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William MacKnight, *University of Massachusetts Amherst*

Walter X. Zukas

N. S. Schneider

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Dynamic Mechanical and Dielectric Properties of an Epoxy Resin During Cure

W. X. ZUKAS, W. J. MACKNIGHT, and N. S. SCHNEIDER¹

Chemical Engineering Department and Polymer Science and Engineering
Department, University of Massachusetts, Amherst, MA 01003

The curing behavior of a commercially formulated epoxy resin composed of a tetrafunctional epoxy, tetraglycidyl methylene dianiline, and a tetrafunctional amine, diaminodiphenyl sulfone, was followed by dynamic spring analysis (DSA) and dielectric relaxation measurements. Both methods yielded two peaks in their loss tangent vs. time traces. The first peak in dynamic spring analysis was used as a measure of the onset of gelation, whereas the second peak appeared to be related to vitrification. The first dielectric relaxation peak was due to a surface charge-related phenomenon while the origin of the second peak is unclear. Results from additional mechanical relaxation studies of thin-films of known cure history support the interpretation of the DSA second peak as due to vitrification and reveal three dispersion regions. In order of increasing temperature these are associated with a glass transition near the temperature of molding (curing), further reaction, and the ultimate glass transition of the "fully cured" network.

The changes which occur in thermosetting resins undergoing cure have been studied by a variety of techniques. Supported sample methods have been used to monitor the relative changes in modulus and damping behavior from the initial low viscosity liquid to the fully cured rubbery or glassy state. Torsional braid analysis (TBA) employs a resin sample impregnated on a

¹ Current address: Polymer and Chemistry Division, Army Materials and Mechanics Research Center, Watertown, MA 02172

glass fiber braid as the mechanical element in a torsion pendulum. This method has been used extensively by Gillham and coworkers (1-13) who developed a pseudo-phase diagram to describe the general features of the thermosetting process. A technique similar to TBA, reported by Lee and Goldfarb (4), involves the use of a resin impregnated glass cloth which is oscillated in the torsional mode of a Rheometrics mechanical spectrometer. An advantage of this method is the ability to observe the frequency dependence of the dispersion phenomena.

Using such techniques, it is generally not possible to obtain the viscoelastic properties of the resin from the measured behavior of the composite (resin plus support). In dynamic spring analysis (DSA) the sample is coated on a spring mounted in the Rheovibron dynamic viscoelastometer (5,6). It was shown by Senich and MacKnight (7) that it was possible to estimate the viscoelastic response of the resin by assuming a simple parallel model of the spring-resin composite and using the measured characteristics of the spring. This method of analysis was applied to the study of the curing of two epoxy resins (8). In addition to the supported sample methods, the viscoelastic properties of partially cured epoxy resins have been obtained directly from temperature scans in the Rheovibron carried out on unsupported films (4,8,9).

Another approach which has received considerable attention involves measuring the changes in the electrical properties of the curing resins, but there is considerable disagreement about the molecular origin of the observed effects. Delmonte (10) determined the change in dissipation factor, dielectric constant, and volume resistivity of several epoxy resins during isothermal cure and attributed a peak observed in the dissipation factor to gelation. Haran et al. (11) used a similar peak to control the physical properties of the cured resins, but did not believe that it represented gelation. Adamec (12) developed an empirical relationship between the a.c. conductivity and the degree of cure represented by the relative concentration of epoxy groups determined by infrared analysis. Dandurant and Huraux (13) observed a broad dielectric relaxation in a Cole-Cole representation of the results of a curing epoxy resin. Other recent studies of the dielectric response by Lawless (14) and by Crabtree (15) used cure cycles which simulate an actual commercial cure process rather than an isothermal cure and therefore were not readily interpreted in terms of the reaction kinetics. A new development in technique was described by Senturia et al. (16) who used a charge flow transistor to monitor isothermally curing resins and developed a simple circuit model to interpret the dielectric response of the resin. A sharp decrease in permittivity and loss factor with cure time was attributed to the rapid rise in viscosity which marks the onset of gelation.

