Measuring the rheology of polymer solutions

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RHEOLOGY AND VISCOSITY

MICRORHEOLOGY

Polymers are versatile materials that play an important role in a diverse range of industrial applications. Polymeric solutions or suspensions provide joint lubrication in the human body, make foods appear rich and creamy, and impart stability to inks and paints. In these and many other applications the rheological characteristics of the polymer solution have a defining influence on product performance and functionality.

Rheology is the study of material deformation and flow, and it can be used to establish a direct link between polymer characteristics - such as molecular weight (MW), molecular size and structure - and product performance. Working towards rheological targets defined in terms of viscosity or viscoelasticity to achieve performance targets is an efficient formulation strategy but relies on measuring relevant rheological data[1].

This whitepaper examines the key rheological characteristics of polymer solutions and the techniques that are available to measure them. These include rotational and microfluidic rheometry and microrheology. Case studies illustrate the data that can be generated and its potential application.

Understanding the role of rheology in formulation

Formulators apply two complementary strategies when working towards defined product performance targets. The first is to change the composition of the formulation; the second is to alter the physical characteristics of the ingredients. In the specific case of formulations incorporating polymers the two most commonly manipulated variables are polymer concentration (composition) and MW (a physical characteristic of the polymer). However, there are a number of other factors that can also impact how polymer solutions behave. These include polymer structure and type, temperature, polymer charge and solvent quality.

Traditionally, formulation has been an empirical process based on making changes to the formulation and measuring aspects of product performance to determine the resulting impact. This can be a lengthy procedure and provides little insight into why a change is associated with an observed effect. Consider the example of experimenting with different grades of a polymeric food additive to achieve a sauce that has an appearance and mouth feel that is appealing to consumers. The tests required to assess both mouth feel and appearance may be time-consuming, and somewhat subjective, and the results may be difficult to correlate with measurable differences in

the grades of additives available. Formulating in this way often yields little information with which to refine ingredient choice.

Rheology can act as a bridge that links changes to the formulation with product performance. Returning to the example above, if we know that a product with a certain yield stress and viscoelastic profile has good commercial appeal then it is possible to set rheological targets to guide the formulation of a new product for the same market. These rheological targets can be used in place of harder to measure product performance metrics.

Using rheology in this way supports faster, knowledge-led formulation but relies on measuring rheological properties that are relevant to the performance of the product. Polymeric solutions can be used simply as thickeners but are also routinely incorporated to impart viscoelasticity. A viscoelastic system is one that can exhibit both liquid- (viscous) and solid-like (elastic) behavior, behavior that underpins the performance of many consumer products. Toothpaste, for example, extrudes easily from a tube under a certain pressure (viscous behavior) but sits immobile on the brush (solid-like behavior), while coatings may be sprayed as liquids during application but form well-defined, discrete droplets on a substrate.

Polymers in solution: understanding intrinsic viscosity

The rheology of any solution or suspension is governed by the volume of dispersed phase within it. Dispersed particles increase viscosity by distorting the flow lines around individual particles and because of friction at the particle surface. Einstein's equation for hard spheres describes the relationship between solids loading and viscosity for dilute systems.

$$\eta = \eta_{medium}\left(1 + 2.5\phi\right)$$

Where η – viscosity of the suspension

η_{medium} – viscosity of the medium

Φ – volume fraction of solids in the suspension

This relationship is linear and suggests that an increase in the number of particles in the solution will induce a corresponding, directly proportional increase in viscosity. It can be extended to polymer solutions if we think of a polymer coil as an impenetrable sphere through which the solvent cannot flow. The equation below shows the Einstein equation rearranged with volume fraction converted to concentration using a measure of molecular density, intrinsic viscosity (IV).

$$\eta = \eta_{medium}\left(1 + [\eta]c\right)$$

η – viscosity of the dispersion

η_{medium} – viscosity of the medium

c – concentration of polymer

[η] – intrinsic viscosity of the polymer in the specific solvent

The parameter IV has units of volume per unit mass and is inversely proportional to molecular density. A less dense polymer molecule will therefore have a higher IV. Because the impact of a polymer on solution viscosity is determined by the volume that it occupies a polymer with a high IV, a larger volume per unit mass, will have a greater impact on solution viscosity than one with a lower IV, all other parameters being equal. Using the equation above the viscosity of a polymer solution can be determined, at any concentration below around 10% (dilute solution), providing that IV is known.

