

Torsional Braid Analysis of the Aromatic Amine Cure of Epoxy Resins

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SYNOPSIS

The cure behavior of diglycidyl ether of bisphenol A (DGEBA) type of epoxy resins with three aromatic diamines, 4,4'-diaminodiphenyl methane (DDM), 4,4'-diaminodiphenyl sulfone (44DDS), and 3,3'-diaminodiphenyl sulfone (33DDS) was studied by torsional braid analysis. For each curing agent the stoichiometry of the resin mixtures was varied from a two to one excess of amino hydrogens per epoxy group to a two to one excess of epoxy groups per amino hydrogen. Isothermal cures of the resin mixtures were carried out from 70 to 210°C (range depending on epoxy-amine mixture), followed by a temperature scan to determine the glass transition temperature (T_g). The times to the isothermal liquid-to-rubber transition were shortest for the DDM mixtures and longest for the 44DDS mixtures. The liquid-to-rubber transition times were also shortest for the amine excess mixtures when stoichiometry was varied. A relatively rapid reaction to the liquid-to-rubber transition was observed for the epoxy excess mixtures, followed by an exceedingly slow reaction process at cure temperatures well above the T_g . This slow process was only observed for epoxy excess mixtures and eventually led to significant increases in T_g . Using time-temperature shifts of the glass transition temperature vs. logarithm of time, activation energies approximately 50% higher were derived for this process compared to those derived from the liquid-to-rubber transition. The rate of this reaction was virtually independent of curing agent and was attributed to etherification taking place in the epoxy excess mixtures. © 1994 John Wiley & Sons, Inc.

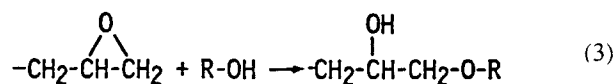
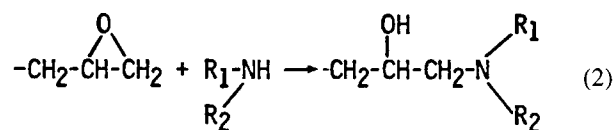
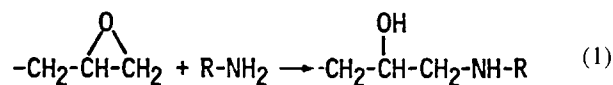
INTRODUCTION

The cure of thermosetting polymers generally proceeds through the transformation of low-molecular-weight liquids to high-molecular-weight amorphous solids by means of chemical reaction. As the material cures, its glass transition temperature (T_g) advances from the T_g of the uncured resin (T_{g0}) up to the T_g of the fully cured resin ($T_{g\infty}$). For cure temperatures below $T_{g\infty}$, the resin will ultimately vitrify. This onset of diffusion control typically stops chemical reaction, leading to a less than fully cured sample. Heating to temperatures above $T_{g\infty}$ typically allows the remainder of reaction to take place and the formation of the fully cured network. The T_g as a function of time has been shown to have a one-to-one relationship with chemical conversion in epoxy-

amine resin systems¹⁻⁵ independent of cure temperature. This allows the easily measured T_g to be used as a means of monitoring the extent of reaction.

Torsional braid analysis (TBA) has been utilized in numerous studies to establish isothermal time-temperature-transformation (TTT) cure diagrams for thermosetting polymers.^{6,7} Its particular advantage is to graphically illustrate the different regions of a thermosetting system in terms of temperature and time (liquid, gelled liquid, glass, gelled glass, etc.). An isothermal cure of an unreacted epoxy-amine system typically proceeds from a liquid to a rubber and finally to a glass for cure temperatures below $T_{g\infty}$. The time required to reach this liquid-to-rubber transition is commonly used as an indicator of molecular gelation and is used to derive an activation energy for the chemical reactions that led to this state of cure.

Epoxy-aromatic amine systems are generally thought to react by the following three reactions:



Reactions 1, 2, and 3 represent primary amine addition to epoxy, secondary amine addition to epoxy, and etherification, respectively. The amine addition reactions are thought to predominate for uncatalyzed epoxy-aromatic amine cure with etherification either not occurring⁸⁻¹⁰ or occurring only in the presence of excess epoxy.^{3,11,12} Riccardi and Williams¹³ concluded that etherification becomes significant in the cure of diglycidyl ether of bisphenol A (DGEBA) with 4,4'-diaminodiphenyl sulfone (44DDS) at cure temperatures greater than 150°C and at intermediate and high extents of reaction. This was attributed to an increasing hydroxyl concentration in combination with the relative inactivity of the secondary amine when compared to the primary amine. On the other hand, Sabra et al.¹⁰ observed no etherification for essentially the same resin system. Previous work in this laboratory,¹⁴ utilizing monofunctional resin compounds, showed the formation of etherification products, even in the presence of excess amine.

In this study TBA was utilized to characterize the cure behavior of three epoxy-aromatic amine systems at stoichiometries varying from excess epoxy to excess amine. Isothermal cures followed by temperature scans were used to measure the liquid-to-rubber transition, vitrification, and resulting network T_g . Activation energies were derived from the liquid-to-rubber transition and from time-temperature shifts of the T_g vs. logarithm of cure time data. These were used to develop a cure profile to better understand the relative importance of the reactions leading to the network formation in an attempt to resolve differences reported in the literature regarding epoxy-aromatic amine cure. The neat resin results reported here are a part of a larger, ongoing study on the formation of an adhesive interphase region due to adherend surface effects on the resin cure. Results of these effects on the above resin systems are the subject of a future paper.

