

Crosslinking of an Epoxy with a Mixed Amine as a Function of Stoichiometry. I. Cure Kinetics via Dynamic Mechanical Spectroscopy

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Synopsis

Variation of the epoxy/curing agent ratio by as much as ± 10 wt % from the stoichiometric 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 as determined by dynamic mechanical measurements. A sample preparation technique was developed for monitoring the cure of glass reinforced epoxy in flexure. Shear measurements were also made on the neat resin. From gel time flexural data, the activation energy of cure passed through a maximum at the stoichiometric ratio of epoxy/amine for a glass cloth composite. In shear for the neat resin, a minimum was observed. By considering the curing of the mixed system to follow third-order kinetics, overall reaction rate constants were estimated after the gel point.

INTRODUCTION

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. This work focuses on the use of dynamic mechanical spectroscopy to study the effect of stoichiometric ratio on the curing behavior of an epoxy system consisting of a diglycidyl ether of bisphenol A (DGEBA) resin cured with a mixed aromatic amine curing agent. A number of workers have studied the effect of stoichiometry on the final mechanical and dynamic mechanical properties of a cured epoxy/amine system.¹⁻³ Although other workers have reported the effect of the epoxy/amine ratio on cure kinetics by DSC and FTIR methods,^{4,5} the effect of stoichiometry on the cure kinetics of epoxy/amine systems using dynamic mechanical spectroscopy is not very prominent in the literature.

Several dynamic mechanical instruments are available to monitor the cure of epoxy resin systems. Senich et al.⁶ used dynamic spring analysis (DSA) to study the curing behavior of two epoxy resins composed of the tetrafunctional amine dicyandiamide. For curing studies, about 15 mg of mixed epoxy sample as a 50 wt % methylene chloride solution was applied to a steel wire spring in a Rheovibron at the isothermal cure temperature and at frequencies of 3.5, 11,

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35, and 110 Hz. The position of the loss modulus maximum with time (t) was found to vary with the isothermal cure temperature (T); from this a plot of $\ln(t)$ vs. $1/T$ for each frequency yielded the activation energy of cure. First-order rate constants (k) were also determined from the slope of a plot of \log viscosity vs. time for several cure temperatures, based on the knowledge of the viscosity frequency product being a constant at the $\tan \delta$ maximum. From a plot of $\ln(k)$ vs. $1/T$, the activation energy of cure was also calculated.

Babayevsky and Gillham⁷ studied the cure reaction of a DGEBA epoxy resin with several aromatic diamines by torsional braid analysis (TBA). In this method, a glass fiber braid was impregnated with the mixed epoxy sample as a 60 wt % acetone solution, dried in vacuum at room temperature for 60 min, and mounted in the apparatus at the isothermal cure temperature. For TBA, information about the rigidity of the specimen during cure is obtained from the natural oscillation frequency of the specimen. Overall activation energies and apparent overall rate constants of the cure reactions based on third-order overall kinetics were determined by assuming that the isothermal relative rigidity is directly proportional to the crosslink density after the gel point in the rubbery state.

Torsion impregnated cloth analysis (TICA) is similar to TBA in that for cure studies the mixed epoxy sample is supported on a glass cloth substrate.⁸ The main difference between TICA and TBA is that the TICA uses a forced torsion technique, whereas the TBA uses a free oscillation technique as described earlier. For TICA, the sample is sinusoidally strained in a fixed frequency mode, and this mode has the advantage of being able to obtain fixed frequency data as well as multifrequency data in a later experiment. Lee⁸ performed the TICA experiments with a Rheometrics spectrometer to characterize the resin curing behavior.

The fixed frequency/multifrequency option used in TICA is also available in the Polymer Laboratories dynamic mechanical thermal analyzer (DMTA), where the sample is flexed through a fixed strain displacement. Wetton et al.⁹ studied epoxy resin curing by mounting the mixed sample on a thin piece of stainless steel shim.

Because of the sample supports used, all of the above methods have the disadvantage of making the evaluation of the absolute value of the resin modulus very difficult for epoxy curing. Vratsanos and Farris¹⁰ minimized the sample support problem by using a soft rubber membrane (e.g., the end of a rubber balloon) to support the mixed epoxy resin during cure in a Dynastat mechanical spectrometer. The soft rubber membrane contributed much less to the overall modulus during cure than the other sample support methods described earlier. Harran and Laudouard¹¹ totally eliminated the need for a sample support by making shear measurements between parallel plates on the neat mixed epoxy resin by use of an Instron rheometer. Polymer Laboratories has recently developed a torsion head for the DMTA by which the neat mixed epoxy resin is placed between parallel plates and dynamic mechanical and dielectric properties can be studied simultaneously during cure of the epoxy sample.¹²

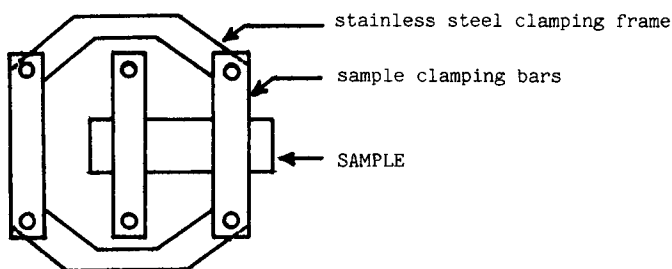
For this work, the epoxy/amine ratio was varied and the dynamic mechanical response was determined for the conversion of the mixed system to a partial B-stage cure condition to yield the isothermal cure kinetics.

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, as shown in Figure 1. For cure kinetics, samples were run in both flexure and shear at isothermal temperatures from 80 to 150°C. A heating rate of 12°C/min was used to ramp from room temperature to the desired isothermal temperature. Each sample was run at a single frequency, primarily at 30 Hz. In the flexural mode, the mixed resin was mounted between two pieces of stainless steel shimstock (0.002 in. thick), and the sample geometry is shown in Figure 2 as well as in an earlier paper.¹³ Two types of samples were prepared for measurements in the flexural mode: the neat resin mounted on the steel shim within a glass cloth border, and a composite sample

FRONT VIEW



TOP VIEW

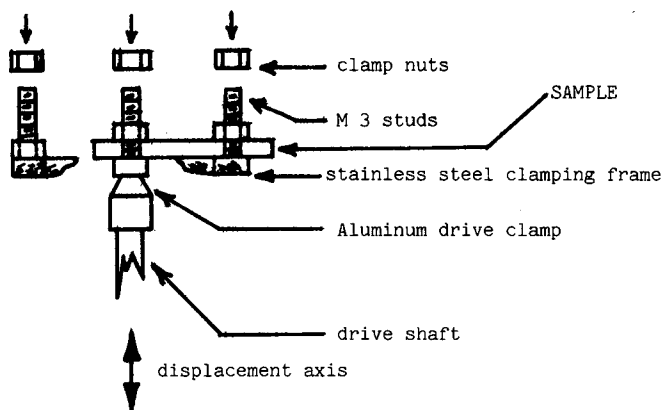


Fig. 1. Sample mounting in the flexural mode with single cantilever bending for the dynamic mechanical thermal analyzer (DMTA).

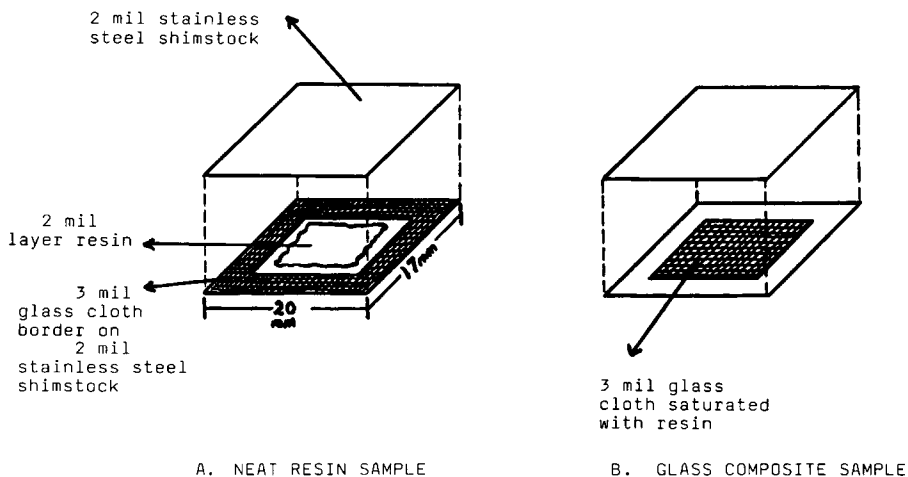


Fig. 2. DMTA flexural measurements: Sample geometry for the mixed system to B-stage cure for the neat resin and a glass cloth composite.

made by rolling the neat resin into the glass cloth with the stem of a disposable pipette. In the latter sample, the epoxy/glass cloth composite contained an average of 50% glass by weight. The glass cloth used was Owens-Corning Fiberglas glass yarn (0.003 in. thick). The method of coating the resin onto steel shim for monitoring the epoxy cure by DMTA analysis is also described by Wetton et al.⁹ For shear measurements, only the neat resin was analyzed using the shear assembly shown in Figure 3. Shear surfaces were covered with copper foil tape to protect the aluminum surface from the epoxy during cure.

