Time to harness the true power of rheology

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The penetration of new analytical techniques follows a well-defined path; first come the early adopters, who find out what new technology can do, assess its value and shape its evolution, and then, with a positive outcome, it transitions to the mainstream. Formulators can use information from a wide variety of techniques which means it can be easy to lose sight of what has become possible. Recent advances in the design of rotational rheometers provide a good example of how technology can transform the accessibility, and consequently the value of the technique, over just a few years.

In this article we look at what today's rotational rheometers can do, contrasting this with the data delivered by typical rotational viscometers. For some time viscometry has been a mainstream technique for formulation, but those leading the way have long since transitioned to the broader capabilities of rheometry. The choices associated with replacing your ageing viscometer may, therefore, be a long way from like-for-like. Here we provide insight to support an up-to-date assessment of the value of upgrading.

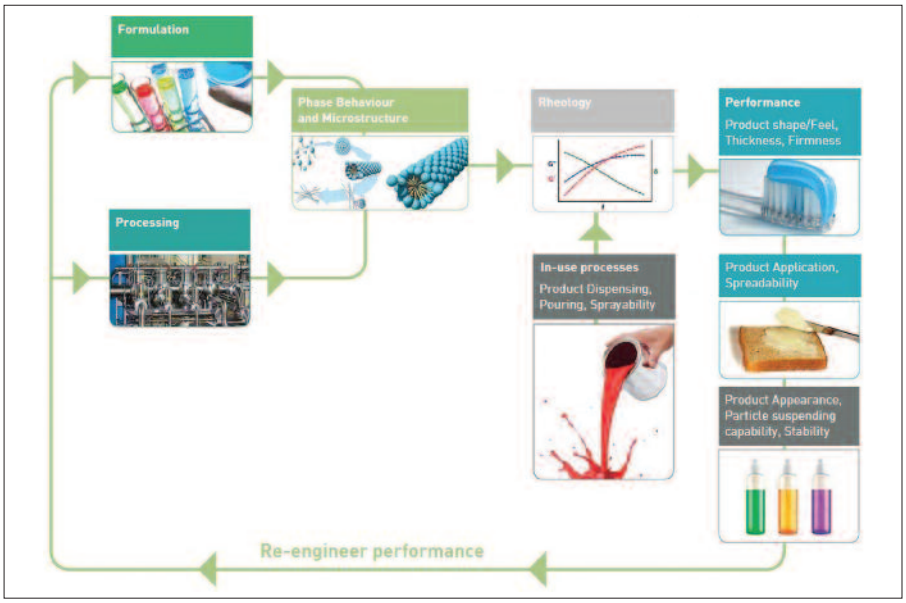

Figure 1: Rheological measurements correlate directly with critical aspects of product performance and help to accelerate formulation to a successful conclusion.

Beyond single point viscosity

A standard rotational viscometer is an efficient tool for measuring viscosity, at a single point or across a moderate range of shear conditions. However, with the majority of commercial personal care products exhibiting complex, non-Newtonian behaviour, viscosity measurements over a narrow range provide an incomplete picture. Furthermore, viscosity is far from being the only parameter that can usefully be measured to determine product performance, or indeed commercial appeal. Other defining rheological properties include: viscoelasticity; yield stress; thixotropy; and tackiness. Rotational rheometry extends access to the comprehensive measurement of all of these parameters and in so doing has the potential to deliver significant value to formulators.

In simple terms the capabilities of a rotational rheometer allow formulators to develop a detailed understanding of performance across all the changing conditions to which a product may be subjected, during manufacture and use. Consumers expect products to behave in a well-defined way and are susceptible to those with 'kerb appeal' - moisturisers with a rich, creamy texture, for example, or face washes containing eye-catching suspended particles. Understanding product performance at rest - on the shelf - and when subjected to the shear associated with actions such as smoothing cream across the skin is crucial, and allows formulators to knowledgeably optimise performance, and appeal, long before the product reaches the shelves (Fig 1).

Complete flow curve measurement

Viscosity measurements remain the most widespread rheological analysis and if carried out over an appropriate range can be highly informative. Non-Newtonian materials 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. Generating a flow curve - a plot of viscosity as a function of shear rate – over a representative shear rate is therefore a valuable core strategy for formulation studies. A particular strength of rheometers, relative to viscometers is that they enable measurement across a broader shear rate range, in particular at the extremely low shear rates associated with storage, and can therefore provide insight into long-term product stability (Fig 2).