Materials

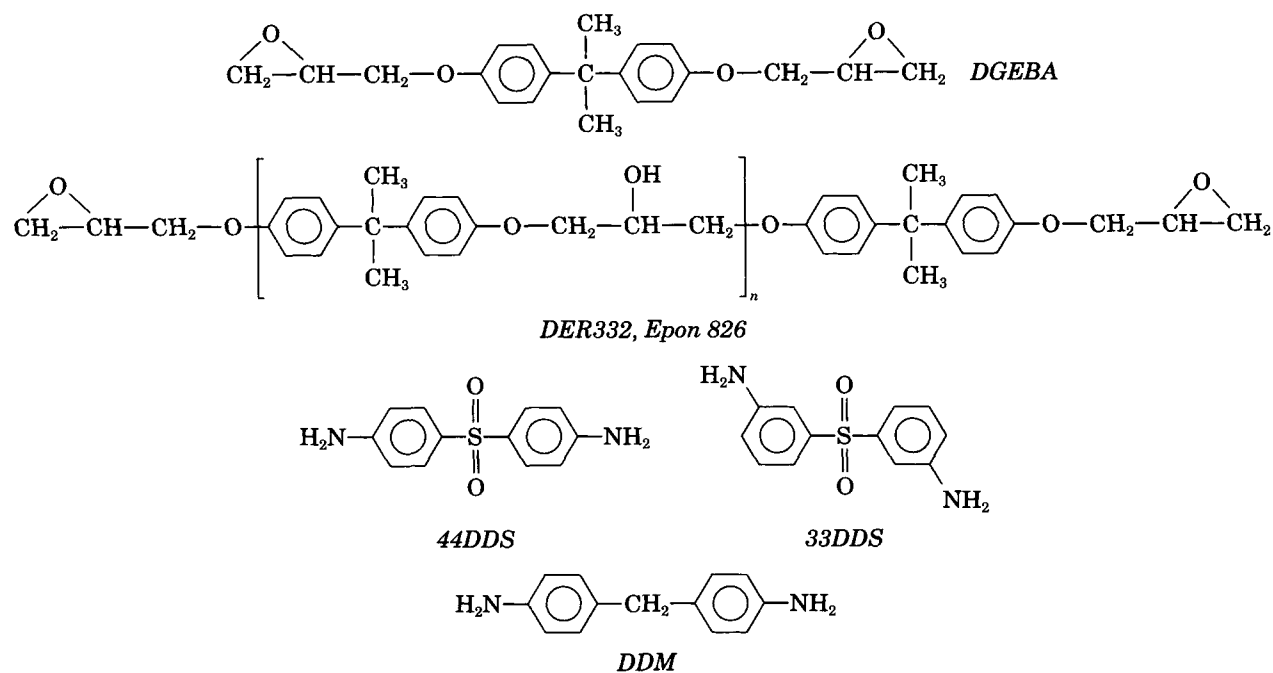
The resin mixture components used in this study are shown in Table I. The epoxy resins were all based on DGEBA: recrystallized DGEBA with an epoxy equivalent molecular weight (EEW) of 171 g/eq; DER332, Dow Chemical Co., EEW of 174 g/eq; and Epon 826, Shell Chemical Co., EEW of 180 g/eq. The curing agents used were the aromatic amines: 4,4'-diaminodiphenyl methane (DDM), 4,4'-diaminodiphenyl sulfone (44DDS), and 3,3'-diaminodiphenyl sulfone (33DDS), all from Aldrich Chemical Co. and used as received. Three stoichiometries were made for each curing agent with an epoxy resin: a two-to-one excess of epoxy to amino hydrogen ($a/e = 0.5$), a one-to-one ratio ($a/e = 1.0$), and a two-to-one excess of amino hydrogen to epoxy ($a/e = 2.0$).

EXPERIMENTAL

Small amounts of resin (~ 0.1 g) were mixed for each TBA run and used as concentrated solutions in tetrahydrofuran. A braid was typically dipped into the solution and allowed to evaporate at room temperature before placing it into the TBA sample oven, preheated to the cure temperature. Isothermal cures were carried out over temperature ranges of 70 to 200°C for DDM mixtures, 110-to-200°C for 44DDS mixtures, and 100 to 200°C for 33DDS mixtures. After isothermal cure, a sample was cooled to 0°C, heated at approximately 3°C/min to temperatures up to 250°C, then cooled at approximately 3°C/min to room temperature. Selected samples were heated a second time at 3°C/min. Typically, three processes were observed during the isothermal segment of the TBA procedure, an isoviscous pregel phenomenon, a liquid-to-rubber transformation (gelation), and vitrification. These are shown in Figure 1 for an isothermal cure of DER332/44DDS ($a/e = 1.0$) at 130°C.

The peak in the log decrement trace of the first heating scan was used to determine the T_g of the isothermally cured material, and the peak in the log decrement trace of the cooling scan was used to determine the T_g of the "fully cured" material. Typically, for the stoichiometric and amine excess samples, the heating scan was enough to complete cure, as evidenced by no further changes in T_g on successive scans. For these samples, the T_g determined from the cooling scan was a measure of the $T_{g\infty}$ of the mixture. The epoxy excess samples typically did not reach "full cure" during the heating scan to elevated temperatures. Attempts to complete cure at

Table I Resin Mixture Component Structures



temperatures higher than 250°C were not carried out in order to avoid degradation of the resin.

RESULTS AND DISCUSSION

The logarithm of the times to the liquid-to-rubber transition were plotted vs. the inverse of the absolute

cure temperature to yield an Arrhenius-type plot. The relative reactivity of the various resin mixtures investigated are shown in such plots in Figures 2 and 3. Figure 2 shows the results for the stoichiometric mixtures of all the curing agents. At any temperature investigated, the DDM mixture is the most reactive, as indicated by the shortest times to

