Molecular interpretation and prediction of the dynamic viscoelastic properties of crosslinked polymers

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The dynamic viscoelastic properties of epoxy resins through the glass transition region are theoretically calculated and molecularly interpreted. Good agreement between the theoretical and experimental results is achieved over a broad range of temperatures and frequencies with a single set of molecular parameters. All molecular parameters are independent of temperature and frequency and can be determined separately. The master dynamic storage modulus and loss tangent are uniquely defined by a single parameter that characterizes the shape of the hole energy spectrum. The transition from a Williams–Landel–Ferry (WLF) (or Doolittle) dependence to an Arrhenius temperature dependence of the relaxation timescale (shift factor) in the vicinity of T_g is predicted and interpreted in molecular terms. The dynamic response of crosslinked polymers is quite similar to that of amorphous polymers. However, the timescale and the hole energy spectrum are orders of magnitude longer and broader, respectively. As a result, we have found higher activation energy, more frozen-in free volume and smaller effect of physical ageing on the dynamic properties of crosslinked systems.

(Keywords: dynamic moduli; time–temperature superposition; glass transition; epoxy resin; physical ageing; free volume)

INTRODUCTION

Mathematical descriptions of the dynamic response of linear viscoelastic properties of solid polymers have been thoroughly developed and given in the form of integral equations and transformations[1-3]. However, the solution of these equations has rarely been reported owing to difficulties in carrying out such calculation precisely. Besides, it is important to recognize that these mathematical descriptions do not have a simple interpretation in molecular terms.

The purpose of this paper is not only to calculate the complete information about the dynamic viscoelastic properties through the glass transition region but also to interpret their time and temperature dependence in terms of a single set of molecular parameters. It is well known that the temperature dependence of viscoelastic relaxation data can be described by the Williams–Landel–Ferry (WLF) equation[4] for $T > T_g$. However, an Arrhenius type of temperature dependence is observed in the glassy state[5-9]. This phenomenon is generally true for amorphous as well as crosslinked systems. By extending the molecular relaxation theory for amorphous polymers[10-12], we will (1) calculate the dynamic mechanical properties of crosslinked polymers, (2) predict the transition of a WLF dependence to an Arrhenius temperature dependence of the shift factor (relaxation timescale), and (3) show the difference in physical ageing between crosslinked and amorphous polymers. The theoretical calculation will be compared with published experimental data.

COMPLEX MODULUS

The constitutive relation of the tensile stress σ and strain e for a viscoelastic material can be written by means of the Boltzmann superposition integral:

$$\sigma(t) = \int_{-\infty}^{t} E(t - \eta)\dot{e}(\eta)\,\mathrm{d}\eta \tag{1}$$

where E is the tensile relaxation modulus and t is time. Put:

$$\omega t = (\omega\tau)(t/\tau) \equiv zy \tag{2}$$

where ω is the angular frequency, τ is the global (macroscopic) relaxation time, and z and y are the non-dimensional frequency and time, respectively. When equation (1) is subjected to the Fourier transform:

$$\sigma(z) = \int_{-\infty}^{\infty} \sigma(y)\exp(-izy)\,\mathrm{d}y \tag{3}$$

it can be written in the form:

$$\sigma(z)/e(z) = E^*(z) = iz\int_{0}^{\infty} E(y)\exp(-izy)\,\mathrm{d}y \tag{4}$$

where the complex tensile modulus can be separated into the real and imaginary parts:

$$E^*(z) = E'(z) + iE''(z) \qquad (5)$$

The real part is called the storage modulus and the imaginary part defines the energy dissipation and is called the loss modulus. We consider that the tensile modulus is related to the normalized relaxation function ϕ by the equation:

$$\frac{E(y) - E_\infty}{E_0 - E_\infty} = \phi(y) = \exp(-y^\beta) \qquad 0 < \beta \leqslant 1 \qquad (6)$$

