

Changes in rotational motion of nitroxide spin probes in epoxy adhesives during the cure reaction

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The decrease in rotational mobility of nitroxide spin probes 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 4-(4-nitrobenzoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (Nitro-TEMPO), dispersed in Epon 828/MBCH (4,4-methylenebiscyclohexylamine) epoxy, was studied during the cure reaction. The larger probe, Nitro-TEMPO, exhibits the T_{50G} transition at a temperature 8°C above the T_g of the fully cured epoxy. During isothermal cure, the T_{50G} transition of Nitro-TEMPO occurs reproducibly at the pregel transition in the viscoelastic time-temperature-transformation diagram. The smaller probe, TEMPO, crosses T_{50G} at 20°C below T_g in the fully cured epoxy, and therefore shows no T_{50G} process during the cure reaction. Detailed analyses of the rotational correlation time τ_R and the rotational anisotropy N were carried out during the cure reaction for TEMPO. The results indicate that an abrupt change in the rotational relaxation behaviour of TEMPO occurs near the pregel transition, interpreted as a hindering of motion around the minor rotational axis. At the vitrification transition, we determine unique values $\tau_R = 4.3 \times 10^{-9}$ s and $N = 10.5$ for TEMPO in Epon 828/MBCH. Investigations of composite samples filled with carbon black and glass beads indicate no significant differences in the cure time dependence of the rotational mobility of the spin probe in filled *versus* neat material.

(Keywords: electron spin resonance; nitroxide spin probes; epoxy cure; viscoelastic transitions; rotational correlation time; anisotropy)

INTRODUCTION

The cure reaction of epoxy adhesives is characterized by three successive viscoelastic regimes, viz. the pregel, gelation and vitrification transitions¹. The molecular origin of the pregel transition is poorly understood, and has been suggested² to be an example of a liquid-liquid transition (T_{LL}). The gelation event corresponds to the initial formation of an infinite network, and the vitrification transition occurs when the glass transition temperature of the system rises to the cure temperature¹. An understanding of how these viscoelastic transitions depend on the reaction conditions is critical to the development of efficient processing methods. With the increasing use of epoxy resins, for example in the manufacture of composite materials, it has become of interest to develop *in situ* techniques that can follow the changes in viscosity which occur during the cure reaction. Several spectroscopic approaches are available which allow one to measure an effective microviscosity by monitoring the mobility of probe molecules dispersed in the epoxy matrix. For example, fluorescence spectroscopy has been employed to monitor the course of epoxy and other polymerization reactions³⁻⁷. One method utilizes fluorescence probes whose emission intensity increases with matrix viscosity because of a decrease in the non-radiative decay of excited fluorophores. Using such probes, correlations have been

established⁵⁻⁷ between the time evolution of the fluorescence intensity and the cure times distinguishing the different viscoelastic regimes for epoxy adhesives.

An alternative approach is to monitor the slowing of rotational diffusion of a dispersed spectroscopic probe molecule as the cure reaction proceeds. One such study has been reported⁴ in which the increase in fluorescence anisotropy of a dissolved fluorophore was studied during epoxy cure. In this report we investigate changes in the rotational mobility of nitroxide spin probes during the course of the epoxy polymerization reaction using electron spin resonance (e.s.r.) spectroscopy. Nitroxide spin probes and labels have been extensively employed to monitor the main-chain and/or side-chain motions of polymers^{8,9} and to measure dynamical transitions in bulk polymers¹⁰. Several monographs are available for review¹¹⁻¹³. Nitroxides have a characteristic three-line spectrum resulting from the hyperfine interaction of the unpaired electron with the nitrogen nucleus. The e.s.r. spectral linewidths are influenced by the rotational correlation time τ_R of the probe and thus depend strongly on matrix viscosity. Comparison of e.s.r. spectra of nitroxide probes with theoretical models enables, in principle, a rather detailed interpretation of the mechanism of rotational diffusion of the dispersed probe.

In this study, nitroxide spin probes of different molecular volumes are incorporated by mechanical mixing into the curing system. As the epoxy polymerization proceeds, dramatic changes in viscosity occur which substantially modify the spectral features. A

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parameter commonly used to characterize the probe mobility is the extrema separation ($2A_{zz}$) of the three-line derivative nitroxide e.s.r. signal. The temperature dependence of $2A_{zz}$ for a spin probe incorporated into a polymeric matrix exhibits a well defined transition, suddenly decreasing from a large value ($2A_{zz} \gg 50$ G) to a small value ($2A_{zz} \ll 50$ G) as the rotational correlation time decreases with a rise in temperature. The temperature at which $2A_{zz}$ equals 50 G is defined to be the T_{50G} transition temperature, and a correlation of T_{50G} with the glass transition of polymeric systems has been suggested¹⁰. It has also been established that T_{50G} is a strong function of the size of the nitroxide probe⁸. The T_{50G} transition corresponds to the crossover from a fast motional region, where the probe rotational relaxation frequency is faster than the Larmor frequency ω_L for the spin transition ($\tau_R^{-1} > \omega_L$), to the slow motional region ($\tau_R^{-1} < \omega_L$). More detailed measurement of spectral parameters allows calculation of the probe rotational correlation time τ_R in the fast and slow motional regions using appropriate theoretical analysis^{14,15}. In the case of a curing epoxy system the viscosity increases monotonically with cure time during isothermal cure. We have therefore investigated the variation of the extrema separation $2A_{zz}$ and the rotational correlation times as a function of cure time for nitroxide probes of different sizes.