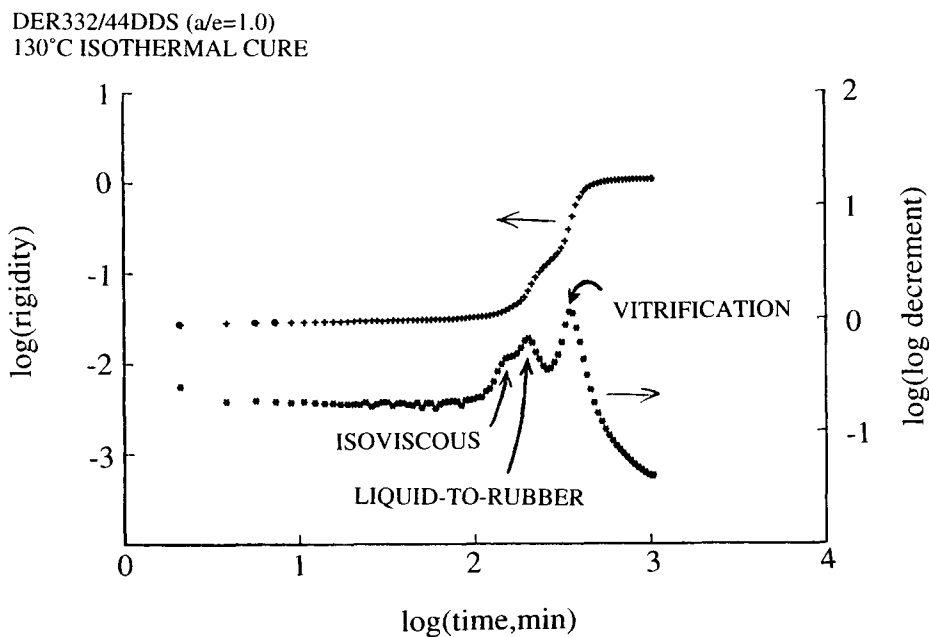


Figure 1 Isothermal TBA at 130°C of a sample of DER332/44DDS (a/e = 1.0).

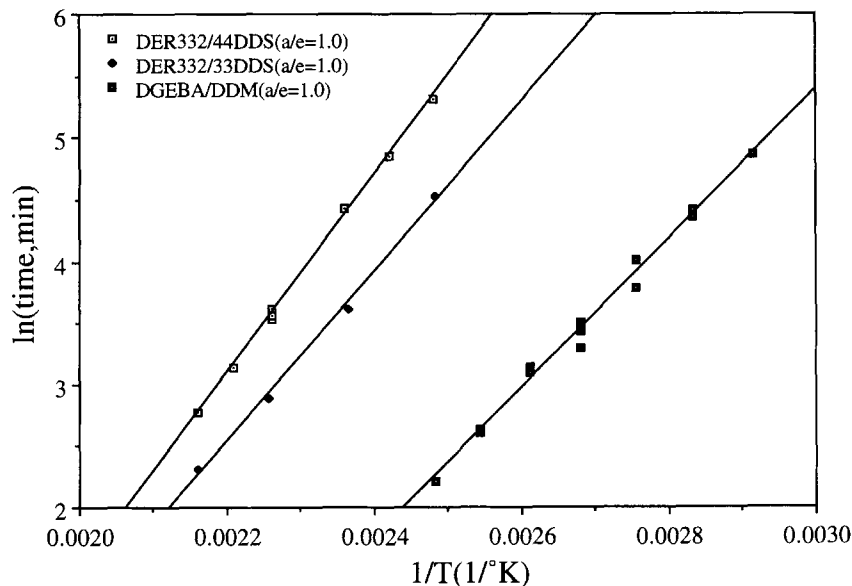


Figure 2 Logarithm of liquid-to-rubber transition time vs. the inverse of absolute cure temperature for stoichiometric resin mixtures.

the liquid-to-rubber transition, followed by the 33DDS, and finally the 44DDS. This curing agent reactivity trend was observed over the range of amine-to-epoxy ratios investigated. Variation in the liquid-to-rubber transition times with stoichiometry is shown in Figure 3 for DDM mixtures at $a/e = 0.5, 1.0,$ and 2.0 . At any temperature investigated, the epoxy excess sample is the slowest to react and the amine excess the fastest. This amine-to-epoxy ratio dependence was observed for all the curing agents used.

The liquid-to-rubber transition is assumed to occur at a resin system dependent, fixed extent of reaction and to be inversely proportional to the rate of reaction at that point. This assumption allows for the derivation of activation energies from the slope of a linear least-squares fit for the Arrhenius-type plots shown in Figures 2 and 3. The results from this analysis are shown in Table II for the resin mixtures investigated. The values of 65 and 50 kJ/mol derived from the liquid-to-rubber transition for stoichiometric mixtures of DGEBA/44DDS and

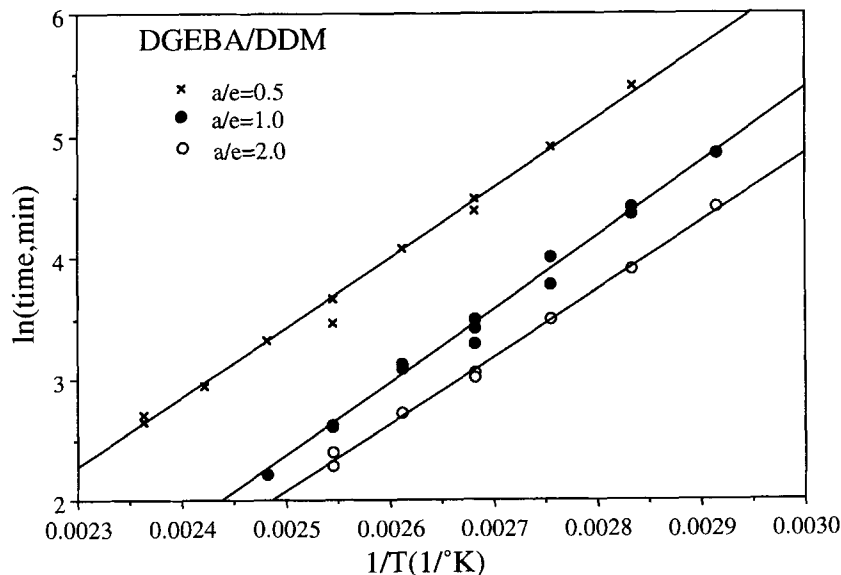


Figure 3 Logarithm of liquid-to-rubber transition time vs. the inverse of absolute cure temperature for DGEBA/DDM at different a/e ratios.

