Appendix 1

The Williams Landau Ferry (WLF) equation and Time Temperature Superposition

The method of reduced variables, or time temperature superposition, has traditionally been applied to pure polymers, where it is used to make predictive measurements of the material. It has also found wider application in the foods area with the treatment of sugar rich hydrocolloid gels and gelatin. A detailed treatment can be found in standard texts such as Viscoelastic Properties of Polymers by Ferry (1) and some basic information is reproduced here.

The fundamental WLF equation can be derived from the Dolittle equation which describes the variation of viscosity with free volume.

$$\ln \eta = \ln A + B([V - V_f]/V)$$

Where η is the tensile viscosity, V and Vf are the total volume and free volume of the system respectively, and A and B are constants.

$$\Rightarrow \quad \ln \eta = \ln A + B(1/f - 1)$$

If it is assumed that the fractional free volume increases linearly with temperature then

$$f = f_g + \alpha_f(T - T_g)$$

where α_f is the thermal coefficient of expansion, f is the fractional free volume at T, a temperature above T_g, and f_g is the fractional free volume at T_g.

Therefore

$$\ln \eta(T) = \ln A + B(1/[f_g + \alpha_f(T - T_g)] - 1) \qquad \text{at } T > T_g$$

And
$$\ln \eta(T) = \ln A + B(1/f - 1) \qquad \text{at } T = T_g$$

subtracting $\Rightarrow \quad \log \eta(T)/\eta(T_g) = -B/2.303 \, f_g[T - T_g]/\{(f_g/\alpha_f) + T - T_g\}$

where the universal constants $C_1 = B/2.303 \, f_g$ and $C_2 = f_g/\alpha_f$

It can be shown that $\log \eta(T)/\eta(T_g) = \log a_T$

The method of extracting the universal constants of the WLF equation is to use the method of reduced variables (time temperature superposition). A number of DMA frequency scans are recorded at a series of isothermal temperatures, and the resulting data displayed on a

screen. A reference temperature is chosen (typically the isothermal temperature from the middle section of data where properties vary most as a function of frequency, equivalent to T_g) and the factors required to shift the responses at the other temperatures calculated so that one continuous smooth mastercurve is produced. Most commercial analysers provide software to create the mastercurve and calculate the shift factors involved. Different approaches have been used to obtain this type of data including a frequency multiplexing approach where a low underlying scan rate is used and the frequency continuously varied. However this means that data collected at each individual frequency will be at a slightly different temperature, and it is best to ensure that truly isothermal conditions are employed.

The factor for the reference temperature (a_T) is 1 with those for temperatures less than the reference temperature being less than 1 and those for temperatures greater than the reference temperature being greater than 1. The mastercurve, in conjunction with either the modulus temperature curve or the shift factors (a_T) relative to a reference temperature (T_{ref}), enables the response of the polymer under any conditions of time and temperature to be obtained.

There is also a correction to be applied in the vertical direction as well as the shift along the x-axis. This is related to the absolute value of temperature, on which the moduli depend, and the change in density as the temperature changes. The entire procedure can be expressed thus

$$E(T_1, t)/\rho(T_1)T_1 = E(T_2, t/a_T)/\rho(T_2)T_2$$

This correction should only be made for the rubbery state, ie above T_g. It is invalid for the glassy state.

By fitting the WLF equation to the shift factors, (y-axis), at a particular temperature, (x-axis) we can obtain an estimate of the universal constants C_1 and C_2 and hence obtain an estimate of T_∞, the underlying true second order transition temperature, where viscosity becomes infinite. The WLF equation can also be expressed in terms of the shear moduli as

$$\log a_T = G(T)/G(T_{ref}) = -C_1(T - T_{ref})/(C_2 + T - T_{ref})$$

and can be rearranged to obtain the universal constants C_1 and C_2 from a linear graphical plot.

$$(T - T_{ref})/\log a_T = -1/C_1(T - T_{ref}) + (-C_2/C_1)$$
$$\mathbf{y = mx + c}$$

If the term $[C_2 + T - T_0]$ went to zero the term $\log a_T$ would tend to $-\infty$ which would correspond to a shift factor of 0 and the response of the polymer at the limiting true transition temperature T_∞.

and
$$T_\infty = T_{ref} - C_2 = T_g - 50$$

if T_g is chosen as the reference temperature.

T_{∞} is thought to be the true underlying 2nd order transition for these materials and only accessible for experiments carried out over very long time scales. In practice the 50°C, which is normally added to the T_{∞}, returns a value for T_g more in keeping with everyday experience and measured values. This procedure places the glass transition somewhere in the transition region.

It can therefore be seen that C_1 can give information on the free volume at the glass transition whilst C_2 can give information on the thermal expansion as well as the underlying glass transition.

WLF Kinetics

It is found for some diffusion limited reactions that the temperature dependence of the rate of the reaction follows a WLF type of equation rather than an Arrhenius equation in the region of the glass transition. This is also true for rheological properties such as shear moduli. Plots which linearise the data are of the form of the logarithm of reaction rate against the reciprocal of terms similar to $T - T_g$, rather than the Arrhenius form, $1/T$. It is only for reactions limited by diffusion, such as the translational motion of a reactant in a glass/rubber. Reactions which are limited by some other non diffusion based step are known as reaction limited and will obey Arrhenius kinetics.

1) Viscoelastic Properties of Polymers, Third edition, Ferry, 1980, Wiley, Pages 280–298