

Crosslinking of an Epoxy with a Mixed Amine as a Function of Stoichiometry. II. Final Properties Via Dynamic Mechanical Spectroscopy

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Synopsis

Variation of the epoxy/curing agent ratio for a system containing a diglycidyl ether of bisphenol-A (DGEBA) and a mixed aromatic amine was found to have a significant effect on the cure kinetics and final dynamic mechanical properties of both the neat resin and glass reinforced epoxy. For a partial B-stage cure to an ultimate C-stage cure, optimum cure temperatures were obtained as a function of stoichiometry. For the ultimately cured (C-stage) resin, the molecular weight between crosslinks (M_c) passed through a minimum, and both the glass transition temperature (T_g) and a secondary (sub- T_g) transition passed through a maximum at the stoichiometric ratio. In addition, the activation energy of the ultimately cured resin passed through a maximum at or near the stoichiometric ratio for both the T_g and sub- T_g transitions.

INTRODUCTION

Epoxy resins are an important engineering matrix material for polymeric composites where a high modulus and glass transition temperature are desirable. Accurate determination of the ratio of epoxy to curing agent is important because a variation of more than ± 2 wt % of the stoichiometric ratio of epoxy to curing agent can have a significant effect on the final mechanical properties of the cured resin.

There are several examples in the literature of the use of dynamic mechanical spectroscopy to determine the final properties of an ultimately cured epoxy-amine system. Murayama and Bell¹ varied the epoxy/amine ratio for a DGEBA resin (Shell Epon 828) cured with methylene dianiline (MDA), and determined its effect on the molecular weight between crosslinks, modulus as a function of temperature, and glass transition temperature (T_g). Senich et al.² studied two epoxy resins cured with dicyandiamide by dynamic spring analysis (DSA). They showed that partially cured samples that were cured below their ultimate T_g had two relaxations when they were scanned in temperature. The first relaxation occurred near the original isothermal cure temperature with a low activation energy, about 250 kJ/mol, whereas the second relaxation occurred near the ultimate T_g , with an activation energy of 500–650 kJ/mol. The large

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increase in activation energy for the T_g relaxation was attributed to the reduction in molecular mobility caused by increasing crosslink density. Gupta et al.³ studied the effect of the epoxy/amine ratio on the dynamic mechanical and tensile mechanical properties of an ultimately cured system of Epon 828 and meta-phenylene diamine (*m*-PDA). Charlesworth⁴ studied the effect of the epoxy/amine ratio on the crosslink density of an ultimately cured system of a DGEBA resin and MDA, as well as other epoxy-diamine systems. The epoxy-amine systems described above are primarily for a single aromatic amine curing agent. For this work, an epoxy-amine system was investigated in which the curing agent was mostly a mixture of two aromatic diamines.

For this work, the epoxy/amine ratio was varied and the dynamic mechanical response was determined for: (a) the maximum change in modulus from a partial B-stage cure to an ultimate C-stage cure of a glass cloth composite, to yield the optimum cure temperatures; and (b) the C-stage cure of the neat resin and glass braid composite as a function of temperature and frequency.

EXPERIMENTAL

The dynamic mechanical properties were studied via a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA), used with: (a) Universal temperature programmer (UTP); (b) Hewlett Packard Model 85 desktop computer and Model 7470-A plotter; (c) flexural/shear deformation head.

Samples mounted in the flexural mode were run with single cantilever bending at a strain amplitude of 0.016 mm. For temperature scanning of the cured resin, samples approximately 1.5–2.0 mm. thick were prepared in an aluminum mold, which is described in an earlier paper.⁵ The molded samples were analyzed from –100 to 200°C at a heating rate of 3–4°C/min and up to five frequencies (0.33–30 Hz).

The epoxy resin used was a diglycidyl ether of bisphenol-A (DGEBA), Shell Epon 828, and the aromatic amine, 360L, was manufactured by the Magnolia Plastics Co. The aromatic amine is primarily a 50/50 wt % blend of methylene dianiline (MDA) and *m*-phenylene diamine (*m*-PDA), with other oligomeric fractions included. Other details of this epoxy system are described in the previous paper.⁵ The recommended stoichiometric ratio of epoxy to amine was 81 to 19 wt %. This ratio is not really stoichiometric, but is 1.2 for the ratio of amine hydrogen equivalents to epoxide equivalents initially. However, we will see later that this epoxy/amine ratio yields maximum values for glass transition temperature, modulus, and crosslink density. Studies were conducted by varying the concentration of Epon 828 by ± 2 , ± 5 , and ± 10 wt % from the stoichiometric value of 81 wt %.

RESULTS AND DISCUSSION

B-Stage to C-Stage Cure

For many applications it is important to determine the optimum cure conditions for obtaining the highest modulus possible for the ultimate cure of a particular epoxy/curing agent ratio. For this work, samples that were B-stage

cured in the DMTA from the mixed resin at different cure temperatures were C-stage oven cured at 149°C for 2 h. These samples, which were glass cloth composites mounted in a steel shim sandwich as described in an earlier paper,⁵ were run in the flexural mode at a frequency of 30 Hz. Figure 1 shows a plot of the change in modulus vs. isothermal cure temperature for several epoxy/amine ratios for the glass cloth composites in flexure. The overall change in modulus was taken from the mixed resin at room temperature to the B-stage cure, plus the B-stage to C-stage cure. For the nonstoichiometric samples, the change in modulus reached a maximum near 100°C, while the stoichiometric samples reached a maximum near 130°C. These maxima should correspond to the optimum cure temperatures needed to obtain the highest values of modulus for these composites at a particular epoxy/amine ratio. These optimum cure temperatures at three epoxy/amine ratios are within 20°C of those shown on a time-temperature-transformation (TTT) cure diagram of the same epoxy system in the previous paper.⁶

Scanning Measurements on C-Stage Cure

Molded samples of the Epon 828-mixed amine system were B-stage and C-stage oven cured at the recommended conditions described earlier. The samples were then scanned in the DMTA from -100 to 200°C. Raw data of $\tan \delta$ and flexural modulus E' (in Pa) vs. temperature at 30 Hz for the -5 and +5 wt % epoxy/amine ratio samples are shown in Figure 2. The sharp drop in modulus, accompanied by a peak in $\tan \delta$, indicates the glass-to-rubber transition of the

