CURE MONITORING OF AN EPOXY–AMINE SYSTEM BY DYNAMIC MECHANICAL THERMAL ANALYSIS (DMTA)

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ABSTRACT

A method has been devised to study the cure of epoxy resins using a dynamic mechanical thermal analyzer (DMTA) in combination with differential scanning calorimetry. Special glass fiber braids ($25 \times 13 \times 0.15$ mm) were impregnated with the liquid epoxy/amine (DGEBA/*m*-PDA) mixture at room temperature and subjected to forced oscillations at elevated cure temperatures. The modulus and the tan δ underwent transitions typical of gelation and vitrification. The times to gelation and vitrification were used to generate the well known time–temperature–transformation diagram proposed by J. Gillham on the basis of torsional braid analysis data. DMTA also provides information about the rate of modulus increase during cure, which was compared with theoretical calculations of the rise in crosslink density.

INTRODUCTION

Thermosetting epoxy resins possess thermal and mechanical properties which make them the preferred choice for polymer composites, aerospace applications, coatings, appliances, adhesives, etc. For optimum performance of the finished product it is of foremost importance to know and monitor the curing reaction. Unfortunately, thermosets are by their very nature difficult to study because of their insolubility and infusibility. The widely used differential scanning calorimetry (DSC) technique provides considerable insight into the reaction mechanism. However, events like gelation and vitrification are not observable by this method. Lately, dynamic mechanical methods have been employed to investigate these features. Gillham's very extensive work [1,2,3] with the torsional braid analyzer (TBA) lead to the introduction of the time–temperature–transformation (TTT) diagram for thermosetting resins. Gill and Blaine [4] used a dynamic mechanical analyzer

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(DMA) to study matrix epoxies in a cone and plate arrangement, while Zukas et al. [5] employed dynamic spring analysis (DSA) to probe the cure of an epoxy resin coated onto a spring. So far, dynamic mechanical thermal analysis (DMTA) has rarely been used for this task, and only one entry in the literature has been found to date [6]. The purpose of this study was to investigate the potential of the method for monitoring the viscoelastic aspects of thermoset cure from the liquid phase through the B and C stages.

TTT diagram of thermosetting resins

The cure of thermosetting resins typically passes through two crucial events: gelation and vitrification. Gelation marks the onset of forming an insoluble gel-fraction, a molecular arrangement of infinite molecular weight, whereas vitrification is understood as solidification of the reaction mixture, owing to the rise of the glass transition temperature upon tightening of the thermoset network. On a molecular level, gelation as a distinct event is defined as the incipient occurrence of one molecule of infinite molecular weight. Gelation occurs at a defined extent of reaction, and does not change the kinetics of the reaction. Thus it cannot be observed by DSC and related methods. However, gelation does change mechanical and electrical properties of the reaction mixture, which makes it detectable by methods based on changes of mechanical, electrical and viscoelastic properties. Vitrification or solidification of a thermosetting resin can occur at any stage of reaction when the rising glass transition temperature of the reacting gel approaches the cure temperature.

Gelation and vitrification can be combined to form part of the TTT diagram of thermoset cure (see Fig. 1). The times to gelation t_{gel} and to vitrification t_{vit} are plotted as a function of the normalized glass transition temperature of the system. In the case of the generalized TTT diagram, the T_g of the cured resin is identical to the cure temperature. $T_{g,0}$ is the glass transition temperature of the unreacted resin mixture; $_{gel}T_g$ is the minimum cure temperature to form a gel; and $T_{g,\infty}$ is the maximum possible glass transition temperature or the minimum cure temperature to achieve full cure. For real systems, however, the assumption of $T_g = T_c$, where T_c is the actual cure temperature does not hold, so that T_c rather than the glass transition temperature is used as the independent variable. The times to gelation and vitrification as a function of cure temperature can be calculated based on the relationship between reaction kinetics and glass transition temperature, as will be shown.

The overall reaction rate $d\alpha/dt$ can be written as an Arrhenius-type function of the extent of reaction α, as long as the reaction is not diffusion controlled. Thus the times to gelation and vitrification can be written as

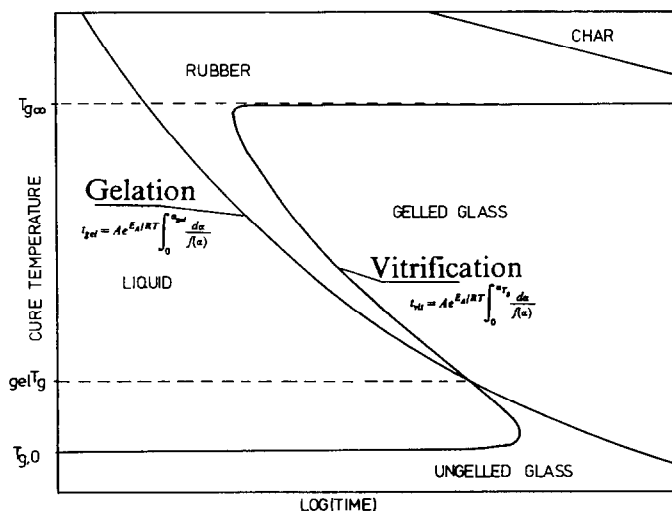$$t_{gel} = A \; e^{E_A/RT} \int_0^{\alpha_{gel}} \frac{d\alpha}{f(\alpha)} \qquad (1a)$$