The majority of viscosity measurements involve the application of a rotational shear force or rate, but rheometers, by enabling the precise control of normal force and the gap between upper and lower geometries, also provide the means to carry out axial testing, a technique that is inaccessible with a standard rotational viscometer. This permits:

- Pull away or tack testing – to quantify stickiness
- Squeeze flow measurements – to extend flow curve measurement for samples with high solids loadings which can fracture during standard viscosity testing.

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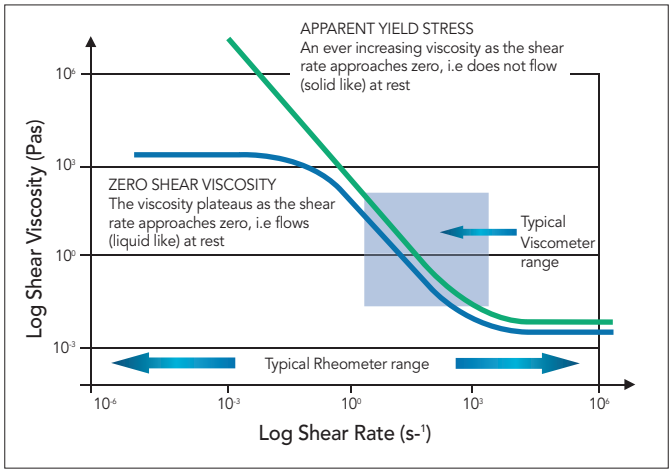

Figure 2: With a rotational rheometer it is possible to extend the flow curve across a much wider shear rate range to understand how a product will behave under all the conditions encountered during routine use.

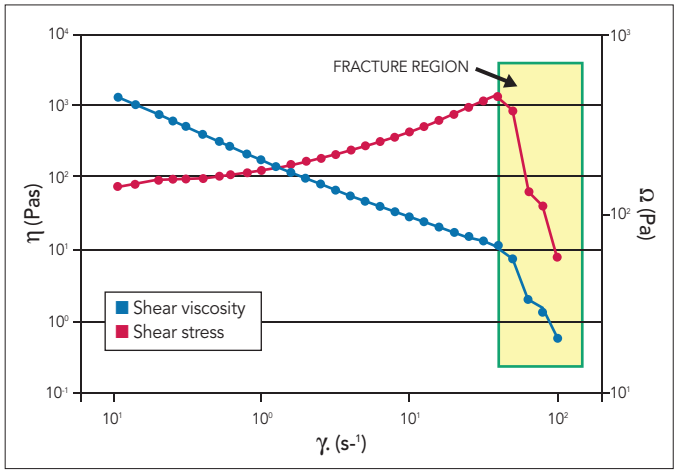

Figure 3: Shear stress/viscosity data for toothpaste highlights the problem of sample fracture in rotational testing, and how it compromises measurement of a complete flow curve that fully spans all the conditions of interest.

Using squeeze flow measurements to characterise the viscosity of toothpaste

Toothpaste is a prime example of a personal care product formulated with a high solids fraction. In viscosity testing toothpaste has a tendency to fracture at relatively low to medium shear rates, compromising the development of a flow curve that covers the complete range of interest. Typically sample fracture occurs at the edge of the geometry and leads to a sudden decrease in the shear stress/strain data (Fig 3).

With squeeze flow techniques, gap and normal force measurements are converted into shear stress and shear rate data in order to calculate shear viscosity as a function of shear rate under the conditions at which sample fracture occurs.[1] Figure 4 shows gap and normal force profiles measured for toothpaste at 25°C using a rotational rheometer (Kinexus, Malvern Instruments) with a Peltier plate cartridge and 60 mm parallel plate. Tests were conducted at two different gapping speeds - 2 and 10 mm/s - using a pre-configured squeeze flow sequence. Sample size was 1g (toothpaste density 1.3 g/cm^3).

The gap and normal force profiles show that 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 5 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 shear 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 achieved.

Probing viscoelasticity

A further primary difference between viscometers and rheometers is that the latter permit oscillatory testing. As the term suggests, oscillatory testing involves subjecting the sample to a relatively small shear force, or displacement, applied in the form of a sinusoidal wave. It therefore calls for bi-directional movement of the upper geometry, relative to the lower, a feature uniquely associated with rotational rheometers. This testing is usually performed in the Linear Viscoelastic Region (LVR) where stress-strain is linearly dependent and the microstructure remains intact.