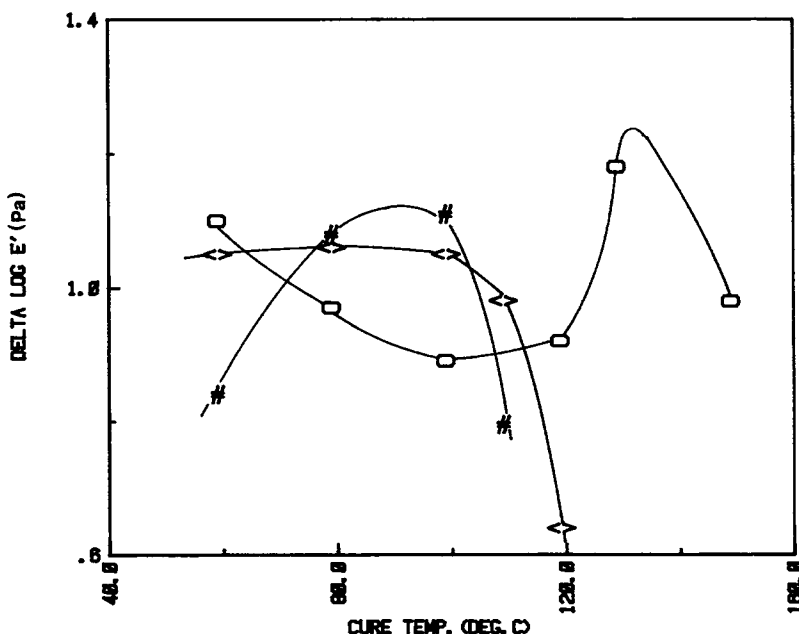


Fig. 1. The change in flexural modulus (in Pa) from the mixed resin to a C-stage cure $\{ [E'(B\text{-st.}) - E'(\text{init.})] + [E'(C\text{-st.}) - E'(B\text{-st.})] \}$ vs. cure temperature for several epoxy/amine ratios on glass cloth/steel shim at 30 Hz: (O) stoichiometric (s.r.); (< >) -10 wt %; (#) +5 wt %.

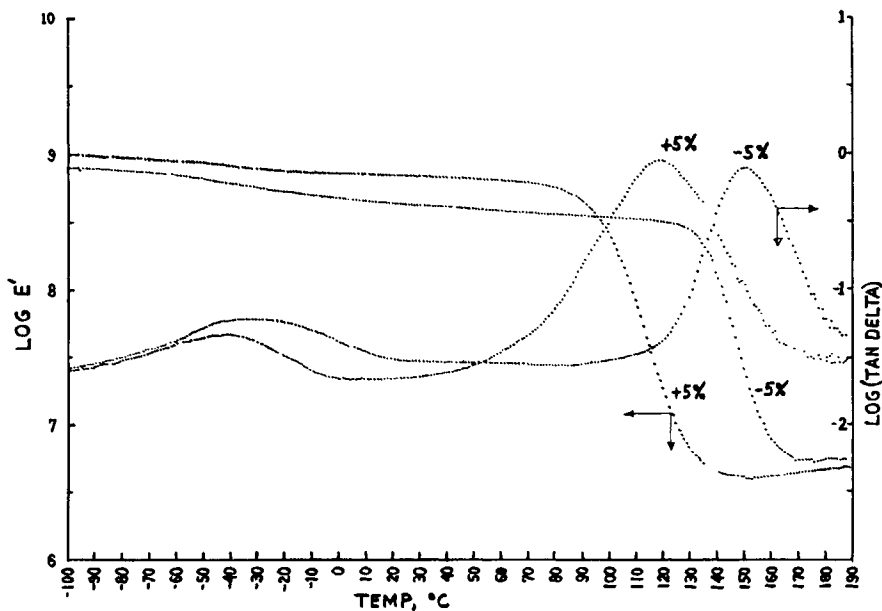


Fig. 2. Flexural modulus ($\log E'$) and $\tan \delta$ vs. temperature showing the sub- T_g and T_g regions for the +5 and -5 wt % epoxy/amine ratio neat resin samples at 30 Hz.

epoxy resin. From the maximum in $\tan \delta$, the glass transition temperature (T_g) can be obtained. The smaller $\tan \delta$ peak at -40 to -30°C in Figure 2 indicates a "sub- T_g ." The sub- T_g is a secondary transition believed to be attributed to the crankshaft rotation of the glycidyl amine linkage ($-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-$) after reaction of the epoxide ring and the amine.⁷ Both the T_g and sub- T_g always increase with increasing frequency over a temperature range, as shown in Figures 3 and 4.

Correlation of Activation Energy and T_g with Stoichiometric Ratio

From the variation of T_g and sub- T_g with frequency, transition maps of $\ln(\text{frequency})$ vs. $1/T$ were made from which the activation energy could be determined from the slope. Such a plot is shown in Figure 5 for several epoxy/amine ratios at a frequency range of 0.33–30 Hz. These transition maps begin to show deviation from linearity at about 30 Hz. The activation energy (E_a) values of the neat resin for both the T_g and sub- T_g were plotted as a function of epoxy/amine ratio in Figure 6, and both curves passed through a maximum near the stoichiometric ratio. The maximum for E_a in the T_g region suggests that molecular mobility is the most restricted at the stoichiometric ratio since the degree of crosslinking is the highest at that ratio. Also in Figure 6, the T_g and sub- T_g for the neat resin both pass through a maximum at the stoichiometric ratio. The values of E_a near the stoichiometric ratio of epoxy/amine for the ultimate T_g (about 160–175 kcal/mol) in Figure 6 agree fairly well with those of 500–650 kJ/mol (119–155 kcal/mol) reported by Senich et al.² for two epoxy resins cured with stoichiometric amounts of dicyandiamide.