Fig. 1. Schematic time–temperature–transformation diagram [1].

and

$$t_{vit} = A\, e^{E_A/RT} \int_0^{\alpha_{T_g}} \frac{d\alpha}{f(\alpha)} \tag{1b}$$

where A is a pre-Arrhenius factor, E_A is the activation energy, $f(\alpha)$ is a function of α reflecting the type and order of the reaction, α_{gel} is the conversion at gelation, and α_{T_g} is a function of $(T_g - T_{g,0})$, T_g being the system's rising glass transition temperature and T_c the cure temperature. α_{T_g} can be calculated by means of the rearranged DiBenedetto equation [7,8], which relates the T_g of the thermoset to the extent of conversion:

$$\alpha_{T_g} = \frac{T_g - T_{g,0}}{T_{g,0}(\epsilon - F) + (T_g - T_{g,0})(1 - F)} \tag{2}$$

Equation (2) inserted into a cure kinetic equation like eqn. (6) yields the time to vitrify under isothermal conditions. The parameters ϵ and F are material constants of the polymer and are determined empirically. The typical sigmoidal shape of the vitrification curve reflects the temperature-dependent interplay of rheology and kinetics [1]. Just above $T_{g,0}$ vitrification is reached in very short times, since only a very low extent of conversion is necessary to lift the T_g of the system above the cure temperature T_c. At slightly higher values of T_c the times to vitrify t_{vit} pass through a maximum, since the rate of conversion is low and the viscosity of the resin is high. Raising T_c shortens t_{vit}, since a higher rate of conversion helps to increase the speed of attaining the extent of conversion necessary to elevate the glass transition temperature above T_c. However, at cure temperatures close to $T_{g,\infty}$ the times to solidify increase again, as a result of the long conversion times necessary to reach the high extent of reaction which is needed to elevate T_g above T_c.

Modulus increase during cure

Ideally, the equilibrium modulus of a thermoset can be calculated following classical rubber elasticity theory as

$$E = 3\frac{\rho RT}{M_c} \tag{3}$$

where ρ is the density of the material, and M_c the number average molecular weight between crosslinks. ρ/M_c can be substituted by ν, the concentration of effectively anchored network chains. In general, eqn. (3) cannot be applied to very dense networks close to full cure, since the assumptions regarding random coil state or equilibrium modulus cannot be met. This relationship nevertheless describes fairly well the modulus changes taking place during formation of the gel at moderate extents of conversion, as will be demonstrated.

It is of interest to see whether the modulus gain data obtained from dynamic experiments reflect theoretical predictions. Although numerous models describe the effects of crosslinking reactions on the change of molecular weight of the sol and the gel, the recursive approach of Miller and Macosco [9] to step growth type crosslinking reaction has been chosen because of its clarity and elegance. The density of network chains ν is the weighted sum of the crosslink densities $[X_m]$,

$$\nu = \sum_{m=3}^{f} \frac{m-2}{m}[X_m] \tag{4}$$

where m is a chain's degree of anchoring in the gel. This must be larger than three to be effective. f is the functionality of the one reaction partner whose functionality is larger than two. The following equation is the application of Miller and Macosco's [9] general procedure to a binary reaction system with functionalities of two (DGEBA) and four (m-PDA), assuming equal reactivity:

$$\nu = [A_4]_0 \left\{ \frac{4}{3} \left[\left(\frac{1}{\alpha^2} - \frac{3}{4} \right)^{0.5} - \frac{1}{2} \right] \times \left[\frac{1}{2} - \left(\frac{1}{\alpha^2} - \frac{3}{4} \right)^{0.5} \right]^3 \right.$$

$$\left. + \frac{1}{2} \left[\frac{1}{2} - \left(\frac{1}{\alpha^2} - \frac{3}{4} \right)^{0.5} \right]^4 \right\} \tag{5}$$

where $[A_4]_0$ is the initial concentration of the four-functional species. By calculating α, the extent of conversion, as a function of time and temperature, one can construct theoretical plots of E vs. time or log E vs. time, and compare with the corresponding DMTA results.

Dynamic mechanical thermal analysis

Measurements of the times to gelation and vitrification were carried out by Enns and Gillham [1] by means of a torsional braid analyzer (TBA). A resin-impregnated glass fiber braid is subjected to dampened torsional oscillations whereby the logarithmic increment of successive amplitudes $\Delta = \log[A_i/A_{i+1}]$ is a measure of energy dissipation or damping of the material, and the relative rigidity $1/P^2$ (P is the period $2\pi/\omega$) is a measure of the sample's stiffness. Gillham could show that several damping maxima occur over time when an epoxy resin is isothermally cured. The two most prominent peaks have been assigned to gelation and vitrification of the resin.

