Introduction

Is your viscometer approaching the end of its life?

Are you starting to feel that your trial and error, ‘rheology-light’ approach to formulation is becoming dated?

Or are there longstanding product performance issues that you’re failing to gain traction with, where you suspect rheology may hold the answer?

If the answer to any of these questions is yes, then it may be time to assess just what a modern rheometer can do, most especially relative to a cheaper viscometer. Rheometer design and functionality has advanced considerably over the course of the last decade and today’s instruments offer an extremely broad range of test capabilities, wrapped in software that makes them accessible to less expert users. Such systems support the industrial adoption of rheology and deliver cost benefits far beyond those returned by viscometers, from R&D, through formulation and into manufacture. Here, we look at the top five measurements offered by rheometers that enhance their value relative to viscometers and provide some example studies to illustrate potential benefits.

1. A Broader Measurement Range – Extend Your Viscosity Flow Curve

A broader measurement range makes it easier to obtain relevant data by subjecting the sample to conditions that reflect those applied during product use or manufacture.

Viscosity is a performance-defining parameter for many industrial products, few of which are Newtonian. A Newtonian fluid exhibits viscosity that is independent of the applied shear rate – a common example being water. Non-Newtonian materials, in contrast, either shear thin, i.e., exhibit lower viscosity at higher shear rates, or, less commonly shear thicken meaning that viscosity increases with applied shear rate. Understanding how a material will behave when used, or processed, relies on knowing its properties under the conditions that are routinely applied. Clearly this is much more challenging for non-Newtonian materials than for those that are Newtonian.
One of the simplest ways of investigating viscosity is to generate a flow curve, a plot of viscosity as a function of shear rate. Measurements are made either by subjecting a sample to different shear stresses and measuring the resulting shear rate, at each applied stress, or by subjecting a sample to a controlled shear rate and measuring the resultant stress. The ability of a rotational rheometer to cover a much broader range of shear rates than a rotational viscometer means that the flow curve generated can be far more comprehensive. Most especially data can be generated at the very low shear rates associated with storage and movement under gravity.

**Eye Surgery**

Ophthalmic Viscosurgical Devices (OVDs) are viscoelastic solutions or gels used during eye surgery, and are typically aqueous polymeric solutions containing one or more of the following constituents: hyaluronic acid; chondroitin sulfate and/or methyl cellulose. The International Standard (ISO 15798:2013) covering OVDs directly specifies rheological measurement because of the impact of product rheology on in-use performance. Carrying out steady state testing at shear \(s^{-1}\) rates in the range 0.001 to 100 determines how a fluid will behave within the anterior chamber and when injected into the eye through a cannula, respectively. The lower end of this range is inaccessible to a typical rotational viscometer.

Figure 2 shows flow curve data for three OVD formulations, each with a different yaluronic acid concentration: 15 mg/ml, 18 mg/ml and 25 mg/ml HA solutions, and their tendency towards Newtonian behavior at the very low shear rates typical of at rest conditions within the eye.

Equilibrium flow curve data shows the shear-thinning behavior of 25 mg/ml (△), 18 mg/ml (+) and 15 mg/ml (○) HA solutions, and their tendency towards Newtonian behavior at the very low shear rates typical of at rest conditions within the eye.

By spanning a much wider range of shear rates than a viscometer, a rotational rheometer is able to provide data of direct relevance to more processes.
Time to Spec Up?
Top Five Reasons to Replace Viscometer with a Rheometer

2. Relevant Yield Stress Measurement – Generate Accurate Data for Every Sample Type

Yield stress defines the consumer appeal of many products. Accurate and relevant measurement, using an appropriate technique, therefore supports faster and more effective formulation.

After viscosity, yield stress is perhaps the most routinely measured rheological property since many consumer products derive value from having one. Complex fluids that exhibit a yield stress transition from solid- to liquid-like behavior when subjected to a stress (or strain) that exceeds a certain value. A number of foodstuffs (e.g., tomato ketchup, mayonnaise and yoghurt) and many cosmetics are invitingly rich and thick on a plate or in a pot (at rest), but at the same time easy to dispense or smooth over skin, respectively, because of their more liquid-like behavior when shear is applied. Yield stress and strain also provide an indication of strength and brittleness, respectively.