The present work is concerned with measurements of the curing

behavior of the Narmco 5208 resin both by the dynamic spring and dielectric methods. This resin is one of the high temperature epoxies which have been developed for aerospace composites and it has been the subject of extensive characterization. Mechanical property characterization of cured resins has been carried out by Morgan et al. (17). Recent studies on such resins also include dielectric and dynamic mechanical by Crabtree (15), FTIR and HPLC analyses by Cizmecioglu (18), FTIR by Mones and Morgan (19), and spin trapping studies by Tsay et al. (20).

EXPERIMENTAL

The subject of this study is a commercially formulated resin (Narmco Materials Division of Celanese Corp.) referred to as Resin 5208. May et. al. (21) have shown that the primary constituents of this resin are Ciba-Geigy Corporation's Araldite MY720, diaminodiphenyl sulfone (DDS), and a glycidyl ether of a bisphenol A based novolac (Celanese SU-8). The principle component of MY720 is tetraglycidyl methylene dianiline (TGMDA).

Resin 5208 is a tacky solid at room temperature and has an approximate amine to epoxy equivalent of 0.6:1.0 (18). Samples were stored in sealed vials at 0°C and briefly warmed to room temperature before removing for analysis. The recommended commercial cure is 177°C for 2 hrs. (22).

The isothermal DSA analysis, utilizing the Rheovibron DDV-IIB dynamic viscoelastometer, has been described elsewhere (7). A steel spring 2.9 mm in outer diameter of 0.30 mm diameter wire, seventeen turns in length was placed in the Rheovibron. The temperature chamber was then brought to constant cure temperature, T_c , the spring stretched to achieve a pitch of 0.1 mm, and the sample applied by hypodermic syringe as a 50% by weight solution in methylene chloride. The viscoelastic response of the spring supported resin was then followed in a dry nitrogen atmosphere as a function of time. About 10 to 15 mg of resin per run was required.

Dielectric measurements were made using a GenRad 1620 Precision Capacitance Measurement System (modified for high loss materials) equipped with a Balsbaugh Three-Terminal Research Cell. Dielectric relaxation data for isothermal cures were obtained from thin-films essentially "compression molded" in the parallel plate measuring cell. The resin was separated from the upper guard electrode by a thin sheet of PTFE and from the bottom electrode by a thin sheet of aluminum foil (Figure 1a). A PTFE shim with a circular hole 50 mm in diameter constrained the resin to an approximate thickness of 0.7 mm (Figure 1b). The measuring cell was first allowed to equilibrate thermally at the cure temperature, then the resin, sandwiched between the PTFE and aluminum sheets, was placed and clamped between the two plates of the measuring cell. After a short (2-5 minutes) thermal equilibration period the isothermal dielectric response was followed as a function of time at frequencies of 0.05, 0.10, 0.20, 0.50, 1.0, 2.0, 5.0, 10, 20, 50, and 100 kHz. This procedure was repeated for various cure temperatures. Approximately 2 g of resin was required for each analysis.

Thin-film samples of specific isothermal cure histories were prepared for dynamic tensile testing on the Rheovibron by compression molding 0.6 to 0.7 mm thick samples at a pressure of 14 MPa. The samples were air quenched after various times at constant cure temperature. The thin-films were then mounted in the Rheovibron and the temperature increased from room temperature to approximately 310°C at 2°C/min in a dry nitrogen atmosphere. DSA and thin-film experiments were carried out at frequencies of 3.5, 11, 35, and 110 Hz.

Results and Discussion

DSA. Isothermal cures of Resin 5208 in the temperature range of 125 to 181°C were examined by the DSA technique. Figure 2 shows the composite loss tangent response as a function of the natural logarithm of time for a cure at 147°C at several frequencies. Two $\tan \delta$ peaks are observed. At fixed temperature both peaks become smaller, shift to longer times, and exhibit improved resolution as the frequency is decreased. Figure 3 displays the composite loss tangent as a function of the natural logarithm of time at a fixed frequency of 3.5 Hz for cures at several temperatures. At this, the lowest frequency of measurement, the two peaks are best resolved, smallest, and occur soonest in time as the temperature is increased.

As noted previously by Senich et al. (8), the usefulness of the DSA technique in following the cure of epoxy curing systems stems from the fact that a relative maximum is produced in the composite loss tangent when the viscosity of the resin reaches a predetermined value. In a previous study (23) which considered a series of polystyrenes of varying molecular weights characterized

Figure 1. Dielectric cell.