The epoxy resin used was a diglycidyl ether of bisphenol-A (DGEBA), Shell Epon 828, and the aromatic amine, 360L, was manufactured by 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

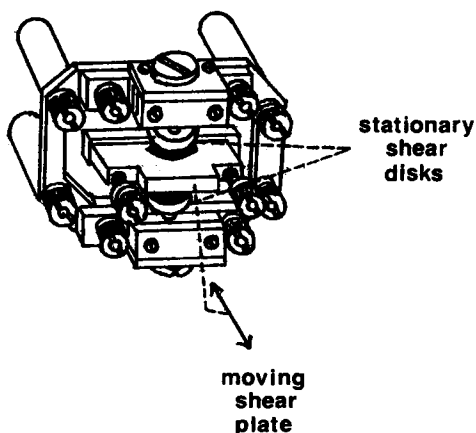
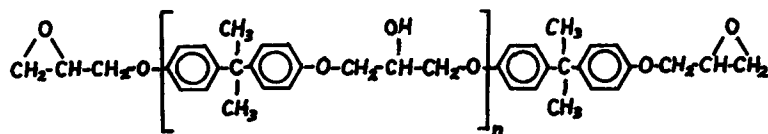


Fig. 3. DMTA shear assembly: Mixed resin is mounted between stationary disks and a moving shear plate. The arrows indicate the direction of shear.

fractions included. The primary components of the epoxy system are shown in Figure 4. Both the resin and curing agent were used without further purity. The resin has an epoxide equivalent weight of 185 and the mixed amine has an active hydrogen equivalent weight of 37. The recommended stoichiometric ratio of epoxy to amine was 81–19 wt %. This ratio is not really stoichiometric, but is 1.2 for the ratio of amine hydrogen equivalents to epoxide equivalents initially. However, we find in this paper and in a later paper¹⁴ that this epoxy/amine ratio yields maximum values for glass transition temperature (T_g), modulus, and crosslink density. The recommended B-stage cure was 250–275°F (129°C) for 30–45 minutes, followed by a C-stage cure of 300°F (149°C) for 2 h. Studies were conducted by varying the concentration of Epon 828 by ± 2 , ± 5 , and ± 10 wt % from the stoichiometric value of 81 wt %. All samples were hand mixed for 2 min and degassed under vacuum for 15 min prior to thermal curing. The degassing step was done to minimize bubble formation in the sample upon curing. The Epon 828/mixed amine system is a slow curing system at room temperature—the gel time of a stoichiometric mixture of epoxy/amine was over 7 h at 30°C. Therefore, the amount of curing that takes place in the 15-min degassing step prior to thermal curing was considered negligible. Samples were also prepared for the epoxy cured with each of the separate amines, MDA and *m*-PDA. A stoichiometric amount of each amine was melted, mixed with the required epoxy, and then quenched in an ice bath to minimize further reaction.

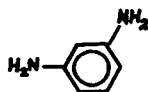
RESULTS AND DISCUSSION

The isothermal cure kinetics of the mixed system to the B-stage was determined by the method outlined by Senich et al.⁶ for two epoxy resins cured with

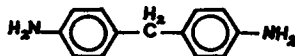


Diglycidyl ether of bisphenol A (DGEBA) epoxy resin

Shell Epon 828 ($n \approx 0.1$)



m-Phenylenediamine (*m*-PDA)



Methylenedianiline (MDA)

Fig. 4. The epoxy system used in this work: A DGEBA epoxy resin (Shell Epon 828) and a mixed aromatic amine curing agent (Magnolia Plastics 360L).

dicyandiamide by dynamic spring analysis (DSA). They used the elapsed time to the peak maximum of $\tan \delta$ as a measure of the rate of the reaction at each temperature and frequency. The slope of a plot of $\ln(t_{\max})$ vs. $1/T$ was then used to determine the activation energy.

Some of the flexural data is shown in Figures 5 and 6 for cure of the epoxy/glass cloth composite with the stoichiometric ratio of epoxy/amine at several isothermal temperatures. In Figure 5, a plot of log flexural modulus (E') vs. time, the highest final value of the modulus is shown at 100°C. The magnitude of the loss peak, $\tan \delta$, is also highest at 100°C as shown in Figure 6. The lowest final values of E' in Figure 5 for the samples cured at 120 and 150°C can be attributed to the cure temperatures approaching the T_g of the fully cured system for the stoichiometric ratio.¹⁰ The 120 and 150°C curves for E' reach a final value near the same lowest cure time; thus 120°C appears to be an optimum cure temperature. Since the viscosity of the curing resin varies with both temperature and time, these two parameters are very important in the processing of thermoset composite parts (e.g., in aerospace applications) where precise viscosity control is required.¹⁵ Figure 6 shows that the $\tan \delta$ peaks for the 120 and 150°C samples are the smallest in area and are similar in size, which is another reason we might choose 120°C as an optimum cure temperature. A smaller area for the $\tan \delta$ peak implies that the material has a greater ability to absorb energy for a given cure temperature. Figures 7 and 8 show that, for shear measurements on the neat resin, the highest final value of the modulus is also at 100°C for both stoichiometric and excess amounts of amine. Shear

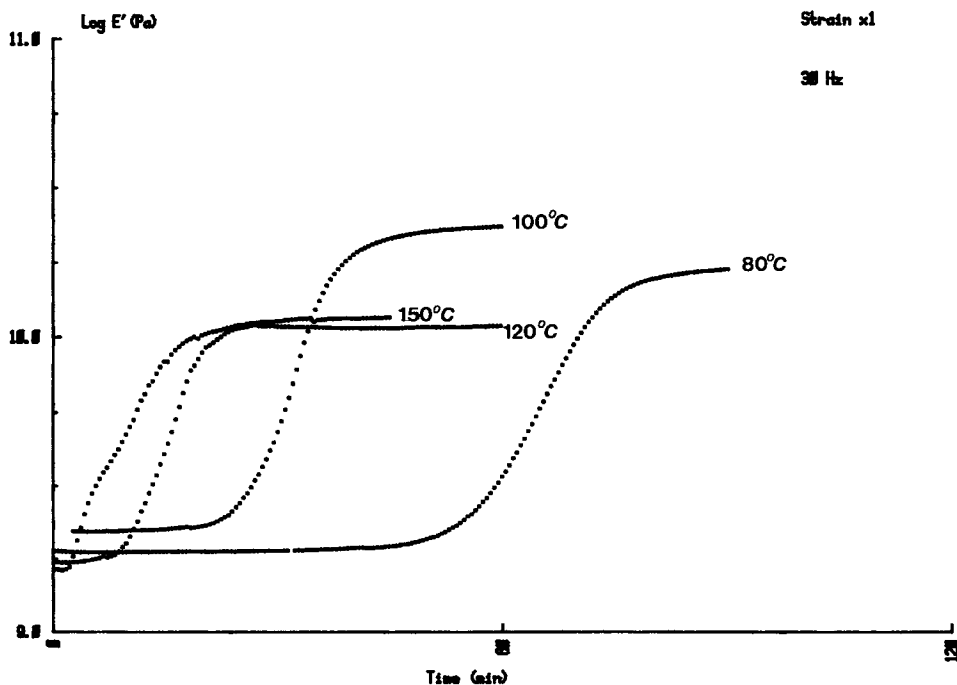


Fig. 5. Flexural modulus E' vs. cure time for the stoichiometric ratio of epoxy/amine on glass cloth at several cure temperatures.

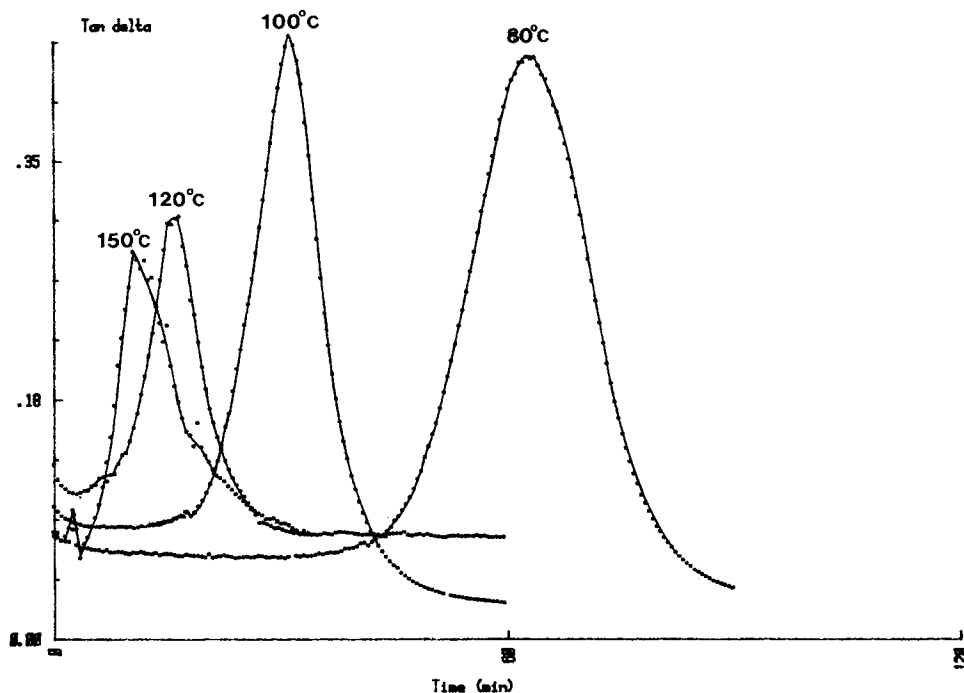


Fig. 6. $\tan \delta$ vs. cure time for the stoichiometric ratio of epoxy/amine on glass cloth at several cure temperatures.

measurements showed the stoichiometric ratio of epoxy/amine to be the optimum ratio for complete conversion at a given isothermal temperature in a plot of modulus versus time, as shown in Figure 9. In Figure 9, the difference between the final modulus values for the -10 wt % and stoichiometric curves appears to be statistically insignificant. However, dynamic mechanical data for the fully cured neat resin¹⁴ later revealed the glass transition temperature for the stoichiometric sample (155°C, 1 Hz) to be considerably higher than that of the -10 wt % sample (113°C, 1 Hz). The crosslink density of the stoichiometric sample was also considerably higher than that of the -10 wt % sample for the fully cured system.¹⁴ In Figure 9, the -10 wt % curve for E' reaches a final value in a shorter time than that of the stoichiometric curve, but the difference in T_g and crosslink density between the two samples must be considered as well. Figure 10 shows a plot of flexural modulus vs. temperature for the stoichiometric ratio of epoxy/amine that was B-stage cured (from the mixed resin to partial crosslinking) at several cure temperatures. There appears to be little difference in the rubbery plateau shear modulus (and, therefore, the degree of crosslinking) for the three samples. But the T_g is strongly dependent on cure conditions in Figure 10, and this is why we must consider other parameters. It is also important to use other techniques such as FTIR and DSC to follow the mechanism of the curing reactions for a particular cure condition, as was done in another paper on this same epoxy system.¹⁶