Determining IV

Although the IV of a polymer is related to molecular weight it is also influenced by structural characteristics such as the degree of branching in the polymer chain, and the type of solvent in which the polymer is being dissolved. The Kuhn-Mark-Houwink-Sakurada equation, often referred to simply as the Mark-Houwink (M-H) equation, describes these relationships. It can be used to determine the IV that a specific polymer will exhibit in any given solution, provided that the M-H parameters of K and α are known. These parameters can be found in published literature for many of the polymer/solvent systems in routine use. Alternatively intrinsic viscosity can be measured using for example either rotational or microfluidic rheometry by measuring viscosity at range of concentrations and fitting the Huggins or Kraemer equations[2].

$$[\eta] = K \times Mw^{\alpha}$$

[η] – intrinsic viscosity of the polymer in a specific solvent

Mw – molecular weight

K and α – are the M-H parameters

Radius of gyration (Rg) (see figure 1) is a parameter that is also used to define the volume occupied by a polymer. It is the average squared distance of any point in the polymer coil from its center of mass. It can be measured by directly by light scattering and correlates directly with IV, via the MW of the polymer. Measurements of Rg can therefore be used to determine and compare the IV of different polymer solutions.
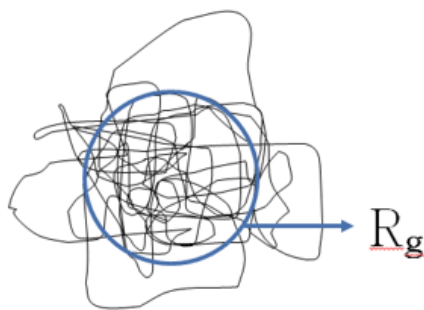

Figure 1: Radius of gyration (Rg), which can be determined from light scattering data, is a useful measure of the size of a polymer coil

In summary then, in dilute solutions, the impact on viscosity of a polymer coil is governed by the volume it occupies in an analogous way as with non-polymeric solutes. The volume which a polymer occupies is related to IV or to molecular density, which can be determined by measuring Rg. However, in more concentrated polymer solutions, the polymer coils begin to interact. At this point the Einstein model begins to break down and the behavior of the solution becomes substantially more complex.

Polymers in solution: the onset of viscoelasticity

In a dilute solution the polymer coils have sufficient space to avoid any interaction. If a dilute solution exhibits viscoelasticity it is therefore attributable to the properties of individual polymer coils. The overall viscoelasticity exhibited by a dilute solution is the viscoelasticity associated with each coil, multiplied by the number of coils present. This behavior is described by the Rouse-Zimm model[2,3].
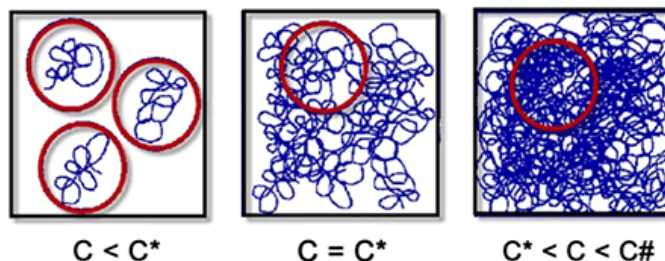

C < C*   C = C*   C* < C < C#

Figure 2: As the concentration of polymer coils within a solution increases, coils begin to interact and entangle[2].

