistency of sour cream. In production, the yield stress determines the force needed to start pumping through a pipeline or fill a container with the product. The stress ramp, in Figure 6, is the most frequently used technique to measure the yield stress today. The stress at the viscosity maximum, which is readily measurable for most structured fluids, provides a reproducible and representative value for the yield stress. The viscosity maximum is pronounced, if the material at

rest behaves viscoelastic and the time dependent stress or viscosity build-up competes with the viscosity decrease due to structure break-down with increasing stress.

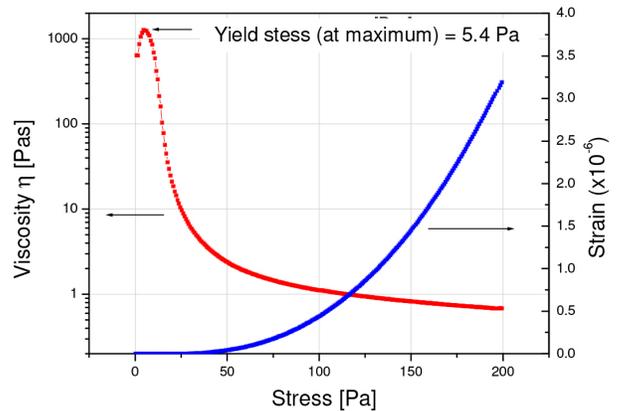


Figure 6: Yield stress measurement of a cosmetic cream based on the viscosity maximum method in a stress ramp

**Critical strain and strain sweep**

Usually the rheological properties of a viscoelastic material are independent of strain up to a critical strain level  $\gamma_c$ . Beyond this critical strain level, the material's behavior is non-linear and the storage modulus declines. So, measuring the strain amplitude dependence of the storage and loss moduli ( $G'$ ,  $G''$ ) is a good first step taken in characterizing visco-elastic behavior: A strain sweep will establish the extent of the material's linearity. Figure 7 shows a strain sweep for a water-base acrylic coating. In this case, the critical strain  $\gamma_c$  is 6%. Below 6% strain, the structure is intact, the material behaves solid-like, and  $G' > G''$ , indicating that the material is highly structured. Increasing the strain above the critical strain disrupts the network structure.

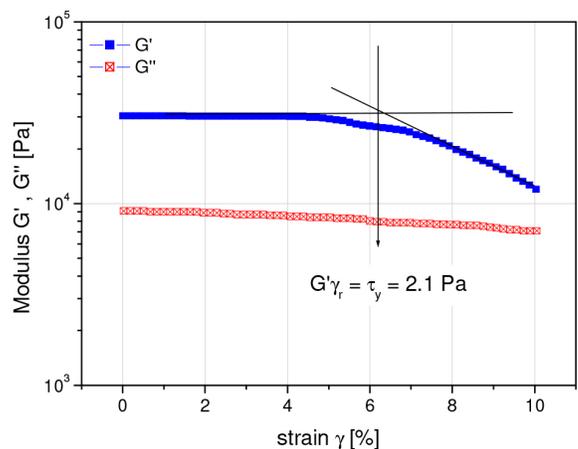


Figure 7: Strain sweep for a water-based acrylic coating

The material becomes progressively more fluid-like, the moduli decline, and  $G''$  exceeds  $G'$  eventually. The strength of the colloidal forces is reflected by  $\tan \delta = (G''/G')$ . A  $\tan \delta$

less than 1 suggests that the particles are highly associated due to the colloidal forces and sedimentation could occur: a high  $\tan \delta$  at given concentration suggests that the particles are largely unassociated. For a stable system, an intermediate  $\tan \delta$  is desired. Critical strains for electrostatically stabilized systems are about 0,01% to 0,5% for sterically stabilized systems, about 1% to 5%.

The product of critical strain  $\gamma_c$  and complex modulus  $G^*$  below  $\gamma_c$  is a good indication of the materials yield stress and correlates well with the yield stress determined from the viscosity maximum obtained in a stress ramp.

### Structure and frequency sweep

After the fluid's linear viscoelastic region has been defined by a strain sweep, its structure can be further characterized using a frequency sweep at a strain below the critical strain  $\gamma_c$ . This provides more information about the effect of colloidal forces, the interactions among particles or droplets. In a frequency sweep, measurements are made over a range of oscillation frequencies at a constant oscillation amplitude and temperature. Below the critical strain, the elastic modulus  $G'$  is often nearly independent of frequency, as would be expected from a structured or solid-like material. The more frequency dependent the elastic modulus is, the more fluid-like is the material. Figure 8 illustrates the transition solid-fluid with frequency sweep data measured on a slurry of a simulated solid rocket propellant at both a low (0,5%) and a high strain amplitude (5%).