In Figure 7, the sub- T_g is plotted as a function of amine/epoxy ratio (in equivalents) for the Epon 828/(*m*-PDA/MDA) system used in this work, and

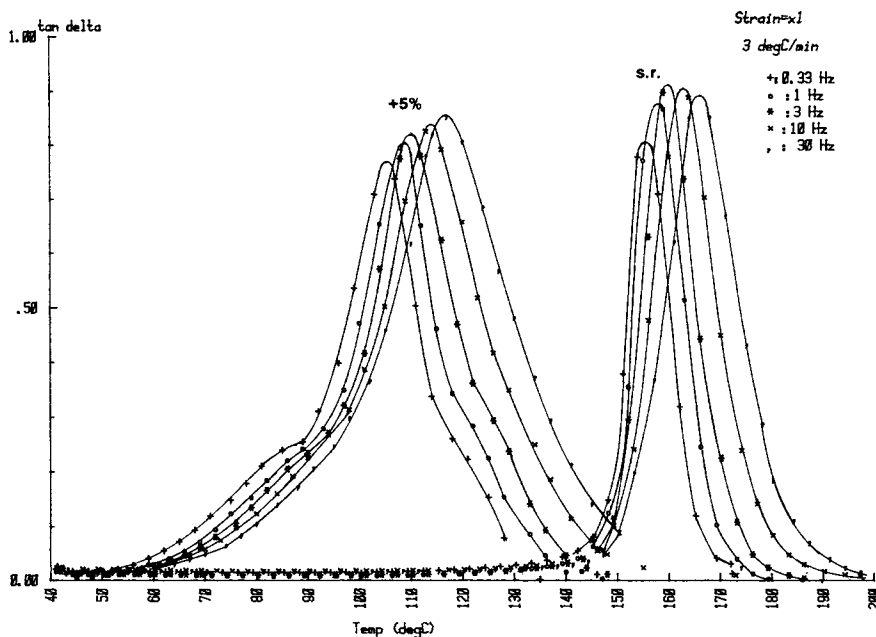


Fig. 3. Tan δ vs. temperature for the +5 wt % and s.r. epoxy/amine ratio neat resin samples showing the effect of frequency on the T_g .

is compared with a Epon 828/*m*-PDA system used by Gupta et al.³ They used a “standard cure” (75°C for 2 h + 125°C for 2 h) as well as a “postcure” (std. cure + 175°C for 6 h in an inert gas environment). The curves for both cure conditions are plotted in Figure 7, and the dynamic mechanical data was obtained from a Rheometrics mechanical spectrometer (RMS) at 0.16 Hz. The curve for the standard cure passes through a maximum at $B = 1.0$, while the curve for the postcure passes through a maximum near $B = 0.8$. In comparison, the curve for the epoxy system used in this work passes through a maximum at $B = 1.2$. This data was obtained from a DMTA at 30 Hz.

Correlation of Molecular Weight between Crosslinks and T_g with Stoichiometric Ratio

The molecular weight between crosslinks (M_c) was determined for each epoxy/amine ratio from the rubbery plateau region of the modulus–temperature curve following the T_g region. Figure 8 shows the rubbery plateau shear modulus G for the neat resin at several epoxy/amine ratios as a function of frequency, and the value of G is the highest at the stoichiometric ratio. Figure 9 compares the rubbery plateau shear modulus of the neat resin with that of a glass braid composite for several epoxy/amine ratios. The glass braid used was two-ply triaxially braided S-2 glass supplied by McDonnell Douglas, and is different from the Owens-Corning glass cloth described earlier. Figure 10 shows a plot of log tan δ vs. temperature for the stoichiometric ratio of epoxy/amine for the

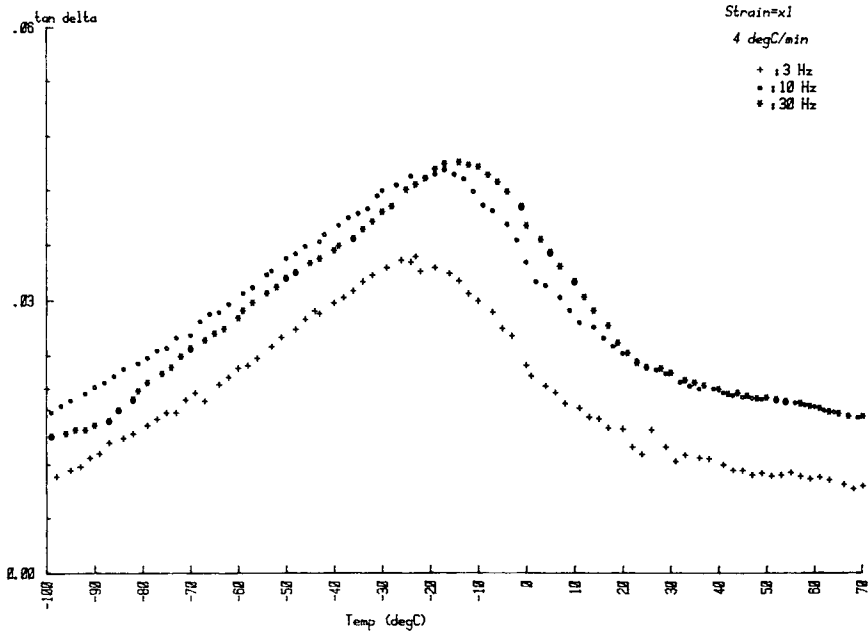


Fig. 4. Tan δ vs. temperature showing the effect of frequency on the sub- T_g for the s.r. epoxy/amine ratio of neat resin.

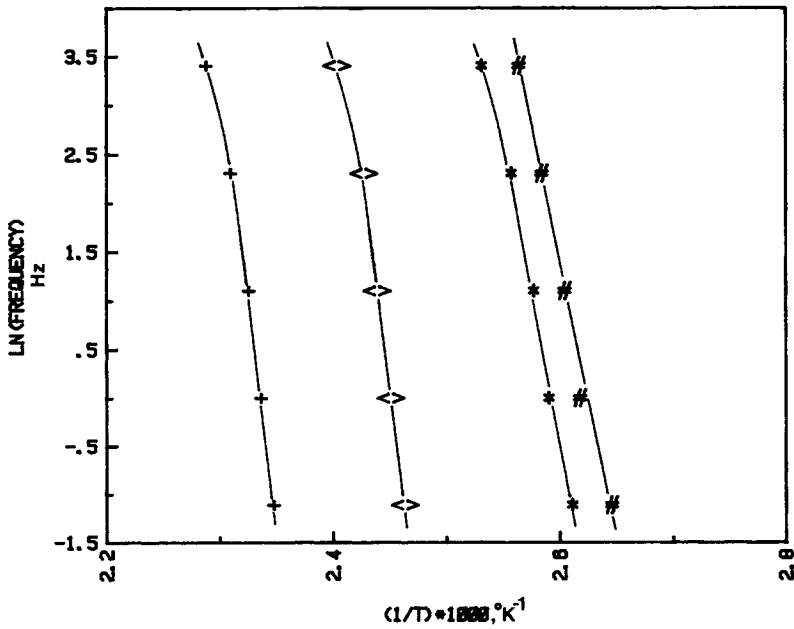


Fig. 5. Transition map of $\ln(\text{frequency})$ vs. reciprocal temperature for the primary T_g of the C-stage cured neat resin samples: (+) s.r.; (<>) -5 wt %; (*) -10 wt %; (#) +5 wt %.

