Using Creep testing as an alternative to Multiwave Oscillation for determining the true gel point of network polymers

Mats Larsson[1], John Duffy[2], Shona Murphy[2], and Adrian Hill[2]

[1] Malvern Instruments Nordic AB, Uppsala, Sweden
[2] Malvern Instruments LTD, Malvern, UK

ABSTRACT

The most common method for monitoring gelation dynamics with a rotational rheometer is to perform Small Amplitude Oscillatory Shear (SAOS) testing at a single fixed frequency while continually monitoring the evolution of G' and G" with time or temperature. The point of gelation being defined as the time or temperature at which G' and G" cross. Winter[1] has shown, however, that with the exception of stoichiometrically balanced network polymers and networks with excess cross-linker the true gel point does not coincide with the intersection of the dynamic moduli and is more accurately identified as the time or temperature at which G'(ω) and G"(ω) become parallel and the loss tangent (tan δ) independent of frequency, the so called Winter- Chambon criteria[2]. Hence, to accurately determine the gel point using SAOS testing requires measurements to be made at multiple frequencies and at various stages of the gelation process. A common approach is to perform Fourier Transform Mechanical Spectroscopy (FTMS) or Multiwave Oscillation whereby the frequency dependent moduli are determined simultaneously at several discrete frequencies by applying a complex waveform consisting of a fundamental frequency and several harmonics[3]. While the approach can significantly reduce the time required to obtain a frequency spectrum and hence assist in the determination of the true gel point it is still, however, limited by the time required to perform a full or partial oscillation at the lowest frequency, which can be substantial. Hence, the approach is only really valid for relatively slow curing systems. Furthermore, the sum of the stress or strains applied at each frequency must be within the Linear Viscoelastic Region (LVR) thereby increasing noise to signal ratio (harmonic distortion) compared with a single frequency test.

In this paper we propose an alternative to Multiwave Oscillation that overcomes many of the limitations cited above. The approach is based on creep testing and the subsequent transformation of J(t) to G'(ω) and G"(ω) using the method proposed by Duffy et al[4], since J(t) contains information about all oscillation frequencies, not just the discrete harmonics used in a multiwave test. Furthermore, it is possible to determine a frequency spectrum in a fraction of the time required for multiwave without the same stress or strain limitations, potentially allowing more weakly structured and faster gelling systems to be evaluated. In this paper we will show that it is possible to determine the true gel point for a number of network polymer systems using this approach.

INTRODUCTION

Multiwave Oscillation is used for testing of processes that utilize a frequency sweep as function of time or temperature to study phenomena including gelation and curing, mainly due to the time reduction available:

Multiwave applies multiple frequencies as complex waveforms consisting of a fundamental frequency and harmonics. The Creep to Modulus method has the advantage of shortening the time scale of experiment and measure on different time scales corresponding to a frequency sweep from high too low frequency. Each creep test contains discrete information about each frequency and strain.

METHOD

The method for the Creep to Modulus conversion is based on microrheology testing using tracer particles, where the mean square displacement of the tracer particle as function of time is monitored using a dynamic light scattering technique. A relationship between the MSD of a tracer embedded in a viscoelastic fluid and the creep compliance of that fluid $J(t)$ can be established since in the Laplace frequency domain $\tilde{J}(s) = 1/s\tilde{G}(s)$, can be shown that $J(t)$ and $\Delta r^2(t)$ are linearly related according to Eq. 1. A microrheology experiment can therefore be considered analogous to a mechanical creep test performed in the linear viscoelastic regime and data can be presented in a common rheological format using $J(t)$ without the need for transformation to the frequency domain

$$J(t) = \frac{\pi a}{k_B T}\left\langle \Delta r^2(t)\right\rangle \qquad (1)$$

Furthermore, the mean square displacement in Eq. 2 can be substituted with the creep compliance to give the following relation,

$$\left|G^*(\omega)\right| \approx \frac{1}{J(1/\omega)\Gamma[1+\alpha(\omega)]} \qquad (2)$$

with $\alpha(\omega)$ defined according to Eq. 3

$$\alpha(\omega) = \left.\frac{d\ln J(t)}{d\ln t}\right|_{t=1/\omega} \qquad (3)$$

Therefore, the methods developed for obtaining viscoelastic properties from the MSD in a microrheology measurement can be equally applied to the creep compliance, thus facilitating an approach for converting the time dependent creep compliance to frequency dependent moduli for measurements made on a rotational rheometer.

The subsequent transformation of $J(t)$ to $G'(\omega)$ and $G''(\omega)$, using the method proposed by Duffy et al[4], contains information about all oscillation frequencies, not just the discrete harmonics used in a multiwave test.

