

Characterizing Gel Properties Using Oscillation Testing on a Rotational Rheometer

Introduction

A gel can be considered as a solid three-dimensional network that spans the volume of a liquid medium. This network structure can result from physical or chemical interactions, resulting in the formation of physical and chemical gels, respectively with varying degrees of stiffness. Chemical gels include materials such as vulcanized rubbers and cured epoxy resins where the cross-links are covalent in nature. Physical gels are formed through intermolecular associations as a result of hydrogen bonding, Van der Waals forces or electrostatic interactions. Such gels include particulate gels, clay dispersions and associative polymers to name a few.

For a fully cured elastic solid, the gel modulus, G , can be estimated from the following expression:

$$G = \nu kT$$

where ν is the number of 'elastically effective' network strands per unit volume, k is the Boltzmann constant and T is the temperature. While physical gels do not necessarily conform to this relationship, the value of G is never the less related to the elastic network characteristics and interactions, which may be dependent on polymer/particle concentration, electrical charge or composition.

Consequently G (or the Elastic Modulus, G' , in dynamic oscillatory tests) is an important parameter for characterizing gels. For an ideal gel, G' should be independent of

frequency since structural relaxation cannot occur; however, many gels show some frequency dependence indicative of structural relaxation over different timescales. This relaxation process is also important when characterizing gels.

One way to capture both characteristics is from a frequency sweep test which captures the change in G' as a function of angular frequency, ω . At the gel point, G' generally shows a power law dependence with frequency, which can be characterized using the following model.

$$G \approx k\omega^n$$

where k is known as the relaxation strength and n the relaxation exponent.

For an ideal gel n has a value of 0 which indicates that no structural relaxation occurs (in the measured frequency range anyway). A value greater than 0 suggests some degree of structural relaxation, quantified by the magnitude of n . Numerically k is just the value of G' at an angular frequency (ω) of 1 rad/s.

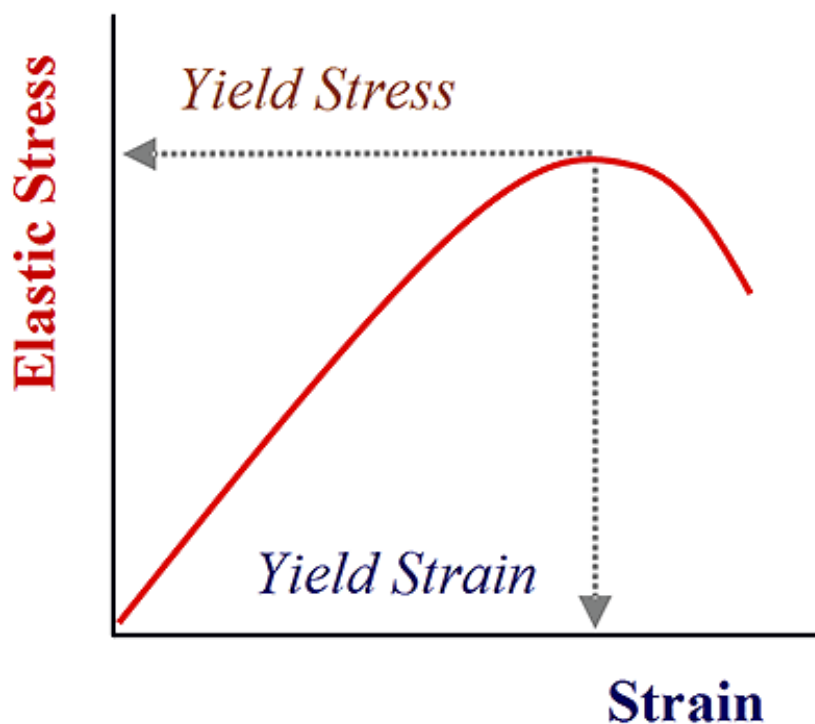
An additional parameter of interest is the phase angle δ , which can reflect imperfections in the gel structure, or parts of the structure, which are not 'elastically effective'. A perfect gel will have a phase angle of zero while any value between 0 and 45° suggests some degree of viscous damping which can facilitate relaxation.

Another characteristic of gels is the yield stress, which is the stress required to break down the three-dimensional network structure and induce flow. There are various methods for determining the yield stress, however, one of the most sensitive methods is an oscillatory amplitude sweep, which involves measuring the elastic stress component, σ' (associated with the elastic structure through G') as a function of strain amplitude. The yield stress is then taken as the peak stress and the strain at which this occurs, the yield strain, which is related to the brittleness of the structure (see Figure 1).

It should be noted that the power law model should only be used to fit data over the measured frequency range since deviations from such behavior may occur at lower or higher frequencies.

Experimental

- Three gel systems including a hair gel, a Xanthan-Mannan gum complex and an associative polymer-surfactant system were evaluated.
- Rotational rheometer measurements were made using a Kinexus rheometer with a Peltier plate cartridge and using cone-plate measuring system¹, and using standard pre-configured sequences in the rSpace software.
- A standard loading sequence was used to ensure that both samples were subject to a consistent and controllable loading protocol.
- All rheology measurements were performed at 25°C.
- The tests involved performing a strain-controlled frequency sweep within the linear viscoelastic range and fitting a power law model to the data to determine k and n as defined in equation 2.
- The yield stress and strain were determined in the same sequence by performing a subsequent amplitude sweep test beyond the critical strain.