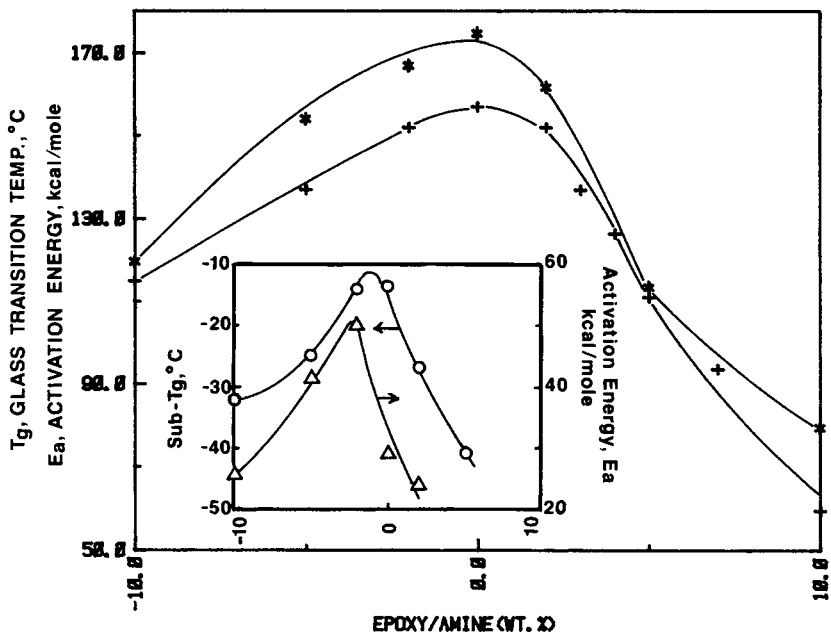


Fig. 6. Glass transition temperature (T_g , 3 Hz), sub- T_g (30 Hz), activation energy (E_a , T_g region and E_a , sub- T_g region) of the C-stage cured neat resin as a function of epoxy/amine ratio: (*) E_a ; (+) T_g , 3 Hz (note that T_g and E_a have the same scale).

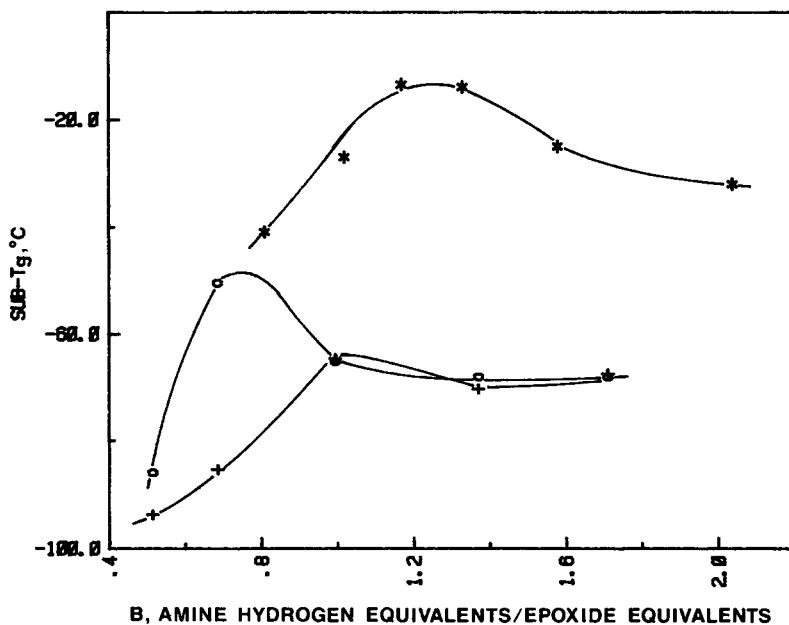


Fig. 7. Sub- T_g vs. amine/epoxy ratio (in equivalents) for: (*) Epon 828/(*m*-PDA + MDA) neat resin in flexure at 30 Hz on a DMTA; (+) Epon 828/*m*-PDA (std. cure) neat resin at 0.16 Hz on a Rheometrics Mechanical Spectrometer (RMS) by Gupta et al.³; (o) Epon 828/*m*-PDA (postcure) neat resin at 0.16 Hz on an RMS by Gupta et al.³

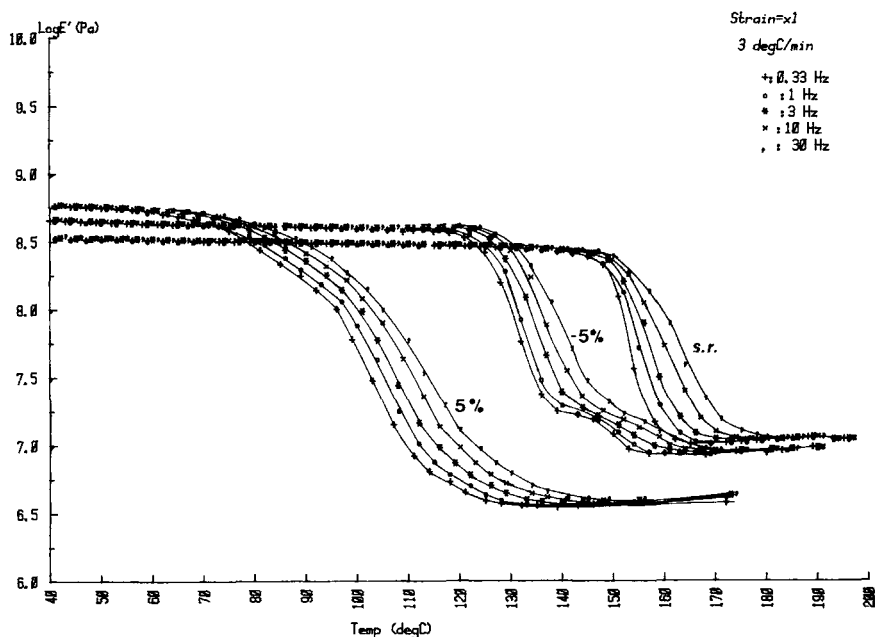


Fig. 8. Flexural modulus ($\log E'$) vs. temperature for several epoxy/amine ratios of neat resin and several frequencies showing the rubbery plateau shear modulus after the T_g region.