Creep data can be converted to modulus data either without model fitting or fitted to a Burgers model given by Eq. 4 below and then converted to modulus data.

$$J(t) = J_g + \sum J_t\left(1 - e^{\frac{t}{-}}\right) + \frac{t}{\eta_0} \qquad (4)$$

The Burgers model result can be determined in a specific time window and fig. 1 shows typical creep to modulus converted data and data converted using a fitted Burgers model.
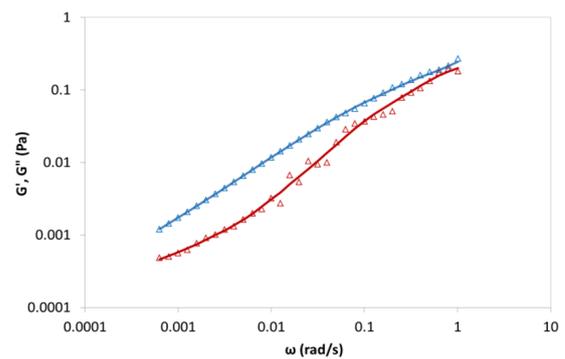

Fig. 1. G′ and G′′ converted data (upper line G′′ and lower line G′ using Burgers model and upper triangle represent G′′ and lower triangles represent G′ without model) on a FLOPAAM polyacrylamide solution (1 mg/ml)

The converted data using the Burgers model can be compared with a frequency sweep for the same sample. The data are shown in fig. 2. representing FLOPAAM polyacrylamide solution (1 mg/ml).
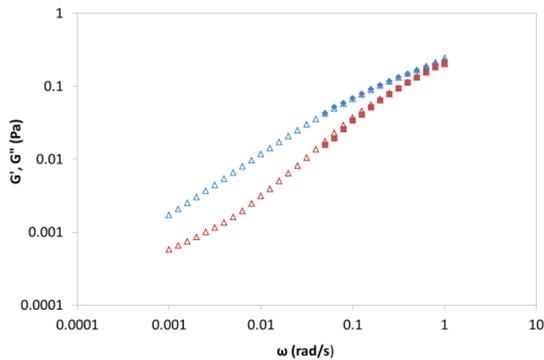

Fig. 2. Comparison of frequency sweep data (G´ shown as squares and G´´ as diamonds) and the modulus data converted from creep data (upper curve G´´ and lower curve G´)

The data in fig. 2. shows a very good agreement between creep converted data and frequency sweep data. The results show that creep recovery experiments can be converted to dynamic data over a wide frequency range for very low viscous solutions.

RESULTS

The data presented below are food grade gelatine blade melted in a concentric cylinder cup at 50°C for 10 min. Sample is equilibrated for 50 min and a temperature gradient is performed in a temperature range from 50°C to 10°C using a gradient of 0.5°C/min. During temperature ramp, a continuous creep measurement is performed for 20s at 10Pa and a recovery phase of 30s.

Creep data for temperatures ranging from 30.3°C to 24.9°C are shown in fig. 3. The gelation of the gelatine can be determined in different ways as discussed in this paper.
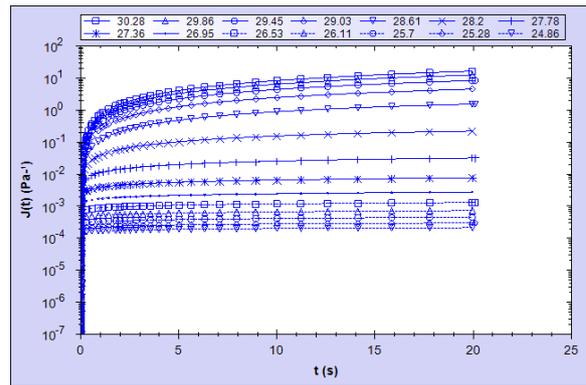

Fig. 3. Creep curves at temperatures from 30.3°C to 24.9°C

By converting the creep data above by using the creep to modulus conversion for the data above the gel point temperature is shown in fig. 4- 6.
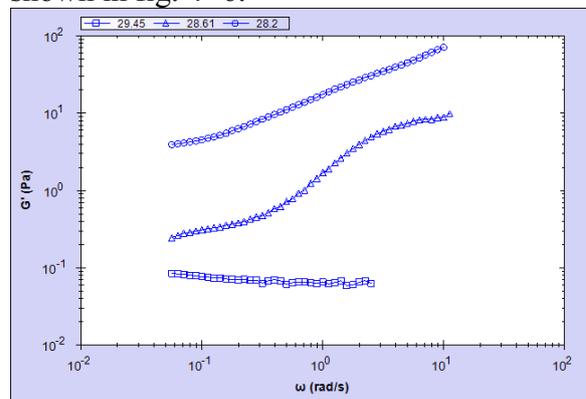