Figure 2. DSA $\tan \delta$ vs. $\ln$ (time, sec) at fixed temperature (147 °C).

Figure 3. DSA $\tan \delta$ vs. $\ln$ (time, sec) at fixed frequency (3.5 Hz).

by DSA, the theoretical basis for understanding the viscosity related peak was established. The study also showed that the Tg or vitrification process was not observed by DSA for this series of PS samples. The appearance of a second peak well beyond the Tg of two high molecular weight polystyrene samples was attributed to the relaxation of entanglements.

The location of the first peak represents the time required to reach a specific viscosity, and, providing the reaction mechanism does not change as a function of temperature, represents the time to reach a fixed chemical conversion for a specific frequency. These peaks can then be used as a measure of the rate of reaction at each temperature where the reaction velocity constant can be treated as inversely proportional to the time to the peak maximum, $t_{\max}$:

$$\ln \left(\frac{1}{t_{\max}} \right) = - \frac{H_a}{RT} + C \quad (1)$$

where H_a is the activation energy of the reaction. The slope of a plot of the natural logarithm of $t_{\max}$ vs. the inverse of absolute temperature can then be used to determine the activation energy. Figure 4 contains the DSA and TBA (24) results on Resin 5208 plotted in this way. A linear least squares fit was applied to the data and the activation energies are listed in Table I. A frequency dependent activation energy results which changes from 14.7 to 16.0 kcal/mole for frequencies of 110 and 3.5 Hz, respectively, for DSA results (125 to 160°C). This may be compared to a value of 19.3 kcal/mole obtained from TBA at a nominal frequency of 1 Hz (150 to 180°C). In addition, the curing times for DSA were found to be approximately 40% longer than the TBA values for similar temperatures (150 to 160°C).

Resin 5208 exhibits a second peak at longer times than the viscosity related maximum. Gillham (1) attributed a second peak observed by TBA to vitrification. Figure 5 displays the plots of the natural logarithm of $t_{\max}$ vs. the reciprocal of absolute temperature for the second peaks from DSA and TBA. The activation energies derived from the slope of a linear least squares fit of the results from both are somewhat different as indicated in Figure 5 and Table I.

Figure 4. Arrhenius plots of DSA and TBA first peaks.

Figure 5. Arrhenius plots of DSA and TBA second peaks.

TABLE I. Dynamic Mechanical (DSA and TBA) Activation Energies

Peak	Frequency (Hz)	Analysis	H_a (kcal/mole)
1st	110	DSA	14.7
	35	DSA	15.3
	11	DSA	15.6
	3.5	DSA	16.0
	~1.0	TBA	19.3
2nd	3.5	DSA	10.5
	~1.0	TBA	13.7

The DSA technique allows for the calculation of the storage and loss components of the resin modulus from the composite response using a simple parallel mechanical model:

$$M_c^* = M_s^* + M_p^* \quad (2)$$

where M_c^* , M_s^* , and M_p^* are the complex moduli of the composite, spring, and material of interest, respectively. Figure 6 shows the results of such an analysis applied to the Resin 5208 cure at 147°C shown in Figure 2. Similar analyses were done for the entire temperature range.

If the above model correctly describes the behavior of the resin then it is possible to identify the behavior in the storage modulus (E') and the loss modulus (E'') responsible for the composite $\tan \delta$ peaks. The first $\tan \delta$ peak corresponds to an increasing resin E' that reaches a value at $t_{\max}$ which is approximately frequency independent for each isothermal cure as shown in Figure 6 for a 147°C cure. This E' value is observed in similarly derived curves ranging from 20 to 55 kPa as the isothermal cure temperatures are lowered from 181 to 125°C. This first peak also corresponds to a shoulder in the resin E'' . Apparently, the increase in the magnitude of E'' with frequency at this position is responsible for the change in magnitude of $\tan \delta$ with increasing frequency seen in Figure 2.