neat resin and the glass braid composite. The $\tan \delta$ maximum is lower for the composite than for the neat resin, suggesting that the glass fibers restrict molecular mobility as the resin becomes more crosslinked. Also in Figure 10, the $\tan \delta$ peak for the T_g region of the composite is broader than for the neat resin. The greater area under the $\tan \delta$ curve for the composite can be taken as a measure of the ability of the composite to absorb energy, i.e., the composite has a greater toughness than the neat resin. Figure 11 shows a plot of the flexural modulus ($\log E'$) vs. epoxy/amine ratio for both the neat resin and the glass braid composite at 40°C and in the rubbery plateau region following the ultimate T_g . At 40°C , $\log E'$ is invariant with the epoxy/amine ratio for both the neat resin and the composite until about 5 wt % excess epoxy. In the rubbery plateau region, $\log E'$ passes through a maximum at the stoichiometric ratio of epoxy/amine for both the neat resin and the glass braid composite. Although the G values are considerably higher for the composite than for the neat resin in Figure 9, they are not a true representation of the composite. To account for the interaction between the epoxy matrix and the glass fibers, the rubbery plateau shear modulus of the composite can be estimated, to a first approximation, from the linear rule of mixtures⁸ by

$$G_c = \frac{1}{V_f/G_f + V_m/G_m} \quad (1)$$

where G_c , G_f , G_m = rubbery plateau shear modulus of composite, fiber, and matrix, and V_f , V_m = volume fraction of fiber and matrix, respectively. A lit-

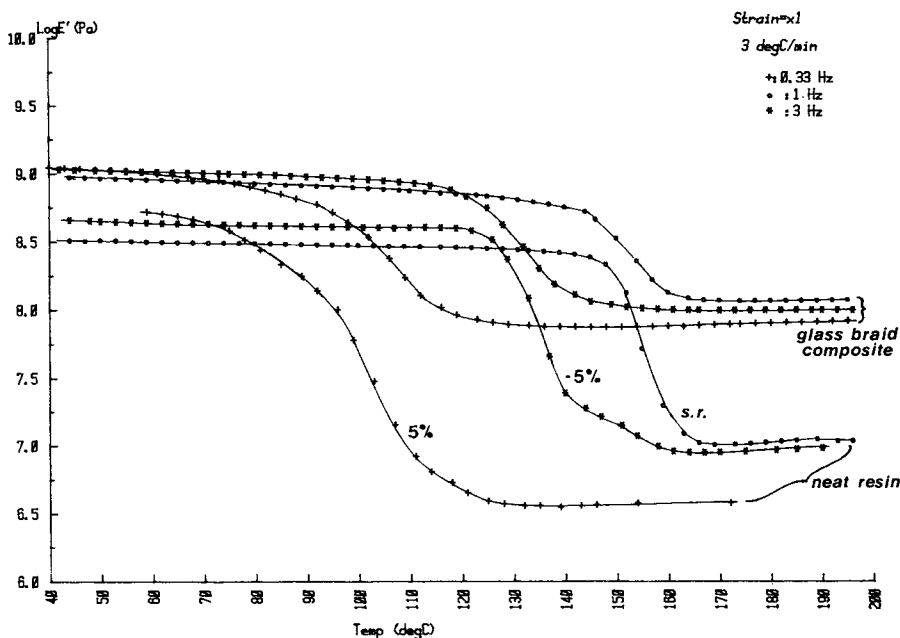


Fig. 9. Flexural modulus ($\log E'$) vs. temperature comparing the rubbery plateau shear modulus of the neat resin with that of a glass braid composite for several epoxy/amine ratios.

erature value of 2.87×10^{10} Pa was used for G_f for S-glass fibers.⁹ The M_c values were calculated from the following equation:

$$M_c = dRT/G \quad (2)$$

where d is the polymer density, R is the gas constant, T is the absolute temperature, and G is the rubbery plateau shear modulus. The M_c was calculated at 185°C for each sample because this temperature was clearly in the rubbery plateau region. The density of the neat resin at 185°C was determined by preparing a block of crosslinked epoxy and measuring its dimensions and weight. The density was nearly invariant for all the epoxy/amine ratios; an average value of 1.13 g/cm^3 was used in calculating M_c for all the samples. From each value of G_c determined from eq. (1), an "effective" M_c was calculated for the glass braid composite. Values of M_c and T_g for both the neat resin and glass braid composite are plotted vs. the epoxy/amine ratio in Figure 12. The T_g passed through a maximum at the stoichiometric ratio, and was only slightly higher for the neat resin than for the composite at 3 Hz. The M_c curves in Figure 12 are not symmetrical about the stoichiometric ratio, but are highly skewed for $> 5 \text{ wt } \%$ excess epoxy samples. For 10 wt % excess epoxy, the neat resin was very brittle and had to be supported by steel shim during flexural measurements. The flexural modulus of the neat resin was estimated from the

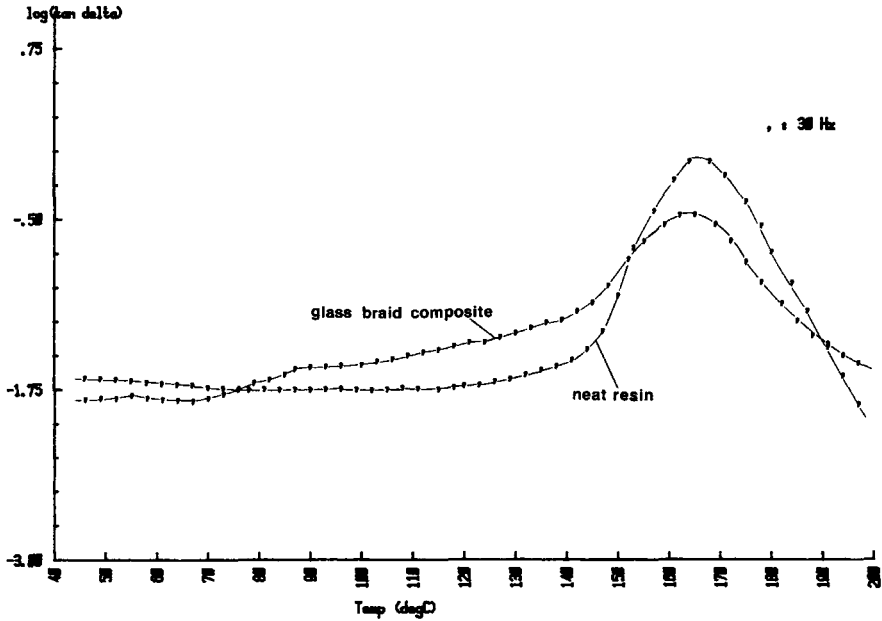


Fig. 10. $\tan \delta$ vs. temperature for the stoichiometric ratio epoxy/amine neat resin and glass braid composite at 30 Hz for the primary T_g region.