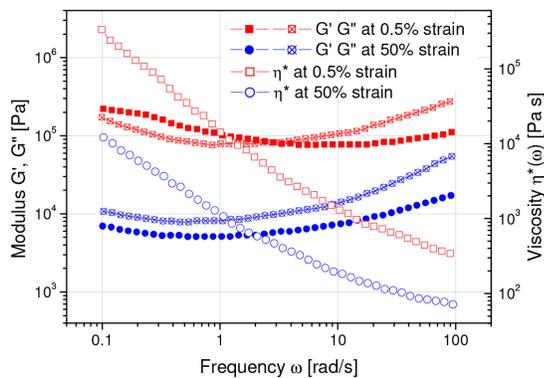


Figure 8: Frequency sweep on a simulated rocket propellant material: shows a more fluid-like behavior at high strain amplitudes ( $G'' > G'$ ), more solid-like at low strains ( $G' > G''$ )

### Yield stress and Creep recovery

The creep test probes the time-dependent nature of a sample. A characteristic creep experiment provides critical parameters such as zero shear viscosity ( $\eta_0$ ) and equilibrium compliance ( $J_{ec}$ ), which measures the elastic recoil of a material. After a sample is allowed to creep under load, the material's elastic behavior can be obtained by abruptly relieving the imposed stress and measuring the extent the sample recovers. Cookie doughs which had nearly the same viscosities showed significant differences in compliance or

elastic recoil, which is important to keep the shape of the dough after extruding to avoid variations in product size (Figure 9).

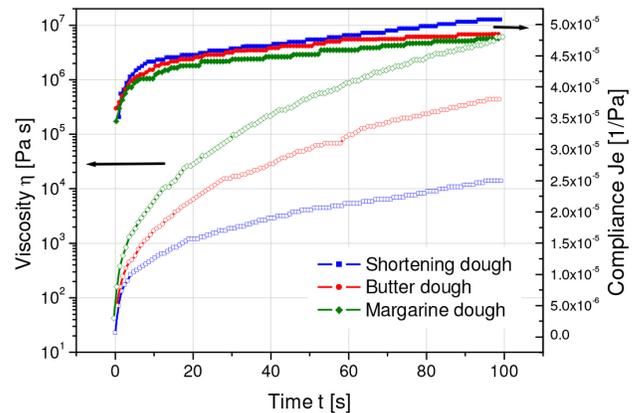


Figure 9: Creep recovery of cookie dough

### Structure changes and thixotropic loop

Thixotropic material will lose structure during shear, and rebuild it on standing. This behavior is a key factor in the ability of a paint or cosmetic to be easily applied to a surface (through structure breakdown in spreading) and then rebuild its structure and viscosity so that it does not drip and run. Latex paints need to flow smoothly as they are sheared by a roller or brush, so the viscosity must break down. A time lag for leveling of the paint (to conceal brush strokes) is necessary, after which the viscosity must rebuild to avoid drips and sagging. Food products also display this important behavior. Mayonnaise being spread on a sandwich or mixed in a salad must break down its structure to be distributed and then rebuild to the right mouth feel so that it doesn't seep into the bread or taste thin and runny in a salad. In figure 10, the thixotropy is shown in the difference of the up and down stress ramps for 3 hand lotions. The area between the curves is an indication of the extent of the thixotropy.

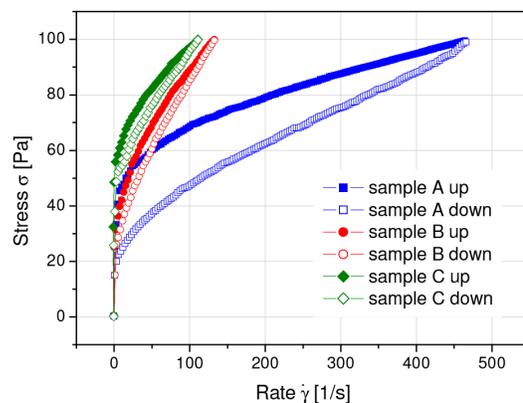


Figure 10: Thixotropy of hand lotions - Stress ramps at 25°C

## Flow curve and step shear rate

The viscosity of a material according to the rate at which it is sheared, provides important information about processing and performance. This can be important in production where stirring, dispensing and pumping of the product will subject it to a variety of shear rates. Low shear rate behavior can be related to storage conditions of materials: sedimentation, phase separation, and structure retention. Single point viscosity information does not profile the material across a spectrum of shear rates. Materials that may behave the same at one end of the flow curve may show dramatic difference at the other, which relates to structural differences in these materials as shown in Figure 11 for two adhesive dispersions.

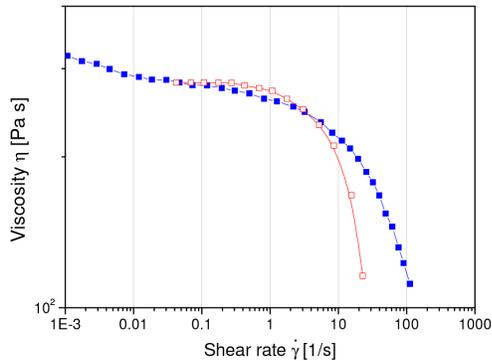


Figure 11: Flow curve of 2 adhesive dispersions. The products differ significantly at high shear rates

## Temperature dependence in oscillatory temperature ramp

A dynamic temperature ramp study does not always mean heating. In the accompanying example (Figure 12), Carrageenan was cooled at 1.5 C/min from 70 to 20 °C and held at the lower temperature for 1 hour. The strain during the cooling period was high: 10%, but during the isothermal period a very low strain, 0.1%, was maintained to avoid disturbing the structure being formed at that low temperature. Dynamic Temperature Ramp studies can simulate production cycles, storage and use conditions or evaluate long term stability of, for example, cosmetic creams. Rheological testing can predict behavior without large costly batch studies.