The second maximum in the composite $\tan \delta$ corresponds to an approximate plateau value of 700 kPa in resin E' and a peak in resin E'' . The frequency shift of the E'' peak to longer times appears to be responsible for the increasing separation of gel and vitrification $\tan \delta$ peaks with decreasing frequency. Higher temperature cures with a well separated second peak show a small inflection in E' very similar in shape to what one would expect for a glass transition, but not of the order of magnitude observed in linear or lightly crosslinked polymers. This supports the contention that the second peak is correlated with a vitrification of

Figure 6. DSA moduli vs. $\ln(\text{time, sec})$ for 147°C cure of resin 5208.

the curing epoxy resin, but the weakness of the DSA transition indicates the limit of sensitivity of the technique is being approached or that the resin is already highly crosslinked before it vitrifies.

Significant differences are observed between the present study on Resin 5208 and the previous studies on two dicy-containing epoxy resins by DSA (8) and by TBA (25).

- Two $\tan \delta$ peaks are observed by DSA compared to one peak in the previous study.
- Differences in the temperature dependence between DSA and TBA are observed in the present study.
- The frequency dependence in the cure times obtained by DSA was not previously observed.

These points will be addressed in order.

First, it is important to recognize that the DSA and TBA peaks do not correspond to the same stage of cure. Figure 7 illustrates the DSA and TBA results for isothermal cures of Resin I at 112 and 92°C from the previous studies and for isothermal cures of Resin 5208 at 180 and 150°C. The TBA logarithm of rigidity and logarithm of the mechanical damping index are plotted as functions of the logarithm of time. The times corresponding to the DSA $\tan \delta$ maxima are indicated as arrows on the TBA rigidity traces. Figure 8 shows E' and E'' for Resin I at 80.2°C computed from the composite DSA results by the analysis used to produce Figure 6. The DSA data were taken from the previous study. A similar frequency independent storage modulus value is observed for Resin I as for Resin 5208 (Figures 6 and 8). The first DSA peak positions indicated on the TBA rigidity curves in Figure 7 also correspond to approximately the same rigidity values. It is apparent that the DSA peak occurs later in the reaction than the TBA peak. The first DSA peak occurs upon the attainment of a modulus close to that of the rubbery plateau while the corresponding TBA peak occurs at the point where the relative rigidity begins to increase. Hedvat (26) has shown that changes in peak position in TBA are possible depending on the ratio of the sample rigidity to the support rigidity. Considering the differences in the nature of the supports and the types of deformation occurring in DSA and TBA it is not possible to rule out effects of this type as an explanation for the differences in the TBA and DSA peak times.

The significant increase in the TBA rigidity after the first DSA maximum is not observed in the derived resin modulus traces from DSA in Figures 6 and 8 indicating lack of DSA sensitivity in the glassy region. A second DSA maximum is apparently observed for Resin 5208. This could be due to the somewhat larger separation in time between the first DSA peak and a more distinct vitrification process observed by TBA (Figure 7). The TBA rigidity traces for Resin 5208 predict the observed larger separation between the two DSA peaks in the logarithm of time as the cure temperatures are increased.

Figure 7. TBA and DSA for Resin I and Resin 5208.

The previous studies showed no significant differences in the temperature dependencies of the first DSA and TBA peaks. Results for Resin I show the DSA peak to occur approximately 25% later in time over the temperature range studied (80 to 112°C) compared to approximately 40% later for Resin 5208. The activation energies derived for Resin 5208 extrapolate to a larger difference between DSA and TBA at temperatures above 160°C and to a smaller difference below 150°C between the two techniques. The fact that the first DSA peak occurs much later in time than the TBA peak means that the reaction responsible for the TBA and DSA peaks might differ due to complexities of the curing mechanism. This could account for some of the differences in activation energy.

The kinetic effect involved in the TBA procedure for an isothermal cure also accounts for some of the differences observed in activation energies for Resin 5208. Typically, a resin solution impregnated braid is introduced to the sample chamber at room temperature (or the temperature of the low boiling solvent) and brought to the cure temperature at a nominal 10°C/min. If the equivalent isothermal curing time is calculated (assuming an approximate activation energy) and the TBA data suitably corrected, an activation energy of 17.5 kcal/mole is observed vs. 19.3 kcal/mole for the uncorrected data (Table 1).