In contrast to torsional braid analysis, using a dynamic mechanical thermal analyzer a sample is subjected to forced oscillations of constant frequency in bending, shear or tension. Loss and storage moduli are recorded, and tan δ is obtained as the ratio of E''/E'. DMTA is primarily a tool for studying the thermo-mechanical response of solid samples. Hence, a composite sample consisting of an inert fibrous support for the liquid resin must be prepared in order to monitor the full range of cure from liquid to solid.

In analogy to the results of the TBA studies, one should expect the same damping maxima as tan δ peaks. When the resin approaches gelation its viscosity increases to eventually become infinite. This results in increased energy dissipation of the network forming liquid. Further crosslinking of the gel and tightening of the network, however, decreases the network's ability to dissipate energy, and hence tan δ passes through a local maximum at the point of gelation.

Vitrification of a curing resin is caused by quenching of the reaction owing to the rise of the glass transition temperature of the system to and above the cure temperature. Since a polymer has a local damping maximum at its glass transition temperature, it is logical that tan δ passes through another local maximum at the time of vitrification.

MATERIALS AND METHODS

The epoxy resin used for this study was a commercially available diglycidyl ether of bisphenol A (DGEBA, Epon 826) cured with an aromatic diamine (*m*-PDA), both used as received. Resin and hardener were mixed at a stoichiometric ratio of 1:1, which in this case amounts to four epoxy equivalents for each *m*-PDA equivalent. The epoxy equivalent weight was determined by titration with HBr according to ASTM D 1652. Mixing was carried out by melting the crosslinking agent at 70°C and dissolving it in the epoxy resin by stirring for 10 min. The system was degassed and stored

at $-70\,^{\circ}C$ until use. This system follows autocatalytic cure kinetics [10] of the type

$$f(\alpha) = \alpha(1 - \alpha)^2 \tag{6}$$

which, substituted into eqn. (1b), yields

$$t_{vit} = A\, e^{E_A/RT}\left\{\left(\frac{1}{1 - \alpha_{T_g}}\right) - \ln\left[\frac{1 - \alpha_{T_g}}{\alpha_{T_g}}\right]\right\} \tag{7}$$

Differential scanning calorimetry

A Perkin–Elmer DSC-4 controlled by a System-4 microprocessor was used to provide conversion data. Total heat of reaction ΔH was determined by integrating the area under a ΔC_p vs. T curve, obtained from a temperature scan of the system. The scan rate was $4\,^{\circ}\,min^{-1}$. Isothermal conversion data were obtained by integrating the areas under the individual ΔC_p traces and relating this to total ΔH. Isothermal experiments were carried out for $T = 30\,^{\circ}C$ to $T = 150\,^{\circ}C$ in $10\,^{\circ}C$ intervals.

Dynamic mechanical thermal analysis

The DMTA equipped with a bending head and a universal temperature programmer was manufactured by Polymer Laboratories. This equipment was interfaced to a Hewlett-Packard 9816 microcomputer. Samples were prepared by submerging a woven glass fiber braid (Du Pont #980228-901) of length 25 mm and width 13 mm in the liquid resin mixture at room temperature. The soaking time was 1 min. The excess resin was blotted off, and the ends covered with aluminum foil to protect the DMTA clamps from the resin. The samples were stored in polyethylene bags at $-70\,^{\circ}C$. Prior to testing, the samples were allowed to equilibrate for 10 min before opening the bag, to avoid condensation. Bending of the sample was carried out in cantilever mode at a frequency of 1 Hz. The free length was 1 mm. Isothermal runs were carried out from $30\,^{\circ}C$ to $190\,^{\circ}C$. The heating rate during heat-up was initially $60\,^{\circ}C\,min^{-1}$ until $20\,^{\circ}C$ below the desired cure temperature, followed by $20\,^{\circ}C\,min^{-1}$ up to $8\,^{\circ}C$ below. The final heating rate was $8\,^{\circ}C\,min^{-1}$. After closing the assembly it took typically 2–2.5 min to reach equilibrium. Although reaction takes place during the initial heat-up period, the authors are confident that gelation does not occur during this period except for temperatures above $170\,^{\circ}C$. At these temperatures the experiment only yielded the times to vitrify (see Fig. 4 below). The times to gelation for high values of T_c were obtained by extrapolation. The temperature was stable within $\pm 1\,^{\circ}C$. Immediately after the isothermal run the sample was cooled to room temperature and subsequently probed in scan-

ning mode to determine T_g. The conditions were the same as for the isothermal mode; the scan rate was 4°C min^{-1}. The DMTA experiments were carried out under static air.

RESULTS AND DISCUSSION

Temperature scan

The temperature scan (Fig. 2) of the uncured epoxy resin shows softening of the reaction mixture at $-12°C$. This corresponds to $T_{g,0}$ in the TTT diagram. The mixture remains a low viscosity liquid until 20°C, beyond which the modulus rises to an intermediate modulus plateau. Reaction as it is recorded by DSC (Fig. 2) starts at 75°C, has its maximum at 133°C, and ends at 180°C. During the first half of the reaction the modulus attains a plateau value reached at the onset of the reaction (70°C). Considerable rise of the modulus takes place after 130°C, and the tan δ peak of 150°C appears to mark the onset of gelation. Since the cure temperature is at any point higher than the T_g of the system, quenching by vitrification does not take place, and the modulus is that of a rubbery material.

