Quiz 6 Polymer Physics 11/2/00

a) The storage and loss curves for a polymer as a function of frequency are typically plotted on a log-log plot. There are several reasons for this.
-Explain how the range of values typically observed for G' leads to the use of a log scale.
-Explain how the functional form of J" for a single relaxation time Debye transition indicates the use of a log frequency axis.

b) Show that the Arrhenius temperature dependence indicates the use of a log frequency scale by
-Writing the Arrhenius function for the relaxation time
-converting this to a log function
-discussing the relationship between the relaxation time and frequency for a simple Debye transition at two temperatures, T_1 and T_2.

c) **-Sketch** a typical time dependent modulus versus time and time dependent compliance versus time curve.
-Give a function that describes time dependent compliance as a function of time at very long times in the terminal region.
-Give a function that describes the time dependent modulus as a function of time at very long times.
-If you used a log axis for the time scale in your sketch explain why based on the functions you gave and the typical range of time involved for a full curve.

d) **-Show** how the Arrhenius shift factor a_T can be obtained form the Arrhenius temperature dependence function.
-Compare this shift factor with the WLF shift factor. Under what condition is the WLF equation the same as the Arrhenius equation.

e) The WLF function for the α-transition contains a constant, C_2, that is a temperature 30 to 70 degrees below T_g.
-What is special about the glass transition that requires this temperature when compared to other lower temperature transitions such as β- or γ-transitions?
-**Is it possible** to observe the glass transition below C_2 at very long times or very low frequencies?
-**Is it possible** to observe β- or γ-transitions at very low temperatures well below the normal transition temperature for long times or very low frequencies?

Answers Quiz 6 Polymer Physics 11/2/00

a) -Typically G' spans 9 orders of magnitude. If a log scale were not used the low values would be swamped in a plot and only the high modulus end could be observed.
-For a single relaxation time Debye transition J'' = $\Delta J\ \omega\tau/(1 + \omega^2\tau^2) = \Delta J/(10^{-\log(\omega\tau)} + 10^{\log(\omega\tau)})$ so the loss peak will be symmetric in $\log(\omega\tau)$.

b) $\tau = \tau_0 \exp(-E_a/kT)$ taking a log of both sides $\log\tau = \log\tau_0 - E_a/kT$
In the equations for a simple Debye relaxation τ and ω always appear as a pair so for observation at two temperatures, T_1 and T_2, the measurement at T_2 can be converted to an equivalent frequency at T_1 by using $\log(\tau_1\omega) = \log(\tau_0\omega) - E_a/kT_1$ that gives the Arrhenius shift factor equation, on a low frequency scale, $\ln a_T = (E_a/k)(1/T_2 - 1/T_1)$.

c)

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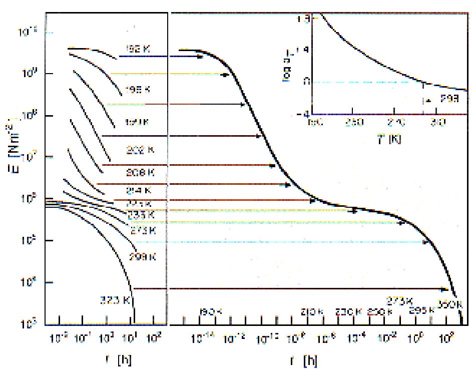

Fig. 5.14. Time dependent tensile modulus of PIB. Measurements at the indicated temperatures (left) and master-curve, constructed for a reference temperature T = 298 K (right). The insert displays the applied shifts. Data from Castiff and Tobolsky [53]

log Modulus versus log time

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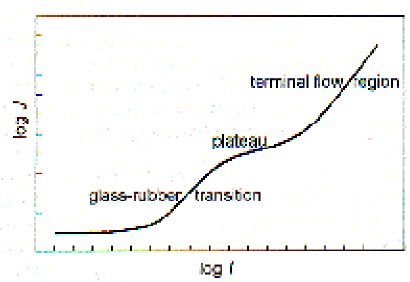

Fig. 5.12. General shape of the complete creep curve of PS, as suggested by the appearance of the different parts shown in Fig. 5.11

log Compliance versus log time

At long times $J(t) = t/\eta$, and $G(t) = J_e^0\ \eta_0^2\ t^{-2}$. The log time scale is used because the time range is 20 orders and the functions at long times in the terminal zone are power-law functions that are naturally presented on a log-log plot to make the power-law regions appear linear.

d) For two temperatures, T_1 and T_2, we can write $\log(\tau_1\omega) = \log(\tau_0\omega) - E_a/kT_1$ and $\log(\tau_2\omega) = \log(\tau_0\omega) - E_a/kT_2$. Subtracting the second from the first we obtain, $\log(a_T) = \log(\tau_2\omega) - \log(\tau_1\omega) = (-E_a/k)(1/T_2 - 1/T_1)$.
The WLF function is $\log(a_T) = -C_1\ (T - T_0)/(C_2 + T - T_0)$, the difference between the two equations involves the second parameter C_2. The two functions are identical when $C_2 = T_0$.

e) The glass transition has a finite temperature limit when it is considered a true second order transition. That is, below C_2 the α-transition can not occur. This is not true of simple Arrhenius transitions such as β- or γ-transitions. For these simple transitions the transitions occur for all temperatures above absolute 0.

When viewed as a true second order transition it is not possible to observe the α-transition below C_2. It is possible to observe the β- or γ-transitions for all temperatures above absolute 0 by looking at very long times or very low frequencies.