where E_0 and E_∞ are unrelaxed and relaxed moduli, respectively. Equation (6) has been used quite successfully in describing the transient viscoelastic behaviour of amorphous and lightly crosslinked polymers[12-15]. In this paper, we shall see whether it is also applicable to the dynamic viscoelastic properties of well crosslinked polymers. There are two important differences between the Williams–Watts equation for dielectric relaxation[16] and equation (6). First, they chose $-\phi'$ instead of ϕ to define the transient decay. Secondly, while they treated β and τ as empirical parameters, which must alter continuously through the glass transition region in order to fit the relaxation data, we acquire a deep insight into the molecular mechanism controlling these parameters. We have found that β is a constant through the glass transition region and τ can be a function of temperature, non-equilibrium glassy state[11], crosslink density[14] and non-linear stresses[12]. Further details will be discussed and examined in the next section.

Substitution of equation (6) into equation (4) gives:

$$\frac{E' - E_\infty}{E_0 - E_\infty} = \frac{\omega\tau}{\beta} \int_0^\infty \exp(-x)[x^{(1-\beta)/\beta}\sin(\omega\tau x^{1/\beta})]\,dx \qquad (7)$$

and

$$\frac{E''}{E_0 - E_\infty} = \frac{\omega\tau}{\beta} \int_0^\infty \exp(-x)[x^{(1-\beta)/\beta}\cos(\omega\tau x^{1/\beta})]\,dx \qquad (8)$$

These two integrals can be evaluated numerically by the Gauss–Laguerre quadrature for small $\omega\tau$. For large $\omega\tau$, the convergence of the numerical integrations becomes so slow that an alternative approach has to be developed.

Replacing $iz = p$ in equation (4), we consider the Laplace transformation of the relaxation function:

$$\phi(p) = \int_0^\infty \exp(-py)\phi(y)\,dy \qquad (9)$$

According to the mathematical theorem[17]:

$$\lim_{p \to \infty} p\phi(p) = \lim_{y \to 0} \phi(y) \qquad (10)$$

we take the series expansion of equation (6):

$$\phi(y) = \exp(-y^\beta) = 1 - y^\beta + \frac{y^{2\beta}}{2!} - \frac{y^{3\beta}}{3!} + \cdots \qquad (11)$$

Substitution of equation (11) into equation (9) gives:

$$p\phi(p) - 1 = \sum_{m=1}^\infty (-1)^m \Gamma(m\beta + 1)/m!p^{m\beta} \qquad (12)$$

where Γ is the gamma function. Thus, for large $\omega\tau$, the storage and loss moduli can be efficiently calculated, respectively, from:

$$\frac{E' - E_\infty}{E_0 - E_\infty} = 1 + \sum_{m=1}^\infty \frac{(-1)^m \Gamma(m\beta + 1)}{m!z^{m\beta}}\cos(m\beta\pi/2) \qquad (13)$$

and

$$\frac{E''}{E_0 - E_\infty} = \sum_{m=1}^\infty \frac{(-1)^{m+1}\Gamma(m\beta + 1)}{m!z^{m\beta}}\sin(m\beta\pi/2) \qquad (14)$$

The leading terms of the above two equations give a useful asymptotic expression for the loss tangent in the glassy state where E_∞ is also negligible in comparison with E_0. That is:

$$\lim_{\omega\tau \to \infty} \tan\Delta = (\omega\tau)^{-\beta}\Gamma(1 + \beta)[\sin(\beta\pi/2) + \cos(\beta\pi/2)] \qquad (15)$$

When $\beta = 1$, equation (15) becomes:

$$\lim_{\omega\tau \to \infty} \tan\Delta = (\omega\tau)^{-1} \qquad (16)$$

which has the familiar form[2,3].