1 Diagram showing how an amplitude sweep can be used to determine the yield stress and strain

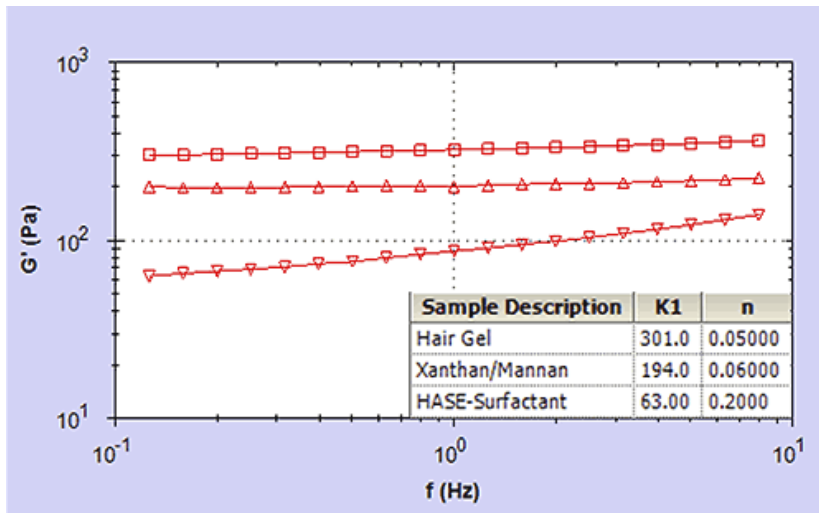
Results and Discussion

Figure 2 shows G' plotted against ω for the different gels performed at 25°C and the model fit parameters. These results show that the hair gel is the stiffest of the three gels with a k value of 301 Pa compared with values of 194 Pa and 63 Pa for the gum complex and associative thickener, respectively.

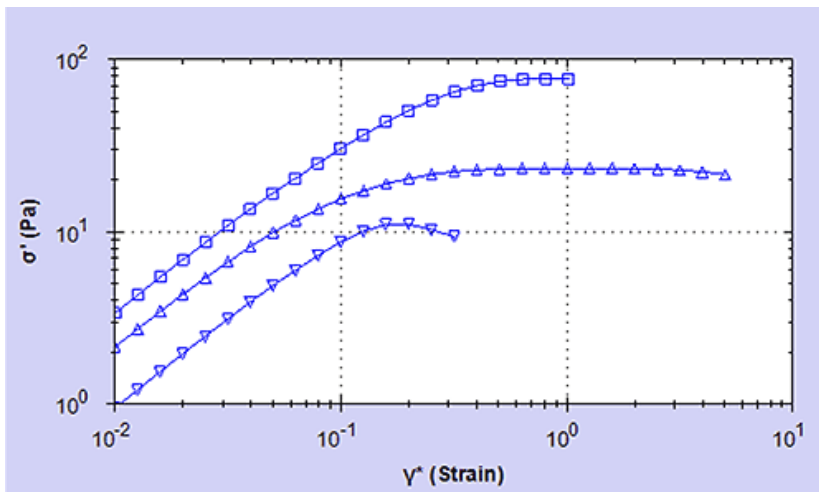
It can also be seen for both the hair gel and gum complex that G' varies very little with frequency suggesting

little structural relaxation is occurring with time. This is reflected in the relaxation exponent n which is close to zero in both cases. In contrast, the associative polymer shows a much steeper gradient corresponding with a higher n value of 0.2.

Figure 3 shows the results from the strain amplitude sweep performed at 1 Hz, including the corresponding values of yield stress and strain, as determined from a peak analysis.



2 G' vs. ω for (□) hair gel (Δ) Xanthan/Mannan gum complex (∇) Associative polymer-surfactant system and associated model fit parameters



Sample Description	Complex shear strain(Strain)	Sigma prime(Pa)
Hair Gel	0.869073	77.33
Xanthan/Mannan	1.47204	23.38
HASE-surfactant	0.193796	11.11

3 σ' vs. γ^* for (□) hair gel (Δ) Xanthan/Mannan gum complex (∇) Associative polymer-surfactant system (at 1 Hz) with yield stress and strain values

The hair gel appears to have the highest yield stress, followed by the gum complex and the associative thickener. The hair gel will therefore require more stress input to initiate flow.

In terms of yield strain, the highest value was measured for the gum complex thus indicating a more ductile structure. The associative polymer has the lowest value, suggesting a comparatively more brittle structure.

Conclusion

Three gels were evaluated using oscillatory testing. Time-dependent gel properties were evaluated from a frequency sweep and the relaxation strength k and relaxation exponent n estimated from a power law model fit of G' . In addition, yield stress and strain were evaluated from a subsequent amplitude sweep. The results demonstrate how such an approach can be used to quantify and compare the properties of different gel systems.

References

- [1] White Paper – Understanding Yield Stress Measurements, NETZSCH-Gerätebau GmbH
- [2] R.G. Larson; The Structure & Rheology of Complex Fluids
- [3] Scanlan JC, Winter (1991), *Macromolecules* 24:47
- [4] HJ Wall et al (2003). *Journal of Rheology*, 47, 847

Please note...

that testing is recommended to be undertaken with cone and plate or parallel plate geometry – with the latter being preferred for dispersions and emulsions with large particle sizes. Such material types may also require the use of serrated or roughened geometries to avoid artefacts relating to slippage at the geometry surface.