Table II Activation Energies (kJ/mol) Derived from the TBA Liquid-to-Rubber Transition

Resin	Activation Energy (kJ/mol) (from TBA Liquid-to-Rubber Transition)		
	$a/e = 2.0$	$a/e = 1.0$	$a/e = 0.5$
DGEBA/33DDS	57	58	58
DER332/33DDS	56	58	58
826/33DDS	—	58	—
DGEBA/44DDS	53	65	69
DER332/44DDS	—	66	70
826/44DDS	—	63	—
DGEBA/DDM	46	50	48
DER332/DDM	—	—	47

a/e = amine/epoxy.

DGEBA/DDM, respectively, are in good agreement with those in the literature. Chan et al.¹⁵ calculated a value of 64 kJ/mol from the liquid-to-rubber transition by TBA for a sample of DER332/44DDS ($a/e = 1.0$). Riccardi and Williams¹³ reported a value of 62 kJ/mol derived from isothermal differential scanning calorimetry (DSC) data for a stoichiometric sample of DGEBA (EEW 187 g/mol)/44DDS and Galy et al.¹⁶ reported a value of 63 kJ/mol derived from dynamic DSC data for a stoichiometric sample of DER332/44DDS. Barton¹⁷ reported values of 53 and 50 kJ/mol for a stoichiometric sample of Epon 825 (EEW 175 g/mol)/DDM derived from dynamic DSC and isothermal DSC data, respectively.

In this study, the DDM and 33DDS mixtures showed no significant variation of activation energy with change in the amine-to-epoxy ratio. However, the 44DDS showed a decreasing activation energy with increasing amine content going from 69 kJ/mol for $a/e = 0.5$ to 53 kJ/mol for $a/e = 2.0$. With the exception of the 44DDS $a/e = 2.0$ sample, the 44DDS mixtures generally had the highest activation energies followed by the 33DDS mixtures then the DDM mixtures. No obvious dependence of activation energy on the epoxy resin hydroxyl content, which increases with increasing EEW, was observed.

Values for $T_{g\infty}$ obtained in this study are shown in Table III. All the values for $a/e = 0.5$ are bracketed. These represent the highest experimental values obtained in this study for this stoichiometry. They typically come from isothermal cures of 180 to 200°C for cure times up to several days. However, these values do not represent $T_{g\infty}$. The TBA relative rigidity and log decrement are still changing after

these long cure times, indicating further reaction leading to higher values for T_g . This is shown in Figure 4 for a sample of DER332/33DDS ($a/e = 0.5$) at 180°C. Clearly, further reaction is underway at long times in the “rubbery” region as evidenced by the slow changes in log decrement and relative rigidity. Attempts at curing for extended times (> 8 h) at 240°C led to lower T_g values, probably resulting from degradation.

Literature values of T_g for similar DGEBA-type resins with the same curing agents used in this study are shown in Table IV.^{15,16,18–22} These values do not necessarily represent $T_{g\infty}$, but rather the T_g obtained for the experimental conditions used. Full cure may not have been obtained, especially in the case of the epoxy-rich systems for which this study clearly shows further reaction at long times. Also, some of the differences reported for the same system in Table IV may be attributed to the different molecular processes measured with the different experimental techniques utilized. However, many of the literature values for the stoichiometric mixtures shown in Table IV agree very favorably with the values of $T_{g\infty}$ reported for this study in Table III. The effect of oligomer content on $T_{g\infty}$ for the stoichiometric mixtures is clearly shown in both Tables III and IV.¹⁹ As oligomer content increases (increasing EEW of the resin), the $T_{g\infty}$ decreases, indicating the expected lower crosslink density in mixtures that primarily react through amine addition to epoxy.

A feature often observed for epoxy-amine systems is a maximum in T_g at a stoichiometric ratio of one when the amine to epoxy ratio is varied. Assuming only amine-to-epoxy addition reactions, a stoichiometric ratio of one should yield the highest crosslink density. Vallo et al.²³ show this to occur for a number of epoxy-amine systems, both from their own work

Table III Ultimate Glass Transition Temperatures (°C) from the TBA Cooling Scans at 3°C/min

Resin	Glass Transition Temperature (°C)		
	$a/e = 2.0$	$a/e = 1.0$	$a/e = 0.5$
DGEBA/33DDS	128	184	[169]
DER332/33DDS	124	177	[174]
826/33DDS	—	174	—
DGEBA/44DDS	157	221	[200]
DER332/44DDS	—	215	[197]
826/44DDS	—	212	—
DGEBA/DDM	102	183	[180]
DER332/DDM	—	—	[174]

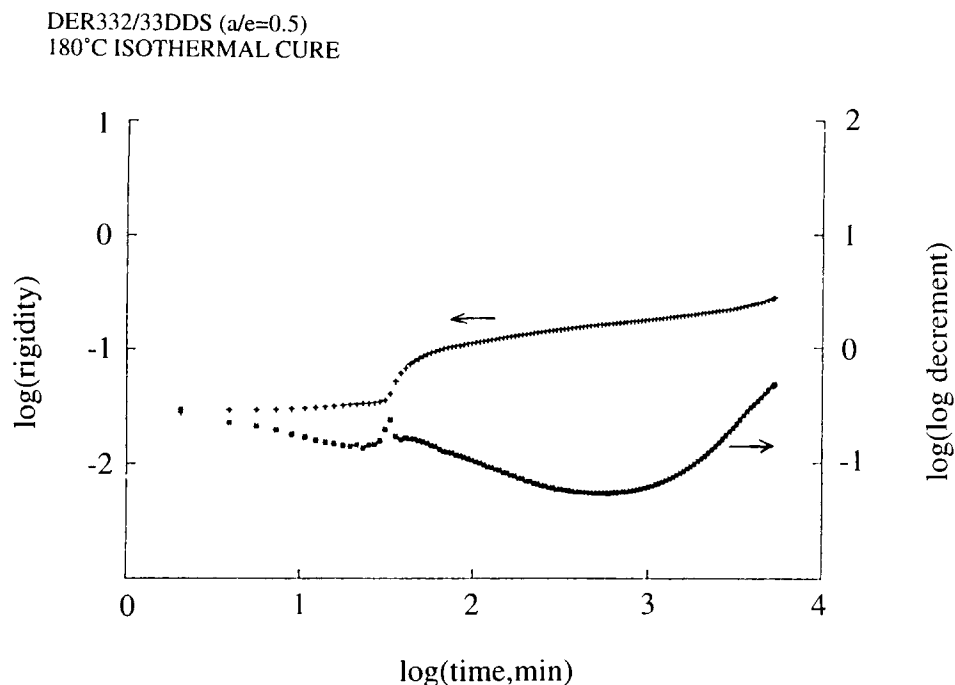


Figure 4 Isothermal TBA at 180°C of a sample of DER332/33DDS ($a/e = 0.5$).