The dependence of E' and E'' on $\omega\tau$ can be calculated from equations (7), (8), (13) and (14) and is shown in *Figure 1* where β is the only adjustable parameter to be determined from experimental data. In analysing the equation of state and physical ageing data on the basis of our molecular model for relaxation in the glass, we have found that $\beta \simeq 1/2$ for most amorphous polymers[11,12]. The calculated curves in *Figure 1* provide a good description to the normalized storage and loss moduli measured (ref. 1, Ch. 15) over a wide range of temperatures for amorphous systems.
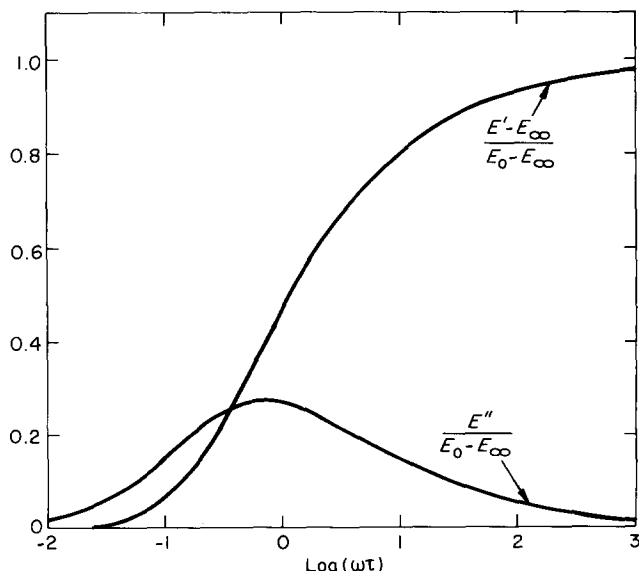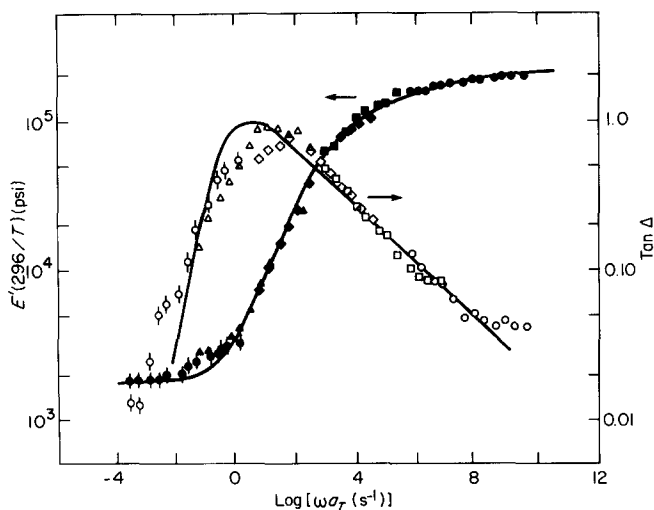

Figure 1 Typical calculation for normalized components of the complex moduli of an amorphous polymer ($\beta = 0.5$)

Figure 2 Comparison of the calculated (curves) and measured (points)[5,18] master curves of dynamic properties of an epoxy resin ($\beta = 0.19$)

A comparison between the theory and experiment for epoxy resins[5,18] is carried out in *Figure 2*. The dynamic viscoelastic data cover a four-decade frequency range from 0.01 to 100 Hz and temperatures from 25 to 200°C. The experimental points in *Figure 2* have been shifted horizontally to form the 'master curves'. The shift factor, a_T, will be discussed in the next section. The reference temperature for the master curves is 165°C. The full curves represent the theoretical calculation where $(E_0, E_\infty) = (2 \times 10^5, 1.8 \times 10^3)(296/T)$ psi. It is interesting to note that the temperature dependence of the relaxed and unrelaxed moduli of crosslinked polymers has exactly the same form as that of amorphous polymers[13]. Using equations (7), (8), (13) and (14), we have determined $\beta = 0.19$, which defines the shape of the curves and the range of timescale for the master storage modulus and loss tangent. Since the abscissa in *Figure 2* is expressed in terms of ωa_T rather than the dimensionless $\omega\tau$, this also enables us to determine $\tau(165°C) = 10^{-3.8}$ s. *Figures 1* and *2* reveal that the timescale for well cured epoxy resins covers the range far broader than that for amorphous polymers.