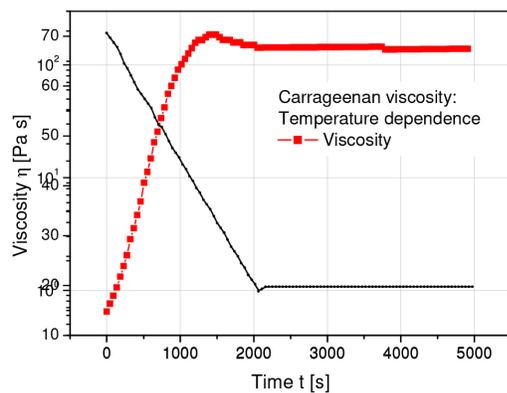


Figure 12: Carrageenan temperature ramp is used to reproduce production cycles, storage or use conditions

## Stress relaxation

Stress relaxation experiments apply a step strain deformation to create an instantaneous strain and to monitor the stress decay as the specimen is held over time in the same constrained state. The profile of stress relaxation is important in materials that will be subjected to repetitive strain, to determine if the stress can be dissipated with the time scale of typical use. Overloading of stress in a material can cause damage and failure in later use. The stress relaxation of human cartilage is shown in Figure 13 after the material has been subjected to a 1% strain at 23 °C. Besides greases, soft solids such as caulks, bread dough, dairy products, and pharmaceutical creams have been studied extensively using stress relaxation tests.

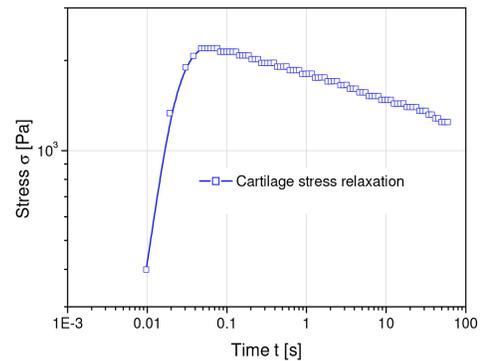


Figure 13: Stress relaxation behavior of human cartilage

## FLUIDS MATERIALS-APPLICATIONS

### Decorative and Protective Coatings

Rheological tests are used widely to evaluate functional coatings in terms of their properties and performance. During manufacturing as they are mixed and transferred, and during application by spraying, brushing, coating, or dipping, coatings are subjected repeatedly to shear and extension over a range of magnitudes, rates and durations. After application the coating may distort, and, inevitably, it ages. Rheological testing provides a convenient way to measure performance- critical rheological changes occurring during the life cycle of decorative and protective coatings. Among the chief performance aspects of coatings influenced by rheology are leveling, sagging, spatter resistance, and brushability.

Leveling refers to the ability of a coating to flow laterally and diminish differences in thickness of adjacent areas of the coating. This is an important property affecting smoothness, gloss, color, and mechanical behavior. Leveling involves changes in surface tension due to solvent loss or reaction and is influenced by the material's yield stress and viscosity. Data from strain sweeps have proven to be an effective predictor of flow and leveling. Table 1 compares the subjective ranking of leveling behavior of six latex paint versus their complex

viscosity at 25% strain.

Paint Type	Sample Number	Leveling Behavior	Viscosity (Pa s) @25% strain
Enamel	A	Good	18
	B	Fair	75
	C	Poor	284
Flat	D	Fair-Good	25
	E	Fair	35
	F	Very Poor	57

Table 1: Comparison of leveling behavior versus complex viscosity of Latex paint

Sagging is undesirable flow of a coating down a vertical surface. Whether a coating will sag or not depends on its thickness and its viscosity at low shear rates. For a coating to resist sagging, the product of its density, the gravitational constant, and its thickness must not exceed its yield stress.

Spatter resistance in spraying is related to the elasticity of the coating and depends strongly on the elongational viscosity of the fluid. Spatter resistance can be predicted from measurements of the elastic modulus  $G'$  at high strains. To achieve the needed combination of low viscosity to pass through small sprayer orifices and yet resist sagging, the coating must be highly pseudoplastic and have rapid viscosity recovery.

Brushability is a matter of the effect of shear rate on viscosity. Newtonian fluids are difficult to brush: highly pseudoplastic coatings brush easily.

## Printing Inks

Two major classes of inks are those used for screen printing in the graphics arts and electronics industry, and those used for printing newspaper. While their compositions differ, they share a characteristic: rheological complexity.

Screen printing is possible because inks can be made thixotropic. Initially highly viscous, these inks shear-thin rapidly under the high shear rates generated as they are squeezed through the mesh. The now low viscosity ink deposits on the substrate in cubical islands, matching the pattern of the openings in the screen. When the screen is removed, the ink, no longer under shear but still at a low viscosity, begins to level, the islands flowing together to form a continuous film. As it flows, the ink's viscosity rebuilds, the timing controlled by proper formulation so that the ink does not bleed beyond the intended printed boundary.