and from the literature. Included in Table IV are some series of resin mixtures that show this phenomenon. Bellenger et al.²¹ vary the amine-to-epoxy

ratio from 0.7 to 1.8 for a DGEBA-type resin (EEW = 186) with DDM with a cure cycle of 1 h at 105°C and 1.25 h at 180°C. The values obtained for the

Table IV Glass Transition Temperatures for Similar Resin Systems

Resin	Amine/Epoxy	T_g (°C)	Technique	Reference
DER332/44DDS	1.0	229	TBA	15
Epon 825/44DDS	1.0	222	TBA	19
Epon 828/44DDS	1.0	211	TBA	19
Epon 834/44DDS	1.0	186	TBA	19
Epon 828/DDM	1.0	166	TBA	19
DGEBA (eew 186)/DDM	0.7	105	DSC	21
DGEBA (eew 186)/DDM	0.8	124	DSC	21
DGEBA (eew 186)/DDM	0.9	149	DSC	21
DGEBA (eew 186)/DDM	1.0	176	DSC	21
DGEBA (eew 186)/DDM	1.2	170	DSC	21
DGEBA (eew 186)/DDM	1.4	138	DSC	21
DGEBA (eew 186)/DDM	1.6	126	DSC	21
DGEBA (eew 186)/DDM	1.8	114	DSC	21
DER332/DDM	0.7	84	DSC	16
DER332/DDM	1.0	165	DSC	16
DER332/DDM	1.4	139	DSC	16
DER332/44DDS	0.6	100	DSC	16
DER332/44DDS	1.0	190	DSC	16
DER332/44DDS	1.4	145	DSC	16
DER332/44DDS	1.0	218	DSC	22
DER332/33DDS	1.0	171	DSC	22
DER332/DDM	1.0	178	DSC	22
Epon 828/DDM	1.0	170	DMA	18
Epon 828/DDM	2.0	115	DMA	18
Epon 828/44DDS	1.0	212	?	20

amine-rich and stoichiometric values compare very favorably with those obtained in this study (Table III). However, a significant difference is observed for the epoxy-rich samples. They report a value 105°C for a sample of $a/e = 0.7$, whereas a value of 174°C is found in this study for a sample with an even larger epoxy excess, DER332/DDM ($a/e = 0.5$). The value of 174°C was obtained after approximately 110 h at 180°C. A sample of DER332/DDM ($a/e = 0.5$) cured for 100 min at 180°C had a T_g of 55°C, much more consistent with their cure and value. Maxima in T_g , at a stoichiometric ratio of one, were also observed by Galy et al.¹⁶ for DER332/44DDS ($a/e = 0.6$ – 1.4) and for DER332/DDM ($a/e = 0.7$ – 1.35) (Table IV). These samples were cured by thermal scans at various heating rates to high temperatures ($> 300^\circ\text{C}$ for 44DDS samples), although only a relatively short time was spent at temperatures greater than 250°C. It thus appears that the differences in T_g between this study and the literature values are due to the length of cure at elevated temperatures.

In the absence of etherification, the epoxy excess mixtures were expected to yield low T_g final products, as observed in the above cited studies. Generally, the values of T_g reported in Table III for the epoxy excess samples are nearly the same as for the stoichiometric samples, with $T_{g\infty}$ for the epoxy excess mixtures most likely higher, as previously discussed. These results are similar to the findings of Simon and Gillham³ who found by DSC for an $a/e = 0.8$ sample of DER332 with the aromatic diamine, trimethylene glycol di-*p*-amino benzoate (TMAB), a second reaction taking place to fully cure the

epoxy. They similarly found that very long cure times were necessary to observe this second process. They attributed this process to homopolymerization of the epoxy and concluded that the epoxy-hydroxyl reaction becomes significant in the excess epoxy sample only after the amine-consuming reaction is nearly complete.

The results of this study are similar to observations made by Gupta et al.¹¹ and Oleinik¹² for changes in T_g of nonstoichiometric DGEBA-type epoxy resins with meta-phenylenediamine (*m*PhDA). Both report a rise in $T_{g\infty}$ in networks only with epoxy excess on postcuring, whereas the cured stoichiometric and excess amine systems show no increases. Both studies concluded that these further changes in this particular aromatic amine system were due to epoxy-hydroxy reactions and not to oxidation or degradation. Both studies addressed changes occurring over hours in the 170 to 180°C range, the same range addressed in this study for the different curing agents. Gupta et al. reported a loss of epoxy groups as measured by infrared spectroscopy in this region to support their claim. Oleinik¹² reported a higher T_g (200 vs. 140°C) for the epoxy excess sample ($a/e = 0.66$) compared to the stoichiometric sample of a diglycidyl ether of resorcinol/*m*PhDA mixture. Clearly, this additional process can be attributed to etherification.

