

Influence of Cure Treatment on Extent of Reaction and Glassy Modulus for BADGE-DDM Epoxy Resin

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ABSTRACT: The extent of conversion of epoxy groups cured with diaminodiphenyl methane, a diamine, at 100°C was approximately 100%, and the glass-transition temperature (T_g^i) was found to be an increasing function of cure time with very large increases with extended postcure treatments at 180°C. However, this considerable increase in the T_g with postcure at 180°C was not due to the reactions of epoxy and amine groups. The specific volume reduced with the T_g to a minimum at 103° for the cured samples but showed a very slight increase with the T_g for the postcured samples. It was also found that the glassy modulus (E_g) was a linear decreasing function of the T_g . There were two separate relationships between the E_g and the rubbery modulus that depended on the cure conditions and suggested that the “structure” formed due to cure at a temperature of 100°C was different than that at postcure, which was 180°C. The most sensitive structural parameter for these cured epoxy resins was their T_g^i . © 20012001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1265–1276, 2001

Key words: cure treatment; extent of reaction; glassy modulus; glass-transition temperature; bisphenol A diglycidyl ether; diaminodiphenyl methane

INTRODUCTION

Epoxy resins are thermosets that require a cure process to attain physical and mechanical properties suitable for industrial applications. There are several texts^{1–4} that survey the chemistry and technology of epoxy resins. The properties of the cured resins depend on a combination of several factors: the structure of the prepolymer, the type and concentration of the curing agent or hard-

ener, the other specific agents such as accelerators or catalysts, and additives and modifiers.⁵

For a specific initial composition of resin plus curing agent the properties are a function of the cure treatment, that is the cure time (t_c) and cure temperature (T_c). For many applications the cure process is stepped, that is, the temperature is raised in stages and held constant for specific times. Often the cure may involve only two steps: a cure for a t_c at a T_c that is followed by a postcure at an elevated temperature (T_{pc}) for a fixed time (t_{pc}), which is the procedure we used.

The physical and mechanical properties change during the cure treatment because of the chemical reaction between the epoxy groups of the prepolymer with the reactive groups of the hardener. The effects of cure on the properties of thermosetting resins was reviewed some years

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ago by Nielsen⁶ and Prime,⁷ and epoxy resins were dealt with by Kaelble and coworkers.⁸ The chemistry of cure is not as simple as is often represented, and the kinetics were reviewed in detail by Ellis⁹ who discussed network formation leading to gelation and formation of a glass. There may also be side reactions other than the direct reaction of the epoxy groups with the functional groups of the hardener.

Studies of the effects of cure variables have involved variations of the structure and molecular weight of the epoxy prepolymer,⁹⁻¹² the ratio of the epoxy and hardener functional groups initially present ($R = [E]_0/[H]_0$), and the cure treatment^{13,14} (i.e., $T_c : t_c$ and $T_{pc} : t_{pc}$). (Here the $[E]_0$ and $[H]_0$ are the initial concentrations of the epoxy groups and reactive amine hydrogen atoms, respectively.)

The reports on the effects of the epoxy resin network structure on their properties are often contradictory as discussed by Morel et al.¹⁵ Thus, the major purpose of the present article was to report a systematic study of the effects of cure variables on the relationships between the extent of reactions (X_e and X_H) for an amine cured (diaminodiphenyl methane, DDM) bisphenol A type epoxy resin and their specific volumes with special reference to the effects of cure on the glassy modulus (E_g).

EXPERIMENTAL

The resin that was used (Shell 828) was mixed with 27 parts/100 of resin (phr) DDM hardener at 100°C. The batch weights of the resin and hardener were 400 ± 0.1 and 108 ± 0.1 g, respectively, and they were cast into slabs using sheet molds. With this ratio of hardener ($R = 0.96$) there is an excess of amine hydrogens to epoxy groups that ensures that essentially all of the epoxy groups react during cure. The molds were placed in an oven for curing at a T_c of 100°C for a t_c of 30 min to 24 h or cured at a T_c of 100°C for a t_c of 30 min followed by postcuring at a T_{pc} of 180°C for a t_{pc} of 30 min to 7 h. Two postcure routes were used: in route A the resin was postcured immediately following cure at a T_c of 100°C for a t_c of 30 min; in route B the sheets were allowed to cool to room temperature, then rested for 3 days at 22°C, and postcured at a T_{pc} of 180°C.