A frequency dependence of activation energies in DSA appears to be fairly well explained by the overlapping of the two $\tan \delta$ peaks observed. The 110 Hz data show only one (superimposed) peak at low temperatures and a shoulder at the higher temperatures. Correcting the times to the first peak would tend to yield a slightly higher activation energy. The opposite would take place with the 3.5 Hz data which are resolved into two peaks at the higher temperatures and overlap at the lower temperatures. Correction would yield somewhat lower activation energies. A linear least squares fit of the completely resolved 3.5 Hz peaks (inclusion of the 181°C data and exclusion of the 125°C data) reduces the activation energy from 16.0 to 15.4 kcal/mole. A frequency independent value of 15.0 to 15.5 kcal/mole would appear to be the result of corrected DSA data (Table 1).

In summary, the differences observed between DSA and TBA can be accounted for to some extent by careful consideration of the meaning of the observed viscoelastic phenomena. An explanation of the frequency dependence of the magnitude of the first peak and strong frequency dependence of the time to the second peak by DSA for Resin 5208 is beyond the scope of this work.

Dielectric Measurements. The dielectric properties of Resin 5208 were followed for isothermal cures of 110, 125, 137, 148, and 162°C at several frequencies. Figure 7 shows the time dependence of the dielectric loss tangent for the combination of the PTFE

Figure 8. DSA moduli ca. $\ln(\text{time, sec})$ for 80.2°C cure of resin 1.

Figure 9. Dielectric composite $\tan \delta$ vs. time for 110°C cure.

film and epoxy resin as experimentally measured. Through the analysis presented in Appendix 1 the actual material response is derived and shown in Figure 10 for the same 110°C cure in Figure 6 as a plot of the logarithm of the dielectric constant, ϵ' , and the dielectric loss factor, ϵ'' , vs. time.

Figure 10 shows a high initial value of about 250 for ϵ' of the resin at the lower frequencies (0.05 to 0.50 kHz) and a low initial value of about 11 for the higher frequencies (20 to 100 kHz). The lower frequencies show a pronounced frequency dependent drop in ϵ' after an initial more gradual decrease through the course of reaction. The fairly steady initial values of the higher frequency runs also show a drop at some frequency dependent point in time with all frequencies showing an approach to an ϵ' value consistent with literature values (27) for cured resins in the range of 3.5 to 4.0. Two main dispersion regions are observed for the time dependence of ϵ'' (Figure 10). Initial high values of ϵ'' develop into a large dispersion with a strong dependence on frequency as the frequency is lowered. A smaller dispersion is also observed at a later time and with a smaller dependence on frequency than the larger, short time dispersion. The smaller dispersion is observed only at the higher frequencies.

An analysis of the dielectric data similar to that for the dynamic mechanical data was undertaken. The natural logarithm of the time to peak maximum vs. $1/T$ was plotted for the two peak maxima observed in the dielectric loss tangent as shown in Figure 11. The activation energies derived from linear least squares fit of the data in these plots are listed in Table II.

TABLE II. Dielectric Activation Energies

Peak	Frequency	H_a (kcal/mole)
1st	50 Hz	11.2
	100	10.8
	200	11.3
	500	11.4
	1000	10.6
2nd	20 kHz	13.3
	50	13.1
	100	13.5

An average activation energy of 11.0 kcal/mole was found for the first peak at frequencies of 50 to 1000 Hz. An average activation energy of 13.3 kcal/mole was found for the second smaller dispersion for the 20, 50, and 100 kHz frequencies. The second peak occurs approximately 40% sooner in time than the DSA second peak. The dielectric relaxation strength ($\Delta\epsilon'$) associated with this peak

Figure 10. Dielectric resin ϵ' and ϵ'' vs. time for 110 °C cure.

Figure 11. Arrhenius plots of dielectric first and second peaks.

is much closer to the magnitudes to be expected from dipolar reorientation mechanisms than is the relaxation strength of the first peak. An approximate frequency shift of the dielectric second peak (20 to 100 kHz) to the dynamic mechanical frequency range (1 to 100 Hz) shows fairly good agreement at similar cure temperatures with the time to vitrification by DSA and TBA. Although good agreement in the temperature dependence with TBA exists and order of magnitude agreement in time with DSA and TBA second peaks exist, the large separation in real time and limited frequency data prevent unequivocal assignment of vitrification as the cause of the second dielectric dispersion.