SHIFT FACTOR

The time–temperature superposition has been extensively studied in the literature to understand the kinetics of polymer relaxation. It has been well established that the linear viscoelastic response obeys the WLF[4] (or Doolittle[19]) shift function at temperatures above the glass transition temperature (T_g). However, an Arrhenius type of temperature dependence of the relaxation time is usually observed in the glassy region. The phenomenon is generally true for amorphous polymers as well as crosslinked systems. Using our statistical mechanical theory of relaxation in the glass, we shall make a theoretical prediction and molecular interpretation of the change from a WLF dependence to an Arrhenius temperature dependence of the shift factor through the glass transition region.

On the basis of the idea of continuous conversion of the number of holes (free volume) and the number of phonons in a polymer lattice, we have introduced[10] a physical picture of quantized hole energy states ε_j with

$j = 1, 2, \ldots, L$. The problem is to determine the distribution of the ensemble characterized by a set of hole numbers $\{n_j\}$ with $\sum_j n_j = n$. The ratio of $n_j/N = f_j$ is the jth contribution to the free volume fraction $(f = \sum_j f_j)$. Minimizing the excess Gibbs free energy due to hole introduction with respect to n_j, the equilibrium distribution of the free volume fraction is obtained[10]:

$$\bar{f}(T) = \bar{f}_r \exp\left[-\frac{\bar{\varepsilon}}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right) \right] \qquad (17)$$

where $\bar{\varepsilon} = \sum_j \varepsilon_j \bar{f}_j/\bar{f}$ is the mean hole energy, R is the gas constant and the subscript r refers to the condition at $T = T_r$ which is a fixed quantity near T_g.

The non-equilibrium glassy state, $\delta(t) = f(t) - \bar{f}$, is determined by solving the kinetic equations that describe the local motion of holes in response to molecular fluctuations during vitrification and physical ageing. In the case of isothermal annealing followed by quenching from an elevated liquid temperature T_0 to T below T_r, the solution is[11]:

$$\delta(T,t) = [\bar{f}(T_0) - \bar{f}(T)]\phi(t/\tau) \qquad (18)$$

with the normalized relaxation function:

$$\phi(t/\tau, a) = \sum_{j=1}^{L} g_j \exp(-t/\tau_{jr}\lambda) \qquad (19)$$

where a and λ are the global and local shift factors, respectively, and g_j is the distribution function of hole energies and is related to ϕ by the discrete Laplace transform. By letting:

$$\frac{\tau_j}{\tau} = \frac{\tau_{jr}\lambda}{\tau_r a} \rightarrow \frac{1}{s} \quad \text{and} \quad g_j \rightarrow g(s) \qquad (20)$$

the summation in equation (19) can be written as an integral:

$$\phi(t/\tau) = \int_0^\infty g(s) \exp(-st/\tau) \, ds \qquad (21)$$

When the distribution is a delta function, $g(s) = \delta(s - 1)$, the distinction between the local and global shift factor disappears and equation (21) reduces to the exponential form, $\exp(-t/\tau)$.

According to equation (18), free volume is frozen-in when the system is quenched from T_0 to T. For $t > 0$, the frozen-in structure starts to relax, and the relaxation function ϕ has been treated as the probability of the holes having not reached their equilibrium states and has the fractional exponential form of equation (6). In this case, equations (20) and (21) reveal the local and global relaxation times cannot be the same because $g(s)$ has a broader distribution and is not limited to a value at $s = 1$. We have found[10-12] that the exponent β in equation (6) not only uniquely defines the shape of the hole energy spectrum $g(s)$, the Laplace inversion of ϕ, but also provides an important link between λ and a. That is[10,11]:

$$\ln a = (\ln \lambda)/\beta = \frac{\bar{\alpha}_r(T_r - T) - \delta}{\beta \bar{f}_r^2} \qquad (22)$$
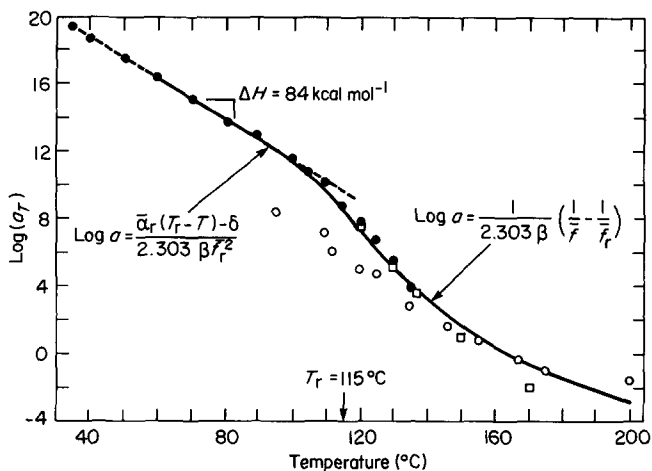
Figure 3 The transition of a WLF dependence to an Arrhenius temperature dependence for the global shift factor of an epoxy. The full curve represents the theoretical calculation and points are experimental data[5] ($\bar{\varepsilon}=4.5\,\mathrm{kcal\,mol^{-1}}, \bar{f_r}=0.13$)

where $\bar{\alpha}_r = \bar{\varepsilon}\bar{f_r}/RT_r^2$. The first term $\bar{\alpha}_r(T_r - T)/\bar{f_r}^2$ in the above equation is controlled by the local activation energy $\bar{\varepsilon}/\bar{f_r}$ and the second term $\delta\bar{f_r}^2$ is related to the non-equilibrium fluctuation in glasses. In the vicinity of T_g, equation (22) is equivalent to[11]:

$$\ln a(T,\delta) = \frac{1}{\beta}\left(\frac{1}{\bar{f}+\delta} - \frac{1}{\bar{f_r}}\right) \qquad (23)$$

which suggests that Doolittle's equation has to be modified to include the non-equilibrium contribution in the glassy state. When $\delta = 0$, equation (23) can be written in the form of the WLF equation, which is known to be valid for $T > T_g$.

When the experimental a_T vs. T data on the epoxy resin above $T_g = 115°C$ are used, equations (17) and (23) give $\bar{\varepsilon} = 4.5\,\mathrm{kcal\,mol^{-1}}$ and $\bar{f_r} = 0.13$. In analysing the data, we consider:

$$\log a_T = 8.58 + \log a \qquad (24)$$

with a (115°C) = 1. Similar to the approach for lightly crosslinked polymers[14], the reference temperature T_r has been chosen to be T_g of an epoxy resin. By using the same set of values for $\bar{\varepsilon}, \bar{f_r}$ and β that were determined in the last section and having $\tau_r = 1\,\mathrm{h}$, equation (22) predicts the temperature dependence of the shift factor in the glassy and transition states. The non-equilibrium glassy state in equation (22) is calculated from[12]:

$$\delta(T,q) = -\frac{\bar{\varepsilon}}{R}\int_{T_0}^{T} \frac{\bar{f}}{T'^2}\exp\left[-\left(\frac{T-T'}{|q|\tau}\right)^\beta\right]\,dT' \qquad (25)$$

where q is the cooling (<0) rate. The numerical solution of the above equation is not affected by the initial temperature of $T_0 > T_g + 10°C$.