The Young's E_g values of the resins were determined from flexural testing of rectangular specimens measuring $120 \times 12.5 \times 4.5$ mm using

four-point loading in a Mayes servoelectric testing machine under displacement control. The inner and outer spans of the loading tests were 20 and 48 mm, respectively, to produce moment arms of 14 mm. The tests were conducted at room temperature ($T_{rt} = 22^\circ\text{C}$), which is well below the glass-transition temperature (T_g^i) of the resins. Most of the tests were performed at a constant displacement rate of 0.5 mm/min with some additional tests carried out at constant rates up to 10 mm/min. The complex Young's modulus (E^*) of the cured resins was measured using a Polymer Laboratories dynamic mechanical thermal analyzer over a temperature range of 20–220°C in an air environment with constant displacement. Measurements were at a fixed frequency of 1 Hz with a temperature scan of 4°C/min. The rubbery modulus (E'_r) was determined from the intercept of the rubbery plateau with the transition slope of the storage modulus ($\log E'$) versus the temperature curve. The T_g^i was determined from the intercept of the glassy plateau with the transition slope of the $\log E'$ versus the temperature curve as defined previously.¹³ The room temperature density (ρ_{rt}) was determined by weighing samples of the resins in air and immersed in water.

The concentration of epoxy groups at different cure times were measured to determine the X_e :

$$X_e = \frac{[E]_0 - [E]_t}{[E]_0}$$

where $[E]_0$ and $[E]_t$ are the concentrations of epoxy groups initially and at time t , respectively. A Perkin-Elmer 300 UV-visible spectrophotometer was used in the near IR spectral region (1–2.5 μm) in the absorbance recording mode at a scanning speed of 450 nm/min. From the spectroscopy measurements the normalized intensity of the epoxy absorption at 2.205 μm was used to determine the concentration of epoxy groups X_e . Because both primary and secondary amines would have reacted with the epoxy, their respective concentrations X_p and X_s were determined from the normalized functional group absorbances at 1.97 and 1.50 μm :

$$X_p = \frac{[H']_0 - [H']_t}{[H']_0}$$

where $[H']_0$ and $[H']_t$ are the initial concentration of amine groups and the concentration of primary amine hydrogen atoms at time t , respectively. The

Table I Extents of Reaction (X_e), Glass-Transition Temperatures (T_g^i), and Glassy Moduli (E_g) for Cured Samples

t'_c (min)	X_e	T_g^i (°C)	E_g (GPa)	N_c^o
0	0.20	—	—	1
30	0.62	93	4.16	2
40	0.72	96	4.35	3
45	0.77	97	4.43	4
60	0.80	99	4.29	5
120	0.87	103	4.18	6
180	0.95	109	4.15	7
280	0.97	113	4.14	8
360	0.99	115	4.14	9
720	0.99	118	3.93	10
1440	0.99	123	4.02	11

t_c (cure time) = $t'_c + 30$ min; N_c^o , cure number.

X_s is the extent of the reaction of the secondary amine hydrogen atoms calculated from their concentration as determined by the difference of the mixed amine band at 1.50 μm and the pure primary amine absorption band at 1.97 μm . Further details of most of the above experimental techniques were given previously.¹³

RESULTS

Tables I and II present the extents of reaction of the epoxy groups of the cured resins and their transition temperatures and glassy moduli. The measured values of the E_g are given in Figure 1,

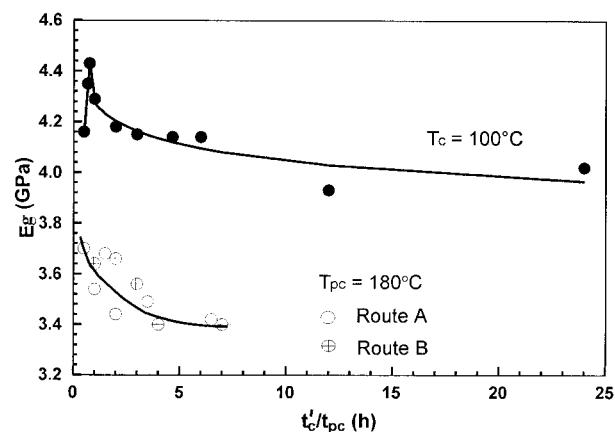


Figure 1 The glassy modulus (E_g) as a function of the cure/postcure time ($t'_c = t_c - 30$ min) is a common axis with t_{pc} .

which illustrates that with postcure the E_g was much lower ($\approx 20\%$) than that for a cure at a T_c of 100°C. There was a sharp maximum in the E_g versus t'_c ($t_c = t'_c + 30$ min), which is illustrated more clearly in Figure 2.

The changes in the extent of reaction of the epoxy and the amine hydrogen atoms are shown in Figure 3 for cure at a T_c of 100°C. It can be seen that X_e is asymptotic to $X_e = 1$ for long cure times. Also, $X_p/2$ tends to its limit of 0.5 for these long cures. In addition, the increase and finally the consumption of the secondary amines is shown as their concentration at t_c ($[N_2]_t$), which is the concentration of secondary amine hydrogen atoms at time t . Finally, all of the secondary amine hydrogens reacted and there was an approximate 1:1

Table II Extents of Reaction (X_e), Glass-Transition Temperatures (T_g^i), and Glassy Moduli (E_g) for Postcured Samples

t_{pc} (min)	X_e	T_g^i (°C)		E_g (GPa)		N_{pc}^o
		Route A	Route B	Route A	Route B	
0	—	—	—	—	—	—
30	0.98	140	—	3.70	—	1
60	0.99	146	148	3.54	3.64	2
90	0.99	155	—	3.68	—	3
120	0.99	160	160	3.44	3.66	4
180	0.99	—	166	—	3.56	5
210	0.99	168	—	3.49	—	6
240	0.99	—	170	—	3.40	7
390	0.99	172	—	3.42	—	8
420	0.99	—	172	—	3.40	9

t_{pc} , postcure time; N_{pc}^o , postcure number. Prior to postcure there was a cure for 30 min at 100°C and then $X_e = 0.20$.