In Figure 6, there is a shoulder at the beginning of the $\tan \delta$ peak at 120°C. At 150°C, the shoulder has become an initial small peak. Enns and Gillham¹⁷

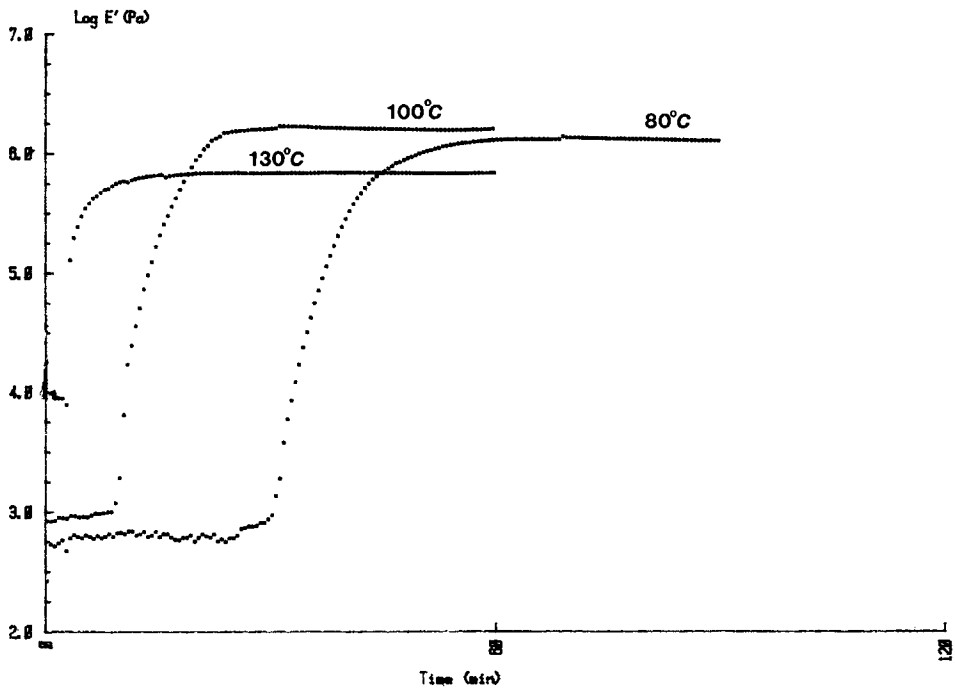


Fig. 7. Shear modulus vs. cure time for the stoichiometric ratio of neat resin at several cure temperatures.

also observed this behavior with increasing cure temperature for torsional braid analysis (TBA) of an amine-cured epoxy. They attributed the first peak to a liquid-to-rubber transformation (gelation) and the second peak to a rubber-to-glass transformation (vitrification). For this work, the gelation peak was difficult to locate at lower isothermal cure temperatures (e.g., $\leq 100^\circ\text{C}$) because of the influence of vitrification. The gel point was found to be easier to obtain by a $\log E''$ vs. time plot than by a $\tan \delta$ vs. time plot. The gel point was identified with a change in slope on the shoulder of the vitrification peak at lower cure temperatures, a method described by Harran and Laudouard.¹¹ Figure 11 shows a plot of $\log E''$ vs. time for the stoichiometric ratio of Epon 828/*m*-PDA on glass cloth in flexure at several isothermal temperatures. The gel point is indicated by the arrows as a change in slope on the shoulder of the vitrification peak at 80 and 100°C . At 120 and 130°C , the gel point is obviously indicated by an initial small peak. In shear, the gel point of the neat resin could be found on the time axis by locating the point at which E' and E'' cross each other. This is a method described by Winter,¹⁸ and is shown for this work in Figure 12 for the excess epoxy and stoichiometric samples of neat resin at 100°C . This technique could not be used for the samples mounted on steel shim in flexure because the shim increased the stiffness of the sample to the degree that E' and E'' never crossed over during the curing reaction.

Arrhenius Plots

Figure 13 shows an Arrhenius plot based on the time to gel for the stoichiometric ratio of epoxy to amine for several samples in flexure and shear at a

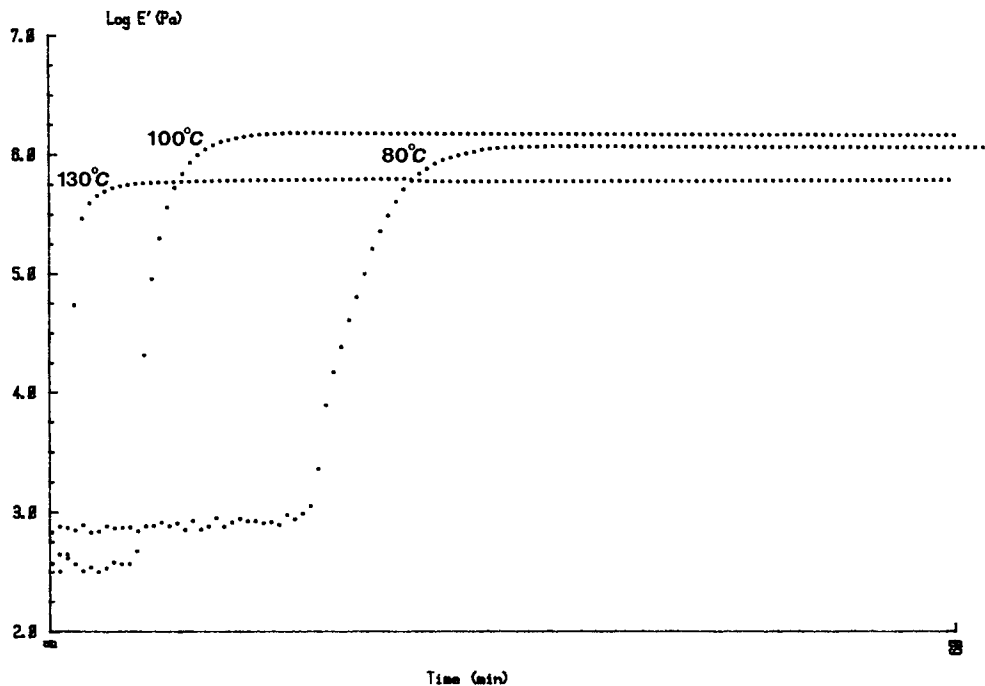


Fig. 8. Shear modulus vs. cure time for the neat resin containing 10 wt % amine in excess of the stoichiometric amount, at several cure temperatures.

DMTA frequency of 30 Hz. Figure 13 shows that the gelation time for the glass cloth composite in flexure is less than that for the neat resin in flexure. This could be due to the glass fiber surface helping to supply the minimum amount of hydroxyl (OH) groups required to initiate autoacceleration of curing.¹⁹ The OH groups from the glass fibers are in addition to the OH groups initially present in the uncured DGEBA epoxy resin. Also, OH groups are formed during the epoxy/amine curing reaction—an OH group is produced for every epoxide group consumed. Figure 13 also shows an attempt to minimize the curing of the sample that takes place in heating the DMTA from room temperature to the isothermal cure temperature. For several runs, the DMTA sample head was preheated to near the cure temperature just prior to loading the sample. The results are shown in Figure 13 for the glass cloth composite, and the plots are almost parallel for the preheated and nonpreheated samples. This indicates that the activation energy is almost the same for each cure condition, but that the gelation times are shorter for the preheated samples. Figure 13 also shows that the gelation times are shorter for the neat resin in shear than for the corresponding sample in flexure. Activation energies of cure (E_a) were determined from the slope of an Arrhenius plot such as Figure 13. Values of E_a and gelation times are summarized for flexural and shear measurements at a frequency of 30 Hz for several epoxy/amine ratios in Table I. The activation energies of the individual amine components (*m*-PDA and MDA) are shown to be close agreement with the E_a of the epoxy-mixed amine system. Table I also compares the data from this work with that of similar epoxy curing systems

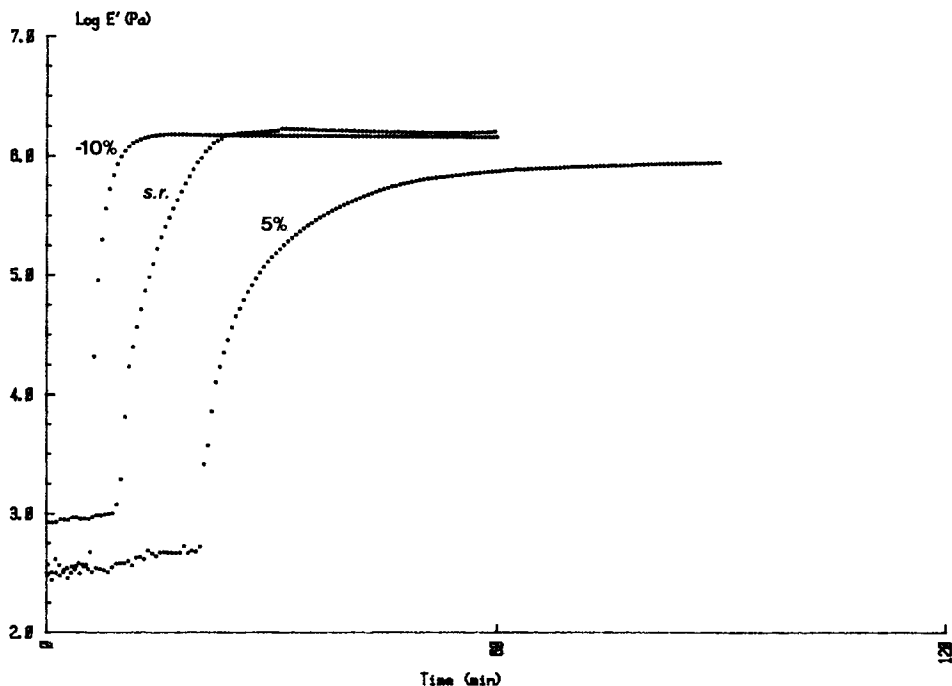


Fig. 9. Shear modulus vs. cure time for several epoxy/amine ratios of neat resin at a cure temperature of 100°C.

in the literature.^{7,11} Although the gelation times from this work are not in close agreement with those in the literature due to different methods of cure monitoring (as well as differences in degassing and mixing times), the activation energies from this work are in good agreement with those in the literature. The data listed in Table I is at 30 Hz; gel time data was also obtained at other frequencies for several epoxy/amine ratios as shown in Figure 14. It was found that gel time was not strongly dependent on frequency except at low cure temperatures (e.g., 60°C), an observation also made by Senich et al.⁶ They used dynamic spring analysis to monitor the cure of two epoxy resins with dicyandiamide at temperatures of 80–110°C and frequencies of 3.5–110 Hz. They also showed that the operating frequency had little effect on the activation energy of cure.