Figure 2 illustrates what happens as the concentration of polymer coils is increased beyond the upper limit that defines a dilute solution (~10%) and the total volume taken up by each coil exceeds the available volume. At this point the coils can no longer remain discrete and become prone to entanglement. The concentration at which this happens is referred to as the critical overlap concentration (c*) and it can be estimated from measurements of Rg or IV since as previously discussed both of these properties are related to the volume occupied by a polymer coil.

The various regimes that occur in polymer solutions can therefore be defined as dilute (c < c*), semi-dilute (c* < c < c#), and concentrated (c > c#). [Note: In the semi-dilute regime coils contract with increasing concentration up to a certain limit. c# is the concentration above which no further contraction can occur.] One way of estimating the overlap concentration is by determining the value at which the product of the number of coils per unit volume (v) and the volume pervaded by a single coil (Rg^3) is unity, using the equation below:

$$c^* = \frac{Mw}{R_g{}^3 N_A}$$

Rg – radius of gyration

Mw – molecular weight

N_A – Avogadro's constant

Alternatively the inverse of IV can also be used as a rough estimate of c* but this approach tends to give lower values.
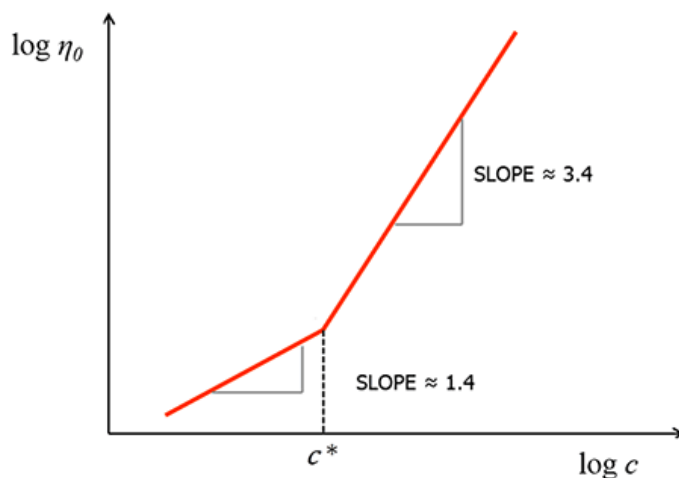
Figure 3: Expected zero shear viscosity profiles for polymer solutions above and below c*

Above c* a polymer solution exhibits greater viscosity dependence on concentration as shown in Figure 3, a logarithmic plot of zero shear viscosity against concentration. This shows a slope 3.4 above c* compared with 1.4 below. The reason for this is that above c* the rheological behavior of the system is governed by interactions between multiple coils rather than by the properties of individual polymer molecules. This results in an increase in polymer interaction and hence viscous drag. Constructing a plot similar to that in figure 3 can therefore also be a useful way of estimating c* and tends to produce a value that correlates with the value calculated using R_g.

This transition from a dilute to semi-dilute and then concentrated regime is also reflected in the viscoelastic properties of the polymer solution. With a viscoelastic system the timescale or frequency over which shear is applied becomes a critical determinant of the rheology exhibited and defines whether viscous or elastic behavior is dominant (see figure 4).
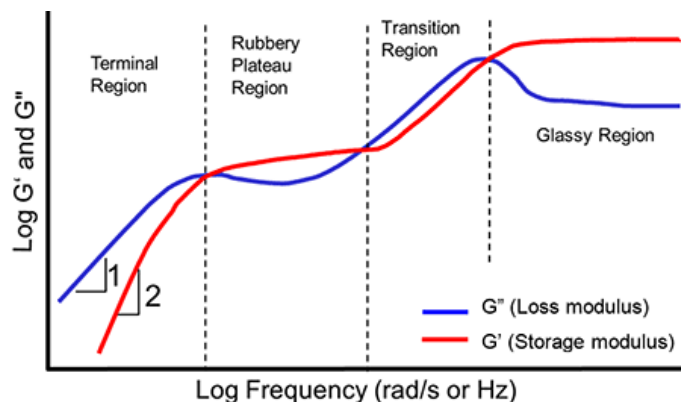

Figure 4: The viscoelastic behavior of polymer solutions is a function of the timescale (inverse frequency) over which shear is applied.