Dynamic tests, including thixotropic analysis and strain, frequency, and temperature sweeps, along with transient stress ramp tests to measure yield stresses, are commonly used to guide graphic ink development.

These tests have been equally beneficial in the evaluation

and development of thick film resistor, capacitor, electrode, solder, and thermoset conductor pastes applied by high speed screen printing onto electronic circuit boards and components.

Newspaper inks encounter high shear rates and abrupt shear rate and shear direction changes as they pass through the nips of the printing press. These deformations generate high shear, normal, and extensional stresses. Accordingly, they require a battery of tests to properly characterize them, including steady and transient shear studies and measurement of normal stresses and elongational viscosity.

Figure 14 shows viscosity versus shear rate and shear stress versus shear rate for three model inks<sup>(3)</sup>. Yield stresses were obtained by extrapolating the steady state shear stress to zero shear rate.

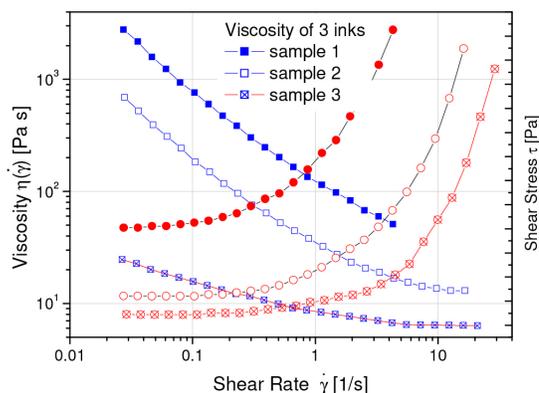


Figure 14: Viscosity and shear stress vs. shear rate for three model inks. The plateau value of the stress at low rate is the yield stress<sup>(2)</sup>.

## Soft solids

Cements, protective caulks, toothpaste, peanut butter and processed cheese spreads are examples of materials rheologically classified as "soft solid. These materials are characterized by a relatively low modulus, but they possess solid properties due such as internal structure and a highly elastic response, when subjected to very small deformations. They, however, exhibit a complex flow behavior if larger deformations are applied. Soft solids frequently have a yield stress.

Processing soft solids is difficult because of their solid-like behavior at low strains, which makes for example startup of pumps very difficult. Once flow starts, the velocity profile may exhibit characteristics of both laminar and plug flow—particularly if a yield stress is present—as well as phenomena such as wall slip.

Though the behavior is rheologically complex, modern rheometer, can easily measure the viscoelastic responses of soft solids under conditions, which simulate those, used in processing the material. The rheological measurements provide information to aid process design, including calculating pump size and pressure requirements. Rotational

<sup>2</sup> J.M. Dealy et al. J. Rheol. 29(4) 471 (1985)

<sup>3</sup> Wang, Scriven, Macosko J.Rheol. 20(5) 1015 (1986)

shear measurements provide the viscosity versus shear rate response of soft solids, and record transient behavior at the onset of flow or changes in flow rate. Dynamic mechanical testing, done at low strains, gives insight into the structure of soft solids. Controlled stress tests (creep, stress ramp) are useful in characterizing these materials at stress levels above and below the yield point. Steady-shear testing and large strain dynamic measurements can be used to predict the flow properties of these materials. Soft solids are generally very sensitive to both strain level and strain history. Accurate characterization requires sensitive stress measurement as well as excellent strain resolution.

Figure 15 shows dynamic strain sweeps for three samples of process cheese spreads, known to differ in pumping ease. Sample A pumped without difficulty; B and C required considerably more pressure to start flowing, than did A. Also, sample C required more pressure to maintain flow than did A and B.

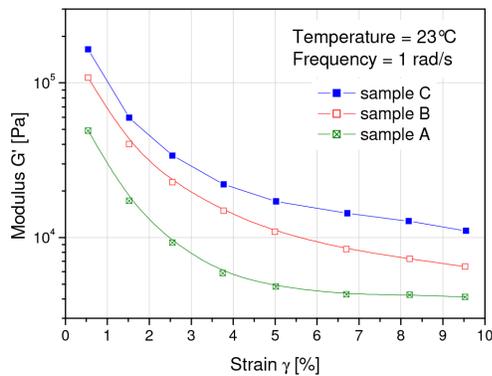


Figure 15: Strain dependence of the storage modulus  $G'$  of process cheese spreads differing in pumping ease

That sample B and C exhibit much higher elastic moduli ( $G'$ ) at low strain amplitudes than does sample A, indicates a higher degree of internal structure in B and C, a more solidlike behavior, and a consequent higher pumping pressure requirement.

### Polymer Solutions

Polymers dissolved in solvents are employed widely as adhesives and coatings. And, with added surfactants, polymer solutions provide the basis for paints, cosmetics, detergents, and other recovery fluids. Both steady and dynamic rheological tests can be used to evaluate these materials. High polymer solutions are used to enhance oil recovery, but they lose effectiveness after extended use. This happens because of a permanent viscosity reduction due to shear degradation of the polymer, under the high shear rates generated by the rotating bit in the well bore. The combination of a high molecular weight polymer and a surfactant can develop high viscosities by formation of complexes insensitive to shear degradation.