Fig. 4. G´ versus angular frequency (squares for 29.45°C, triangles for 28.61°C and circles for 28.2°C)
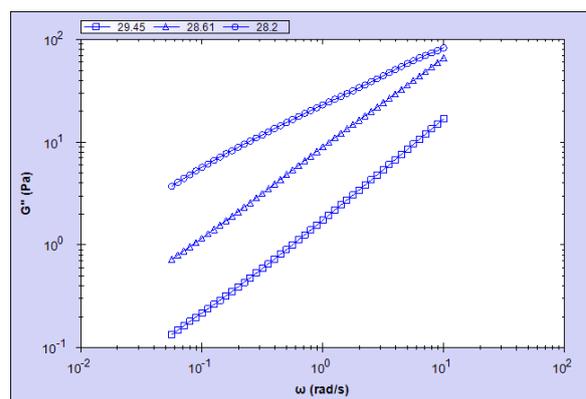

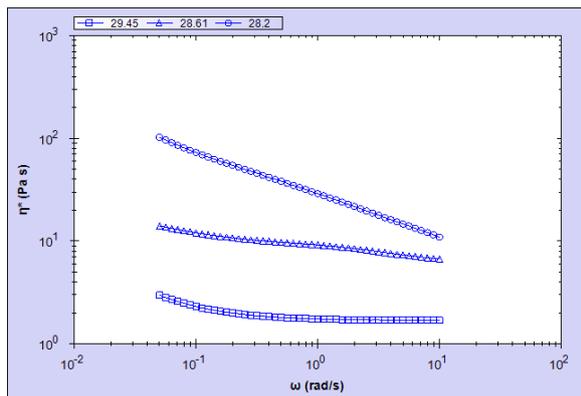Fig. 5. G´´ versus angular frequency (squares for 29.45°C, triangles for 28.61°C and circles for 28.2°C)

Fig. 6. η* versus angular frequency (squares for 29.45°C, triangles for 28.61°C and circles for 28.2°C)

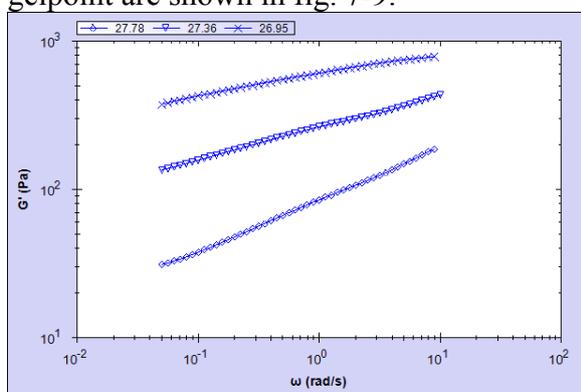The corresponding data below the gelpoint are shown in fig. 7-9.

Fig. 7. G´ vs angular frequency (diamonds for 27.78°C, triangles for 27.36°C and crosses for 26.95°C)
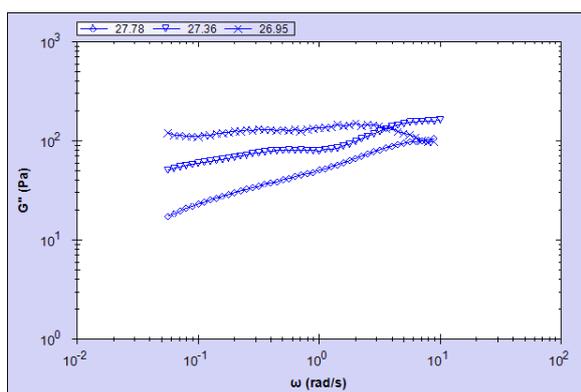

Fig. 8. G´´ vs angular frequency (diamonds for 27.78°C, triangles for 27.36°C and crosses for 26.95°C)
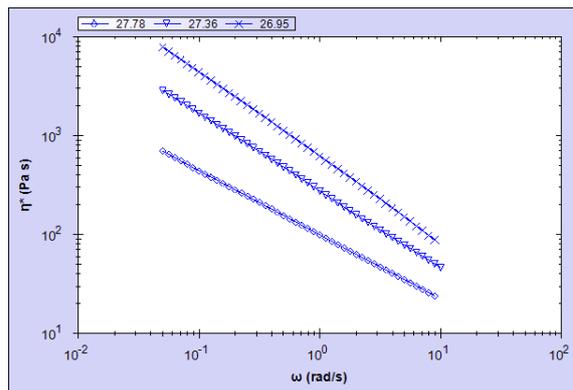