Some well documented reasons exist concerning difficulties in interpretation of dielectric data. The dielectric loss spectrum will be significantly affected by material electrical conductance. McCrum et al. (28) show the d.c. conductivity can be separated from the total dielectric loss factor as follows:

$$\epsilon''(\omega) = \epsilon_0''(\omega) + \epsilon_1''(\omega)$$

where $\epsilon_0''(\omega)$ is the part due to conductivity, G_0 :

$$\epsilon_0''(\omega) = \frac{G_0}{\omega C_0}$$

and $\epsilon_1''(\omega)$ is the part due to the actual material dielectric loss mechanisms. Increasing the frequency should decrease the ϵ_0'' term which is observed in Figure 10. Starting values for d.c. conductivity in the temperature range studied agree in order of magnitude with those observed by Delmonte (10) and Adamec (12) (1×10^{-6} to 1×10^{-7} ohm⁻¹ cm⁻¹). The PTFE film in Figure 1a was originally utilized to prevent shorting across the guard ring.

According to Blythe (29) polarization effects at electrodes become most prominent when the material of a specimen shows some appreciable bulk conductivity. At low frequencies there is sufficient time for any slight conduction to transfer charge to the specimen surface forming an ion double-layer. The result is an enormous increase in the measured capacitance which is observed in Figure 10. A Cole-Cole plot of the data from Figure 9 is shown in Figure 12 as a large dispersion modelled by a single Debye-type relaxation time at 15, 50, 100, and 200 minutes into the 110°C cure. This single relaxation time appears to be associated with charge transport in a viscous medium. The relaxation stems from charge migration to form the ion double-layer instead of from polymer dipolar orientation. Dipolar reorientation in polymers invariably results in a broad distribution of relaxation times. The decrease in the size of the Cole-Cole semicircle with time is

consistent with the above interpretation of the dispersion because of the increase in viscosity of the medium during cure decreases the rate of migration of ions. The second peak in time is much smaller and is difficult to resolve from the main peak. It is observable as a shoulder on the low ϵ' end of the 200 minute Cole-Cole plot (Figure 12).

Similar to the findings in other electrical property studies, correlations may be drawn between electrical and mechanical data, but the large effects of conduction and ion double-layer formation mask such correlations in the present case.

Thin-Films. Dynamic tensile testing was carried out on thin-films of Resin 5208 molded with specific isothermal cure histories. The temperature dependence of the loss tangent at several frequencies of one of these samples cured at 124°C for 5 hours is shown in Figure 13. The state of the cure of the sample corresponds to that of a resin studied isothermally by DSA at a time between the two observed DSA $\tan \delta$ peaks.

The frequency dependence of the loss peak in a temperature scanning experiment indicates whether it arises from viscoelastic relaxation or is associated with chemical reaction. One would expect a peak associated with a viscoelastic relaxation to occur at higher temperatures at higher frequencies, which is true for the lowest and highest temperature peaks observed (Figure 13). For a peak associated with chemical reaction (leading to increased molecular weight) one would expect the peak to occur at lower temperatures at higher frequencies as observed for the intermediate temperature peak (Figure 13). For longer compression molding times at 124°C (or higher temperature cures) the intermediate temperature peak becomes less well resolved from the lowest temperature peak because the extent of further reaction decreases.

Figures 14a and 14b show the logarithm of the storage, E' , and loss, E'' , moduli vs. temperature for specimens cured at 124°C for 5 and 11.5 hours, respectively. The 5 hour sample, as mentioned above, corresponds to a time between the two DSA peaks at 3.5 Hz isothermal scans while the 11.5 hour sample corresponds to a time longer than those of both DSA loss tangent peaks. The E' shows an initial decrease (greater in the case of the 5 hour sample than the 11.5 hour sample) followed by an increase and a final decrease at about 250°C. E'' exhibits three dispersion regions in order of increasing temperature. The first is associated with the softening manifested by the decrease in E' , followed by a peak due to chemical reaction, and finally a peak associated with the glass transition of the fully cured resin. The softening peak in E'' at 3.5 Hz for the 5 hour cure occurs at about 91°C while the same peaks for the 11.5 hour cure occur at approximately 129°C. This indicates the resin is significantly below its glass transition temperature at times after the first DSA peak in the isothermal 124°C scan, whereas the resin is in the

Figure 12. Cole-Cole plots as a function of time for 110 °C cure.

Figure 13. Thin-film $\tan \delta$ vs. temperature for 5 hr premolded at 124 °C.