Figure 16 shows zero shear viscosity measurements of a

0.5% aqueous solutions of a hydrophobically modified hydroxyethylcellulose as a function of the surfactant concentration tetradecyltrimethyl-ammonium bromide (TTAB) and cetyltrimethylammonium bromide (CTAB)<sup>(1)</sup>.

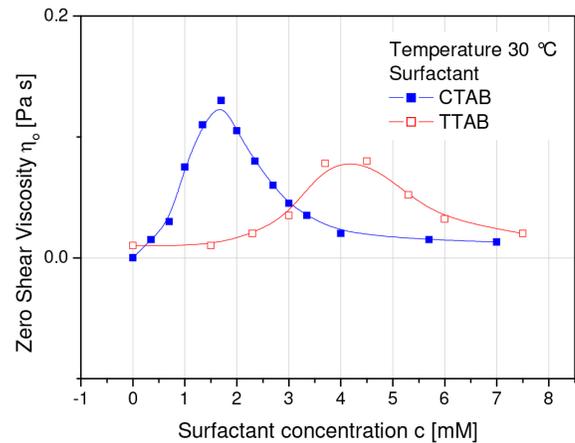


Figure 16: Zero Shear Viscosity versus CTAB and TTAB concentration for 0.5% aqueous hmHEC sample at a shear rate below 1-100 1/s

As surfactant is added, the viscosity of the polymer solution increases due to bridging of the hydrophobe clusters by surfactant micelles. The viscosity increases with the number of effective associating junctions. At higher surfactant concentrations, the hydrophobes are individually solubilized, or masked by an excess of spherical micelles, resulting in a disruption of associations and a decrease on viscosity.

Rheological tests are also used widely in studies of solutions of reactive systems. Dynamic time tests are particularly suitable for measuring the viscoelastic changes these materials undergo while they react and the products attain the intended final form. Such tests provide a convenient way to assess product applicability as well as to establish causal relationships in problem-solving efforts.

### Magnetic suspensions

A mixture of acicular iron oxide particles dispersed in a polymer solution forms the basis for many magnetic coatings used to make audio, video, and digital recording media, and hard and floppy computer disks.

Knowing how magnetic coatings behave at low stresses and high shear rates is important during application. The high shear rate viscosity determines pumping pressures and coating roll separating forces and torques. And the yield stress is critical for leveling, as well as pick-out in rotogravure coating, and thickness uniformity in spin coating. The yield stress may also affect drying behavior and cause flow instability. The shear modulus is a measure of the magnetic forces between particles, their topology, and the extent they are orientable by an external magnetic field.

Figures 17 and 18 show stress rheometer creep data for a model iron oxide magnetic suspension in which a silicone<sup>(3)</sup>

oil was used in place of the usual volatile solvent. The data in Figure 19 were obtained at a stress of 2 Pa, and show that all of the strain during the creep portion of the test is recovered, indicating that no permanent deformation occurred, and the sample is below its yield stress. Figure 19 shows data for the material at higher stress levels.

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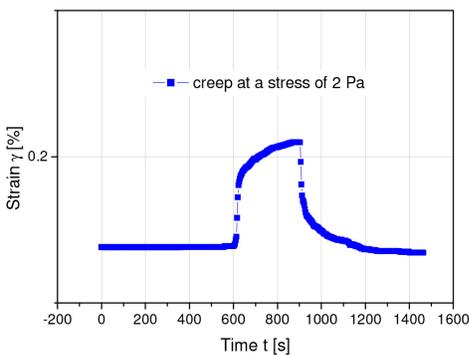


Figure 17: Creep and creep recovery for a model magnetic suspension after imposing a stress of 2 Pa, below its yield stress<sup>(3)</sup>

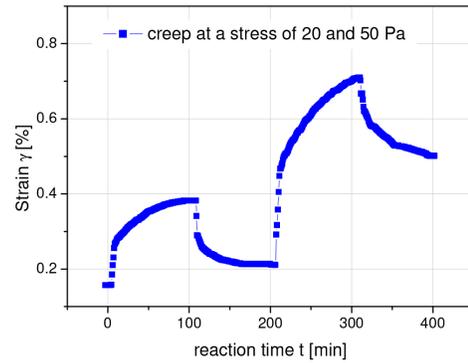


Figure 18: Creep and creep recovery for a model magnetic suspension after imposing its yield stress (20 Pa) and a stress substantially higher<sup>(2)</sup>

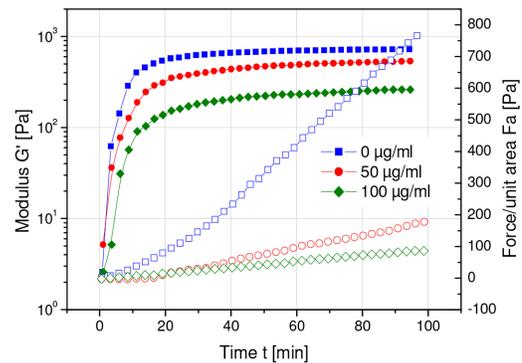


Figure 19: Effects of tetrameric concanavalin A on the clot rigidity ( $G'$ ) and contractile force of platelet-fibrin clots<sup>(4)</sup>

At 20 Pa some deformation is irrecoverable, and at 50 Pa, the material flowed. Data from steady shear and dynamic strain sweep tests, as well as calculations using a Casson model, established a yield stress of approx. 20 Pa also.