As in the previous report⁷ we are interested in comparing the decrease in mobility of the e.s.r. spin probes with the different regimes of viscoelastic behaviour encountered during the cure reaction. We therefore chose to investigate the Epon 828/MBCH (4,4-methylenebis-cyclohexylamine) epoxy material whose viscoelastic properties during cure have been extensively explored by Enns and Gillham¹. The nitroxide spin probes TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) and Nitro-TEMPO (4-(4-nitrobenzoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl) were incorporated into an Epon 828/MBCH epoxy system, and isothermal cures at different temperatures were carried out in order to facilitate comparison with the viscoelastic data of Enns and Gillham¹. For reference, we show the structures of the spin probes in Figure 1.

EXPERIMENTAL

Shell Epon 828 epoxy resin and Aldrich Chemicals 4,4-methylenebis-cyclohexylamine (MBCH) hardener were used as received. Nitroxide spin probes 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 4-(4-nitrobenzoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (Nitro-TEMPO) were obtained from Aldrich Chemical Co. (Milwaukee, WI). The spin probes were added to the epoxy resin at a concentration of 5×10^{-5} M and the solutions stirred for a minimum of 12 h at 60°C. Filled epoxy samples were prepared by mixing, respectively, carbon black and glass beads of 100 μ m diameter into the TEMPO-doped epoxy resin. Filler concentration was 5 wt % in each case.

To investigate the e.s.r. spectrum of nitroxide probes in epoxies during the cure reaction, samples were prepared in the following manner: A stoichiometric amount of the MBCH hardener was added to the epoxy resin and the solution rapidly mixed with a mechanical stirrer at 60°C for 1 min. A small amount of the epoxy/resin mixture was then rapidly transferred to a standard e.s.r. sample tube.

The tube was immersed in a dewar containing dry ice/acetone to quench the reaction rapidly and stored in the bath until the start of the experiment.

E.s.r. spectra were recorded on a Varian E112 Century Series Spectrometer in the X band frequency range (≈ 9.5 GHz) with 100 kHz modulation frequency. The sample cavity was equipped with a variable-temperature accessory that was calibrated with a digital thermocouple prior to each run. Spectra were recorded with power level and modulation amplitude low enough to avoid distortion or saturation effects. Sample tubes were transferred from the dewar to the spectrometer cavity (preheated to the cure temperature) and allowed to equilibrate for 1 min prior to recording spectra.

The outermost peak-to-peak separation (in gauss) of the three-line nitroxide spectrum along with peak intensities and widths were measured directly from the recorded spectra. Rotational correlation times, estimated using equations given below, as well the extrema separation were determined as a function of cure time for both probes during a series of isothermal cures at temperatures ranging from 55 to 68°C.

Direct comparison with the viscoelastic data of Enns and Gillham¹ was possible after verifying that the cure kinetics of the Epon 828/MBCH system used by us was identical to that used in their work. The reaction kinetics were established by following the disappearance of the epoxide infra-red absorption band using Fourier-transform infra-red spectroscopy, and details of this procedure are described in our earlier paper⁷.

RESULTS AND DISCUSSION

In Figure 2a we show the time dependence of the e.s.r. derivative spectra of TEMPO dissolved in 1:1 (stoichiometric ratio) Epon 828/MBCH at 65°C during isothermal cure. Initially the spectra exhibit a well resolved triplet characteristic of rapidly tumbling spin probes. As the cure reaction proceeds, peak intensities

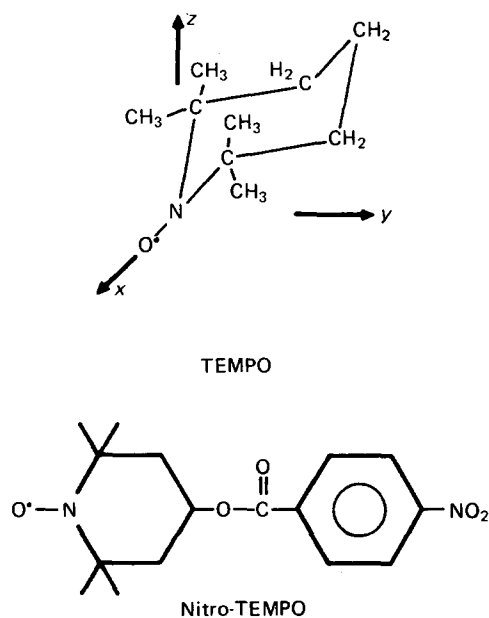


Figure 1 Chemical structure of nitroxide spin probes. The coordinate axes for the g tensor and hyperfine interaction tensor are shown for TEMPO