Isothermal cure

Examples for isothermal cure monitoring by DMTA are given in Fig. 3. This represents modulus and tan δ traces for $T_c = 130$ and 140°C. The
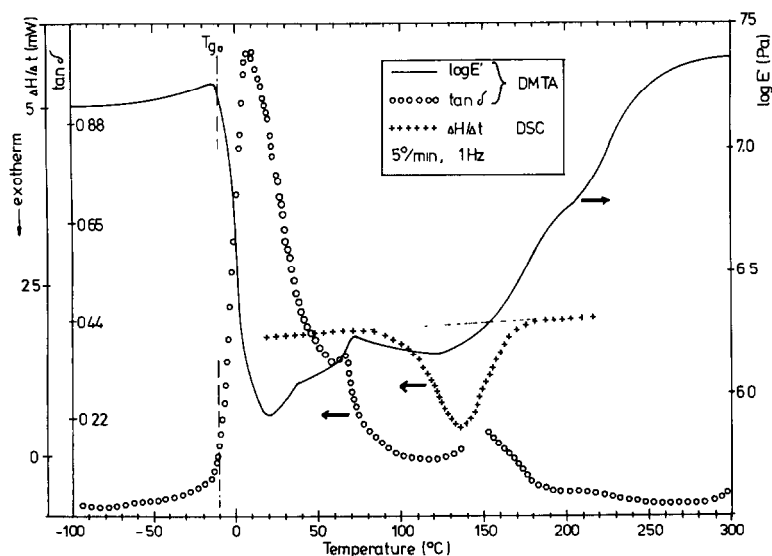

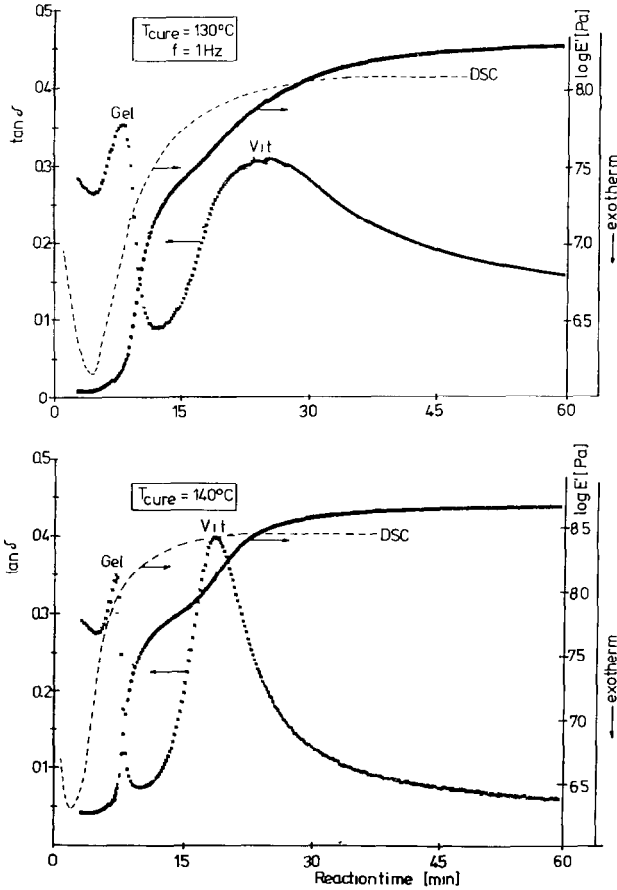Fig. 2. Temperature scan of DGEBA/m-PDA.

Fig. 3. Isothermal traces of DGEBA/m-PDA.

superimposed DSC trace is drawn as a dashed line. The absolute value of the modulus is not representative of the true modulus of the resin, since it is that of the composite sample. Nevertheless, assuming that classical rubber elasticity theory holds, the slope dE/dt is proportional to the rise in crosslink density and the decrease of M_c. Two identifiable linear portions of the log modulus slope coincide with the two tan δ maxima, gelation and vitrification, which means that the crosslink density rises logarithmically with cure time.