In *Figure 3*, the full curve represents the theoretical calculation and the experimental points correspond to those in *Figure 2*. We have shown[12] that the cooling rate has little effect on the calculated slope $\partial\log a/\partial T$ in the glassy state ($T < T_g - 10°C$). Following equation (22), we

obtain the activation energy:

$$\Delta H \simeq -RT_r^2\,\partial\ln a(T,\delta)/\partial T = (1-\mu)\bar{\varepsilon}/\beta\bar{f_r} \qquad (26)$$

where

$$\mu = -\frac{1}{\bar{\alpha}_r}\frac{\partial\delta(T,\delta)}{\partial T} \qquad (27)$$

It reaches a constant value of 0.54 for $T < T_g - 10°C$ and approaches zero for $T > T_g$. The activation energy near T_g changes from $\bar{\varepsilon}/\beta\bar{f_r} = 182.2$ to 84 kcal mol^{-1} = $(1-\mu)\bar{\varepsilon}/\beta\bar{f_r}$ in *Figure 3* as the epoxy resin is cooled through the glass transition region. Similar to that of amorphous polymers, this transition phenomenon can be interpreted in terms of μ for crosslinked polymers. In the glassy state, the value of ΔH obtained in *Figure 3* is larger than those reported for amorphous polymers[12,15], which are in the range of 30–50 kcal mol^{-1}.

Struik[20] has introduced the same constant μ in the glassy state to characterize the physical ageing rate observed in his isothermal creep experiments. Recently, we have derived[12] the Struik equation for the shift factor at longer ageing times (t_e) from equations (18) and (22):

$$a(T,t_e) \sim t_e^\mu \qquad (28)$$

The exponent μ is no longer an empirical constant but can be calculated directly from the same molecular parameters ($\bar{\varepsilon}, \bar{f_r}, \beta$ and τ_r) mentioned earlier. All molecular parameters are independent of temperature and frequency (or time) and can be determined separately. The value of μ for epoxy resins is lower than that of amorphous polymers[12,20,21] in the glassy state.

From equations (15) and (28), we have:

$$\tan\Delta \sim (\omega\tau)^{-\beta} \sim t_e^{-\beta\mu} \qquad (29)$$

which reveals that the effect of physical ageing on crosslinked systems is much smaller in the dynamic than in the transient measurements. The value of $\beta\mu$ drops from 0.4 for amorphous polymers to 0.1 for epoxy resins.

Comparing with amorphous polymers, we have seen that epoxy resins have smaller β and larger $\bar{f_r}$ and ΔH. The formation of crosslinks slows down the molecular motion of chain molecules and the global relaxation time has to increase[14]. This can be interpreted as the result of stronger cooperative interaction due to broader hole energy spectrum, smaller β in equation (22), for crosslinked systems. The slowdown process contributes to more free volume frozen-in near the glass transition, which is consistent with the reported anomalous results[22] for epoxy resins.

CONCLUSIONS

The dynamic moduli, loss tangent and the frequency and temperature shift factor of epoxy resins have been quantitatively calculated through the glass transition regions on the basis of our quantized hole energy model. The timescale for the theoretical evaluation of experimental data covers the frequency range from 0.01 to 100 Hz and temperatures from 25 to 200°C. The corresponding timescale for the master curves covers more than a ten-decade time or frequency range. We have shown how the slow convergence problem encountered in

the calculation can be solved and how the molecular parameters are determined separately. The master curves of the dynamic properties of an epoxy resin are uniquely determined by β, which characterizes the shape of the hole energy spectrum. The mean hole energy $\bar{\varepsilon}$ and the reference free volume fraction $\bar{f_r}$ are obtained by fitting the $\log a_T$ versus T data above T_g. Using these predetermined molecular parameters, we predict the temperature dependence of shift factor in the glassy and transition states. The transition of a WLF dependence to an Arrhenius temperature dependence of the relaxation timescale in the vicinity of T_g is related to the physical ageing rate μ, which can be calculated from the non-equilibrium glassy state in terms of the same set of molecular parameters. The dynamic response of crosslinked polymers is quite similar to that of amorphous polymers. However, the hole energy spectrum is found to be much broader. As a result, we have found higher activation energy, more frozen-in free volume, and smaller effect of physical ageing on the dynamic viscoelastic properties of crosslinked systems.

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