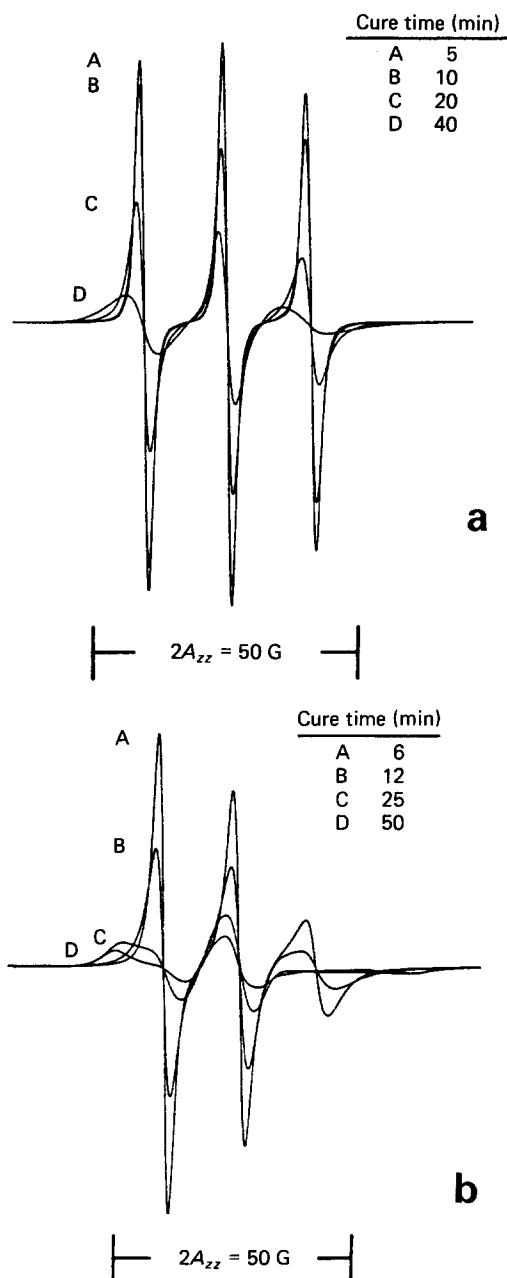


Figure 2 First-derivative e.s.r. spectra of (a) TEMPO and (b) Nitro-TEMPO during the Epon 828/MBCH polymerization reaction at 65°C

decrease, linewidths broaden and $2A_{zz}$ increases as matrix viscosity increases. At 40 min the lines are considerably broadened but the fairly sharp triplet is still evident.

This behaviour is contrasted in *Figure 2b* which shows the changes in the e.s.r. spectrum of the larger Nitro-TEMPO probe under the same cure conditions. In the initial stages of cure, peak intensities of the central and high-field lines are already considerably smaller than the low-field peak and the high-field line is greatly broadened. As the cure reaction proceeds, the increase in spectral broadening and decrease in peak intensities are much more pronounced than for the small probe. At a cure time (t_c) of 25 min the spectrum of Nitro-TEMPO exhibits a doublet in the low-field peak. Such features occur in the vicinity of T_{50G} and have been attributed to the superposition of fast and slow motion spectra^{8,9} or to a distribution of rotational correlation times resulting from

a distribution of free volume within the matrix¹⁶. For these spectra, an estimate of a single rotational correlation time will be imprecise, and detailed spectral simulation must be performed to determine τ_R accurately.

Changes in the spectra of TEMPO and Nitro-TEMPO throughout the cure reaction result from a hindrance to probe rotation as the viscosity of the system increases with cure time. There is no experimental evidence to suggest that the spin probes are involved in the epoxy polymerization reaction. Nitroxide spin probes are known to be exceedingly stable¹³ due to the shielding of the free radical by the adjacent methyl groups (see *Figure 1*). If radical consumption were to occur, peak intensities of the three-line spectrum would rapidly decay and disappear at an early stage in the cure reaction. Superposition of fast and slow motional spectra for Nitro-TEMPO (*Figure 2b*) shows a portion of the probe population to be mobile. It may be argued that at least a fraction of the immobile component could be due to chemical combination. However, epoxy chemistry does not appear to suggest such a mechanism¹⁷. Consider moreover the extreme dilution of probe vs. the highly reactive amine crosslinking agent.

In *Figure 3* the dependence of $2A_{zz}$ on cure time t_c for both small and large probes in Epon 828/MBCH at 68°C is shown. We also indicate by arrows the cure times where this system crossed the pregel, gel and vitrification transitions as estimated from the work of Enns and Gillham¹. The behaviour of each of the spin probes is consistent with the expectation that, as the matrix viscosity increases during polymerization, the rotational mobility is hindered and $2A_{zz}$ increases. The relative

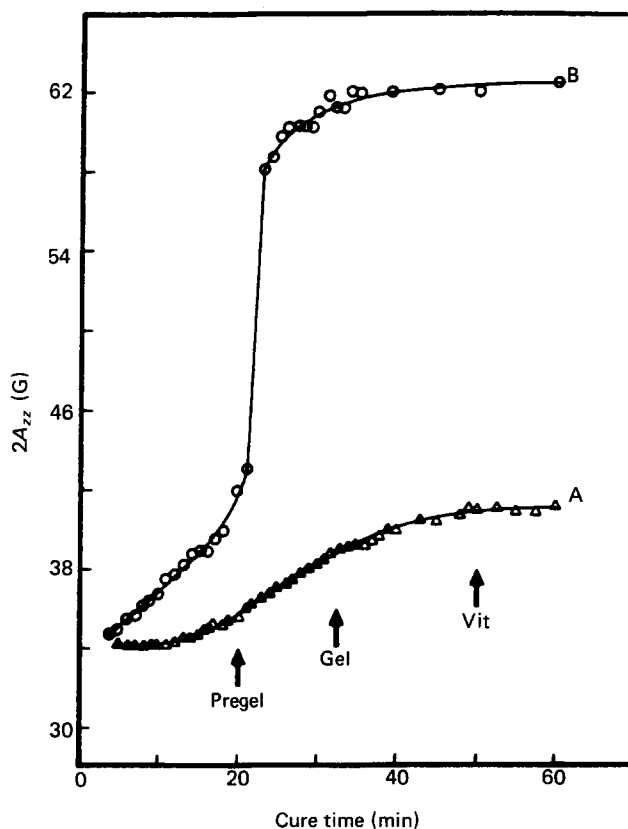


Figure 3 Outermost peak-to-peak separation $2A_{zz}$ of TEMPO (A) and Nitro-TEMPO (B) during the Epon 828/MBCH polymerization reaction at 65°C