A better way to illustrate this reaction is through the slow growth in T_g with time as shown in Figure 5 for a sample of DER332/DDM ($a/e = 0.5$) at 180°C. This sample reaches the liquid-to-rubber transition at this cure temperature in approximately 6 min and a T_g of approximately 55°C at this point

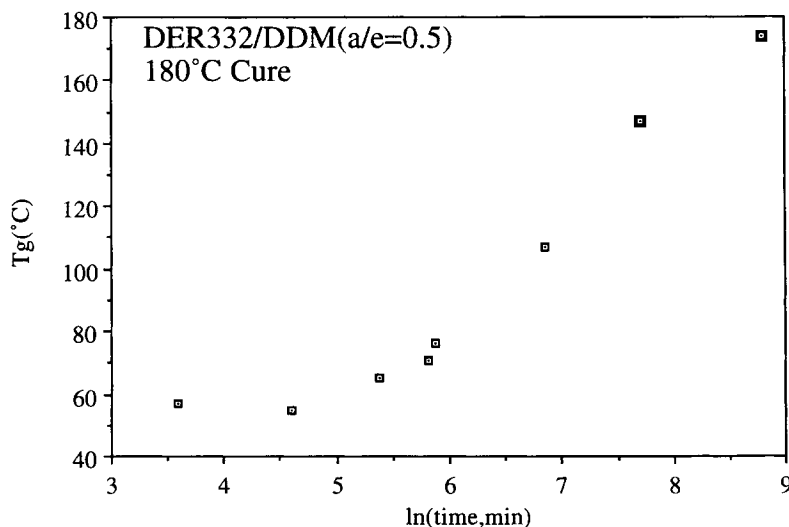


Figure 5 Glass transition temperature vs. logarithm of time for 180°C cures of DER332/DDM ($a/e = 0.5$).

in time. After the relatively fast initial formation of the rubbery material (thought to be primarily through amine addition reactions) the T_g increases dramatically, though slowly, to a value approaching 180°C, where diffusion control of the reactions is most likely becoming significant. Similar T_g vs. logarithm of time plots are shown in Figure 6 for a series of cure temperatures from 160 to 200°C for a sample of DER332/44DDS ($a/e = 0.5$).

Wisnarakit and Gillham¹ described a time-temperature shift technique applied to T_g vs. logarithm of time data for a stoichiometric mixture of DER332/TMAB at different isothermal cure temperatures. This was carried out to establish a master curve for the kinetically controlled region of reaction. Applying this technique to the data in Figure 6 and using the 180°C cure data as the arbitrary reference curve, yields the "master curve" shown in Figure 7. This technique does a very reasonable job of overlapping the data as shown in Figure 7. The scatter at longer times is due to the onset of diffusion control as the T_g of the sample approaches the different cure temperatures. Since the shifting is carried out in the kinetically controlled reaction region, an activation energy can be derived from linear least-square fits of the time shift factor vs. the inverse of the absolute cure temperature to which it applies. The results from such derivations were shown by Wisnarakit and Gillham to be independent of the selection of the reference curve. Figure 8 shows such

a plot for the shift factors used in Figure 7 and similar plots were made for each of the DER332 $a/e = 0.5$ samples in this study. The activation energies derived from these plots are listed in Table V along with the activation energies derived from the liquid-to-rubber transition data for the same samples. A much higher activation energy is found than those derived from the liquid-to-rubber transition thought to primarily be associated with the initial amine addition to epoxy reactions (85 to 89 kJ/mol vs. 47 to 70 kJ/mol). This higher activation energy is similar to the values reported by Galy et al.¹⁶ (90 kJ/mol) and Heise and Martin²⁴ (85 and 88 kJ/mol) for homopolymerization of DGEBA initiated by benzyl dimethyl amine and 2,4-ethylmethyl imidazole, respectively.

Simon and Gillham³ had carried out similar time-temperature shifts for their DER332/TMAB resin system. They, however, carried out this kind of shift for the early reaction in their epoxy excess ($a/e = 0.8$) sample and found that the shift factor required for the early process also overlapped the later process as well. They concluded that similar activation energies applied to both the early epoxy-amine addition reactions and the later epoxy-hydroxyl reactions (65 kJ/mol). The differences between this study and the work of Simon and Gillham may be attributed to two factors. First, the smaller excess of epoxy in the work of Simon and Gillham led to a smaller change in T_g associated with the

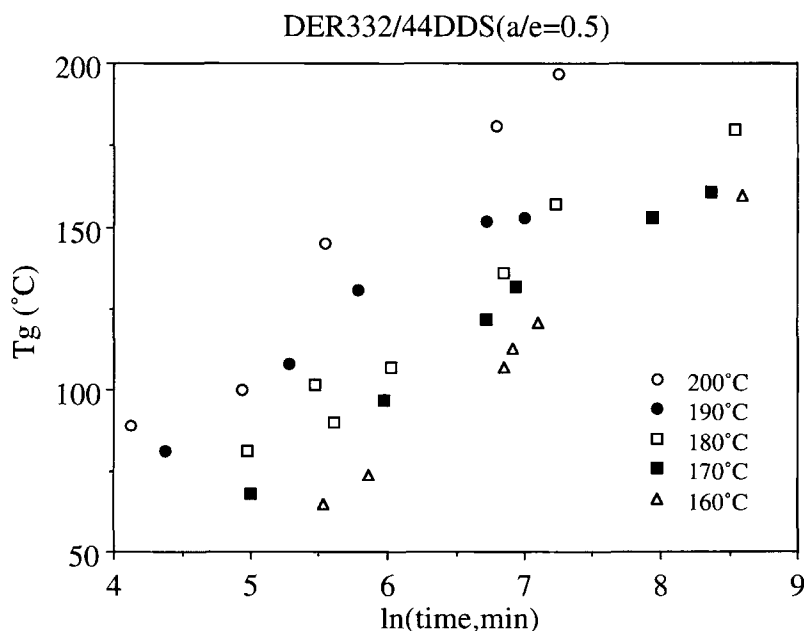


Figure 6 Glass transition temperature vs. logarithm of time for isothermal cures of DER332/44DDS ($a/e = 0.5$) at various temperatures.