Figure 15 shows an Arrhenius plot based on the time to vitrify (from the $\tan \delta$ maximum) for several epoxy/amine ratios in flexure. The curved portions of the plots indicate that gelation begins to dominate at higher cure temperatures, but that vitrification dominates when the cure temperature is sufficiently below that of the glass transition temperature of the ultimately cured resin.²⁰ The E_a values for vitrification, as well as those for gelation from Table I, are plotted as a function of stoichiometry (B , amine hydrogen eq/epoxide eq, initially) in Figure 16 for data at 30 Hz. For gelation, the E_a of the glass cloth composite in flexure passed through a maximum at $B = 1.2$, while the E_a of the neat resin in shear passed through a corresponding minimum. For vitrification, the E_a appears to approach a limiting value as the amount of amine is increased

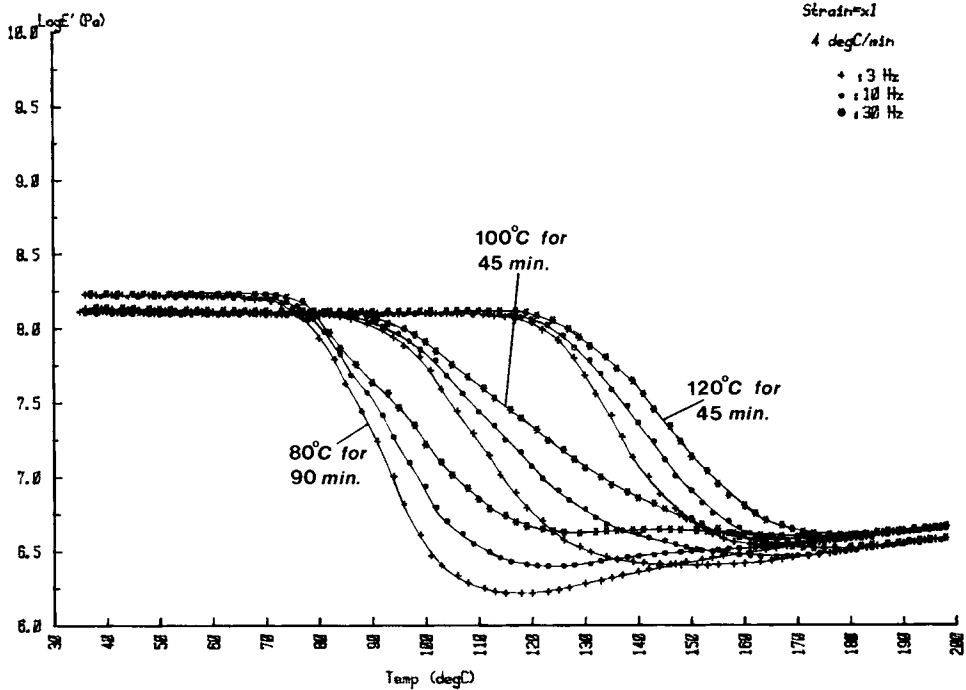


Fig. 10. Flexural modulus vs. temperature for the stoichiometric ratio of neat resin at several B-stage cure temperatures.

in excess of the stoichiometric amount. The E_a values calculated from rate constant data are shown to pass through a minimum at $B = 1.2$ for both the glass cloth composite in flexure and the neat resin in shear. Also shown in Figure 16 is DSC data by Foun et al.²¹ for an epoxy system very similar to the one used in this work. Instead of using a single DGEBA resin, they used a 80/20 mixture of a DGEBA resin (Shell Epon 826) and butanediol diglycidyl ether, DGBE. For the curing agent they used Tonox 60/40, which is a mixed aromatic diamine and is essentially the same as the Magnolia 360L used in this work. They calculated two activation energies, E_1 and E_2 , which were obtained from an autocatalytic mechanism involving two rate constants (k_1 and k_2). The rate constants k_1 and k_2 correspond to the consumption of primary amine and the formation of secondary amine, respectively. Figure 16 shows that the data by Foun et al. passes through a maximum near $B = 1.1$ for both E_1 and E_2 .

Actually, the activation energy of cure should be independent of stoichiometry if one considers the curing reaction between a diepoxide and a diamine. For the most simple rate expression, the rate of disappearance of epoxide can be expressed as

$$-dE/dt = k[E][H][OH], \quad k = A \exp(-E_a/RT) \quad (1)$$

where $[E]$ is the concentration of epoxide, $[H]$ is the concentration of equivalent amine hydrogens in the diamine, $[OH]$ is the concentration of hydroxyl groups

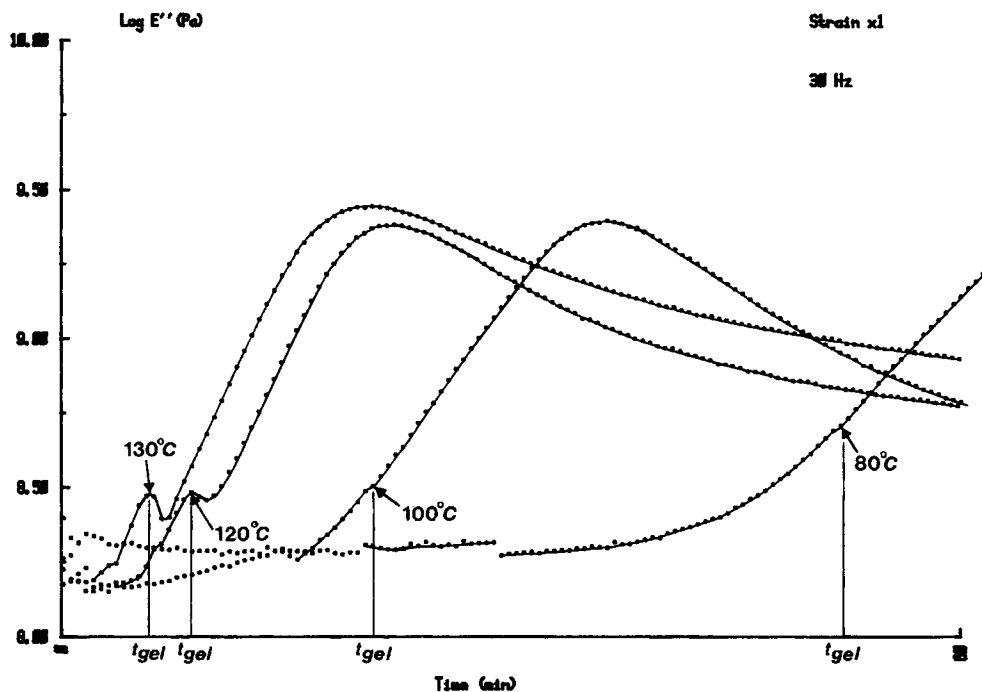


Fig. 11. Loss modulus E'' vs. time for the stoichiometric ratio of Epon 828/*m*-PDA on glass cloth in flexure at several isothermal temperatures.

initially present in the diepoxide, plus those that are formed during the reaction and act as a catalyst, and k is the rate constant. Since the activation energy term E_a is contained in the rate constant k in eq. (1) and is outside of the concentration terms, E_a should be independent of stoichiometry.²² We do not observe this in Figure 16, even though not many data points are shown for this work. However, it is shown in another paper¹⁴ that when more data points were included, the activation energy for a *fully cured system* also passed through a maximum at $B = 1.2$. The fact that the activation energy shows some dependence on stoichiometry is not surprising if one considers that the epoxy-amine curing reaction is not a "clean" reaction. For stoichiometric and excess amounts of amine, the additions of the primary and secondary amino group to the epoxy group are the normal reactions. However, when excess epoxy is used, the epoxy groups react with the forming hydroxyl groups.²³

TTT Cure Diagrams

The times to gelation and vitrification can be shown on the same plot as a function of cure temperature in a time-temperature-transformation (TTT) cure diagram, as described by Enns and Gillham²⁴ for thermosetting resins. Several of these diagrams are shown for data from this work in Figures 17-19 for flexural measurements made at a frequency of 30 Hz. Figure 17 shows data for glass cloth composites with several epoxy/amine ratios. The glass transition temperature of the ultimately cured resin, $T_{g\infty}$, was determined by taking sam-