Yield stress varies as a function of temperature, and the timescale over which the stress or deformation is applied, and can be measured using a range of techniques. By enabling application of the widest range of these methods rotational rheometers make it possible to gather far more relevant yield stress data than can be measured using a rotational viscometer. One of the simplest approaches, with a stress-controlled rotational rheometer, is to apply a stress ramp. This involves steadily increasing the stress applied to the sample, measuring the resultant strain, and determining a peak viscosity (see figure 3). Careful control of the stress ramp rate, or measurement at different ramp rates, enables assessment of the effect of timescale on measured values.

Alternatively, yield stress data may be generated via oscillatory testing (see below), or more specifically an amplitude sweep. An amplitude sweep involves subjecting the sample to a sinusoidal strain profile of gradually increasing amplitude. When the material microstructure is intact G’, the elastic modulus remains constant (see ‘Viscoelasticity’ box), but as structure breaks down it falls rapidly. The region in which G’ remains constant is referred to as the Linear Viscoelastic Region (LVER) and its edge point can be taken as defining the yield point, though some rheologists use the stress or strain at which G” becomes greater than G’ although this is less preferable. Most generally the true yield point occurs somewhere between these two transition points and can be correlated with a peak in the elastic stress (stress component of G’).
Non-Drip Ketchup

Figure 5 shows stress ramp test data for three samples of commercially available tomato ketchup: value; supermarket own brand; and branded. The tests were carried out using a Kinexus rotational rheometer with a 40 mm serrated parallel plate geometry. The data show that each sample has a yield stress with the branded product exhibiting most structure with a yield stress of 22 Pa. This suggests that the branded product will flow least easily, making it less easy to dispense but satisfyingly non-drip during use!

3. Oscillatory Testing – Characterize Microstructure and Control Solid-Liquid Transitions

Oscillatory testing probes the viscoelasticity of a sample providing a microstructural fingerprint that can be used to quantify stability and to sensitively refine critical aspects of product performance.

A defining benefit of rotational rheometers is their oscillatory testing capability. With oscillatory testing, the sample is subjected to a relatively small shear force or displacement applied in the form of a sinusoidal wave. Rotational rheometers are specified to apply the bi-directional movement of the upper geometry, relative to the lower, that is required to achieve this. Rotational viscometers are not, and apply shear in just one rotational direction.

Since oscillatory testing is carried out in the LVER, it enables non-destructive investigation of the viscoelastic characteristics of a material. Testing over a range of frequencies – performing a frequency sweep – provides insight over timescales that are relevant to the way in which the product will be used or manufactured.

4 An amplitude sweep identifies the LVER of a sample, the region in which it exhibits solid-like behavior; a longer LVER is indicative of greater structure in the sample

5 The high yield stress of the branded tomato ketchup (red), relative to the supermarket (blue) and value (green) alternatives is indicative of greater structure and suggests that it will be less prone to spreading on a plate or dripping during use
Such analysis generates a very characteristic fingerprint of a material that is closely associated with structural features. It indicates whether a sample has greater viscous tendencies, i.e., is more likely to flow, or is predominantly elastic with more structure and stability, under specific conditions (see figure 6), and can also provide textural information by quantifying total stiffness (via $G'$) and springiness (via $\delta$). Testing can also be carried out at different temperatures to further define product performance under typical use conditions.

*Shower Gels with Shelf Appeal*

The functionality and/or shelf appeal of shower gels is routinely enhanced through the inclusion of suspended components. For these products, stability often relies on the combined action of surfactants and an associative polymer such as a HASE (hydrophobically-modified alkali soluble emulsion) polymer. By associating with surfactant micelles, these polymers can form an interconnected network with an apparent yield stress which immobilizes the suspended component in a desirable distribution. Where this is the formulation strategy, then determining an optimal level of associative thickener is clearly crucial.

Figure 7 shows oscillatory test data for shower gel samples containing different levels of an associative polymer: A=0%, B=2%, C=4%, D=6% and E=8% (GL2) %. The tests were carried out using a Kinexus rotational rheometer with a cone-plate geometry. Measurements were made in the LVER and over a frequency range of 0.005 Hz to 10 Hz. At low concentrations (0 - 4% inclusive), $G''$ exceeds $G'$ at all frequencies. This means that liquid-like behavior is dominant, that the shower gel has no yield stress and that stability is likely to be relatively poor. However, samples D and E exhibit different behavior. At levels of 6 and 8%, the HASE polymer induces a networked structure and an associated apparent yield stress of 0.8 and 3.8 Pa, respectively, as determined from an amplitude sweep test. These levels of polymer inclusion are therefore likely to deliver the stability needed for commercial success.
Rheology Basics – Viscoelasticity

Materials that exhibit viscoelasticity transition between liquid- (viscous) and solid- or gel-like (elastic) behavior, depending on the conditions they are subjected to. Oscillatory testing subjects a sample to the application of shear stress (or shear strain) in a sinusoidal wave pattern and the shear strain (or shear stress) measured. The complex modulus ($G^*$) is defined as the maximum shear stress divided by the maximum shear strain and is a measure of the overall stiffness of the material.