### Body fluids

Rheological testing has been used widely to advance the understanding of human and animal body fluids in many phases of medical, pharmaceutical, and personal hygienic products research and development. For example, steady, dynamic, and transient tests have been used to characterize and evaluate synthetic polypeptides to study the role of some side groups in naturally occurring proteins; monitor protein network formation in biological fluids; study the aging of the fluid lubricant secreted by synovial membranes in joints; develop water-soluble polymers for controlled drug release pharmaceuticals; develop synthetic body fluids for bandage and sanitary napkin evaluations; measure the erythrocyte aggregation energy index of red blood cells; establish the kinetics of blood platelet gelation; and study the mechanism of blood clotting.

In an effort to unravel the molecular basis for the binding of polymerizing fibrin strands and platelet membranes (the

major constituents of a blood clot), the role of platelet membrane glycoproteins in platelet-fibrin interactions during clot formation was investigated<sup>(4)</sup>.

Figure 19 shows the measured effects of tetrameric concanavalin A (a nonglycoprotein lectin) on the clot rigidity ( $G'$ ) and contractile force/unit area of platelet fibrin clots. The contractile force was measured using the sensitive normal force measuring capability of the ARES rheometer.

## RHEOLOGY OF FLUIDS—CASE STUDIES

### Solve Suspension Slurry Pumping Problems

A chemical formulator using a new lot of titan dioxide slurry burned out a pump motor during a routine transfer of material because the  $TiO_2$  particles settled unexpectedly overnight—hence his quality control problem could have been averted by rheologically testing each batch of material before use. When stored at rest, many suspensions have an internal structure that will not disrupt until a critical yield stress is reached. Overcoming this unexpected yield stress was the cause of the pump burn-out. Whether or not a given suspension will develop a yield stress can be assessed by testing the suspensions that have been stored undisturbed. Measuring the stress growth in a startup experiment provides the required information to avoid pump problems (Figure 20). Troublesome materials will exhibit a stress overshoot, and the maximum stress level reached has to be overcome to pump the slurry.

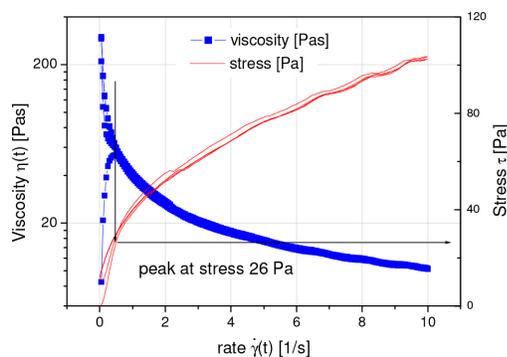


Figure 20: Stress growth experiment (rate ramp) to simulate pumping startup of  $TiO_2$  slurry

### Predict the texture of food products

In today's market, low fat foods represent a huge area of growth and diet conscious shoppers try to make every calorie count. One of the biggest problems in low fat foods is mouth-appeal. A food with less fat content has a different rheological profile, as shown here with peanut butters (Figure 21). The differences in viscosity can have negative effects on customer perception for spreading and mouth feel during consumption. A lower  $G'$  (storage energy) can mean problems with long term settling of the product, which will also be a negative effect on consumer preference.

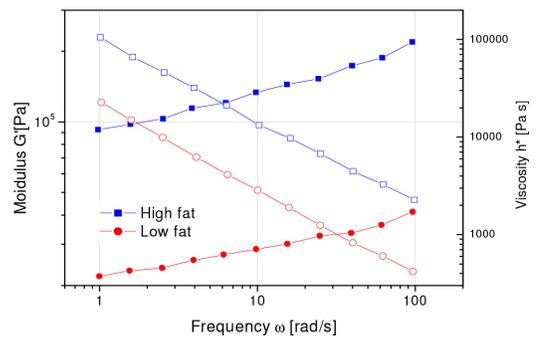


Figure 21: Peanut butter frequency sweep for low and high fat content

### Storage stability of emulsified products

Food products such as mayonnaise, and other important emulsified products, if not properly formulated, have poor storage stability. Gauging this using ordinary empirical shelf-life testing is time consuming and not practical. Dynamic mechanical rheological testing can provide a rapid solution. In emulsions, the underlying structure and interaction of the fluid droplets is what holds the stability of the product against settling or separation. The storage modulus  $G'$  of an emulsion is a good index of the emulsion's solid-like character that arises from the network structure. Raising temperatures of testing can increase the effects of settling in many cases, enhancing the comparison of results. Thus, products with poor storage stability can be weeded out before ever reaching the consumer. When an emulsion separates, it loses its solid-like character, becoming more fluid. Measuring  $G'$  as a function of time at an elevated temperature provides an easy method for judging emulsion stability (Figure 22).