Gelation is an iso-conversion event, and occurs in this case at 52% extent of reaction as measured by DSC. The theoretical conversion at gelation for this system is 58% [9]. This is in contrast to observations by Enns and Gillham [1] that the gelation peak measured by TBA for a similar system occurs above 70%. The second peak, although labeled as vitrification, does not mark the end of network formation; rather it indicates that the system's glass temperature has reached the cure temperature. Hence, the T_g of the isothermally cured resin is higher than the cure temperature.
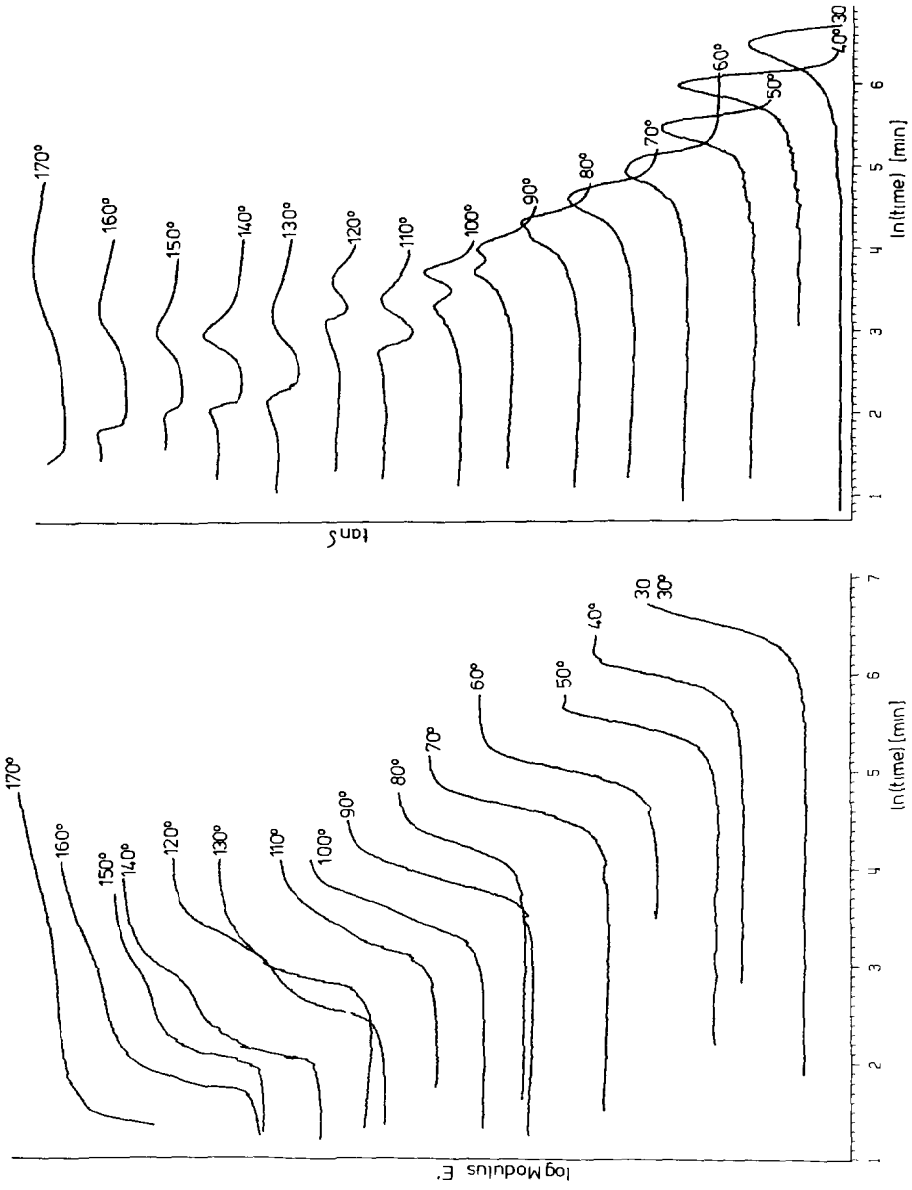
Fig. 4. Summary of isothermal traces (DGEBA/*m*-PDA).

This procedure was carried out for temperatures ranging from 30 to 190°C, and the results are summarized in Fig. 4. Typically, the single tan δ peak of the low temperature cured samples tells that solidification takes place before the necessary conversion into a gel has been reached. A splitting of the peak can be observed at approximately 60°C. The gap between the peaks widens with increasing T_c. The higher the cure temperature, the earlier both gelation and vitrification occur. Above 150°C, however, the vitrification peak moves to the right, and it disappears at high temperatures, indicating that the cure temperature approaches the glass transition temperature of the fully cured resin, $T_{g,\infty}$, which is about 180°C for this system. At low cure temperature ($< 60°C$) the modulus rises linearly in a one-step fashion; this is followed by a splitting of the slope into two linear portions above 60°C. At high temperatures the approach of $T_{g,\infty}$ is marked by the disappearance of the second part of the slope.