The phase angle of the resultant strain (or stress), quantifies the extent of the lag between the application of stress and its impact, thereby defining whether viscous or elastic behavior is dominant and how much each component contributes to $G^*$.

$$G' = G^* \cos \delta$$

$$G'' = G^* \sin \delta$$

$$G^* = \sqrt{(G'^2 + G''^2)}$$

$$\tan \delta = G''/G'$$

If $G'>G''$ then elastic properties – solid-like behavior – are dominant.
If $G'<G''$ then viscous properties – liquid-like behavior – are dominant.

The frequency of the sinusoidal waveform applied during testing correlates with the timescale over which shear is applied. High-frequency measurements assess behavior in a way that is relevant to relatively short timescale processes involving rapid deformation, while low-frequency testing is relevant to slow deformation.
Better Butter?

Spreadable butters are formulated specifically for ease-of-use when the product is removed from the fridge. Here then, it is the temperature dependence of behavior, that is crucial. Figure 8 shows the results from a single frequency oscillatory temperature ramp performed on two butter samples: one spreadable; the other normal. The samples were evaluated over the temperature range 4°C to 35°C via small amplitude oscillatory testing using a Kinexus rotational rheometer with a roughened parallel plate geometry to minimise slippage. Standard loading and pre-configured test sequences were applied. The applied temperature ramp rate was 2 °C/min.

At 4°, a typical fridge temperature, the G' of the normal butter is an order of magnitude greater than that of the spreadable alternative, indicating that it is far stiffer in texture. For both samples, the phase angle, δ, is very low (less than 10°), indicating that solid-like behavior is dominant. With increasing temperature, the modulus values for both samples decrease, as the crystalline milk fat melts and the structure of the products begins to soften. This drop is more pronounced for the normal butter than for the spreadable sample and is associated with a peak in the phase angle – an indicator of more liquid-like behavior - which occurs at a slightly higher temperature with the normal butter. These test data therefore directly quantify the key characteristics of the spreadable product relative to normal butter, showing that it will be less stiff when taken out of the fridge, and will also soften at a lower temperature.
4. Axial Testing – Quantify Tackiness and Extend Viscosity Measurement Capabilities

Precise normal force and gap control makes it possible to measure tack or stickiness and the rheology of samples with high solids fractions.

The majority of rheological testing involves the application of rotational shear; however, there are a small number of commercially useful tests that require axial testing. By enabling the precise control of normal force and the gap between upper and lower geometries, rotational rheometers deliver two key test types that are inaccessible with a standard rotational viscometer:

- Pull away or tack testing – to directly quantify stickiness
- Squeeze flow measurements – for the characterization of samples with high solids loading which can fracture during standard viscosity testing

Tackiness or stickiness may be desirable – tapes, labels, adhesives – or an unwanted property, in materials such as bone cements, which must be tack-free (ISO5833) to avoid adherence to gloves or application aids, and certain foods and personal care products. Controlling tackiness is therefore a routine formulation goal. Performance under the application of different amounts of pressure can be important, as can the time period over which tackiness decays. Tack testing with a rotational rheometer involves measuring the force required to separate two parallel plates with a defined volume of material between them. Testing begins with the plates in a stationary position, with no initial pressure applied.

The fracture of samples with high solids fractions, toothpaste being a prime example, can occur at relatively low to medium shear rates, compromising the generation of adequate flow curve data. Sample fracture typically occurs at the edge of the geometry gap and gives rise to a sudden sharp decrease in the shear stress/strain data (see figure 10).

For samples such as these, squeeze flow techniques extend the range of conditions over which viscosity can be reliably determined, into areas of industrial relevance. These techniques involve loading a sample between parallel plates and then measuring the normal force generated by the sample as the gap between the plates is closed at a constant speed. Gap and normal force measurements are converted into shear stress and shear rate data to allow the calculation of shear rate viscosity as a function of shear rate$^2$ (Laun, Rady and Hassager 1999).
Just the right degree of tackiness

For re-usable adhesives such as Blu-tack®, stickiness or tackiness is clearly a defining characteristic, with the user applying sufficient pressure to achieve a desirable result. To assess the impact of application pressure, the tack properties of Blu-Tack® were measured over a range of contact forces: 5 N; 10 N; 15 N; and 20 N. Measurements were carried out using a Kinexus rotational rheometer using a 20 mm upper plate and 65 mm lower plate (stainless steel) and standard pre-configured test sequences, at a temperature of 25°C. A 1.3 g ball of sample was placed in the center of the lower plate and the upper plate was then lowered into contact with the sample at a speed of 10 mm/s until the required contact force was attained. After a contact period of 2 seconds, the gap was increased linearly at a rate of 10 mm/s (see figure 11).