Oscillatory testing probes the viscoelasticity of a material – the extent to which it exhibits viscous (liquid-like) or elastic (solid-like) behaviour, or indeed transitions between the two under different conditions. Key test variables are the frequency of oscillation (ω), which correlates with the timescale over which deformation is carried out ($t \approx 1/\omega$), and temperature, which is similarly tailored to reflect in-use conditions. The metrics measured include the complex modulus, G*, which indicates total material stiffness and which can be broken down in to its elastic and viscous moduli, G′ and G″ by utilising the phase angle or phase difference, δ, between the applied stress and measured strain. For a fuller discussion of oscillatory testing please refer to Reference 2, but in summary:

- If the phase angle is zero, the applied stress and resultant strain are in phase, and the material is behaving as an ideal solid.
- If the phase angle is π/2 radians (a quarter of a cycle) out of phase then the material is behaving as an ideal liquid.
- Viscoelastic materials have a phase angle between 0 and π/2 radians.

and

- If G′>G″ then elastic properties – solid-like behaviour - are dominant.
- If G′<G″ then viscous properties - liquid-

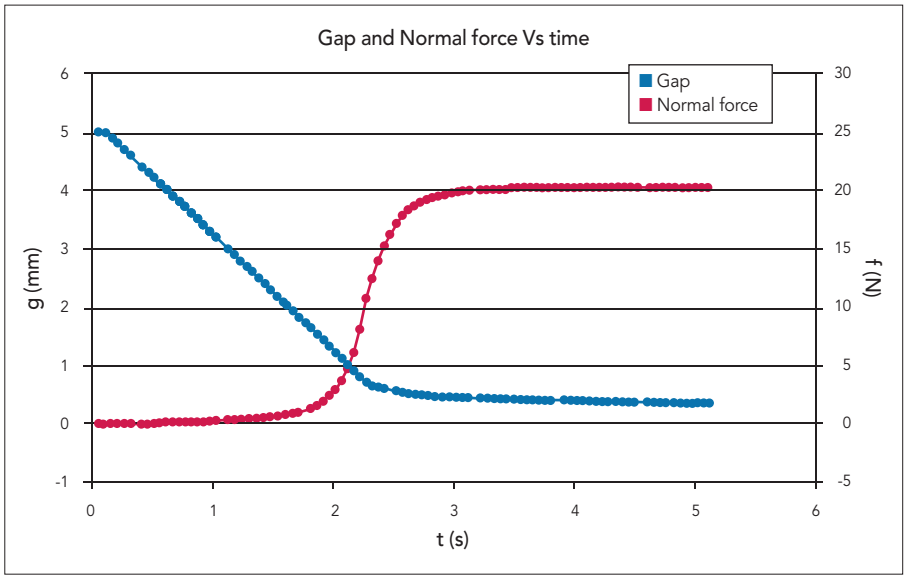

Figure 4: The gap (blue) and normal force (red) profiles for toothpaste illustrate the force generated in the sample as the gap closes at a speed of 2 mm/s.

like behaviour – are dominant.

Oscillatory testing supports the development of a microstructural fingerprint that provides insight into important aspects of product performance such as stability by identifying conditions under which structure develops in the product (Fig 6). It can also quantify characteristics such as spreadability, as a function of temperature for example, and provides textural information by quantifying stiffness (via G*) and springiness (via phase angle).

Using oscillatory testing to develop a stable shower gel

The stability of personal care products with suspended particles, such as shower gels, 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 are able to form an interconnected network with an apparent yield stress. Products with a yield stress behave in a solid- or gel-like way at rest, and until applied stress exceeds a certain value, at which point they begin to flow like liquids. Developing a formulation with a yield stress can therefore help with immobilisation of a suspended component.

Figure 7 shows oscillatory test data for shower gel samples from an experiment designed to determine an optimal level of HASE addition. The samples contain different levels of an associative thickener: A=0%, B=2%, C=4%, D=6% and E=8%. At low concentrations (0% – 4% inclusive) G'' exceeds G' at all frequencies meaning that liquid-like behaviour is dominant, that the shower gel has no yield stress and that stability is likely to be poor.