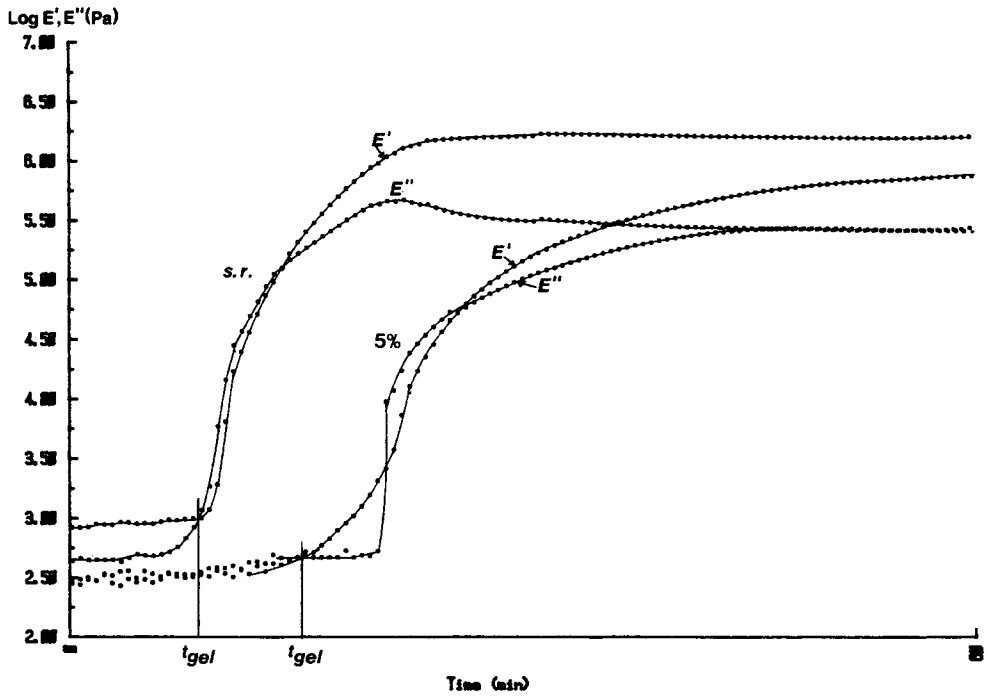


Fig. 12. Location of gel time by crossover of loss and storage moduli for two epoxy/amine ratios of neat resin in shear at a cure temperature of 100°C.

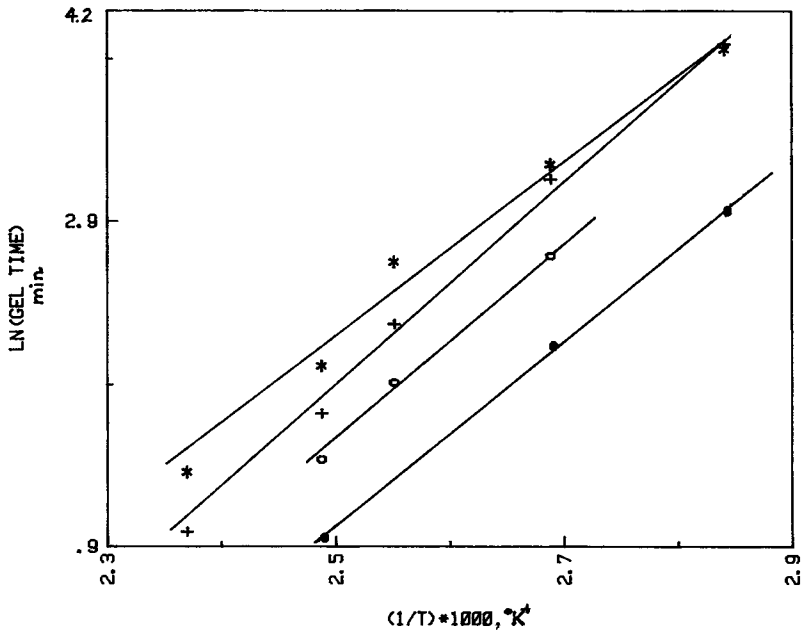


Fig. 13. Arrhenius plot based on gel time for the stoichiometric ratio of epoxy/amine for several conditions: (*) neat resin in flexure; (+) glass cloth composite in flexure; (O) glass cloth composite in flexure for the DMTA preheated prior to data collection; (●) neat resin in shear.

TABLE I
Gelation Times and Overall Activation Energies of Cure for Epoxy/Diamine Reactions by Dynamic Mechanical Analysis at 30 Hz

Reactive system	Epoxy/amine ratio (wt %)	Mode of measurement	Reinforcement	Gelation time t_g (min)										F_g (kcal/mol)	Corr. coeff.
				60°C	80°C	100°C	110°C	120°C	130°C	140°C	150°C				
DGEBA/mixed amine ^a	0 (stoic.)	Flexure	Glass cloth	129	50.7	23.5	—	9.7	5.6	—	2.7	12.0	0.997		
	0	Flexure	None	137	52.4	25.8	—	14.2	7.5	—	3.9	10.8	0.996		
	0	Shear	None	—	19.4	8.5	—	—	2.6	—	—	11.3	0.999		
	-10	Flexure	Glass cloth	75.4	30.6	15.3	11.4	7.1	—	—	—	9.9	0.998		
	-10	Shear	None	—	14.4	6.1	—	—	1.5	—	—	12.8	0.998		
	+5	Flexure	Glass cloth	179	85.8	40.1	29.5	—	—	—	—	9.2	0.999		
DGEBA/MDA	+5	Shear	None	—	50.0	15.6	—	—	5.0	—	—	12.9	0.996		
	0	Flexure	Glass cloth	—	47.2	17.3	—	8.7	—	4.2	—	11.5	0.999		
	0	Shear	None	—	39.4	19.4	—	—	4.9	—	—	11.9	0.994		
	0	Torsion ^b	Glass braid	—	—	—	—	12	—	8	6	9	0.980		
	0	Shear/rheometry ^c	None	—	111.5	46	33	22	18	11	7.5	10.8	0.996		
	0	Flexure	Glass cloth	—	52	20.2	—	8.7	5.9	—	—	12.3	0.999		
DGEBA/ <i>m</i> -PDA	0	Torsion ^b	Glass braid	—	55	30	—	13	—	6	—	11	0.995		
	0	Shear/rheometry ^c	None	—	92	44	30.5	22	15	12	8	10.4	0.999		

^a Mixed amine = primarily a 50/50 mixture of *m*-PDA and MDA (this work).

^b Work by Babayevsky and Gillham at 1 Hz.⁷

^c Work by Harran and Laudouard at 30 rad/s.¹¹

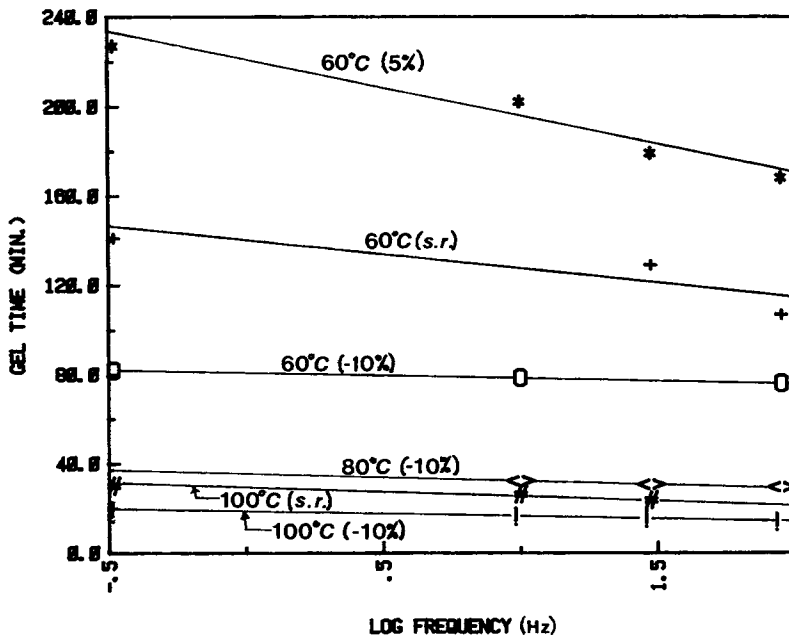


Fig. 14. Gel time vs. log frequency for several epoxy/amine ratios and cure temperatures.

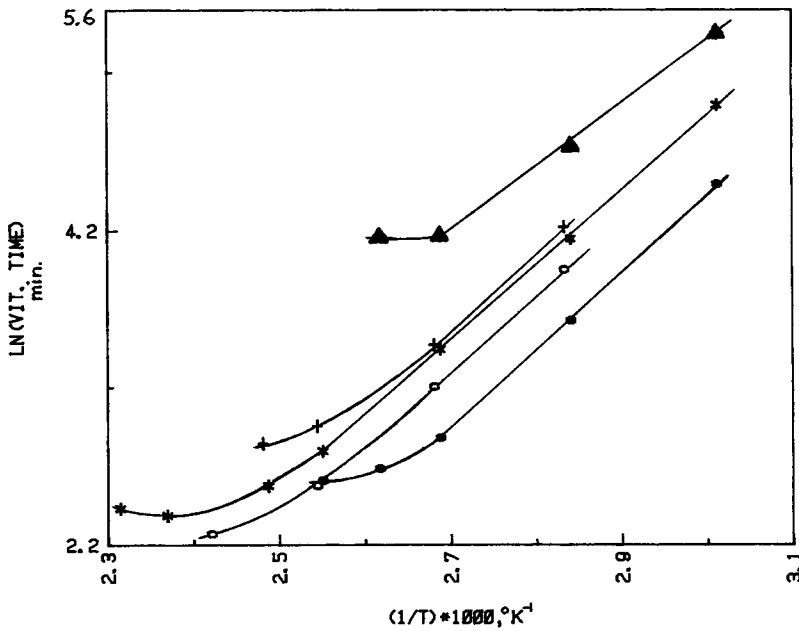


Fig. 15. Arrhenius plot based on vitrification time for several DGEBA-amine systems on glass cloth: (▲) +5 wt % (mixed amine); (+) stoichiometric (*m*-PDA); (*) stoichiometric (mixed amine); (○) stoichiometric (MDA); (●) -10 wt % (mixed amine).

