Quiz 5 Polymer Physics 10/27/00

When a polymer gels during a chemical end-linking reaction, the dynamic mechanical properties reflect a "self-similar" behavior in frequency. That is, a power-law relationship has been proposed to exist between the time dependent modulus G(t) and time, $G(t) = S\, t^{-n}$ [1], where S is the gel stiffness and n is the relaxation exponent (both constants). Under this approach only two parameters are needed to completely describe the mechanical properties at the gel point. The relaxation time spectrum for this process is given by,

$$H(\tau) = S/\Gamma(n)\ \tau^{-n} \text{ for } \tau_0<\tau<\infty$$

The dynamic storage modulus, G'(ω), and the dynamic loss modulus, G"(ω), for the same gelling system are related by,

$$G'(\omega) = G''(\omega)/\tan\delta_c = S\ \omega^n\, \Gamma(1-n) \cos \delta_c$$

where δ_c is a constant in frequency reflecting the phase angle between stress and strain. δ_c depends on the relaxation exponent, n, $\delta_c = \pi n/2$. Γ(n) is the gamma function,

$$\Gamma(n) = \int_0^1 \left(\ln(1/x)\right)^{n-1} dx\ .$$

[1] A. Izuka, H. H. Winter, T. Hashimoto, Macromolecules 30 6158 (1997). Attached.

a) -**Is** relaxation at the gel point, as described by the self-similar laws given above, a Debye Process?

-Show why or why not.

b) -**Sketch** the loss and storage modulus as a function of log(ωτ) for a single relaxation time Debye Process

-and for the process above (remember $\omega^n = 10^{n\log\omega}$.)

c) -Make a Cole-Cole plot of G" versus G' for the Debye process and for the self-similar process.

-What are the differences?

-Explain in simple terms the reason for the differences.

d) Winter in the cited paper and in other work (published in Rheologica Acta 1996) has focused on the relaxation time spectrum as the important feature for discussion of dynamic mechanical properties.

-What is the relaxation spectrum, for a single relaxation time Debye Process? (Sketch).

-Make a sketch of the relaxation spectrum, H versus log τ, for the self-similar process discussed above (remember $\tau^{-n} = 10^{-n\log\tau}$).

e) Winter notes that the phase angle, δ_c, is independent of frequency for a critical gel.

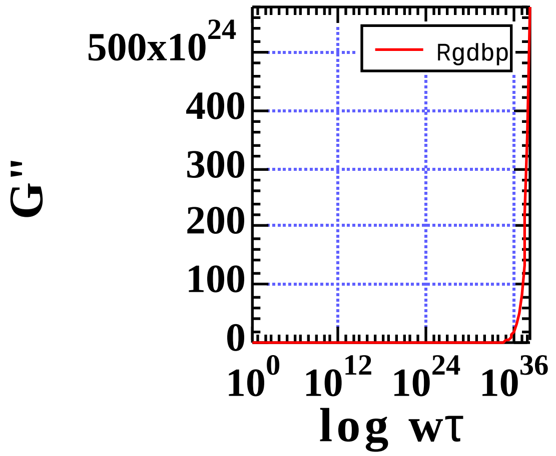
-Is the phase angle independent of frequency for a Debye Process?

-How does the relaxation angle, δ, relate to the Cole-Cole Plot?

-What is the physical significance of a constant phase angle for a gel?

Answers Quiz 3 Polymer Physics 10/27/00

a) No, This is not a Debye Process because the G" versus log(ωτ) plot looks like the one below. (G' versus log(ωτ) is a similar plot.)



Also see "c" below.

b)

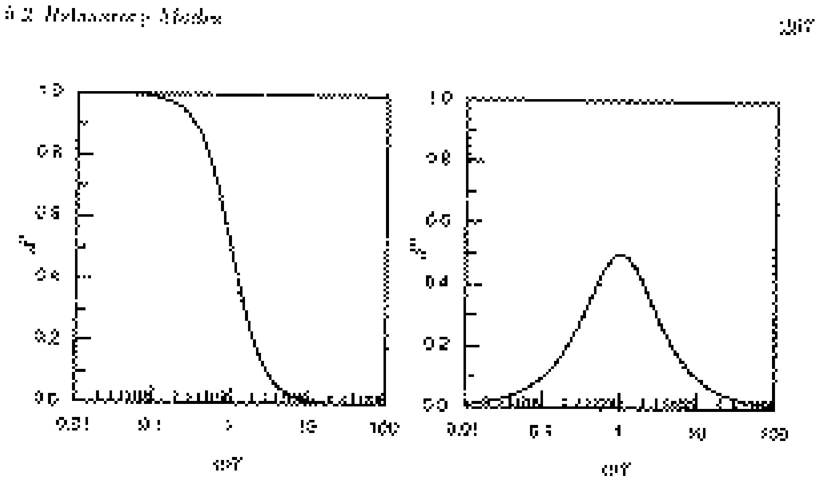
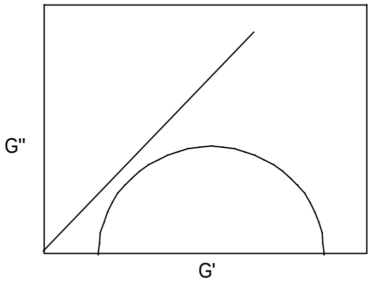


Fig. 5.5. Real part (left) and imaginary part (right) of the dynamic compliance associated with a mechanical Debye-process

The plot is appropriate because the loss curve becomes symmetric about ωτ = 1 if a linear/log plot is used. For the self-similar curve G" = S sin δ_c at ωτ = 1, it goes rapidly up at higher frequency and rapidly drops at lower frequencies. There isn't a single relaxation time for the self-similar function, i.e. there is a power law distribution of relaxation times as described by H(λ).

c)



They are completely different. The self-similar curve is like the superposition of a series of circles with increasing radius.

d) The relaxation time spectrum is a continuous spectrum of single time relaxations of the Debye-type basically. For a single Debye process the relaxation time spectrum is a single value.

For the self-similar spectrum the spectrum is a power-law decay in τ, i.e. $H(\tau)$ is porportional to τ^{-n}.

Some people propose a Gaussian spectrum (bell shaped curve) or a series of discrete spectral peaks associated with specific relaxations.

e) This feature is seen in the Cole-Cole plot where each point reflects a given frequency and the phase angle is the angle a line makes with the x-axis from the origin to the point on the circle, i.e. it changes with frequency. For the self-similar process it is constant as reflected in the line shown in the answer to part "c".

The physical significance of a constant phase angle involves the concept of a gel being self-similar in time and space. This means that at high or low magnifications and at long and short times the gel "looks" the same. Because the gel "looks" the same it displays the same phase angle between G' and G". From this we can conjecture that τ_0 (equation for $H(\tau)$) is the time associated with motion of the smallest piece of the gel, i.e. a base unit of the branched structure.