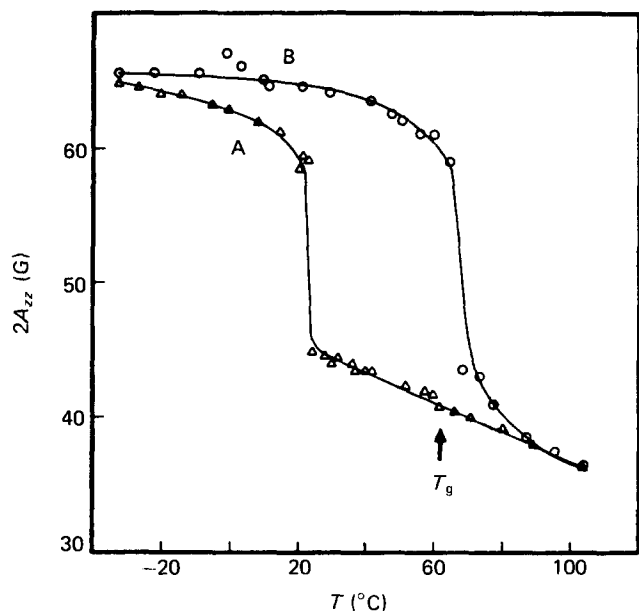


Figure 4 Temperature dependence of the outermost peak-to-peak separation of TEMPO (A) and Nitro-TEMPO (B) in a fully cured Epon 828/1,4 diaminobutane/*N,N'*-dimethyl-1,6-diaminohexane epoxy with $T_g = 62^\circ\text{C}$ as determined by d.s.c.

variation in $2A_{zz}$ for the Nitro-TEMPO probe throughout the cure is, however, much larger than observed for the smaller TEMPO probe. At early stages in the cure reaction both probes are mobile as evidenced by the small value of $2A_{zz}$. As t_c increases, the dissimilar behaviour of large and small probes is clearly evident. The larger Nitro-TEMPO probe exhibits a much faster initial increase in $2A_{zz}$ and a sharp transition from the fast motional behaviour to the slow motional region is observed near $t_c = 20$ min. A characteristic cure time, t_{50G} , may be defined as the time during the reaction at which $2A_{zz}$ equals 50 G. Beyond t_{50G} , $2A_{zz}$ reaches an asymptotic value and the probe is no longer sensitive to changes in the degree of crosslinking.

On the other hand, the small TEMPO probe remains in the fast motional region throughout the course of the reaction and no transition from fast to slow motion is seen. Compared to Nitro-TEMPO, TEMPO is insensitive to polymerization in the early stages and $2A_{zz}$ begins to increase at a much slower rate approximately 12 min into the cure. The overall magnitude of the change in $2A_{zz}$ is much smaller than for the larger probe and an asymptotic value is reached at a later stage in the cure. By analogy with our earlier use of fluorescence probes⁷, we may characterize the variation of $2A_{zz}$ of TEMPO by the cure times at which $2A_{zz}$ exhibits a point of inflection and those at which $2A_{zz}$ reaches its asymptotic value. These parameters were determined for cures at different isothermal temperatures and will be compared with the mechanical measurements of Enns and Gillham¹. The above observations indicate that the molecular volume of the spin probe determines the region of sensitivity to the changes in viscoelastic properties occurring during cure. The large probe, Nitro-TEMPO is sensitive to viscosity changes during the early stages of cure; the small probe TEMPO shows mobility changes extending to the vitrification transition.

To facilitate quantitative interpretation of the data presented in Figure 3, we have investigated the temperature dependence of the e.s.r. spectra of TEMPO and Nitro-TEMPO in fully cured epoxies, as shown in Figure 4. In each case, $2A_{zz}$ increases with decrease in temperature and undergoes a T_{50G} transition at a well specified temperature consistent with previous studies of probes dispersed in conventional thermoplastics⁸⁻¹⁰. However, the T_{50G} for the larger probe, Nitro-TEMPO, occurs at a temperature approximately 8°C above the epoxy T_g as measured by d.s.c. analysis, whereas T_{50G} for TEMPO occurs 20°C below the T_g . These observations are consistent with Figure 3 in that the Nitro-TEMPO probe exhibits the T_{50G} transition at a cure time earlier than t_{vit} . On the other hand, the TEMPO probe does not show a T_{50G} transition during the cure reaction. Instead the $2A_{zz}$ increases to an asymptotic value which is numerically equal to the value, $2A_{zz} = 40.75$ G, for TEMPO in the fully cured epoxy at T_g . The observations summarized in Figure 4 are consistent with similar results in the literature. For example, rotational correlation times τ_R for spin probe rotation in the fast motional region above T_g can be estimated using theoretical expressions described below. Activation energies can then be calculated from Arrhenius plots of τ_R versus T^{-1} . For TEMPO, in the region $T > T_{50G}$ of Figure 4, we calculate an activation energy $E_a \approx 16$ kJ mol⁻¹. Sandreczki and Brown¹⁸ have investigated the temperature dependence of τ_R for nitroxide spin probes in epoxy samples of varying crosslink density above T_g . For small probes, over comparable ranges of temperature $T > T_{50G}$, they observe an Arrhenius contribution to τ_R with an activation energy $E_a \approx 19$ kJ mol⁻¹. At temperatures higher than those accessed in our work, the activation energy increases and exhibits non-Arrhenius behaviour. Kovarskii *et al.*¹⁹ have reported similar observations. Thus, the temperature dependence of the e.s.r. spectrum seen in our work is consistent with these earlier observations^{9,18,19}.