Comparative data for all of the contact pressures, and the corresponding tensile (resistance to pull way) force that corresponds with tack, are shown in figure 12. The peak in each curve indicates the ‘tack’ of the sample which increases with increasing contact pressure, though the difference between 15 and 20 N is relatively small. The area under the curve, on the other hand, equates to the adhesive strength of the sample. This increases with contact force up to 15 N before decreasing at 20 N, suggesting there is an optimum contact force for maximum adhesion. The time taken for the force to decay is similar for all contact pressures with the exception of the 20 N data which suggests a slightly quicker failure rate.
Squeezing Toothpaste

The squeeze flow behavior of toothpaste was measured to extend shear viscosity data into a commercially relevant regime inaccessible via conventional rotational testing. Tests were carried out at 25°C using a Kinexus rotational rheometer with a 60 mm parallel plate and a pre-configured squeeze flow sequence.

Measurements were made at two different gapping speeds: 2 mm/s and 10 mm/s/cm. Sample size was 1 g (toothpaste density 1.3 g/cm³).

The gap and normal force profile for the toothpaste (see figure 13) shows how, as the gap is closed the normal force exerted by the sample increases relatively quickly. Once the upper geometry reaches the defined end gap, the compressive force becomes constant as the progressive squeezing stops. Figure 14 shows the shear viscosity data generated from gap/normal force measurements at both gapping speeds along with data generated at lower shear rates, by traditional rotational rheometry. The squeeze flow data matches up extremely well with the rotational data, with measurements at the two different speeds successfully extending the shear rate range that can be characterized.
5. Sophisticated Test Sequences – Delve Deeper into Process and Product Performance

Beyond the measurement of specific rheological parameters, rotational rheometers make it possible to apply test sequences that directly simulate in-use behavior to provide valuable data for product optimization.

The sensitivity and performance of rotational rheometers, coupled with the ability to closely control the test environment, and the capacity for axial testing means that the ability to simulate specific processes is enormously broad. Those working at the forefront of rheological analysis have, for example, used a rotational chewing development that can bring objectivity to the assessment of how a food is likely to be perceived and enjoyed, when eaten. Simpler examples include the study of curing and thixotropy.

Products that cure, prime examples being adhesives and nail varnish, transition from liquid to solid or gel over a certain time period, frequently in the presence of UV light. Crosslinking polymers are often responsible for this transition. When these products are in their liquid state, they are easily manipulated and applied but once cured they become more fixed. Ensuring that the ‘operational time window’ is optimal for product use is crucial, as are the properties of the cured material. With an appropriate test set-up, oscillatory protocols can be applied to quantify both aspects of behavior.

Time is also a critical factor when it comes to optimizing shear thinning or thickening characteristics. Engineering a shear thinning profile is often desirable but in many instances the structural changes that rebuild viscosity when shear stress is reduced do not occur instantaneously; rather the material exhibits thixotropy. The longer it takes for a material to regain viscosity the more thixotropic it is. Understanding thixotropy is therefore important not only for making reproducible measurements but also for controlling product performance.

Nasal sprays are often thixotropic and here it is desirable for structure to build over a very short timescale so that the low viscosity liquid easily atomized by the nasal pump can quickly become sufficiently viscous to be retained in the nose. With paints, on the other hand, a very short rebuild time may leave visible brushstrokes, slightly longer relaxation times allow some time for levelling though too long is likely to result in drips.

A faster manicure

Many commercially available nail varnishes are effectively ‘daylight’ curing, but UV curing products – ‘hybrid’ and ‘soak-off’ gels – are increasingly popular in a market that has evolved dramatically over the last decade or so. The curing process for soak-off gels tends to involve a relatively high degree of polymer cross-linking which results in a finish with substantial resistance to acetone. A fast cure has obvious benefits, especially since these soak-off products are primarily applied by beauticians, but finish is clearly critical.