At lower frequencies (longer timescales) relatively concentrated polymer solutions may exhibit Rouse-Zimm type behavior, as observed in a dilute system, where G" exceeds G'. Here polymer chains have sufficient time to free themselves from the constraints of entanglement and are able to slip past one another by a process of 'reptation'. At higher frequencies a 'rubbery plateau' region is observed in which the elastic modulus (G') dominates relative to the loss modulus (G"). On these timescales the polymer chains have insufficient time to free themselves from entanglements causing tension in the chain segments between coupling points and hence elastic dominant behavior. The

length of this plateau relates to polymer MW and concentration since these correspond with the number of entanglements and hence relaxation time.

Note the angular frequency at which G' and G" intersect at low frequencies is equal to $1/\tau_{max}$, where τ_{max} is the longest relaxation time or time required for approx. 63% of the stored elastic energy to be converted to viscous energy and dissipated. At even higher frequencies, which correspond to short timescales, polymer solutions undergo a further phase transition and begin to exhibit glassy behavior, where the polymer becomes largely immobile except for localized vibrational and rotational modes of deformation.

This analysis highlights the need to measure rheology across a range of different conditions to gather data that are relevant to the specific application of an individual polymer solution. For low molecular weight and low concentration polymeric solutions the important dynamics tend to occur on shorter timescales hence a need to make measurements at higher frequencies.

Characterizing viscoelasticity

When it comes to characterizing the viscoelasticity of a polymer solution it is important to quantify under what circumstances the solution will flow in a liquid-like way, and, conversely the conditions that will induce solid- or gel-like behavior. One way to do this is via oscillatory testing using a rotational rheometer.

Oscillatory testing involves the application of a shear strain as a sinusoidal wave. Measurements of the resultant stress may be in phase with the applied strain, or there may be a lag, which can be quantified by the parameter phase angle. Phase angle is zero (in phase) for an ideal solid and π/2 radians (quarter of a cycle) out of phase for an ideal liquid. Viscoelastic materials have a phase angle somewhere between these two boundaries. The parameters storage or elastic modulus (G') and loss or viscous modulus (G"), are derived from measurements of phase angles and therefore identify whether viscous or elastic behavior is dominant under any given conditions.

If G' > G" then elastic properties dominate and the sample exhibits solid-like behavior

If G' < G" then viscous properties dominate and the sample exhibits liquid-like behavior

The relative size of G' and G" tends to vary depending on the timescale over which shear is applied so it is critical to carry out testing at a relevant angular frequency. Testing at high frequencies is relevant to short timescale processes, in other words rapid deformation while low frequency testing is more representative of behavior over long timescales, during storage, for example.

Surveying the rheological toolkit for polymer solutions

All rheological techniques are based on measurement of the relationship between applied force or stress and the resulting movement or deformation of the material. However, different techniques vary considerably in terms of the way in which they apply stress, and are therefore variously well-suited to probing rheological behavior, most especially viscoelasticity under different conditions.

Rotational rheometry

A rotational rheometer is one of the most versatile rheological tools available and can be configured for a number of different test methods. Some of the most useful tests for polymer solutions include those that generate simple viscosity flow curves (plots of viscosity against shear) and oscillatory tests for the quantification of viscoelasticity.

In a rotational rheometer samples are loaded between two plates, or other similar geometry such as cone and plate or a cup and bob. Applying a torque to the top plate exerts a rotational shear stress on the material and the resulting strain or strain rate (shear rate) is measured. Testing can be based on the application of uni-directional rotational shear, or a sinusoidal applied stress pattern – oscillatory testing.

Modern rotational rheometers have been optimized to allow precisely controlled testing over many decades of torque. In practical terms this enables the measurement of a diverse range of sample types, from relatively weakly structured fluids through to gels and pastes. However rotational rheometers may reach measurement limitations in the high shear region, at shear rates usually in the region of 1000 -10,000 s^{-1}, depending on the sample. These may be due to sample fracture as a result of elasticity generation under rotational shear, turbulence or shear heating. This can be problematic when assessing the performance of polymeric solutions under conditions that are relevant to, for example, spraying applications or inkjet printing. Furthermore mechanical stabilities can inhibit oscillatory measurements at very high frequencies.