following relationship (based on the neat resin being supported on each side by the steel shim)¹⁰:

$$E'_c = E'_s X^3 + E'_p (1 - X^3)$$

E'_c = modulus of the steel/epoxy composite

E'_s = modulus of the steel shim

E'_p = modulus of the epoxy polymer

X = thickness fraction of steel shim, calculated from

$$X = \frac{2d_1}{d_2 + 2d_1} \quad (3)$$

where d_1 = steel shim thickness and d_2 = epoxy sample thickness. Since the M_c values are so high for the +7 and +10 wt % neat resin samples, it is possible that there is an asymptotic value of M_c somewhere in this range of epoxy/amine ratios.

The T_g and M_c values of the neat resin as a function of stoichiometry for this work were compared with dynamic mechanical data by other workers for similar epoxy systems,^{1,3,4,11} as shown in Figure 13. The epoxy systems from the literature shown in Figure 13 are for a DGEBA resin cured with a single aromatic amine (MDA or *m*-PDA). No literature examples were found for

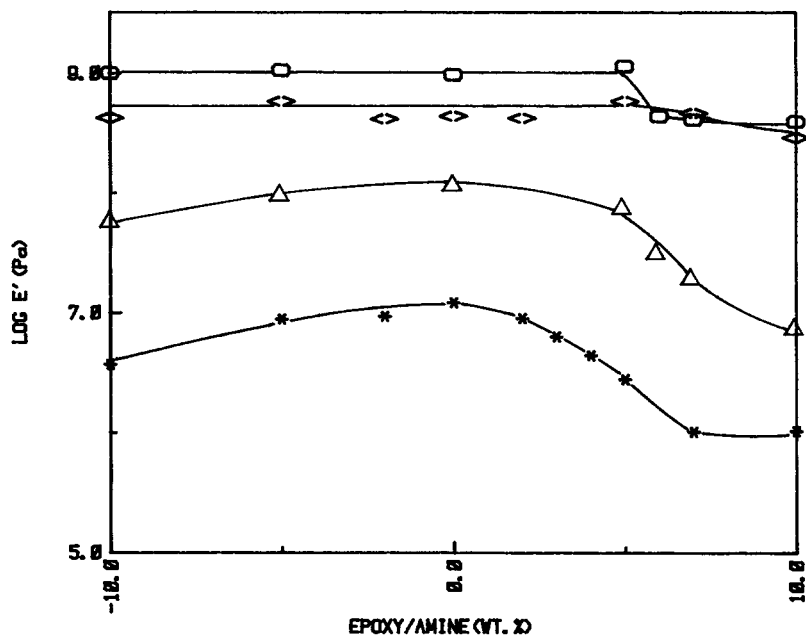


Fig. 11. Log flexural modulus vs. epoxy/amine ratio for both the neat resin and glass cloth composite at 40°C and for the rubbery plateau shear modulus after the T_g region: (O) glass braid composite at 40°C; (<>) neat resin at 40°C; (Δ) glass braid composite (rubbery plateau); (*) neat resin (rubbery plateau).

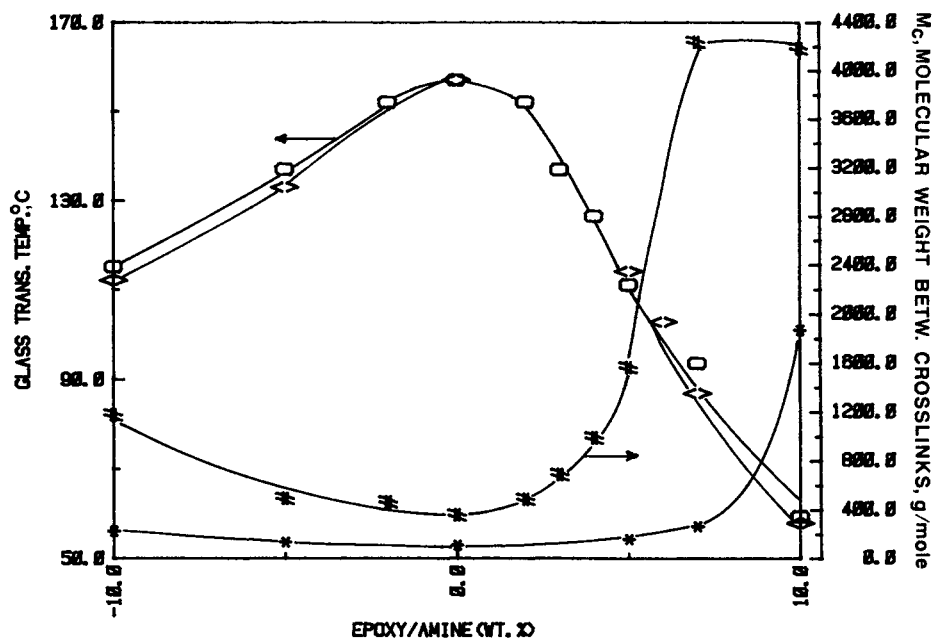


Fig. 12. Glass transition temperature (T_g) and molecular weight between crosslinks (M_c) vs. epoxy/amine ratio for the neat resin and glass braid composite: (O) T_g (3 Hz) for neat resin; (<>) T_g (3 Hz) for glass braid composite; (#) M_c for neat resin; (*) M_c for glass braid composite.