Tests were carried out to study the UV curing profile of a number of different soak off gels: gold glitter; red; pink and black. Testing was carried out using the Kinexus rotational rheometer with parallel plates. UV light of fixed intensity was applied to the gels for 30 seconds and a curing profile was then generated by measuring the change in $G’$, a measure of stiffness, as a function of time (see figure 15).

The results highlight clear differences between the products with the gold glitter gel (clear varnish with suspended glitter particles) curing most rapidly, and to the highest stiffness. The black gel cures most slowly and has a much lower shear modulus. To further investigate the properties of the finish, post-cure amplitude sweeps were carried out for each product. These revealed that the black gel has a longer LVER than the gold glitter gel. Taken together the results provide comprehensive insight into the nature of the products: The glitter gel will cure quickly to give a brittle finish that may be difficult to remove, while the black gel will cure far slower to a more flexible coating that is easier to remove. The other products exhibit behavior between these two extremes.

Oscillatory testing for nail varnishes reveals clear differences in their curing profiles which would directly impact customer experience
Thixotropy of nasal sprays

Thixotropy can be assessed using viscometry testing by monitoring the time evolution of viscosity on stepping from one shear rate to another, as shown in figure 16. For example, with paint, a high shear rate is used to replicate brushing and a low shear rate to represent the film rebuild on the wall. Viscometry is very useful for assessing thixotropy but it is not capable of monitoring the full recovery of a gel structure since the application of a shear rate will continually break the reforming gel structure down. This is where oscillation testing is useful as it is possible to apply a constant shear rate to break the structure down then follow the recovery process in oscillatory mode allowing both pre-gelation and post-gelation processes to be followed through the evolution of $G'$ and $G''$.

Figure 17 shows small amplitude oscillatory data for two allergy relief nasal sprays before and after the application of a shear rate. The tests were carried out using a Kinexus rotational rheometer with a cone-plate geometry. Stage 1 and Stage 3 are oscillatory measurements made in the LVER (0.1% strain) before and after the application of a constant shear rate of $10\,\text{s}^{-1}$ (Stage 2) which breaks the structure down. Sample A is quite thick and highly gel-like with $G'$ (550 Pa) $\gg G''$ (110 Pa). It is also quite thixotropic, taking approximately 800 seconds for $G'$ to recover its original value (stage 1) following unidirectional shear. In comparison, Sample B is quite thin but appears to have a weak gel structure at the frequency measured with $G'$ (0.2 Pa) $> G''$ (0.15 Pa). It is not thixotropic since it recovers its structure after just a couple of seconds. Sample A is marketed as a thixotropic gel spray and Sample B as a standard nasal spray.
Next Steps – Scrutinizing a Spec

If evaluation of the available test methods and capabilities suggest that upgrading to a rotational rheometer may be advantageous, choosing the right instrument is the next step. This can be tricky as the published specifications for rheometers can be misleading. There is no standard way of generating instrument specifications and it can be difficult to interpret in terms of the measurement capabilities that you need. With this in mind, it’s worth keeping the following points at the forefront of your mind when you start window shopping:

- If you are not a rheology expert, then it’s critical to have a software interface that you are comfortable with. System performance is important but can become irrelevant if your own skills inhibit you accessing it. The software that drives rheometers has progressed substantially in recent years with systems such as our own rSpace (for Kinexus) enabling SOP-type (Standard Operating Procedure) testing. These help you choose the right test for investigating specific behaviors, guide you through measurement, and support interpretation of the resulting data. Software of this type can have a major impact on who can use the instrument and the value it delivers.

- Sensitivity, including torque, angular displacement, gap and temperature resolution is important also. Sensitive systems with precision control deliver the very practical benefit of better quality data and at the same time let you gather accurate data with less sample. This can be crucial in the early stages of development. Higher sensitivity also enables the characterization of a wider range of sample types over a wider range of measurement conditions.

- Be realistic and specific about what you want to do, both now and into the future. For example, are you interested in quality control or formulation and product optimization? What types of samples do you need to measure – a wide range with distinctly different properties, or a narrow group of closely similar materials? And what information are you really looking for? This will help you focus in on a product that is well-matched to your needs – sufficiently sophisticated to meet requirements, but cost-effective.

- Above all, test your samples on any instrument that makes it into your shortlist. See how easy it is to make a measurement and push the specifications that are important to you if you are working towards the limits of what can be measured. This is the meaningful way to test a published specification and ensure that you purchase a rotational rheometer that enables you to exploit all the benefits of this powerful science to meet your commercial goals.

References

1 Understanding Yield Stress Measurements, Whitepaper