Samples D and E however exhibit different behaviour, with the data

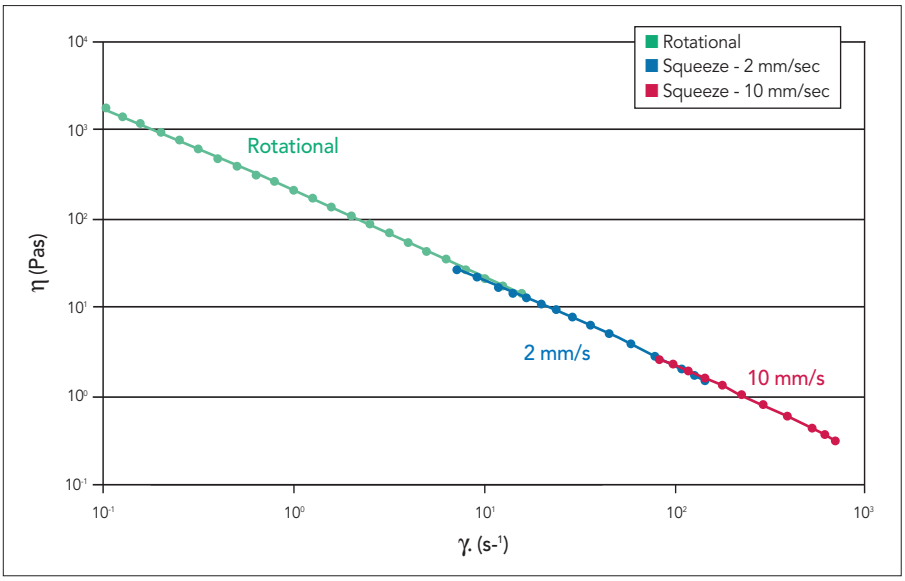

Figure 5: Squeeze flow testing extends the shear rate range over which viscosity data can be measured for the toothpaste sample.

suggesting that a networked structure begins to form at these higher concentrations. These two samples have an apparent yield stress of 0.8 and 3.8 Pa respectively and are therefore able to offer better suspension (product) stability.

Advanced testing to quantify specific aspects of product performance

When tailoring rheological testing to maximise informational insight formulators closely define the test conditions applied and may even link different types of testing to ensure that the results generated are as representative as possible. While mechanical performance improvements have been important in extending the application of rheology, advances in software have been equally transformative. Modern rheometers have an inviting interface that makes it easy to decide which tests to perform, to perform them, and to analyse the resulting data, as well as offering the flexibility for customised sequence development. Curing is a good example of a process that can be simulated and followed directly using a rotational rheometry sequence as the following data shows.

Assessing the curing behaviour of nail polish

As a nail varnish cures it transitions from a liquid to a solid- or gel-like finish often as a result of exposure to UV light which catalyses the crosslinking of polymeric components of the formulation. Many commercially available nail varnishes are effectively 'daylight' curing, but UV curing products – 'hybrid' and 'soak-off' gels – are becoming increasingly popular. The curing