Figure 14. Thin-film moduli vs. temperature for 5 and 11.5 hr premolded at 124 °C.

glassy state at times after the second DSA peak in the isothermal 124°C scan. This implies that the second peak in DSA is associated with vitrification and that significant reaction takes place between the two DSA peaks observed for Resin 5208 in isothermal scans at 3.5 Hz and 124°C.

The viscoelastic response of a sample previously heated to approximately 310°C is shown in Figure 15a. In this case only a single relaxation region exists and this is associated with the glass transition temperature of the fully cured resin formed at 2°C/min.

Previous work (8) on partially cured thin-films of two other epoxy resins showed much less temperature separation between softening, further reaction, and ultimate glass transition than is the case with Resin 5208. In fact, overlap between the dispersion regions made it impossible to identify the chemical reaction process.

Keenan et. al. (30) observe a peak due to the softening of the sample and another peak associated with the glass transition of the fully cured resin on similar type resin systems. Samples in their study were molded at higher temperatures thus no evidence of a reaction peak was observed. They also report the existence of two other processes during the thermal scan of thin films. a β transition at approximately -50°C attributed to the crankshaft motion of the glycidyl portion of the polymeric chain and a ω transition at approximately 100°C attributed to the motions of unreacted molecular segments and/or inhomogeneities arising from dissimilar crosslink densities. Thermal scans of the samples in this study were not carried out in this β transition region and no evidence of the ω transition is observed for the fully cured resin as seen as in Figure 15 for Resin 5208 between 40 and 300°C. The lower molding temperatures in this study apparently give rise to large softening and reaction effects which possibly mask the observation of the ω transition in the partially cured materials.

Conclusions

DSA analysis of Resin 5208 exhibits two dispersion regions. The first is related to gelation and the second is related to vitrification. The first DSA peak occurs on the attainment of a value for the resin storage modulus slightly lower than that of the rubbery plateau. The first TBA peak occurs at the point where the composite (braid and resin) attains measurable rigidity.

Activation energies are derived from the dynamic mechanical experiments assuming that the kinetic mechanism does not change with temperature. The thus arrived at activation energy represents a lumped kinetic parameter for the reactions which have led to the point in time of the dynamics mechanical dispersion being measured. Activation energies for the first dispersion by DSA

Figure 15. Thin-film E' , E'' , and $\tan \delta$ vs. temperature for $T_g \infty$.

range from 14.7 to 16.0 kcal/mole whereas the TBA value is 19.3. Activation energies of 15.0 to 15.5 kcal/mole for DSA and 17.5 for TBA were derived by elimination of the overlap of the second dispersion in DSA and consideration of the kinetic effect in the heating procedure of TBA. The first peaks by DSA and TBA occur at significantly different times (extents of reaction) into the cure and a change in reaction mechanism may account for the difference observed.

Molecular dipolar polarization was difficult to define from dielectric measurements. A large first dispersion in time for isothermal cures of Resin 5208 is attributed to charge migration in a viscous medium. High values of dielectric constant and dielectric loss factor are attributed to the formation of an ion double-layer and sample conductivity, respectively. Limited frequency data on a smaller second dispersion prevent unequivocal assignment of its relationship to molecular changes.

It is useful to make a comparison of the capabilities and limitations of the three techniques used in this work for characterizing the isothermal curing behavior of epoxy resin formulations. DSA has the advantage that storage and loss modulus values for the resin can be computed employing a simple model for the resin-spring composite. The data are reliable only during the early stages of cure due to a loss of sensitivity as the resin vitrifies and greater deformations occur in the ends of the spring. With DSA it is also possible to examine the frequency dependence of the changing viscoelastic characteristics of the resin during cure. TBA allows a broader relative view of the entire process, but adds the mathematical complexity of the braid/resin composite and allows observations only at a resonant frequency. The dielectric analysis first dispersion appears to arise from the influence of the changing viscosity during cure on charge migration rather than from the rapid change in viscosity which marks the onset of gelation in the other two techniques. This method could provide an accurate means of measuring the change in viscosity during the cure. Due to the strength of this dispersion the vitrification region is masked in the equivalent mechanical frequency range of the dielectric analysis. Thus, it appears that the three methods are complementary in the information which they are capable of providing about the properties and characteristics of the resin during cure.