Microfluidic rheometry

Microfluidic rheometry is a relatively new rheological technique closely aligned to capillary rheometry. It is especially relevant for characterizing low viscosity polymeric solutions at ultra-high shear rates, in excess of 1,000,000 s^{-1}, and finds practical application in the analysis of drinks, inkjet inks, personal care products and other types of material, when rotational rheometry may be less suitable. Compared with rotational rheometry, microfluidic rheometry more sensitively differentiates samples of low viscosity and enables testing under higher shear rate conditions.

With microfluidic rheometry a sample is forced down a microfluidic channel and the resulting pressure drop is measured. Micro Electro Mechanical System (MEMS) pressure sensors embedded within the channel are used to determine pressure drop with a high degree of accuracy and only small amounts of sample are required for precise measurement. A particular benefit of microfluidic rheometry is that is can be used to study apparent extensional rheology, the behavior of a fluid under 'stretching' conditions by employing a rectangular microfluidic channel with parabolic contraction that accelerates and extends the fluid through the contraction.

Microrheology

Microrheology is an evolving technique being developed by researchers working at the forefront of rheological characterization. Unlike the preceding mechanical approaches it involves determining the rheological properties of a fluid from the movement of probe particles within it. Small particles within a fluid move as a result of Brownian motion. This motion can be tracked using, for example, light scattering techniques and viscoelastic properties can then be determined from the resulting data. This is the operating principle that underpins dynamic light scattering (DLS) microrheology.

DLS microrheology does not rely on the application of a mechanical stress and therefore has significant potential for measuring low viscosity and weakly-structured, strain-sensitive samples such as polymer solutions. In particular the technique is valuable for investigating rheology at the very high frequencies needed to measure the critical short timescale dynamics of polymer systems for certain applications. Microrheology can be used to investigate the viscoelastic profile of a material over a very wide frequency range and over much shorter timescales than can be accessed using rotational rheometry, and with smaller sample volumes.

By applying these techniques in a complementary and systematic way it is possible to fully scope the rheological performance of polymer solutions under conditions that are closely relevant to a specific industrial application. The following example studies illustrate that this approach.

Case study 1: Measuring the concentration dependence of polymer solution viscosity

Figure 5 shows viscosity profiles for a series of polymer solutions of increasing concentration. All solutions had a concentration in excess of the critical overlap concentration. Shear viscosity was measured as a function of shear rate for each polymer solution over a wide range of shear rates using a rotational rheometer, Kinexus (Malvern Instruments, UK).
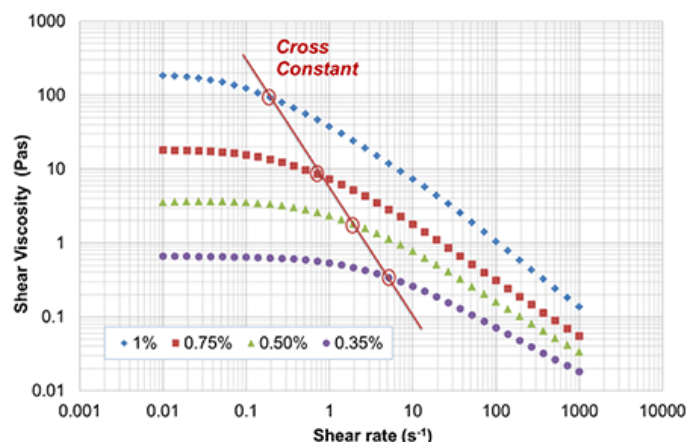

Figure 5: Viscosity profiles for polymer solutions of increasing concentration measured using a rotational rheometer

At low shear rates a constant shear viscosity plateau termed the zero shear viscosity (η_0) is observed. In this region the disruption of the entangled polymer coils happens so slowly that re-entanglement can occur simultaneously. As a result there is no net change in the extent of entanglement and viscosity remains constant. In contrast, at higher shear rates the rate of disruption exceeds the rate of re-entanglement and the solution becomes less viscous. Shear thinning is observed. This transition to shear thinning behaviour happens at lower shear rates for more concentrated solutions, because they are more prone to greater entanglement.