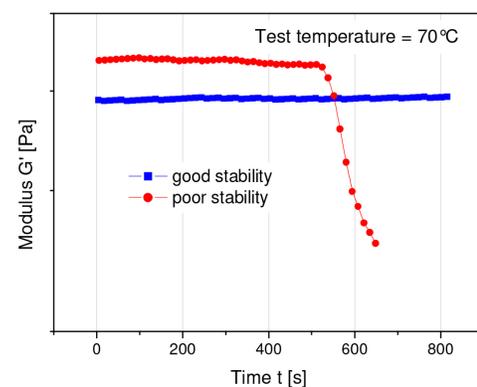


Figure 22: Mayonnaise emulsion stability

### Performance of personal products

The example in Figure 23 shows a dynamic time sweep of toothpaste at  $30^\circ C$  shearing the paste specimen at two different stresses. The higher stress level destroys the emulsion's structure, then the lower stress allows the slow rebuild of the viscosity. Time dependent experiments such as this provide

clues for optimal product usage. Too slow a rebuild and the product is unappealing, too fast and it is poorly suited for its application.

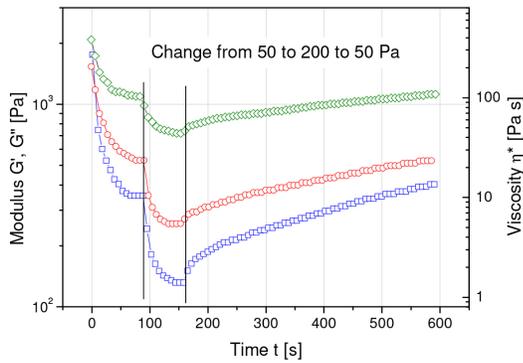


Figure 23: Structure break down and buildup of an emulsion

The dynamic time sweep in Figure 24 shows the behavior of a hand lotion under minimal and high strain. The important feature is ability of the hand lotion to break down its structure to flow smoothly across the skin, followed by a rebuilding of the structure when the strain is removed. This keeps the lotion on the skin, so that it does not continue to flow, or feel greasy. The dynamic time sweep allows continued monitoring of an event to see if the behavior is decaying or steady state. The ability of a product to achieve a steady state can be crucial to product performance.

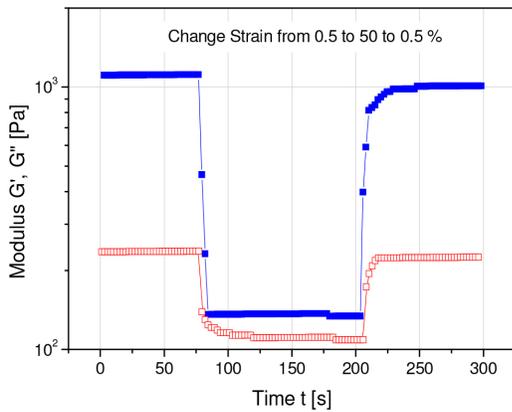


Figure 24: Hand lotion-structure break down and build up

### Phase Separations with temperature of polymer solutions

Dilute polymer solutions that have upper and lower critical solution temperatures can form one or two phases, depending on the temperature. A similar phenomenon is found for polymer blends. The phase transition temperature is called the consolute temperature. The consolute temperature of a given mixture can be determined by first measuring the storage ( $G'$ ) and loss ( $G''$ ) moduli of the material versus temperature, and then plotting  $\log G'$  versus  $\log G''$ . (Figure 25) This is a "modified Cole-Cole plot." The temperature corresponding to the point on the graph at which the data

begin to deviate from the common line is the consolute temperature.

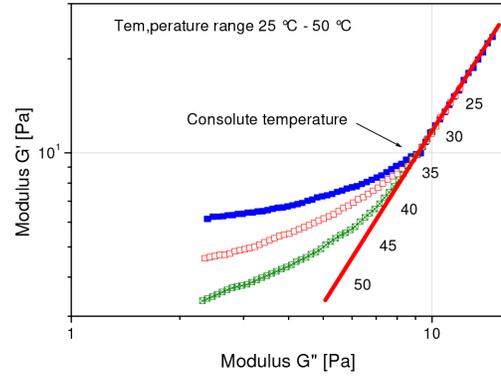


Figure 25: Consolute temperature of a polymer solution

### Measure Electrorheological Fluid Viscosity and Structure Build-Up

Electrorheological (ER) fluids increase in viscosity under the influence of an electric field. However, to understand the behavior of these materials, measuring the viscosity is not sufficient. Figure 26 shows the effect of increasing electric field voltage on an ER fluid. As the voltage is increased, the viscosity of the sample increases associated with consequent structure buildup over time. Though the viscosity changes almost instantly, the storage modulus ( $G'$ ), an indicator of the material structure, builds more slowly (Figure 27). After the electric field is removed, this particular ER fluid does not return completely to its original state, retaining some of the electrically induced structure. These effects, as well as the effects of changing frequency and current, can be studied using the ER Materials Analysis Package.