Although the second tan δ peak is taken as indication for vitrification, conversion sometimes continues past this point. Hence, the final T_g of an isothermally cured sample below $T_{g,\infty}$ should be higher than the cure
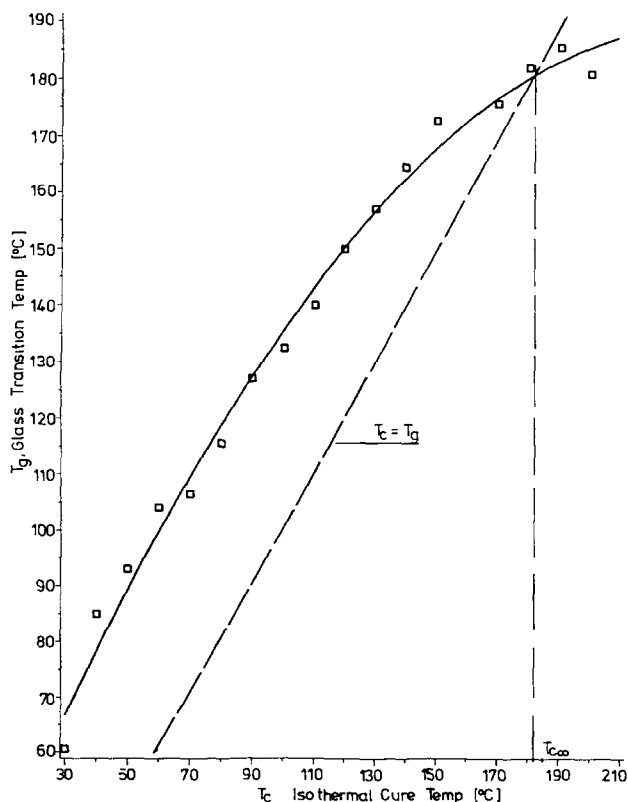

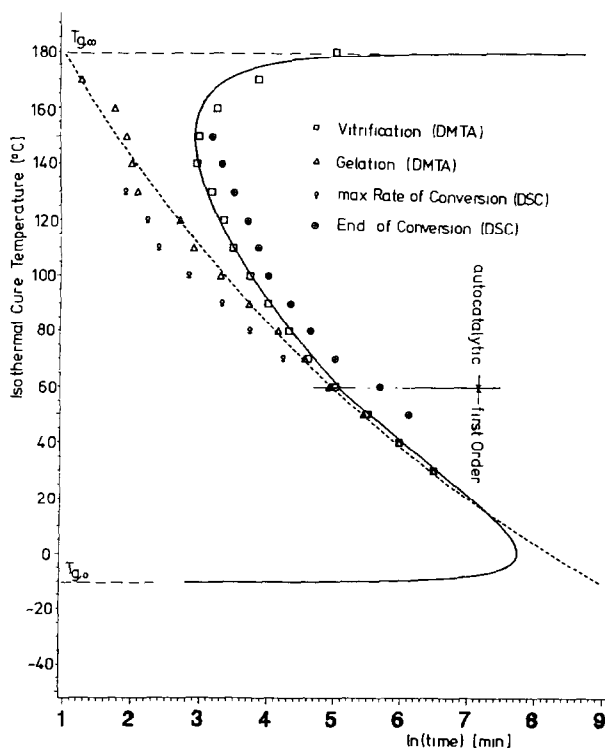Fig. 5. Glass transition temperature vs. cure temperature of isothermally cured DGEBA/m-PDA.

Fig. 6. TTT diagram of DGEBA/m-PDA.

temperature. In order to show this phenomenon, the glass transition temperatures that were taken immediately following the isothermal cure experiments are plotted against isothermal cure temperature (Fig. 5). The dashed line represents $T_g = T_c$. Below $T_c = 150\,°C$, the glass transition temperature is considerably higher than the cure temperature. The gap closes at about $180\,°C$, which can be regarded as the glass transition temperature of the fully cured resin, $T_{g,\infty}$.

DMTA and DSC data are combined to form the TTT diagram of this system (Fig. 6). The triangular data points represent the time to gel formation, and the squares reveal the time to vitrification. Both are taken from the tan δ peaks of the DMTA measurements. The maximum and end of conversion as obtained from DSC are also included. The lines for gelation and vitrification were calculated using eqns. (1a) and (7). Above ca. $60\,°C$ an autocatalyzed approach (see eqn. (6)) was found to best represent the experimental data. Below this point, however, first order kinetics fit the data better. This transition was also observed by Enns and Gillham [1], although a first to second order kinetics transition rather than a first order to an autocatalytic approach was used. The minimum cure temperature to reach full conversion, or $T_{g,\infty}$, as it is asymptotically approached by the vitrification line, is $180\,°C$; the other extreme, the maximum storage temperature
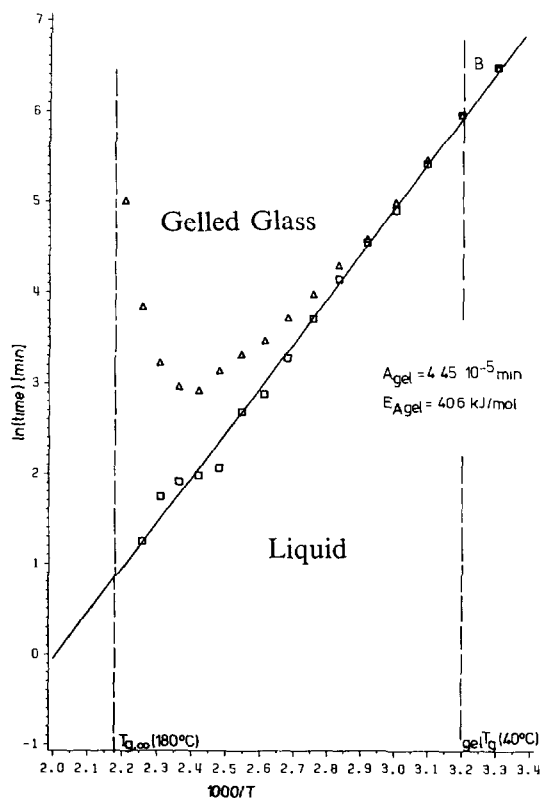
Fig. 7. Arrhenius-type TTT diagram of DGEBA/m-PDA.