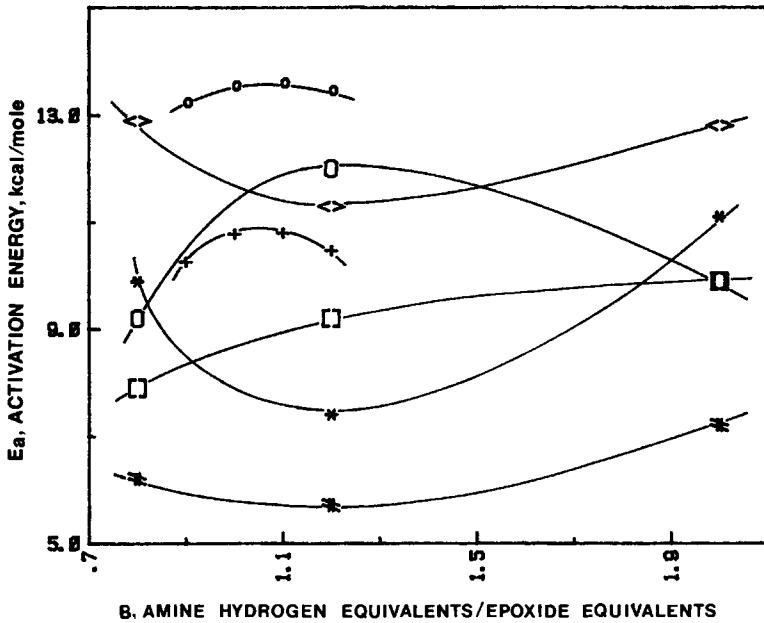


Fig. 16. Activation energy of cure vs. epoxy/amine ratio for the DGEBA/mixed amine system for several conditions: (O) = gel time (flexure) for glass cloth composite; (\diamond) gel time (shear) for neat resin; ([]) vitrification time (flexure) for glass cloth composite; (*) calculated rate constant for neat resin; (#) calculated rate constant (flexure) for glass cloth composite; (o) Foun et al.²¹ (DSC work for rate constant k_1); (+) Foun et al.²¹ (DSC work for rate constant k_2).

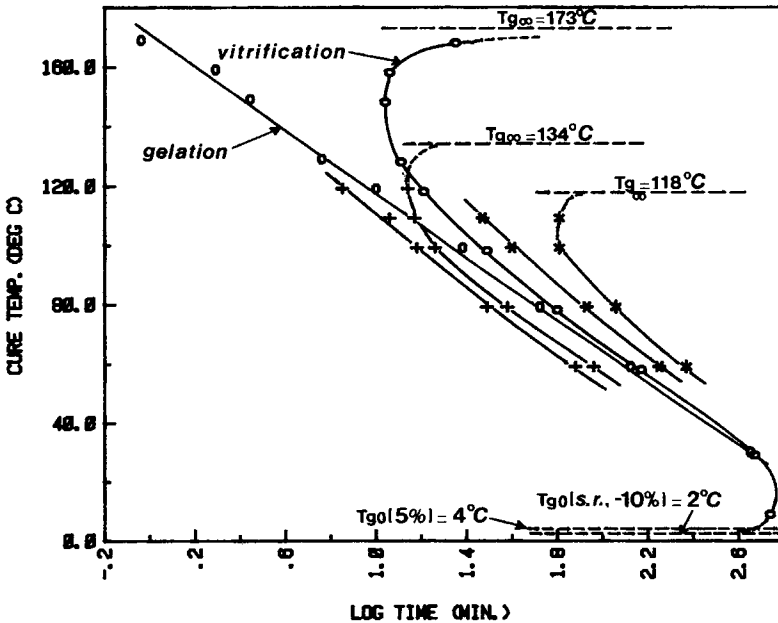


Fig. 17. Time-temperature-transformation (TTT) cure diagram for several epoxy/amine ratios on glass cloth in steel shim sandwich at a frequency of 30 Hz: (+) -10 wt %; (O) stoichiometric (s.r.); (*) +5 wt %.

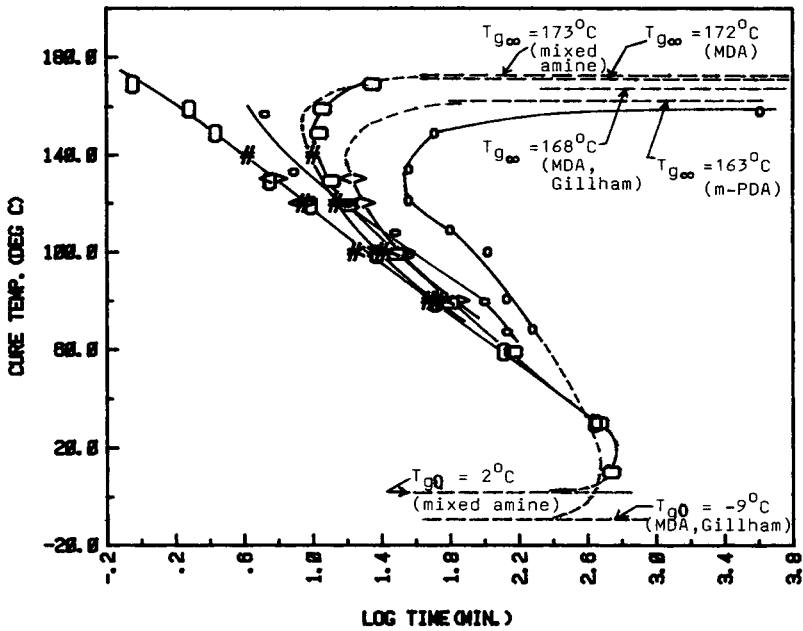


Fig. 18. Time-temperature-transformation (TTT) cure diagram for the stoichiometric amount of several epoxy/amine systems on glass cloth at a frequency of 30 Hz: (O) Epon 828/mixed amine; (◇) Epon 828/*m*-PDA; (#) Epon 828/MDA; (○) Epon 828/MDA (Enns and Gillham²⁶).

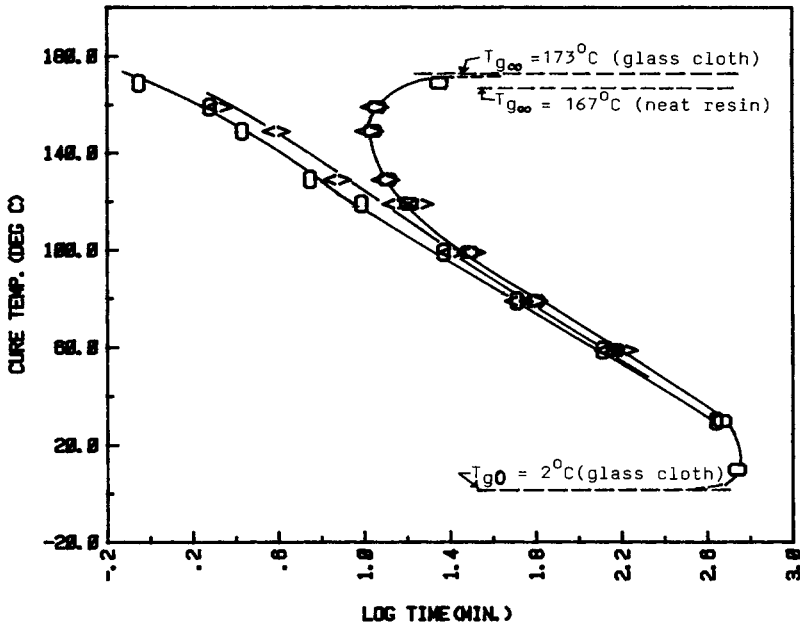


Fig. 19. Time-temperature-transformation (TTT) cure diagram for the stoichiometric ratio of Epon 828/mixed amine as the neat resin and a glass cloth composite in a steel shim sandwich at a frequency of 30 Hz: (◇) neat resin; (○) glass cloth composite.

ples that were partially cured at several isothermal temperatures and curing them at a C-stage cure of 149°C for 2 h. These samples were then scanned in temperature at 30 Hz to obtain $T_{g\infty}$. An average value of $T_{g\infty}$ was obtained at a given epoxy/amine ratio. The glass transition temperature of the freshly mixed uncured resin, T_{g0} , was obtained for each epoxy/amine ratio from a single temperature scanning experiment at 30 Hz. Figure 17 shows that T_{g0} was about the same, within experimental error, for all three epoxy/amine ratios. The vitrification curve is shown to S-shaped. At higher cure temperatures the time to vitrification passes through a minimum due to the opposing influences of the reaction rate constant and the decreasing concentration of reactants at vitrification as $T_{g\infty}$ is approached.²⁴ Knowledge of this minimum time and the corresponding temperature is useful in molding technology.²⁵ The minimum time and corresponding temperature [time (min), temp (°C)] are shown in Figure 17 for the stoichiometric, 10% excess amine and 5% excess epoxy samples, respectively: [11, 150], [14, 120], and [63, 105]. Thus, the stoichiometric ratio of epoxy/amine appears to give the optimum cure conditions for molding or other processing techniques.

Figure 18 shows a TTT cure diagram for the stoichiometric ratio of Epon 828/amine on glass cloth at 30 Hz for several amines. Figure 18 shows that the gelation and vitrification curves for the Epon 828/(*m*-PDA + MDA) system are very similar to those of the Epon 828/*m*-PDA and Epon 828/MDA systems. Figure 18 also shows the curves for the Epon 828/MDA system from the data obtained by Enns and Gillham²⁶ for torsional braid analysis (TBA) at 1 Hz. For TBA, a glass braid is used for a sample support as was used for this data. However, although the separate amines were melted for this work prior to mixing with the epoxy and mounting on the glass cloth, for the TBA the separate amine was mixed with the epoxy in a solution of methyl ethyl ketone prior to dipping the glass braid in the solution. The specimen was then mounted in the TBA at the temperature of cure, whereas the specimens used in this work were heated in the DMTA at 12°C/min from room temperature to the cure temperature before data was collected. These factors—type of instrument used, measurement frequency, sample preparation, and onset of cure—help to explain the difference between the experimental and literature curves in Figure 18. No data was obtained for this work for the T_{g0} values of the Epon 828/separate amine. However, Enns and Gillham²⁴ obtained a value of -9°C for the Epon 828/MDA system by TBA.