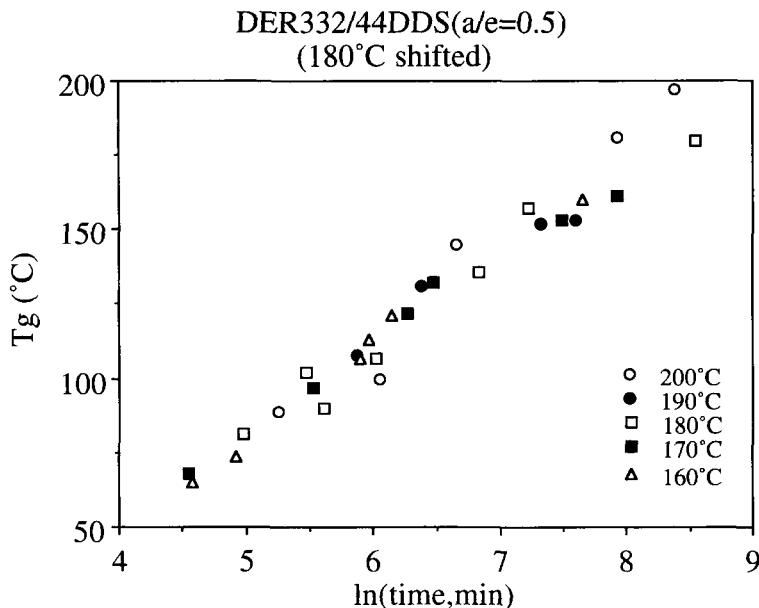


Figure 7 Shifted glass transition temperature vs. logarithm of time data for isothermal cures of DER332/44DDS ($a/e = 0.5$) using 180°C as the reference temperature.

epoxy-hydroxyl reaction portion of cure. Differences in the overlap of the later stages of cure may not be as clear. Second, the changes in T_g , which they were measuring for the later stages of cure, were much closer to the cure temperatures than those measured in this study. The onset of diffusion control of the reactions in the later stages of cure may be an important factor in their results.

The T_g vs. logarithm of time data for all the epoxy excess DER332 mixtures in this study at 180°C are shown in Figure 9. With the exception of some small differences at short times (most likely due to the different reactivity of the amine) the curves are very similar. This independence of curing agent on T_g is further indication that etherification is occurring in these systems. Once the amine has reacted, further reaction takes place through the same reactions in all the systems. This distinction between the two regions of reaction is greatest for the DDM mixture

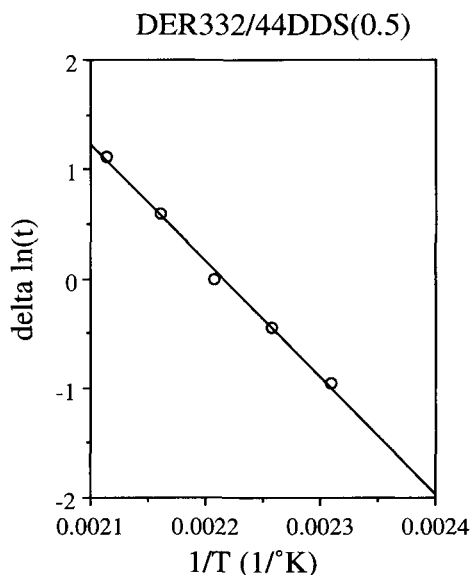


Figure 8 Logarithm of shift factor vs. the inverse of absolute cure temperature for DER332/44DDS ($a/e = 0.5$).

Table V Activation Energies (kJ/mol) Derived from the TBA Liquid-to-Rubber Transition and from Time-Temperature Shifts of T_g vs. In Time Plots

Resin	Activation Energy (kJ/mol)	
	$a/e = 0.5$	$a/e = 0.5$
DGEBA/33DDS	58	—
DER332/33DDS	58	87
826/33DDS	—	—
DGEBA/44DDS	69	—
DER332/44DDS	70	89
826/44DDS	—	—
DGEBA/DDM	48	—
DER332/DDM	47	85

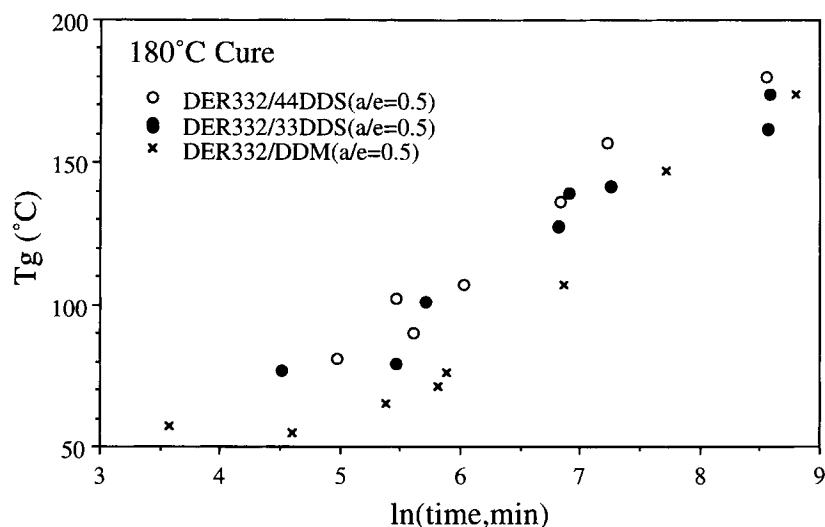


Figure 9 Glass transition temperature vs. logarithm of time for 180°C cures of DER332 $a/e = 0.5$ mixtures.

since it is the most reactive amine. These mixtures quickly reach a plateau T_g value of approximately 55°C, which then eventually continues to react to higher T_g s. The DDM system is the only resin in this study that clearly shows a plateau at the completion of the epoxy-amine reactions. The 33DDS and 44DDS mixtures both show an inflection, but since the amine is much less reactive in these systems, there exists a region in time where both epoxy-amine and etherification reactions are taking place simultaneously.