In Figure 5, e.s.r. data of the type presented in Figure 3 are compared with torsional braid analysis (t.b.a.) of the epoxy cure as measured by Enns and Gillham¹. Enns and

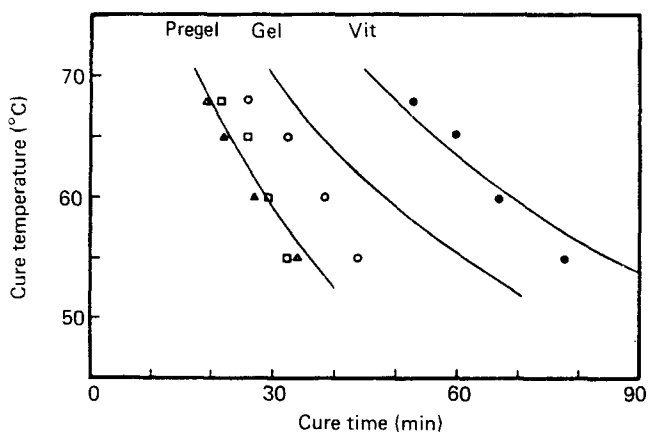


Figure 5 Comparison of e.s.r. probes dynamical transitions to viscoelastic transitions determined by torsional braid analysis measurements. Viscoelastic transitions are indicated by full curves. The cure times at which the inflection points and asymptotes occur in $2A_{zz}$ for TEMPO are indicated by the symbols \circ and \bullet respectively. The symbol \triangle locates the transition in τ_R for TEMPO during cure (see Figure 6) and \square indicates the location of the T_{50G} transition for Nitro-TEMPO during cure

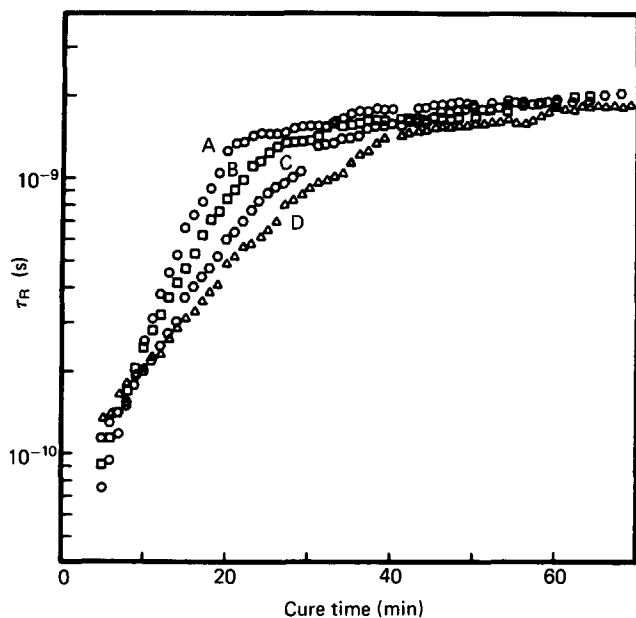


Figure 6 Rotational correlation times τ_R calculated via equation (1) plotted versus cure time for TEMPO in Epon 828/MBCH, cured at 68°C (A), 65°C (B), 60°C (C) and 55°C (D)

Gillham¹ have developed time-temperature-transformation (*TTT*) diagrams that locate the viscoelastic transitions on a plot of the isothermal cure temperature versus the cure time. Thus, in *Figure 5* the full curves indicate the cure time required to reach the pregel, gel and vitrification transitions as measured by t.b.a. On this figure we have superimposed values of the T_{50G} transition for Nitro-TEMPO and the time to reach the asymptotic value of $2A_{zz}$ for TEMPO at different cure temperatures. The latter values show good correlation, within experimental error, with the vitrification transition and indicate that TEMPO is capable of accurately measuring the time to vitrification of the curing system. For the TEMPO probe we also show the location of the points of inflection on the $2A_{zz}$ cure curves corresponding to the point where the rate of increase of $2A_{zz}$ with cure time slows down. These values lie in the region between the pregel and gelation transitions. Likewise, *Figure 5* demonstrates that the t_{50G} data for Nitro-TEMPO show excellent correlation with the location of the pregel transition. The pregel, gel and vitrification transitions delineate the range of cure times where the matrix mobility rapidly decreases and it is evident that the e.s.r. spectra of each of the nitroxide probes show corresponding changes which can be quantitatively related to the matrix properties.

Since TEMPO remains in the fast motional regime throughout the cure reaction, we can carry out a more quantitative analysis of the change in probe mobility during the cure reaction. In *Figure 6* the rotational correlation time τ_R of TEMPO is displayed as a function of cure time. Here we have used τ_R values based on an equation due to Kivelson¹⁴:

$$\tau_R = C[(I_0/I_{-1})^{1/2} - (I_0/I_{+1})^{1/2}]W_0 \quad (1)$$

where W_0 is the width of the central peak in gauss; I_{-1} , I_0 and I_{+1} are, respectively, the peak-to-peak heights of the

low-, central, and high-field peaks; and C ($C = 5.55 \times 10^{-10} \text{ s G}^{-1}$ for TEMPO) is a constant depending on the value of the resonance field H_0 , the hyperfine coupling constant A and g -factor anisotropies. Equation (1) is valid only for the fast motional region and assumes that the rotation of the probe is isotropic. *Figure 6* shows that the variation of τ_R vs. cure time shows a well defined transition from a fast to a slower rate of increase with cure time. The position of the transition is estimated by performing a least-squares linear regression on the straight-line segments before and after the crossover. The cure times calculated at these crossovers were compared with the mechanical data of Enns and Gillham in *Figure 5* and found to occur at the location of the pregel transition. This is consistent with our finding that the point of inflection on the $2A_{zz}$ curve occurs near the pregel transition. Similarly, our earlier studies⁷ of mobility of fluorescence probes during epoxy cure showed their maximum rate of change near the pregel transition.