without cure taking place, or $T_{g,0}$, is $-10\,^\circ$C. From these calculations, the values of ϵ and F (see eqn. (2)) were calculated to be 0.34 and 0.198, respectively. From the Arrhenius-type TTT diagram (Fig. 7), the activation energy of gelation E_A was calculated to be 40.6 kJ mol^{-1}. This is somewhat lower than reported elsewhere for the same system [11].

The slopes of log E vs. time (Fig. 4) reveal two distinct linear portions, one at about gelation and the other towards the end of cure (or vitrification). The slope data are summarized in Fig. 8 in Arrhenius form. Typically, the logarithmic values of the slopes of log E vs. time during gelation lie on a straight line, with an activation energy of 39.6 kJ mol^{-1} ($R^2 = 0.995$). The corresponding data for vitrification lie on a semicircle, and this reflects the fact that at higher cure temperature the rate of modulus rise is small. This can be explained by the fact that at higher cure temperatures, most of the system's final modulus is gained during and after gelation, and, on the other hand, the vitrification time is considerably longer.

Theoretical values of increases in log modulus over time were calculated using eqn. (4). A conversion range of between 0.58 and 0.74 was chosen for the modulus rise during which the system passes through gelation. The
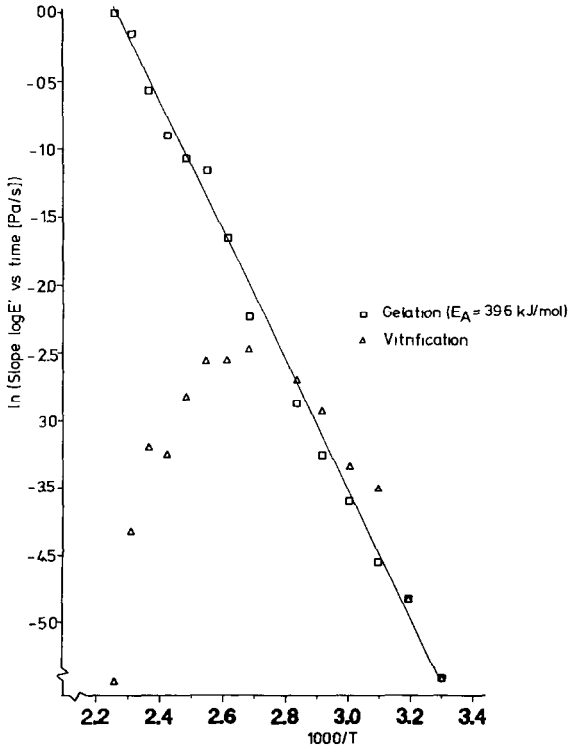
Fig. 8. Arrhenius plot of slopes of log E vs. time (DGEBA/m-PDA).

initial concentration of $[A_4]_0$ of m-PDA is 1430 mol m^{-3}. The theoretical data are in good agreement with the experimental DMTA data (Fig. 9). Although the theoretical values are slightly higher than the corresponding experimental data, the two curves follow a closely similar trend, which indicates that the gain in modulus at moderate extents of conversion as it is measured with this method is in close agreement with that predicted by rubber elasticity and the Miller–Macosco theory. The same procedure was applied to the second linear portion of the modulus rise taking place during vitrification (Fig. 10), with the notable difference that these events do not happen at fixed conversions but rather at temperature-dependent conversions and cure times. Hence, the actual beginning and termination points on the time scale of the linear portion of the DMTA signals were used to calculate the extents of conversion using eqns. (1b) and (7). The results are summarized in Fig. 10. Clearly, the agreement is inferior by far to that achieved in the case of gelation. Although the theoretical data mirror somewhat the trend of the fastest rise in modulus occurring at around 100 °C, the absolute values are too small. The failure of the theory to represent the DMTA results can be attributed primarily to the fact that very dense networks are too far from ideality to be represented by classical rubber elasticity. The discrepancy between the DMTA data and theory at
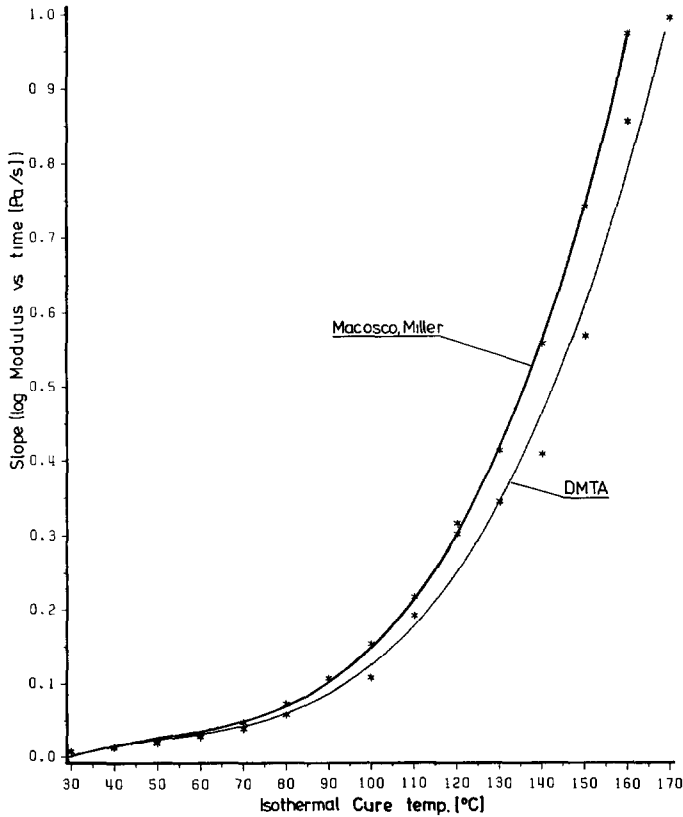
Fig. 9. Slope of log modulus vs. time during gelation. Theoretical data are calculated following Miller and Macosco [9].