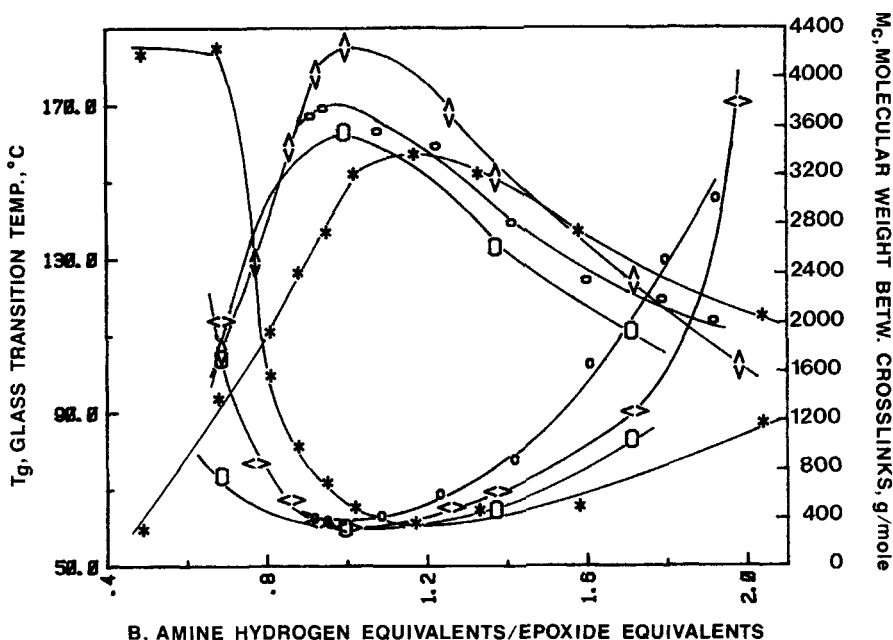


Fig. 13. Glass transition temperature (T_g) and molecular weight between crosslinks (M_c) vs. amine/epoxy ratio (in equivalents) comparing this work with several epoxy-amine systems in the literature analyzed by dynamic mechanical methods: (*) this work [Epon 828/(MDA + *m*-PDA)] on a DMTA at 3 Hz; (o) Murayama and Bell¹ [Epon 828/MDA] on a Vibron at 11 Hz; (O) Gupta et al.³ [Epon 828/*m*-PDA] on a Rheometrics mechanical spectrometer (RMS) at 0.016 Hz; (< >) Charlesworth⁴ [DGEBA/MDA] on a torsional pendulum at 1 Hz.

dynamic mechanical analysis of a DGEBA/mixed amine system like the one used in this work. Although it is difficult to make direct comparisons between the literature data and the data for this work in Figure 13 due to different cure conditions and measurement frequencies, some observations can be made. The maxima and minima in Figure 13 for the literature curves occur at $B = 1$, where $B =$ amine hydrogen equivalents/epoxide equivalents, initially, and $B = 1$ for perfect stoichiometry between the epoxy and the amine. However, the maxima and minima in Figure 13 for this work occur at $B = 1.2$, which shows that optimum cure conditions require some excess amine in the system. It is not certain why the T_g maximum for the mixed amine system is lower than the maximum in T_g for the single amine systems. In the previous paper,⁶ we found that the T_g values for ultimately cured Epon 828-aromatic amine systems ($B = 1.2$) of glass cloth composites in flexure on the DMTA at 30 Hz were as follows: (*m*-PDA + MDA), 173°C; MDA, 172°C; *m*-PDA, 163°C. This data is reasonable in comparison with that of Foun et al.¹² for similar epoxy-amine systems ($B = 1.0$). They concluded that the high viscosity of the DGEBA/MDA mixture and the large MDA molecule (larger than the *m*-PDA molecule) both contribute to more restricted molecular mobility. Thus, the DGEBA/MDA system has a higher ultimate T_g than the DGEBA/*m*-PDA system. Foun et al.¹² also used Tonox 60/40, essentially the same mixed amine used in this work, and concluded that the high percentage of oligomeric fractions in this curing agent contributes to reduced molecular mobility. Thus, our results from

the first paper⁶ showing the ultimate T_g 's of the DGEBA-MDA and DGEBA-mixed amine systems about equal seems reasonable. The M_c values in Figure 13 for this work were calculated from eq. (2), as were the values by Murayama and Bell.¹ Charlesworth⁴ did not calculate M_c values, but we calculated them from eq. (2) for ease of comparison in Figure 13. Gupta et al.³ determined M_c values from an empirical relationship.

Fox and Loshaek¹³ found that the glass transition temperature (T_g) of a polymer could be expressed as a linear function of the molecular weight (M) by the relationship:

$$T_g = T_{g\infty} + K/M \quad (4)$$

where K is a constant for a particular polymer, and $T_{g\infty}$ is the glass transition temperature for a polymer of infinite molecular weight. Equation (4) can also be applied to the molecular weight between crosslinks (M_c) for a crosslinked polymer, and the results are shown in Figure 14 for the ultimately cured neat resin of the DGEBA/mixed amine system used in this work. A fairly good correlation was obtained, and the values of K and $T_{g\infty}$ are shown in Table I in comparison with values obtained for uncrosslinked systems¹³ and other crosslinked systems involving a DGEBA resin cured with several aliphatic diamines.¹⁴

Figure 15 shows a plot of $\tan \delta$ maximum vs. M_c for this work for both the neat resin and the glass braid composite. Data by Murayama and Bell¹ for the Epon 828/MDA neat resin system is also shown in Figure 15 for comparison. The increase in $\tan \delta$ maximum with increasing M_c reflects the increasing ability of the polymer to absorb energy as the molecular constraints are reduced. As