Case study 2: Investigating viscoelasticity using rotational rheology and microrheology

Figure 6 shows oscillatory test data for a series of hyaluronic acid (HA) solutions, all with concentrations above the critical overlap concentration, measured using a Kinexus (Malvern Instruments, UK). For each solution a clear crossover point is observed when G' the elastic modulus exceeds G" the viscous modulus. These results reflect the expected generic polymer solution rheological behaviour represented in figure 4 with the crossover point marking the transition to the rubbery region where the solution exhibits solid-like (elastic dominant) behavior. At lower concentrations the crossover point occurs at higher frequencies and the rubbery region is less extensive due to a reduction in the number of entanglements.
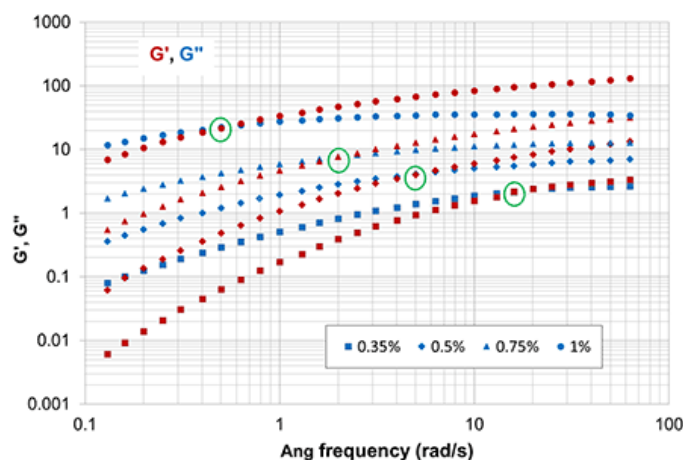
Figure 6: Measuring the viscoelasticity of Hyaluronic Acid (HA) using rotational rheometry

The crossover frequency at which rubbery behaviour establishes is an important value since it can be used to determine the longest relaxation time of the polymer τ_{max}. Relaxation time is simply taken as the inverse of the angular frequency at the crossover point, circled in green in Figure 6. The longest relaxation time tends to increase with molecular weight and concentration and is a measure of how long it takes for polymer molecules within the solution to disentangle. From a practical perspective the key factor defining material behaviour is the time of the applied stress relative to the relaxation time of the material, as defined by the so-called Deborah number (De), where De = τ_{max} /t or $\omega\tau_{max}$. When De > 1 solid like behaviour dominates and for De < 1, liquid like behaviour dominates. The relevant timescale will depend on the application, so for example the pulse time for an inkjet printer may be on the order of 10μs or 10^5 rad/s, while the contact time when chewing food is in the order of 1s or 1 rad/s.

To extend this investigation to lower polymer concentrations, in this case around 0.1% by weight of the high MW HA being measured, necessitates a switch of rheological technique since the mechanical limitations of rotational rheometer inhibit its application in the low concentration/high frequency regime. Here DLS microrheology is applicable.