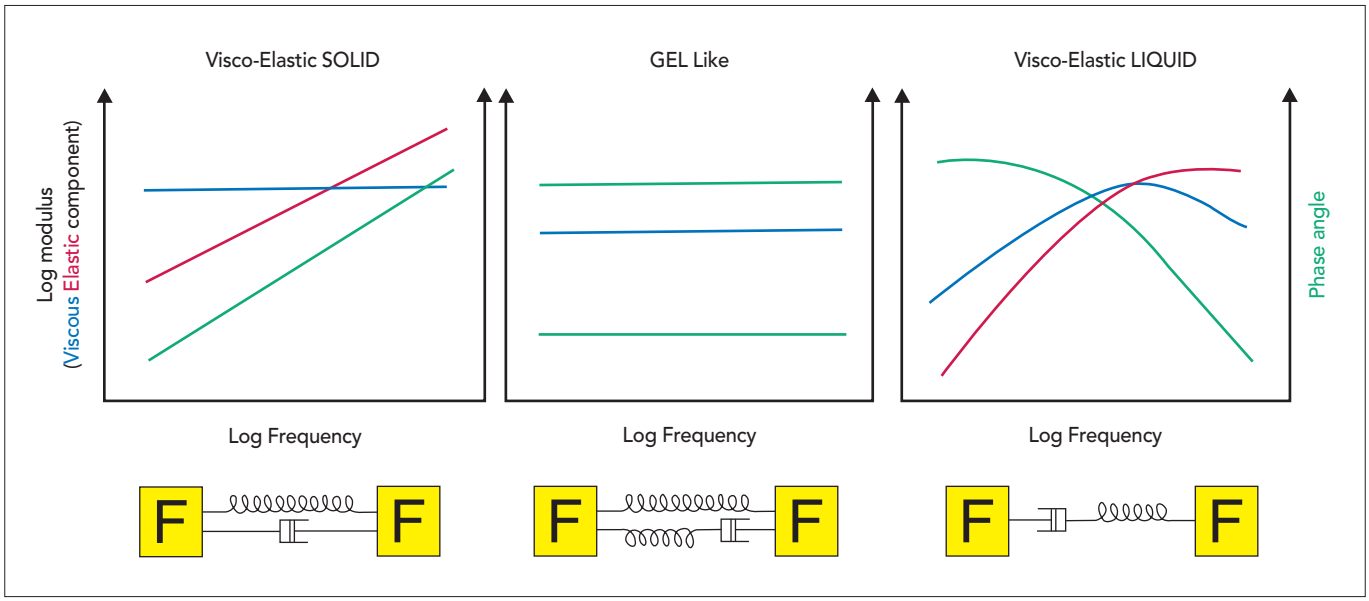

Figure 6: Oscillatory test data across a range of frequencies indicates whether a sample will behave as a visco-elastic solid, as a gel or as a visco-elastic liquid.

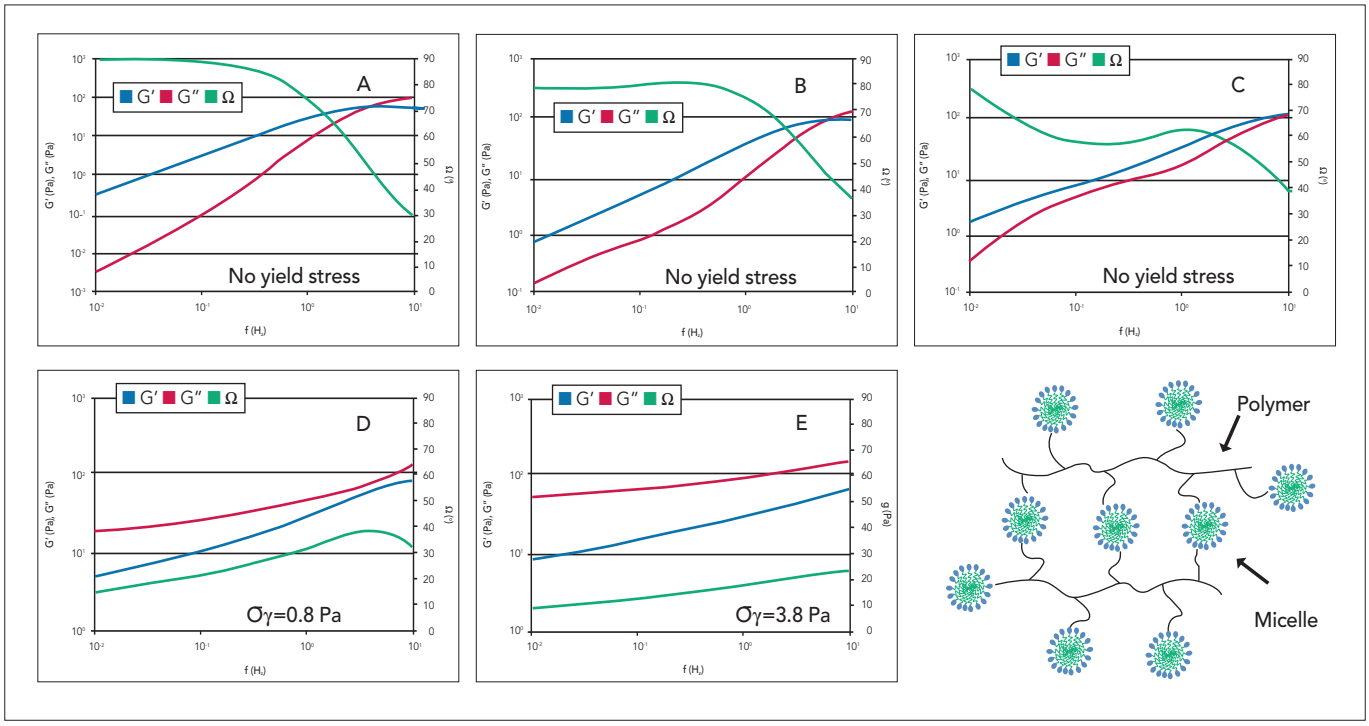

Figure 7: Oscillatory test data for shower gel samples identifies an associative thickener levels of 6 or 8% as being sufficient to induce the microstructure associated with product stability. [Elastic modulus, G′ is shown in red; Viscous modulus, G″ is shown in blue; phase angle is shown in green.]