Thin-films of Resin 5208 with specific isothermal cure histories exhibit three dispersion regions upon heating. The first is attributed to softening, followed by further chemical reaction and finally a peak due to the glass transition of the fully cured resin. Dynamic mechanical testing on thin-films shows that significant reaction takes place between the two DSA loss tangent peaks and that the second DSA peak is associated with vitrification.

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Appendix

Composite Dielectric Analysis. The dielectric response from the experimental set-up shown in Figure 1 is that of the epoxy resin and upper PTFE sheet. In order to observe the dielectric response of the resin alone one must first subtract the PTFE response from the total response.

The total complex capacitance (C^*_{total}) can be expressed as a series combination of the complex capacitances of the resin and PTFE sheet (C^*_{resin} and C^*_{PTFE}) as follows:

$$\frac{1}{C^*_{total}} = \frac{1}{C^*_{PTFE}} + \frac{1}{C^*_{resin}} \quad [1]$$

A complex capacitance can be expressed as the product of the complex dielectric constant, ϵ^* , and a geometrical constant, C_0 , of the sample:

$$C^* = \epsilon^* \cdot C_0 \quad [2]$$

where the complex dielectric constant is defined by a real (ϵ') and an imaginary ($i\epsilon''$) component as follows:

$$\epsilon^* = \epsilon' - i\epsilon'' \quad [3]$$

Assuming no dielectric loss factor ($\epsilon''_{PTFE} = 0$) for the PTFE response over the temperature range studied, combining [1], [2], and [3] shows:

$$\frac{1}{(\epsilon' - i\epsilon'')_{\text{total}} \cdot (C_0)_{\text{total}}} = \frac{1}{\epsilon'_{\text{PTFE}} \cdot (C_0)_{\text{PTFE}}} + \frac{1}{(\epsilon' - i\epsilon'')_{\text{resin}} \cdot (C_0)_{\text{resin}}}$$

Rearranging [4] for the complex resin dielectric constant yields:

$$\epsilon'_{\text{resin}} - i\epsilon''_{\text{resin}} = \frac{1}{(C_0)_{\text{resin}}} \cdot \left(\frac{\epsilon'_{\text{total}} \cdot \epsilon'_{\text{PTFE}} \cdot (C_0)_{\text{total}} \cdot (C_0)_{\text{PTFE}}}{\epsilon'_{\text{PTFE}} \cdot (C_0)_{\text{PTFE}} - \epsilon'_{\text{total}} \cdot (C_0)_{\text{total}}} \right) + \left(\frac{-i\epsilon''_{\text{total}} \cdot \epsilon'_{\text{PTFE}} \cdot (C_0)_{\text{total}} \cdot (C_0)_{\text{PTFE}}}{+i\epsilon''_{\text{total}} \cdot (C_0)_{\text{total}}} \right) \quad [5]$$

Separating and equating the real and imaginary parts of [5] yield the actual resin response:

$$\epsilon'_{\text{resin}} = \frac{1}{(C_0)_{\text{resin}}} \cdot \left(\frac{A \cdot C - B \cdot D}{C^2 + D^2} \right) \quad [6]$$

$$\epsilon''_{\text{resin}} = \frac{1}{(C_0)_{\text{resin}}} \cdot \left(\frac{A \cdot D + B \cdot C}{C^2 + D^2} \right) \quad [7]$$

where A, B, C, and D are all functions of experimentally measurable quantities:

$$A = \epsilon'_{\text{total}} \cdot \epsilon'_{\text{PTFE}} \cdot (C_0)_{\text{total}} \cdot (C_0)_{\text{PTFE}} \quad [8]$$

$$B = \epsilon''_{\text{total}} \cdot \epsilon'_{\text{PTFE}} \cdot (C_0)_{\text{total}} \cdot (C_0)_{\text{PTFE}} \quad [9]$$

$$C = \epsilon'_{\text{PTFE}} \cdot (C_0)_{\text{PTFE}} - \epsilon'_{\text{total}} \cdot (C_0)_{\text{total}} \quad [10]$$

$$D = \epsilon''_{\text{total}} \cdot (C_0)_{\text{total}} \quad [11]$$

A somewhat similar analysis for a conducting layer and a parallel non-conducting layer is presented by Hill (31).

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