It is of interest to compare our observations with literature studies of e.s.r. spin-probe mobility in thermoplastics^{8-10,19-21}. Analysis of the temperature dependence of τ_R above T_g indicates that a distinct transition is observed²⁰ in the Arrhenius plot of $\log(\tau_R)$ versus $1/T$. For a given nitroxide probe the transition in rotational motion occurs at the same value of τ_R in different polymeric matrices. Comparison with mechanical data indicates that this change in activation energy of τ_R occurs at the so-called liquid-liquid transition temperature (T_{LL}). T_{LL} is believed²⁰ to delineate a transformation from a polymer melt exhibiting short-range order to true liquid-like behaviour. Smith²² has further concluded that, at T_{LL} , there is a change in the characteristics of anisotropic rotation of the spin probe. An additional study, by Cameron *et al.*²¹, has demonstrated the dependence of anisotropic probe rotation on temperature as well as probe size for nitroxide spin probes incorporated in a thermoplastic.

The changes observed in the e.s.r. spectrum of the spin probes at the pregel transition of epoxies, viz. a significant broadening in the low-field peak and concurrent reduction in peak intensity, are very similar to those observed in the transition from above to below T_{LL} in thermoplastics. Our observations are therefore consistent with the suggestion of Enns and Gillham² that the pregel transition during epoxy cure is equivalent to a T_{LL} transformation. Following Cameron *et al.*²¹ and Smith²², it is therefore of interest to evaluate the degree of anisotropy N of the spin-probe rotation, at different points during the cure reaction. N , defined as the ratio of the components of the diffusion tensor parallel and perpendicular to the principal symmetry axis of rotation, can be estimated from the e.s.r. spectra using theoretical arguments presented by Goldman *et al.*²³ (which incorporate anisotropy into the model for probe rotational motion).

Experimentally, the measured e.s.r. linewidths $\Delta\nu(M)$ are related to the nitrogen nuclear spin quantum number M by the equation:

$$\Delta\nu(M) = A + BM + CM^2 \quad M = 0, \pm 1 \quad (2)$$

from which it follows necessarily that:

$$A = \Delta\nu(0) \quad (3)$$

$$B = \frac{1}{2}[\Delta\nu(1) - \Delta\nu(-1)] \quad (4)$$

and

$$C = \frac{1}{2}[\Delta\nu(-1) + \Delta\nu(1)] - \Delta\nu(0) \quad (5)$$

The theoretical analysis of Goldman *et al.*²³ leads to an equivalent expression relating a linewidth parameter T_2^{-1} to M :

$$T_2^{-1}(M) = A' + B'M + C'M^2 \quad (6)$$

T_2^{-1} is proportional to the peak-to-peak separation $\Delta\nu(M)$ corresponding to a given line in the derivative spectrum and the constants A' , B' and C' are, in general, functions of the rotational diffusion, hyperfine and g tensors of the probes.

We utilize simplified forms of the expressions for B' and C' , derived by Goldman *et al.*²³:

$$B' = \frac{16}{3} \frac{\pi}{10} \omega_0 [g(0)F(0)\tau(0) + 2g(2)F(2)\tau(2)] \quad (7)$$

$$C' = \frac{8}{3} \frac{4\pi^2}{5} [F(0)^2\tau(0) + 2F(2)^2\tau(2)] \quad (8)$$

with

$$g(0) = (6)^{-1/2} [2g_z - (g_x + g_y)] \quad (9)$$

$$g(2) = \frac{1}{2}(g_x - g_y) \quad (10)$$

$$F(0) = (|\gamma_e|/2\pi) [2(6)^{1/2}]^{-1} [2A_z - (A_x + A_y)] \quad (11)$$

$$F(2) = \frac{1}{4} (|\gamma_e|/2\pi) (A_x - A_y) \quad (12)$$

$F(0)$, $F(2)$, $g(0)$ and $g(2)$ are the irreducible components of the nitrogen hyperfine (A) and g tensors expressed in the coordinate system (x' , y' , z') of the rotational diffusion tensor²³; γ_e is the hyperfine splitting in angular frequency units and ω_0 the microwave frequency in rad s^{-1} . The rotational correlation times $\tau(0)$ and $\tau(2)$ are defined in terms of the anisotropy N and an average rotational correlation time τ_{Rav} as follows:

$$\tau(0) = \tau_{\text{Rav}} N^{1/2} \quad (13)$$

$$\tau(2) = 3\tau_{\text{Rav}} [N^{1/2}/(1+2N)] \quad (14)$$

where

$$N = D_3/D_1 \quad D_{\text{av}} = (D_3 D_1)^{1/2} \quad \tau_{\text{Rav}} = (6D_{\text{av}})^{-1} \quad (15)$$

Here D_3 is the component of the diffusion tensor parallel to the symmetry axis of rotation and D_1 the perpendicular component. The above equations for B' and C' (equations (7) and (8)) do not include contributions from non-secular terms²³. These contributions are most significant²³ for extremely narrowed spectra were $\tau_{\text{R}} < 1 \times 10^{-11}$ s. The calculated τ_{R} (Figure 6) data for TEMPO in the polymerizing Epon 828/MBCH system show $\tau_{\text{R}} \approx 1 \times 10^{-10}$ s at $t_c = 5$ min. In addition, examination of Figure 2a indicates that some line broadening is present at early stages in the cure reaction as evidenced by the variation in peak intensities. The effect of including the non-secular terms would be a slight increase in the calculated value of N in the early stages of cure ($t_c < 15$ min). At later cure times the non-secular terms

become constant and have no effect on the magnitude of N .