process for soak-off gels tends to involve a high degree of polymer cross-linking and results in a finish that is highly resistant to acetone. In its liquid state, nail varnish is easily manipulated and applied but once cured it becomes fixed. Fast curing has obvious benefits for the customer but ensuring that the 'operational time window' is adequate for easy product use is essential, as is the quality of the resulting finish.

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 a rotational rheometer (Kinexus, Malvern Instruments) with parallel plates. UV light of fixed intensity was applied to the gels for 30 seconds and a curing profile generated by measuring the change in G′, a measure of elastic stiffness, as a function of time (Fig 8).

The results show clear differences between the products; the gold glitter gel (clear varnish with suspended glitter particles) cured fastest, and to the highest stiffness, while the black gel cured slowest, to give a more flexible finish with a much lower shear modulus. To further investigate the properties of the finish, post-cure amplitude sweeps were carried out. This is an oscillatory test in which the amplitude of the applied oscillation is steadily increased. This analysis revealed that the black gel has a longer linear viscoelastic region than the gold glitter gel meaning it is more flexible (less brittle). In combination these results provide comprehensive insight into the nature of the products: the glitter gel will cure quickly resulting in a brittle finish that may be difficult to remove, whereas the black gel will cure far slower to a more flexible, easily removed coating.

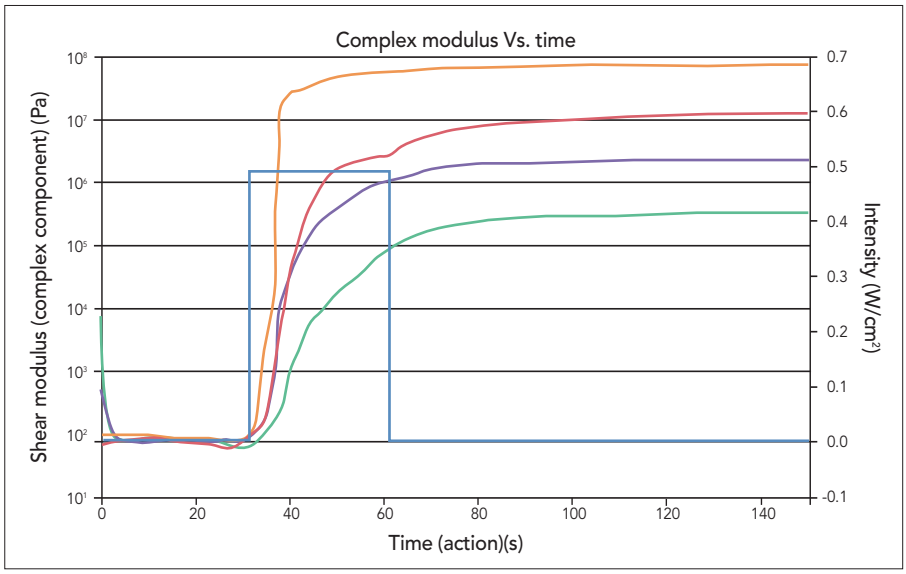

Figure 8: Oscillatory testing for nail varnishes reveals clear differences in their curing profile that would directly impact customer experience.

Looking ahead

In recent decades the formulation of personal care products has transformed from black art to advanced science, a process that continues as productive analytical strategies emerge. Formulating to fully meet consumer expectations is vital for commercial success and there is intense time pressure on formulation and reformulation programmes. By offering enhanced sensitivity, and a wider range of test capabilities rotational rheometers answer more far more fully to current formulation requirements than traditional rotational viscometers, more effectively supporting a knowledge-led approach to product development. Upgrading to a rotational rheometer can therefore pay significant dividends in the form of faster, more secure formulation and, ultimately, competitive product performance. PC

References

1 Laun HM, Rady M, Hassager O. Analytical solutions for squeeze flow with partial wall slip. Journal of Non-Newtonian Fluid Mechanics 1999; (81): 1-15.

2 Barnes HA, Hutton JF, Walters K. An introduction to rheology, Elsevier, 1989.