Figure 7 shows measurements of G' and G" as a function of frequency at a HA concentration below the critical overlap concentration, made using a Zetasizer ZSP (Malvern Instruments, UK). Without DLS data it may be inferred that G' and G" would intersect at increasing frequencies as in figure 6, however, microrheology data shows that this is in fact not the case and classic Rouse-Zimm behaviour, which describes

dilute polymer solution behaviour is observed. This behaviour is well documented in the various text books on polymer rheology and predicts that G' and G" will run parallel with an approximate gradient of 2/3 when plotted logarithmically, which is what is observed.
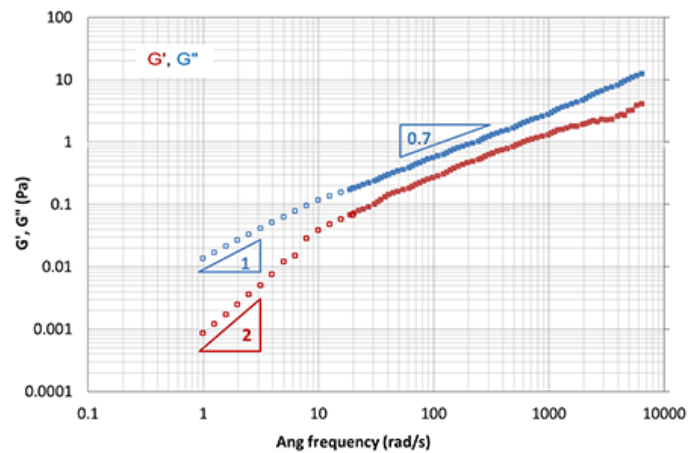

Figure 7: Using microrheology it becomes possible to study the viscoelastic behaviour of dilute polymer solutions at high frequency

Case study 3: Combining rheological techniques to fully scope the behaviour of polymer solutions

In this study the aim was to investigate the behaviour of a polyacrylamide (HPAM) solution over a very wide range of conditions, to comprehensively scope rheological performance. The polyacrylamide used has a relatively high molecular weight of around 4,000,000 and was constituted to form a relatively concentrated solution (0.1% w/v) which was above c*. The first technique applied was oscillatory testing with a rotational rheometer (see figure 8).
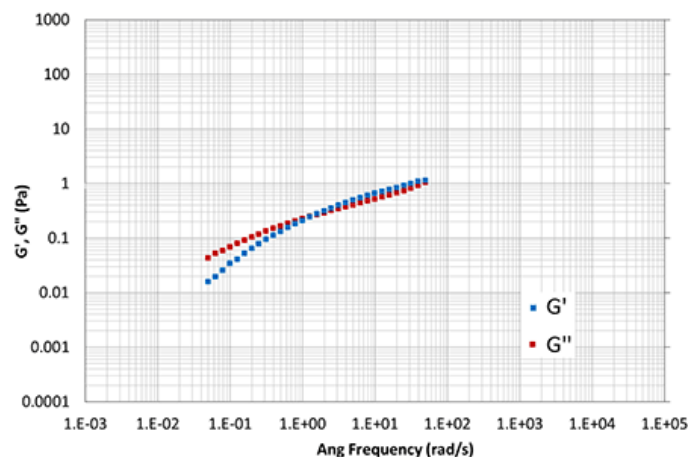

Figure 8: For a moderately concentrated HPAM solution rotational rheometry enables measurement in the terminal region and detection of the start of the rubbery plateau

Using an oscillatory test method it is possible to successfully measure performance in the terminal region and to detect the onset of rubbery behaviour. However, there are clearly areas where oscillatory testing with a rotational rheometer does not provide data. It is possible to go lower in frequency using oscillation testing with the only real

restriction being the time of the test, since ideally you would want to complete a full oscillation cycle or a significant fraction of a cycle at each frequency which can be time consuming. Figure 9 shows how creep testing, an alternative rotational rheometry method and microrheology provide the complementary information needed extend the viscoelastic spectrum to high and low frequencies.
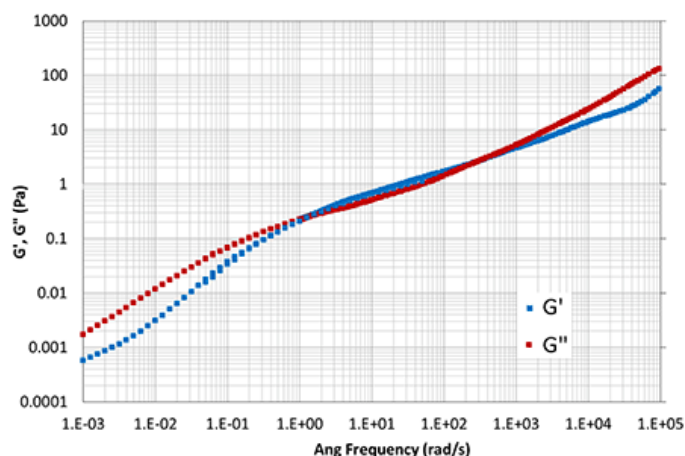