In order to implement the method of analysis summarized by equations (2) to (15), an e.s.r. experiment was performed in which the linewidths of the low-field ($M=1$), central ($M=0$) and high-field ($M=-1$) peaks of TEMPO were sequentially measured at high resolution (scale expansion $4 \times$) throughout the cure reaction. The resulting widths of the $M=0, \pm 1$ lines, determined for TEMPO in Epon 828/MBCH at 65°C , are shown in Figure 7 as a function of cure time. The corresponding values of the coefficients B and C determined from equations (4) and (5) are plotted against each other in Figure 8. The straight line shown in Figure 8 represents a least-squares fit of the first 12 pairs of B, C values to equations (7) and (8), with τ_{Rav} and N as variables, and corresponds to an assumption that the anisotropy is unchanged during the initial phase of the reaction. For this calculation we found it necessary to locate the principal symmetry axis (z') for rotation along the y axis of the coordinate system which defines the g tensor and hyperfine interaction tensor of the spin probe (see Figure 1). The straight line in Figure 8 indicates that, up to $t_c = 26$ min, the linewidth data are consistent with a constant value of anisotropy parameter N and a monotonically increasing τ_{Rav} . After $t_c = 26$ min, fits to the experimental B, C values to equations (7) and (8) indicate that both N and τ_{Rav} are increasing functions of t_c . The computed values of N and τ_{Rav} are shown as a function of cure time in Figures 9 and 10. Figure 9 shows that N remains constant at $N = 2.7 \pm 0.5$ up to $t_c = 26$ min, and then increases rapidly to $N = 10.5 \pm 0.3$ at the vitrification

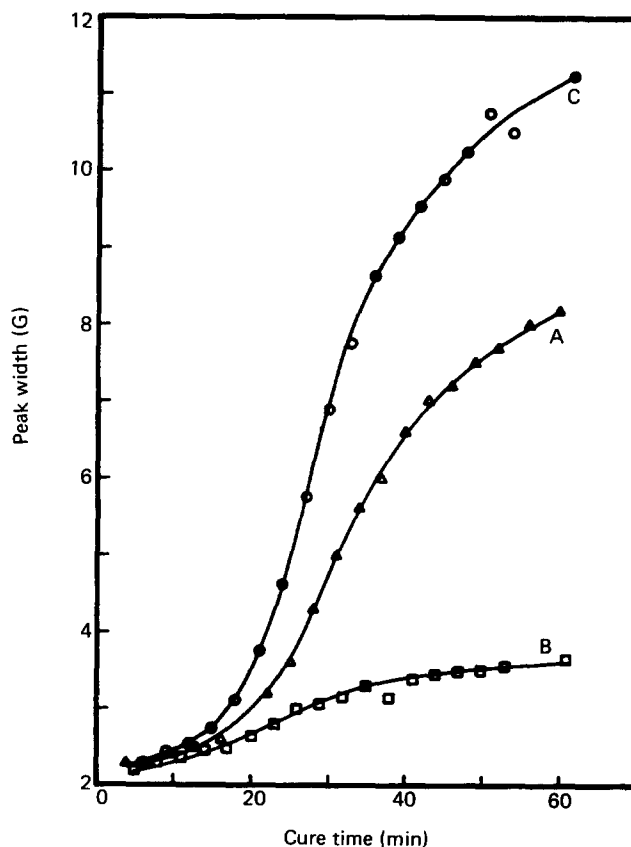


Figure 7 Variation of the peak-to-peak separation $\Delta\nu(M)$ of low-field (A), central (B) and high-field (C) first-derivative peaks of TEMPO during the cure of Epon 828/MBCH at 65°C

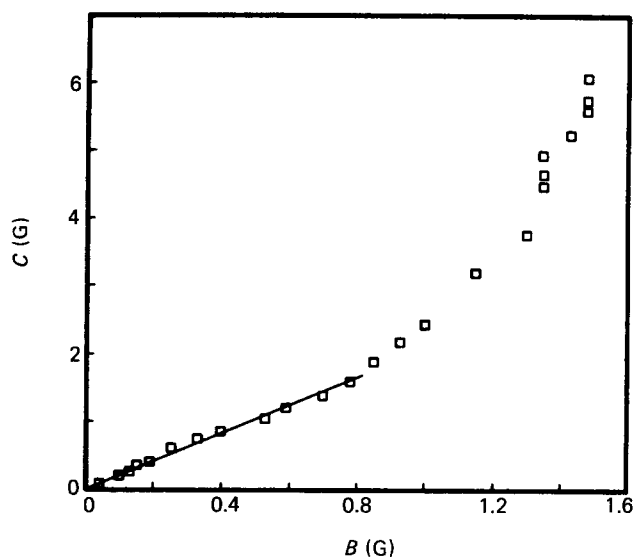


Figure 8 Experimental values of B and C compared for TEMPO during cure of Epon 828/MBCH at 65°C

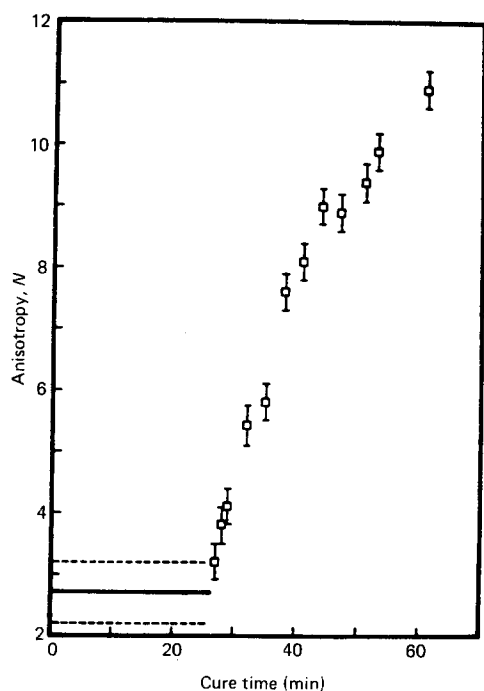


Figure 9 Degree of rotational anisotropy N as a function of cure time for TEMPO in Epon 828/MBCH. Broken lines indicate statistical accuracy of calculated anisotropy, $N=2.7\pm 0.5$ from $t_c=0$ to $t_c=26$ min, based on a fit of equations (6)–(15) to the first 12 pairs of B , C values