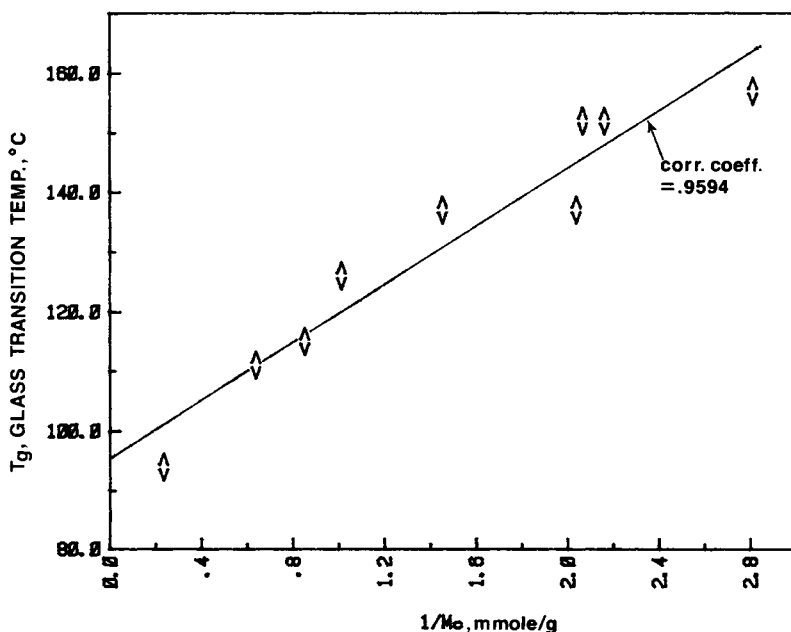


Fig. 14. Glass transition temperature (T_g) vs. $1/M_c$ for the ultimately cured neat resin of the Epon 828/mixed amine system.

TABLE I
 T_g-1/M Relationships

Polymer	$T_{g\infty}$ (K)	K , (g °C/mmol)	Ref.
Polystyrene	373	120	Fox and Loshaek ¹³
PMMA	378	60-150	
DGEBA/mixed amine	369	24.2	This work
DGEBA/EDA ^a	—	52.3	Horie et al. ¹⁴
DGEBA/TMDA ^b	—	46.1	
DGEBA/HMDA ^c	—	39.5	

^a Ethylenediamine.

^b Trimethylenediamine.

^c Hexamethylenediamine.

the distance between crosslinks becomes larger, $\tan \delta$ maximum becomes independent of M_c at the point where M_c equals the length of a statistical chain segment. After this point, a further increase in M_c has little effect on $\tan \delta$ maximum.¹ For the data of Murayama and Bell, it appears that the molecular weight of a statistical segment is about 900. For the data from this work there is considerable scatter, but it appears that the molecular weight of a statistical segment is at least 3000. For the glass braid composite corrected for the interaction between the epoxy matrix and glass fibers, the molecular weight of a statistical segment is about 300. Figure 15 also shows that $\tan \delta$ maximum is

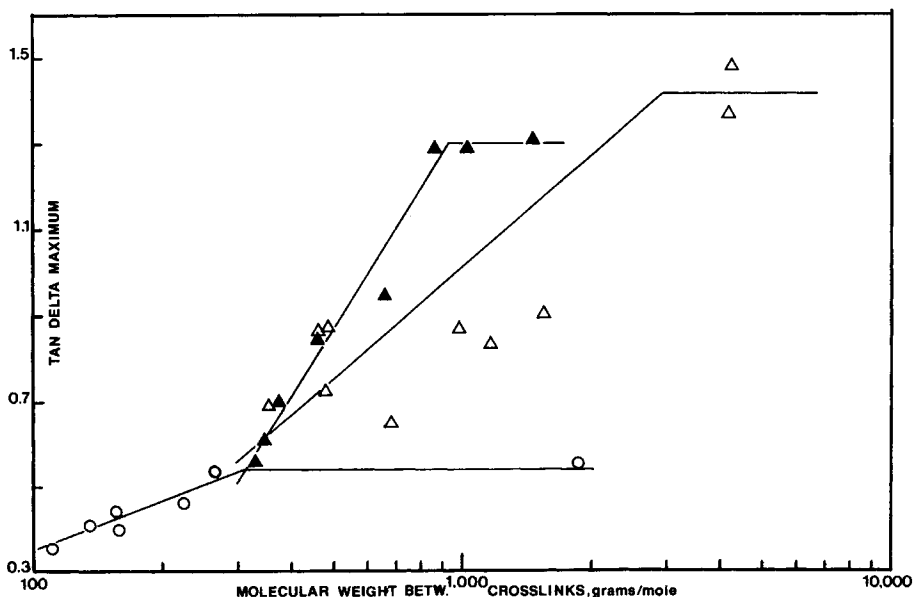


Fig. 15. $\tan \delta$ maximum vs. molecular weight between crosslinks for the neat resin and glass braid composite: (Δ) this work [Epon 828/(MDA + *m*-PDA)] for neat resin on a DMTA at 10 Hz; (\blacktriangle) Murayama and Bell¹ [Epon 828/MDA] for neat resin on a Vibron at 11 Hz; (\circ) this work [Epon 828/(MDA + *m*-PDA)] for glass braid composite on a DMTA at 10 Hz.

less for the composite than for the neat resin, which is expected since the glass fibers restrict molecular mobility.

SUMMARY

This work utilized dynamic mechanical spectroscopy to determine the effect of varying the epoxy/amine ratio on the final properties of an ultimately cured epoxy system containing a DGEBA-type resin and a mixed aromatic amine curing agent. Although there are several examples in the literature of the use of dynamic mechanical spectroscopy to determine the effect of stoichiometric ratio on the final properties of an ultimately cured epoxy-amine system, they are primarily for a single amine curing agent.

For this work, optimum cure temperatures were determined as a function of stoichiometry by measuring the change in modulus from a partial B-stage cure to an ultimate C-stage cure for dynamic mechanical flexural measurements. The optimum cure temperature for the stoichiometric ratio of epoxy/amine was about 30°C higher than that for the excess epoxy or excess amine ratios. These results are similar to those obtained from a time-temperature-transformation (TTT) cure diagram for the same epoxy system in our earlier paper.

From temperature scans on the ultimately cured neat resin, the glass transition temperature (T_g) and activation energy (E_a) passed through a maximum at the stoichiometric ratio. The molecular weight between crosslinks (M_c) passed through a corresponding minimum. The T_g of the ultimately cured neat resin was found to be a linear function of $1/M_c$. The sub- T_g and E_a (sub- T_g) of the ultimately cured neat resin, which are associated with a secondary molecular transition, also passed through a maximum near the stoichiometric ratio. The use of two-ply glass braid filler in the epoxy system had little effect on the value of the primary T_g , but did lower the $\tan \delta$ maximum and also broadened the $\tan \delta$ peak in the T_g region. However, the molecular weight between crosslinks (M_c) of the glass braid composite was considerably lower than that of the neat resin for the range of stoichiometry considered. The M_c values of the composite, which were estimated from the linear rule of mixtures, account for the interaction between the epoxy matrix and the glass fibers.

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