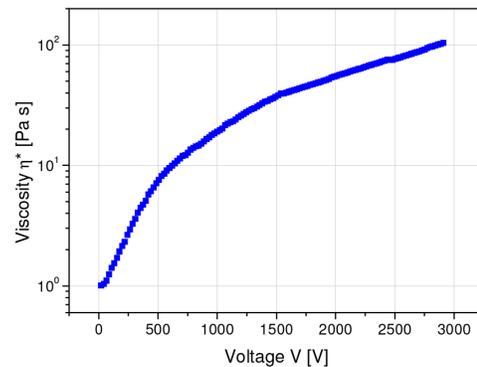


Figure 26: Effect of the voltage on the viscosity of an ER fluid

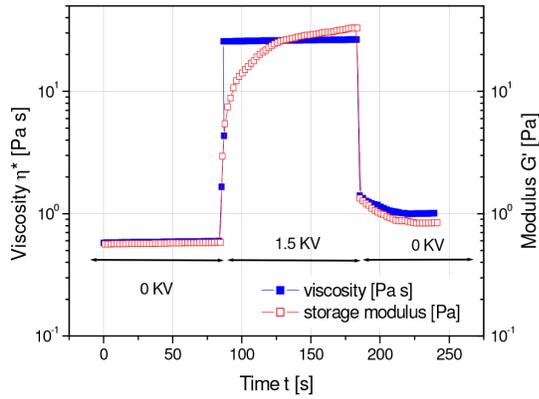


Figure 27: Viscosity and Modulus in a step voltage change for an ER fluid

insufficient degree of structure to avoid settling of the fruit juice particles.

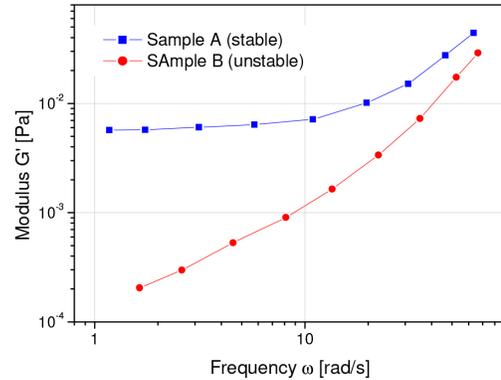


Figure 29: Storage modulus correlates with fruit juice stability

### Immersion Study

A number of materials are used in conditions of immersion. The behavior profiles usually differ dramatically when tested dry and in-situ. The ability to dissipate stress and the degree of frequency dependence of a material must be monitored in the conditions it will see in its application. The data in Figure 28 show a Fibrin Gel immersed in water and its behavior over a wide frequency range. Without in-situ testing such as this, product applicability cannot be determined.

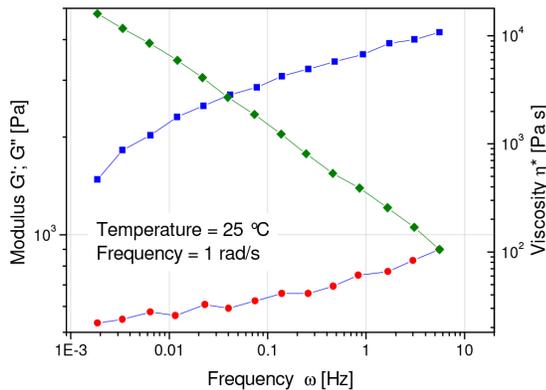


Figure 28: Frequency sweep of an immersed fibrin gel

### Sol-Gel transition of PVC gels

A polymeric gel is a three dimensional network forming from flexible chains through chemical or physical interactions. The transition from liquid state (sol) to the solid state (gel) is the sol-gel transition and the critical transition point is the gel point. The gel point can be determined rheologically, when the loss tangent becomes independent of frequency as a function of the concentration. Figure 30 shows the concentration dependence of  $\tan \delta$  for a series of frequencies from 0.1 to 100 rad/s for poly vinyl chloride in bi(2-ethylhexyl) phthalate (PVC in DOP). The gel point can be easily obtained from the common point in the multifrequency plot of  $\tan \delta$  (at constant frequency) versus concentration. The critical concentration at the gel point is 12.5 g/l for this system at 40°C.

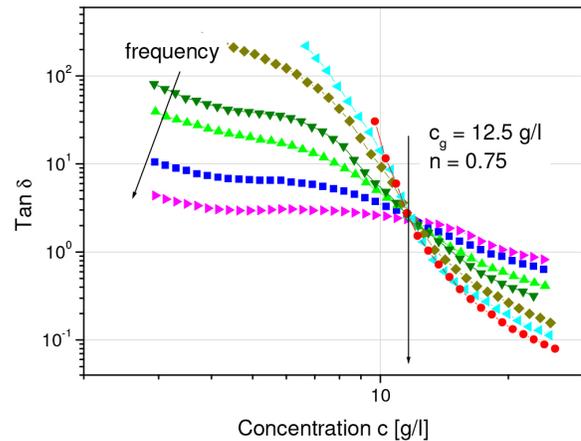


Figure 30: Sol Gel transition of PVC gels

### Predicting the Stability of Fruit Juice Blends

Soft drink concentrates were found to be unstable, depending on how they were mixed and bottled. Too thin concentrates showed fruit juice particles settling out, too thick concentrations were stable but hard to mix later. The optimum concentration, stable but not too thick to be easily mixed, could be evaluated in a frequency sweep as shown in Figure 29. The solid content of the juice blend was increased until  $G'$  reached a plateau value. A pronounced plateau value towards low frequency stands for higher elasticity and indicates a higher degree of internal structure, which makes the product more stable. In the unstable blend the plateau value at low frequency was not reached, so there was an

Revised by A. Franck.

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