Figure 19 shows a TTT cure diagram of this work for the Epon 828/mixed amine system at the stoichiometric ratio of epoxy/amine for both the glass cloth composite and the neat resin mounted on steel shim. As shown, there is very little difference between the gelation and vitrification curves for the two sample types.

Rate Constant Determination

Apparent overall rate constants for the cure reactions were determined using a method by Babayevsky and Gillham for torsional braid analysis,⁷ which assumes that the relative modulus (if a sample support is used) is directly proportional to the crosslink density after the gel point in the rubbery state of the epoxy system. Therefore, the extent of the cure reaction from the gel point can be calculated by using the equation

$$\alpha' = \frac{(E')_t - (E')_0}{(E')_\infty - (E')_0} \quad (2)$$

where α' is the extent of reaction from the gel point, $(E')_t$ is the modulus at time $(t - t_g)$ from the gel point, $(E')_0$ is the modulus at the gel point, and $(E')_\infty$ is the modulus of the ultimately cured specimen in the rubbery state. Values of $(E')_\infty$ were obtained by taking the B-stage cured samples and C-stage curing them at 300°F (149°C) for 2 h, and then scanning them as a function of temperature in the DMTA to obtain the rubbery plateau shear modulus. If the reactions for the epoxy-amine system are considered to be third order (one each in epoxy, amine, and hydroxyl concentration), the apparent overall rate constant (k') of cure can be determined from the slope of a plot of $1/(1 - \alpha')^{n-1}$ vs. $(t - t_g)$. The value of n , the reaction order, is 3, as mentioned above. One of these plots is shown in Figure 20 for the stoichiometric ratio of Epon 828-mixed amine neat resin on steel shim in flexure at 30 Hz at several cure temperatures. Figure 20 shows that the plots are linear only in the initial stages of cure after the gel point. Deviation from linearity indicates the influence of vitrification. The data points in Figure 20 are for the model; the straight lines represent the best fit through the points in the early stages of the reaction. Values of α' were calculated from eq. (2) based on a plot of flexural modulus ($\log E'$) vs. time such as that shown in Figures 5 and 7-9.

A plot of $\ln k'$ vs. $1/T$ is shown in Figure 21 for the neat resin in shear at several epoxy/amine ratios. Values of k' are shown to increase as the amount

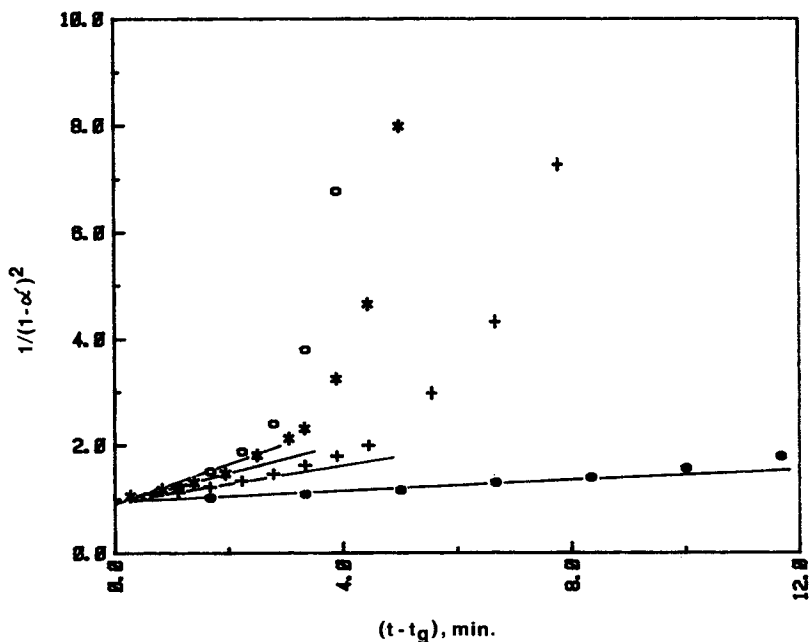


Fig. 20. Plot of $1/(1 - \alpha')^2$ vs. $(t - t_{gel})$ for determining the overall rate constant k' for the stoichiometric ratio of epoxy/mixed amine neat resin on steel shim in flexure for several cure temperatures: (●) 60°C; (+) 80°C; (*) 100°C; (○) 120°C.

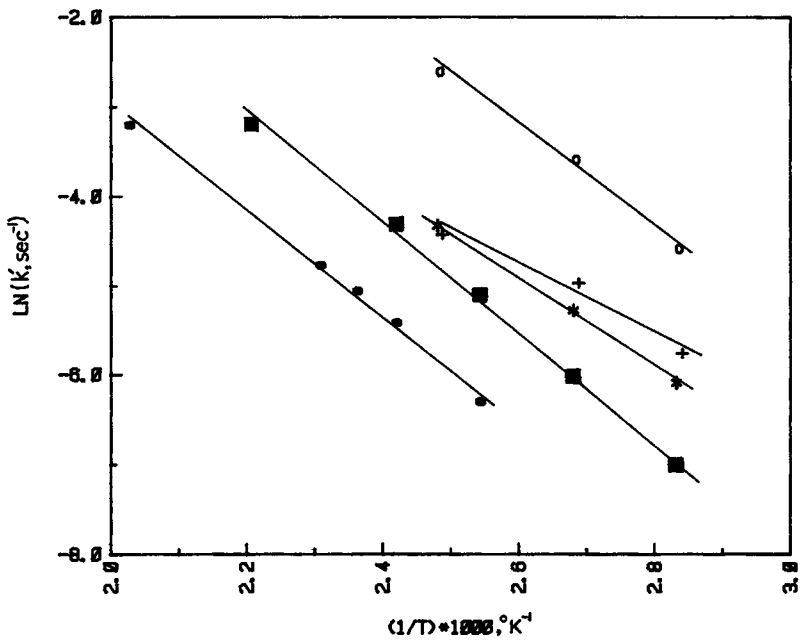


Fig. 21. Arrhenius plot based on calculated overall rate constants for several neat resin systems in shear: (O) -10 wt % epoxy/mixed amine; (+) stoichiometric ratio of epoxy/mixed amine; (*) +5 wt % epoxy/mixed amine; (■) Epon 828/*m*-PDA (s.r., Babayevsky and Gillham⁷); (●) Epon 828/MDA (s.r., Babayevsky and Gillham⁷).

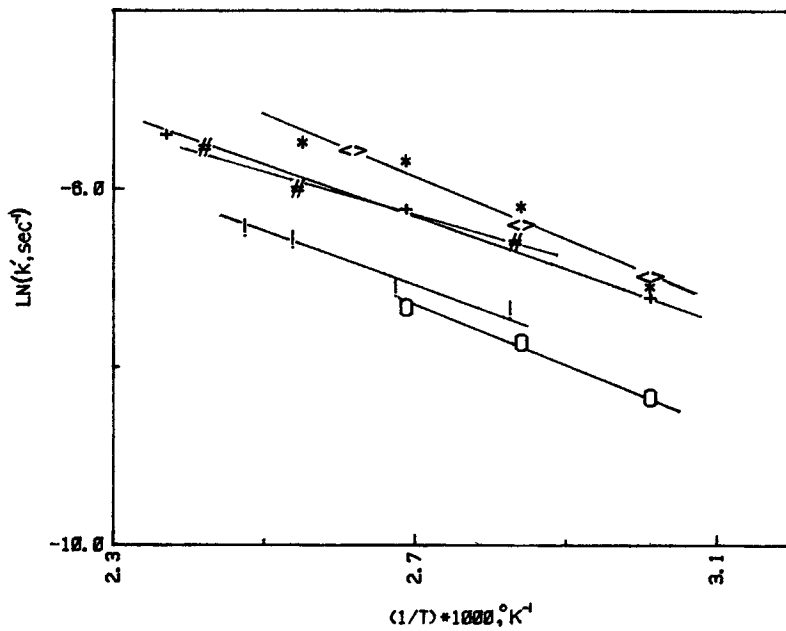


Fig. 22. Arrhenius plot based on calculated overall rate constants for several epoxy systems on glass cloth/steel shim in flexure: (*) neat resin for s.r. epoxy/mixed amine; (◇) -10 wt % epoxy/mixed amine; (+) s.r. epoxy/mixed amine; (O) = +5 wt % epoxy/mixed amine; (#) s.r. epoxy/MDA; (!) s.r. epoxy/*m*-PDA.

TABLE II
Overall Apparent Rate Constants and Overall Activation Energies of Cure After Gelation for Epoxy/Diamine Reactions by Dynamic Mechanical Analysis at 30 Hz

Reactive system	Epoxy/amine ratio (wt %)	Mode of measurement	Reinforcement	Rate constant k' after gel point ($s^{-1} \times 10^5$)								E_a (kcal/mol)	Corr. coeff.		
				60°C	80°C	100°C	110°C	120°C	130°C	140°C	150°C				
DGEBA/mixed amine ^a	0 (stoic.)	Flexure	Glass cloth	0.73	—	2.0	—	—	—	—	—	—	4.5	5.7	0.999
	0	Flexure	None	0.82	2.0	3.4	—	4.2	—	—	—	—	—	7.1	0.974
	0	Shear	None	—	3.2	7.0	—	—	—	11.9	—	—	—	7.4	0.983
	-10	Flexure	Glass cloth	0.92	1.6	—	3.8	—	—	—	—	—	—	7.2	0.999
	-10	Shear	None	—	10.2	27.5	—	—	—	73.5	—	—	—	11.1	0.997
DGEBA/MDA	+5	Flexure	Glass cloth	0.24	0.44	0.65	—	—	—	—	—	—	—	6.2	0.996
	+5	Shear	None	—	2.3	5.1	—	—	—	13.2	—	—	—	9.9	0.999
	0	Flexure	Glass cloth	—	1.4	—	—	2.5	—	—	—	3.9	—	5.0	0.988
	0	Shear	None	—	2.4	4.4	—	—	—	29.3	—	—	—	14.4	0.978
	0	Torsion ^b	Glass braid	—	—	—	—	1.9	—	—	4.6	—	—	11.8	0.998
DGEBA/ <i>m</i> -PDA	0	Flexure	Glass cloth	—	0.64	0.81	—	1.4	1.6	—	—	—	—	5.5	0.983
	0	Torsion ^b	Glass braid	—	0.9	2.4	—	6.0	—	—	13.3	—	—	12.2	0.999

^a Mixed amine = primarily a 50/50 mixture of *m*-PDA and MDA (this work).