Figure 9: Creep testing and microrheology provide complementary data to oscillatory testing to fully scope polymer solution behaviour across a very wide range of frequencies.

Creep testing is a technique used to assess behaviour over long timescales/low frequencies and is similar to the approach used in DLS microrheology in that one applies a stress to the material for a given time period and the inverse of each discrete time point equates to an angular frequency. Using Kinexus (Malvern Instruments, UK) an algorithm is applied to the creep data in the rSpace software to convert creep data in to values of G' and G". A full description of techniques for creep testing lies beyond the scope of this paper but it is clear that the resulting data enables measurement well into the terminal region. In contrast, microrheology provides access to very high frequency data and can therefore be used to detect the transition phase beyond the rubbery plateau that precedes the development of glassy behaviour.

Looking beyond viscoelasticity to the simpler issue of viscosity highlights the role of microfluidic rheology in completing the assessment of rheological behaviour. Figure 9 shows a viscosity profile for the HPAM solution. Although rotational rheometry enables measurement across a wide range of shear rates it does not provide access to the ultra-high shear rates that prevail in certain industrial processes such as spraying. In this region microfluidic rheometry is a valuable technique that allows extension of the viscosity profile across a wider range of conditions.
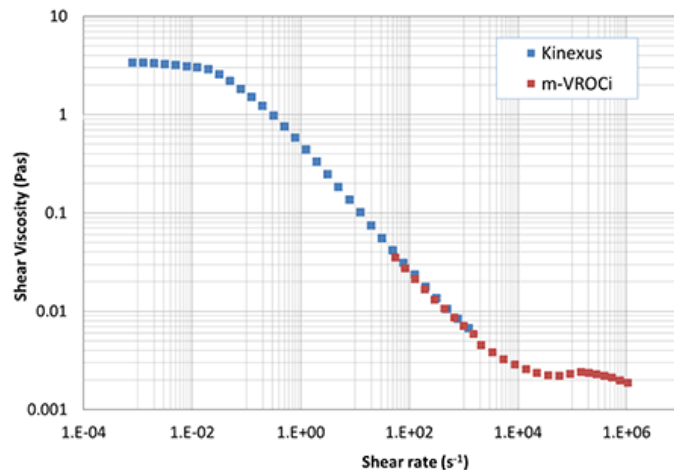
Figure 10: Rotational rheometry and microfluidic rheometry provide complimentary viscosity data at low and high shear rates

In conclusion

Polymer solutions exhibit complex but industrially valuable rheological behaviour. Measuring rheology under relevant conditions is essential to gain the insight and understanding needed to successfully exploit this behaviour and use polymer solutions to reach formulation goals. The case studies presented here show how rotational rheometry, microrheology and microfluidic rheometry can be applied in combination to fully scope the rheological performance of polymer solutions to support their beneficial use.

Further reading/information

To find out more about polymer solutions listen to a recording of the webinar: Polymer solution characterization Part 4: Rheology and viscosity or "stretch and flow". http://www.malvern.com/en/support/events-and-training/webinars/W140916PolymerSolution4.aspx

For an introduction to rotational rheometry and creep testing go to: http://www.malvern.com/en/products/technology/rheometry-rotational/

Additional references

1. "The science of beauty – Characterizing Hyaluronic Acid, the molecule behind anti-aging creams" Recorded webinar available for download at: http://www.malvern.com/en/support/events-and-training/webinars/W140625ScienceOfBeauty.aspx

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