this level of conversion is not caused by the influence of diffusion control on the reaction kinetics, since only the linear portions of the log E' slopes have been included in the calculations of the concentration of active network chains. The onset of diffusion control takes place after vitrification, which is also characterized by a change in the corresponding log E' slope. Corrections of eqn. (4) to account for entanglement effects lead to only a slight increase in the corresponding slopes.

CONCLUSION

The cure of an epoxy system (DGEBA/m-PDA) was monitored isothermally by DMTA in bending mode at a fixed frequency (1 Hz). The resin was supported by an inert glass fiber braid. It could be shown that a dynamic mechanical system utilizing forced oscillation such as DMTA is a fast and reliable tool for monitoring the cure of an epoxy–amine system, and gives
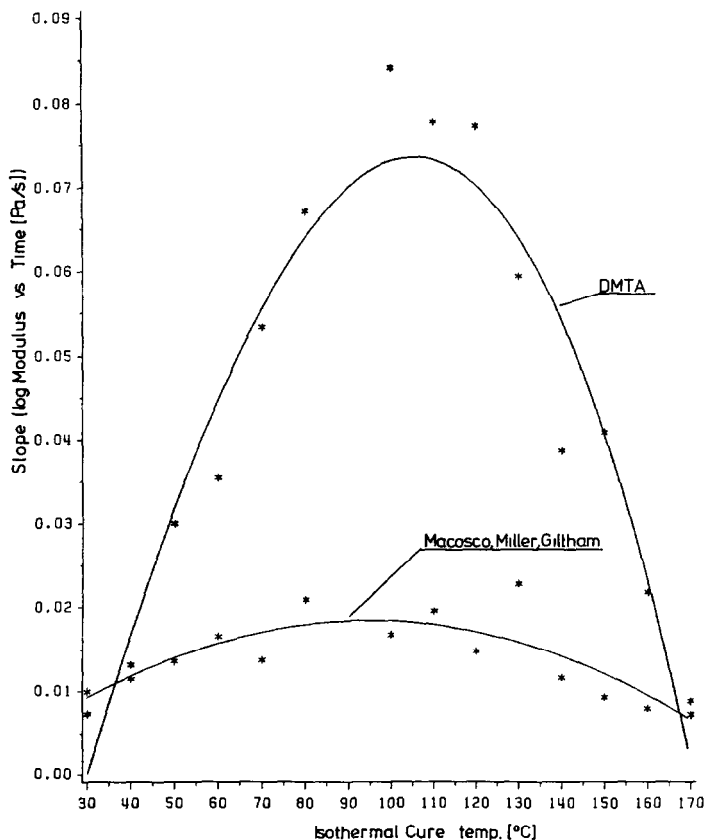
Fig. 10. Slope of log modulus vs. time during vitrification. Theoretical data are calculated following Miller and Macosco [9] and Enns and Gillham [1].

results comparable to those obtained by free oscillation methods such as TBA.

Typically, the damping (tan δ) passes through two maxima, designated as gelation and vitrification. From the tan δ data, a TTT diagram was developed, and the times to gelation and vitrification were calculated. The activation energy of gelation was 40.6 kJ mol^{-1}. The increase in log E was linear for both gelation and vitrification, but the slopes were different. From this, the activation energy of gelation was calculated to be 39.6 kJ mol^{-1}. Comparison of theoretical slope data of log E vs. time based on rubber elasticity theory with actual DMTA values of modulus rise during cure yielded very good agreement for the range of $\alpha = 0.58$–0.74, but the agreement failed for the high conversion portions of the diagram. This can be explained by the fact that classical rubber elasticity cannot be applied to very dense networks. This study has shown that DMTA is a useful and reliable method for monitoring all stages of the cure of an epoxy thermoset.

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