Fig. 9. η* vs angular velocity (diamonds for 27.78°C, triangles for 27.36°C and crosses for 26.95°C)

To determine the gelpoint a technique based on Winter[5] the gelpoint can be established as the slope in complex viscosity vs angular frequency approaching a slope of -0.5 as shown in fig. 10. The figure shows that a very small change in temperature changes gelation properties.
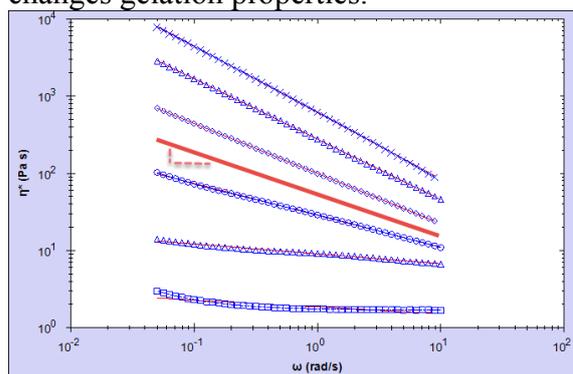

Fig. 10. Complex viscosity vs. angular frequency for temperatures ranging from 29.45°C to 26.95°C with insert of slope of -0.5.

Table 1 shows the slope for complex viscosity versus angular frequency at different temperatures. The shear viscosity is reported at an angular frequency of 1 rad/s.

Sample Description	Shear viscosity (complex component)(Pa s)	n	Correlation coefficient
26.95	614.7	-0.8610	0.9999
27.36	277.1	-0.7838	1.000
27.78	99.40	-0.6490	1.000
28.2	28.62	-0.4129	0.9998
28.61	9.040	-0.1286	0.9943
29.45	1.854	-0.08846	0.8648

112

Table 1. Slope and complex shear viscosity for temperatures 29.45 to 26.95

Another approach for gelation is to do Time Resolved Mechanical Spectroscopy (TRMS) according to Mours and Winter[6] outlining that the data can be resolved on the time domain or temperature domain as shown in fig. 11, where data from 29.45°C to 26.95°C are shown.
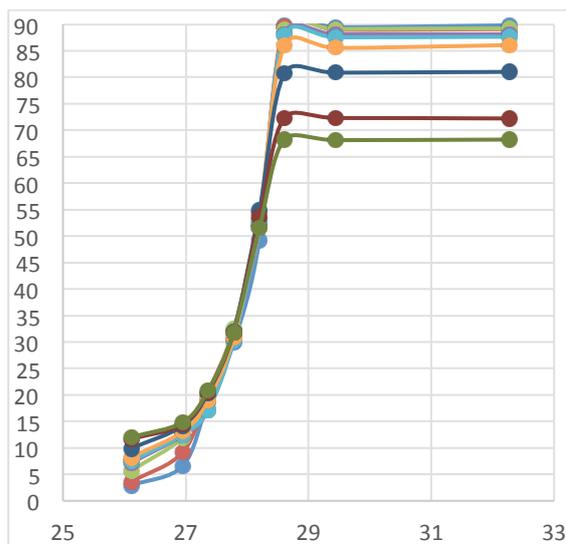

Fig. 11. Phase angle vs temperature for 7 angular frequencies from

The gelpoint in fig. 11 is the crossover for all the frequencies and it occurs at 28°C.

REFERENCES

1. Winter; H.H. (1987), "Can the gel point of a cross-linking polymer be detected by the G′–G ″crossover?", *Polymer Engineering & Science*, **27**, 1698-1702

2. Winter H.H. and Chambon, F. (1986), "Analysis of linear viscoelasticity of a crosslinking polymer at the gel point", *Journal of Rheology*, **30**, 367-382

3. Holly, E.E, Venkataraman, S.K., Chambon, F. and Winter H.H. (1988), "Fourier transform mechanical spectroscopy of viscoelastic materials with transient structure", *Journal of non-Newtonian Fluid Mechanics*, **27**

4. Duffy, J.J., Rega, C.A., Jack, R., and Amin, S. (2016), "An algebraic approach for determining viscoelastic moduli from creep compliance through application of the Generalised Stokes-Einstein relation and Burgers model", *Appl. Rheol*. **26(1)**

5. Winter H.H., (1987), "Evolution of rheology during chemical gelation", *Progr. Colloid & Polymer Sci.*, **75**

6. Mours M., Winter H.H. (1994), "Time-Resolved Rheometry", *Rheol Acta*, **33**