^b Work by Babayevsky and Gillham at 1 Hz.⁷

of amine is increased, which is to be expected. Plots for the individual amines in the mixed amine are also shown from work done by Babayevsky and Gillham.⁷ Figure 22 shows that the neat resin mounted on the steel shim has higher values of k' (and E_a) than does the resin/glass cloth composite mounted on steel shim. This observation is in agreement with the work done by Mijovic²⁷ with a DSC for an epoxy system reinforced with glass microspheres (40% by wt). He suggests that the lower rate constants for the reinforced system implies that the reinforcement restricts the molecular mobility of reactive species.

Table II summarizes overall apparent rate constants and overall activation energies of cure after gelation for flexural and shear measurements on several epoxy/amine ratios. The values of k' and E_a are somewhat lower for the glass cloth composites in flexure than for the neat resin in shear. Aside from the observation made by Mijovic,²⁷ this could also result from the stiffness of the steel shim masking the buildup in relative modulus as a function of time for the resin on the glass cloth, since the k' and E_a values are determined from the log E' -time plot.

Figure 23 shows conversion-time curves for the Epon 828/mixed amine system by DMTA as well as DSC analysis at several cure temperatures for the stoichiometric ratio of epoxy/amine on glass cloth in flexure. The DSC data was obtained by Wingard et al.²⁸ on the same epoxy system used in this work.

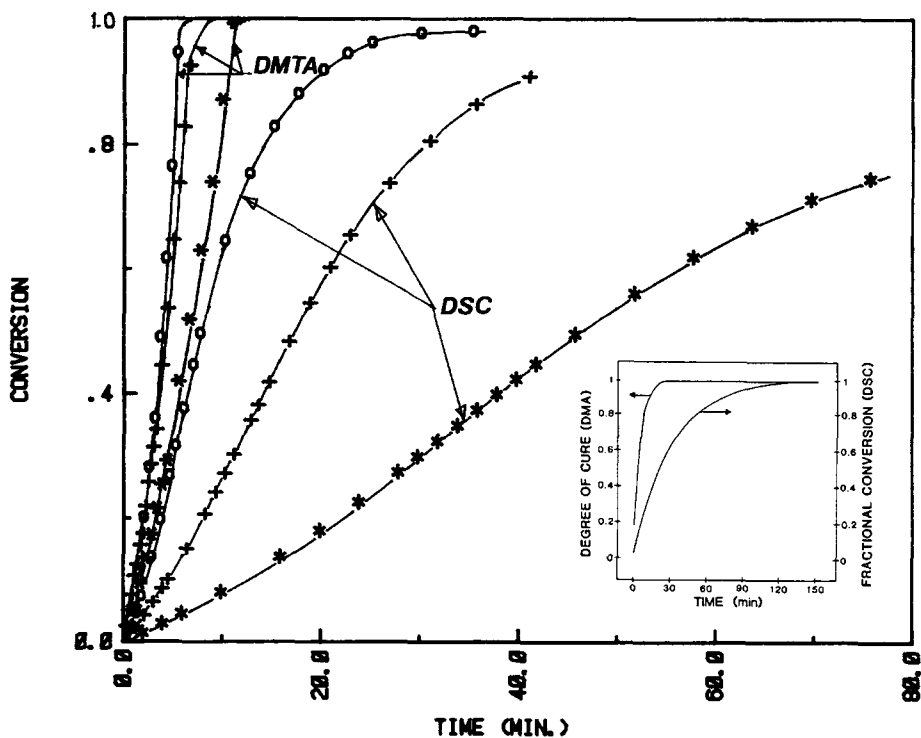


Fig. 23. Conversion vs. time curves for the Epon 828/mixed amine (s.r.) system by DMTA (in flexure) and DSC analysis at several cure temperatures; compared with a similar curve by Provdar et al.²⁹ for Epon 825/MDA by DMA and DSC analysis at 150°C: (*) 80°C; (+) 100°C; (O) 120°C.

Also shown is a similar plot comparing results by DSC and DMA (DuPont 981 Mechanical Analyzer) for the Epon 825/MDA system at a cure temperature of 150°C.²⁹ The DMA uses a fiberglass braid support for the mixed resin similar to that used for this work on the DMTA. Provder et al.²⁹ explain that the discrepancy between DSC and DMA conversion-time curves may be due to the vitrification of the sample before complete chemical reaction has been achieved, as well possibly being due to the DMA's sensitivity to the rigidity of the amine molecule MDA. Figure 24 shows conversion-time curves for DSC and DMTA (in shear) analysis at several cure temperatures. Ten percent excess amine for the Epon 828/mixed amine neat resin was used. Although there is some discrepancy between the DSC and DMTA shear curves in Figure 24, it is less than for the flexural data curves shown in Figure 23.

SUMMARY

This work focuses on the use of dynamic mechanical spectroscopy to characterize the cure kinetics of a system containing a DGEBA epoxy resin and a mixed amine curing agent. Accurate determination of the ratio of epoxy to curing agent is important because a variation of more than ± 2 wt % of the stoichiometric ratio can have a significant effect on the final mechanical prop-

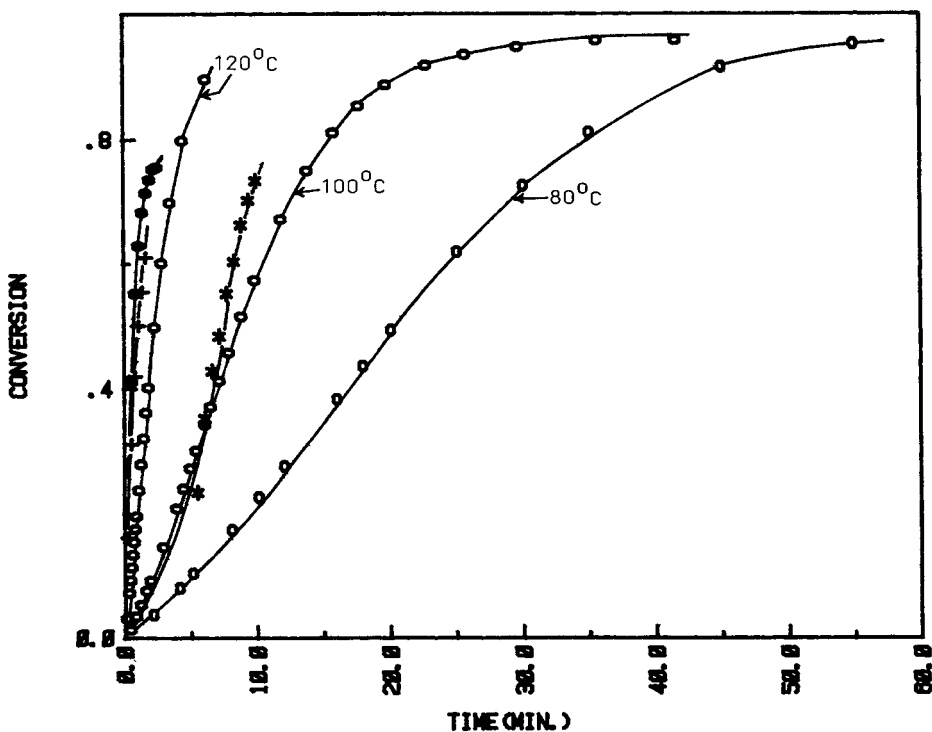


Fig. 24. Conversion vs. time curves for the Epon 828/mixed amine system (10 wt % excess amine) by DMTA (in shear) and DSC analysis at several cure temperatures: (*) 80°C (DMTA); (+) 100°C (DMTA); (●) 120°C (DMTA); (○) DSC (all cure temps).

erties of the cured resin. From gel time flexural data, the activation energy of cure passed through a maximum at the stoichiometric ratio of epoxy/amine for a glass cloth composite mounted in a steel shim sandwich. For shear measurements on the neat resin, a corresponding minimum was observed. However, a simple kinetic model for the reaction of a diepoxide and a diamine shows that the activation energy of cure should be independent of the stoichiometry of the reactants.

From the buildup in modulus during cure, an optimum cure temperature of about 120°C could be chosen for both the neat resin and the glass reinforced epoxy for the stoichiometric ratio of epoxy/amine. From a time-temperature-transformation (TTT) cure diagram, an optimum cure temperature of 150°C was observed for stoichiometric conditions, with a considerably lower optimum cure temperature observed for nonstoichiometric conditions.

By considering the curing of the mixed epoxy system to follow third-order kinetics, overall reaction rate constants were estimated after the gel point. The epoxide conversion after the gel point was compared with the conversion determined by differential scanning calorimetry (DSC). The conversion determined by the DMTA had a much faster rise with cure time than did the conversion by DSC. This could be due in part to the vitrification of the sample before complete chemical reaction has been achieved.

The authors would like to thank McDonnell-Douglas Astronautics, Inc. in Titusville, Florida for partial financial support of this research as well as the Microstructure of Materials Center of Excellence, Department of Materials Science and Engineering, College of Engineering, University of Florida. The use of the Polymer Laboratories dynamic mechanical spectrometer owned by Polymer Products and Services, Inc. of Gainesville, Florida is gratefully acknowledged.

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Received April 30, 1989

Accepted August 9, 1989