Venditti and Gillham⁵ present a model for T_g vs. conversion, x , representing the one-to-one relationship between these two parameters for thermosetting systems, including the DGEBA/TMAB resin systems investigated by Simon and Gillham.³ This model is as follows:

$\ln(T_g)$

$$= \frac{(1-x)\ln(T_{g0}) + (\Delta cp_\infty / \Delta cp_0)x \ln(T_{g\infty})}{(1-x) + (\Delta cp_\infty / \Delta cp_0)x}$$

where Δcp_∞ is the change in heat capacity of the fully cured resin at its T_g , $T_{g\infty}$, and Δcp_0 is the change in heat capacity of the uncured resin at its T_g , T_{g0} . Use of this model for the $a/e = 0.5$ samples in this study would require the assumption of a value for the unknown $T_{g\infty}$ and a value for the ratio of the change in heat capacity for these samples. However, the DDM mixtures show a plateau T_g value of 55°C where the epoxy-amine reactions appear to be complete and etherification has not occurred to any significant extent ($x = 0.5$). Using a measured T_{g0} value of 0°C and a value of 0.5 for the change in

heat capacity ratio (similar to the one reported by Venditti and Gillham⁵ for their epoxy-rich mixture), a value for $T_{g\infty}$ of 200°C was calculated. This appears to be a very reasonable estimation. The TBA results showed $T_{g\infty}$ must be higher than 174°C and Chang²⁵ estimated a T_g of approximately 190°C for a fully cured 2,4-EMI homopolymerized DGEBA. So a T_g vs. x relationship can be derived for at least one resin system in this study. The 33DDS and 44DDS $a/e = 0.5$ mixtures did not show a distinct plateau T_g before etherification became significant, so a similar derivation for $T_{g\infty}$ was not possible for these curing agents.

Plots of conversion vs. time were derived using the above model for the TBA T_g data obtained for the DER332/DDM ($a/e = 0.5$) cures. The initial cure is assumed to occur through epoxy-amine reactions and a rate for these reactions was calculated from the T_g at the liquid-to-rubber transition. For a sample cured at 180°C, a T_g of 48°C was measured for a cure time of 7 min. This corresponds to an epoxy-amine reaction rate of $6.6 \times 10^{-2} \text{ min}^{-1}$. A rate of etherification of $3.4 \times 10^{-4} \text{ min}^{-1}$ was calculated from the slope of the derived conversion vs. time plot of the 180°C data. The rate of epoxy-amine reactions are thus approximately 200 times faster than the etherification reactions at 180°C for DER332/DDM ($a/e = 0.5$). A similar rate of etherification is expected for all the curing agents for the $a/e = 0.5$ mixtures, as observed in the similar long time behavior shown in Figure 9. Using the inverse of the time to the liquid-to-rubber transition as a measure of the relative rate of the various curing

agents used in this study leads to the conclusion that the *rate* of the epoxy-amine reactions in the 33DDS $a/e = 0.5$ mixture are approximately 40 times faster and in the 44DDS $a/e = 0.5$ mixture 20 times faster than etherification at 180°C.

Expressing the rate of amine addition to epoxy as

$$\text{rate(AE)} = k_1[E][A]$$

where k_1 , $[E]$, and $[A]$ represent the rate constant for the epoxy-amine reactions, the epoxy concentration, and the amine concentration, respectively, and the etherification rate as

$$\text{rate(EE)} = k_2[E][\text{OH}]$$

where k_2 and $[\text{OH}]$ represent the rate constant for etherification and hydroxyl concentration, respectively, the ratio of the rate constants can then be expressed as

$$\frac{k_1}{k_2} = \frac{[E][\text{OH}]\text{rate(AE)}}{[E][A]\text{rate(EE)}}$$

The initial rate of epoxy-amine reactions is assumed to be represented by the rate derived from the liquid-to-rubber transition ($[E] = [E]_0$ and $[A] = [A]_0$) and the etherification rate is derived from where the amine addition reactions are essentially complete and etherification has just begun ($[E] = \frac{1}{2}[E]_0$ and $[\text{OH}] = [A]_0$). This leads to the following expression:

$$\frac{k_1}{k_2} = \frac{1}{2} \frac{\text{rate(AE)}}{\text{rate(EE)}}$$

from which rate constant ratios of 100 for DDM, 20 for 33DDS, and 10 for 44DDS are derived for $a/e = 0.5$ mixtures at 180°C. This is in good agreement with the rate constant ratio of 6 to 9 reported by Riccardi and Williams¹³ for a stoichiometric DGEBA/44DDS resin mixture in the 180 to 200°C temperature range derived from a kinetic model for DSC results. Thus, through the use of a model of the one-to-one relationship between T_g and conversion, a ratio of the rate constants of epoxy-amine reactions and etherification were derived. These approximate ratios may be somewhat lower than actual since the assumed rate of epoxy-amine reactions may be lower than the initial rate. Since etherification is shown as a much higher activation energy process, the above derived ratios should decrease as the cure temperature is raised for all the curing

agents investigated. This indicates that the ratio of the rate constants for amine addition and etherification can be very similar in a "postcure" temperature region for the commonly investigated DGEBA/44DDS resin system. The ratio of the *rates* of reaction for this system become more dominated by the concentration of functional groups than the rate constants as the cure temperature is raised.

CONCLUSIONS

TBA was utilized in this study to characterize the cure of three aromatic amines with DGEBA over a range of stoichiometries. Distinct differences in the reactivity of the curing agents were observed in the times to the liquid-to-rubber transition. DDM was the most reactive and 44DDS the least. Also, the higher the amine-to-epoxy ratio, the faster the rate of reaction for each of the curing agents. The stoichiometric and amine-rich samples all showed an ultimate T_g obtained on scanning to 250°C. The epoxy-rich samples for all the curing agents, however, continued to react, as indicated by large increases in T_g over very long times at elevated temperatures. This slow process was attributed to etherification and occurred after amine addition to epoxy was essentially complete and appeared to be independent of curing agent. Time-temperature shifts of T_g vs. $\ln(\text{time})$ data allowed for the calculation of an activation energy for etherification approximately 50% higher than those derived for amine addition reactions from the liquid-to-rubber transition. Through the use of a model of the one-to-one relationship between T_g and conversion, a ratio of the rate constants of epoxy-amine reactions and etherification were derived. At 180°C, approximate rate constant ratios of 100 for DDM mixtures, 20 for 33DDS mixtures, and 10 for 44DDS mixtures with DER332 were found.

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