transition. It is not possible to make direct numerical comparisons with other systems because of differences in both matrix and probe. However, we note that for a nitroxide probe of moderately large molecular volume dispersed in poly(vinyl acetate) in a range $80 \leq T - T_g \leq 140$, there results²¹ $1 \leq N \leq 4$, comparing favourably with the above value prior to the pregel transition. On the other hand, Figure 10 shows that at $t_c=26$ min, the rate of increase of $\tau_{R\text{av}}$ with cure time slows dramatically. By comparison, for Epon 828/MBCH at this temperature, t_{pregel} and t_{gel} are estimated to be 24 and 38 min, respectively. Contrasting Figures 6 and 10,

it is clear that the behaviour of $\tau_{R\text{av}}$, calculated from equations (2)–(14), and τ_R , determined from the Kivelson theory (equation (1)), are qualitatively similar. There is a numerical difference in that the asymptotic value of $\tau_{R\text{av}}$ at vitrification is 4.4×10^{-9} s, while the τ_R asymptote is 2.4×10^{-9} s. Since equations (2)–(15) provide a more detailed accounting of the relationship between probe rotation and the e.s.r. spectrum, we assume $\tau_{R\text{av}}$ is a more accurate estimate of the mean rotational correlation time.

Figures 9 and 10 indicate a substantial change in the mechanism of rotational diffusion of TEMPO near t_{pregel} . The observed increase in rotational anisotropy is indeed rather similar to that observed near the T_{LL} transition in thermoplastics²⁰. Thus our study reinforces the idea that the pregel transition is equivalent to a T_{LL} process and further suggests that T_{LL} represents a change in structure of the matrix on a length scale similar to that of the nitroxide probe, TEMPO. It is pertinent to note that, in Epon 828/MBCH epoxy, the pregel transition occurs at a conversion of 55%. Using standard equations²⁴, this corresponds to a mean molecular weight between crosslinks $M_c \approx 624$. If the monomer molecular weight of Epon 828/MBCH is 320, this leads us to conclude that there are approximately two monomers between crosslinks. At this crosslink density ($\rho_x = 8.8 \times 10^{-4}$ mole crosslinks/cm³) there is apparently a change in mobility of the epoxy matrix which leads to a change in the mechanism of probe rotation corresponding to a hindering of rotation around the minor rotation axes.

Comparison of the cure characteristics of filled versus unfilled systems indicates that the TEMPO probe is unaffected by the presence of filler. Owing to the low (5 wt %) concentration of filler incorporated in the resin, bulk properties such as viscosity and modulus will be altered significantly, but matrix properties such as crosslink density and microviscosity should be relatively unaffected. Since the TEMPO probe samples the microviscosity it is anticipated that addition of fillers will have little effect on the measured τ_R and $2A_{zz}$ cure profiles. Our results indeed show excellent agreement between filled and unfilled samples in the τ_R values determined using equation (1), and similar consistency in the measured values of $2A_{zz}$. Thus, the application of e.s.r.

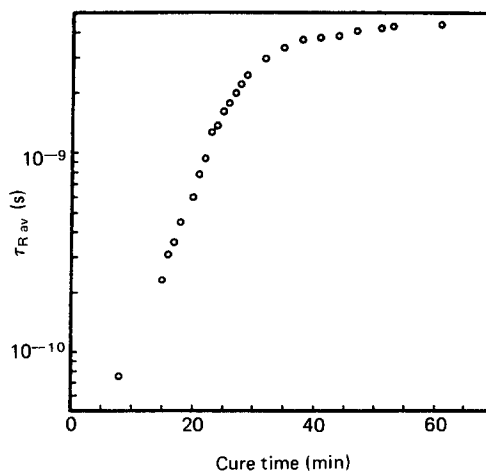


Figure 10 Average rotational correlation time $\tau_{R\text{av}}$ for TEMPO during cure of Epon 828/MBCH at 65°C , computed via equations (6)–(15)

spin probes to monitor changes in viscoelastic behaviour during cure of the epoxy matrix in opaque composite materials seems realistic.

SUMMARY

The decrease in mobility of e.s.r. nitroxide spin probes during cure of epoxy adhesives can be correlated quantitatively with the changes in viscoelastic properties that accompany the cure reaction. The large probe, Nitro-TEMPO, exhibits a T_{50G} transition in a fully cured epoxy at a temperature just above the epoxy glass transition temperature (Figure 3). During the cure reaction, Nitro-TEMPO shows the T_{50G} transition at the pregel transition as determined by torsional pendulum measurements (Figure 4). The small probe, TEMPO, exhibits its T_{50G} at 20°C below the epoxy T_g (Figure 3), and therefore does not show a T_{50G} during the cure reaction (Figure 4). However, the rotational mobility of TEMPO, as monitored by the extrema separation $2A_{zz}$, shows a well defined change near the pregel transition, and approaches a unique asymptotic value upon vitrification (Figure 2). Comparison with molecular dynamic theory indicates that, at the pregel transition, the rate of increase during cure of the rotational correlation time reaches a maximum and begins to decrease (Figure 10). At the same time, the degree of anisotropy of rotation suddenly begins to increase, suggesting that the pregel transition involves a change in dynamics of the network involving a structural length scale comparable to that of the TEMPO probe (Figure 9). Finally, the unique value of the rotational correlation time of the TEMPO probe in the Epon 828/MBCH epoxy system at the vitrification transition is $\tau_{R_{av}} = 4.3 \times 10^{-9}$ s with a degree of rotational anisotropy $N = 10.5$ (Figures 10 and 9 respectively).

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