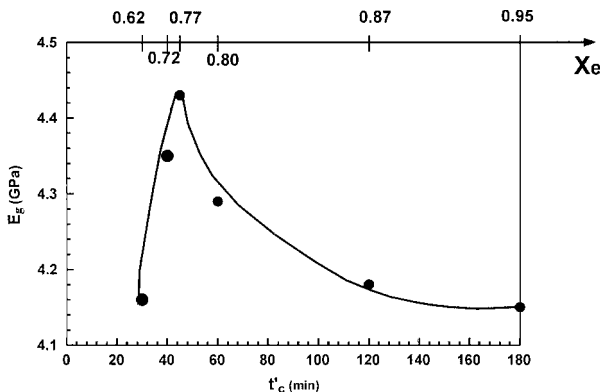


Figure 2 The detail from Figure 1 for $30 \leq t'_c \leq 180$ min. Note that $0.62 \leq X_e \leq 0.95$.

relationship between X_H and X_e (Fig. 4) as required by the approximately stoichiometric initial concentrations of epoxy and amine functional groups, $R = [E]_0/[H]_0 = 1$ (actually a small excess of amine, $R = 0.96$). The extent of the amine reaction was calculated as follows:

$$X_H = \frac{X_p}{2} + \frac{X_s}{2}$$

Similar data are given for the postcured resins in Figure 5.

The changes in the rubbery modulus with the extent of reaction are given in Figure 6, which shows that it increases monotonically with the extent of cure up to $X_e = 0.99$ and remained constant as $X_e \rightarrow 1.0$. The changes in the rubbery modulus due to postcure at a T_{pc} of 180°C were not related to the extent of epoxy-amine reac-

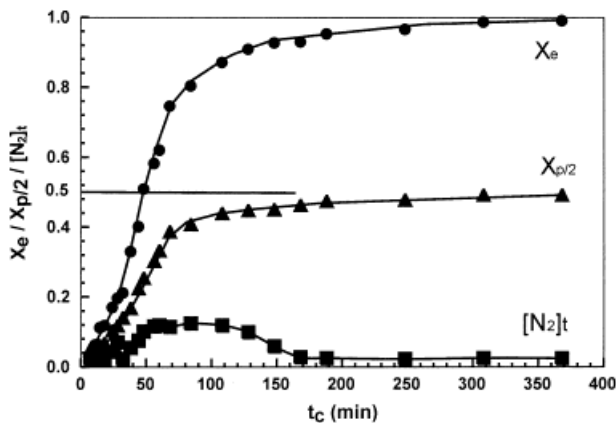


Figure 3 The extent of the reaction versus the cure time (t_c) for curing at 100°C .

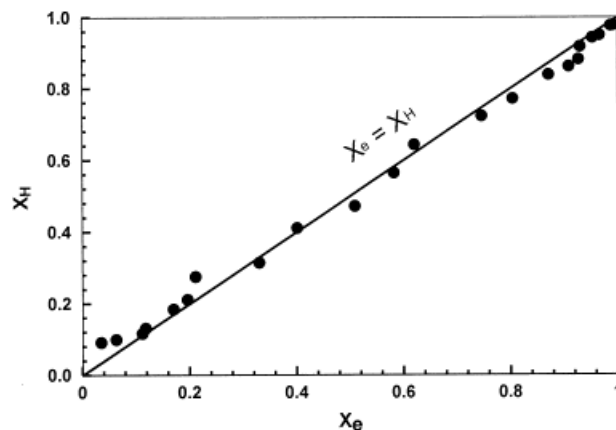


Figure 4 The extent of the reaction of amine versus epoxy groups for a cure at 100°C .

tions. Also shown in Figure 6 are the changes in the E_g with the extent of reaction, which shows that it reached a maximum at $X_e \approx 0.77$ and was reduced as $X_e \rightarrow 0.99$. Again the changes due to postcure were not related to the extent of reactions. The changes in E_g were systematic as previously shown in Figures 1 and 2.

A detailed discussion of the changes in density with the cure treatment¹³ (see Fig. 4) showed that there was a sharp maximum similar to that of the E_g versus t'_c given in Figure 1. Thus, presentation of the data and discussion is not repeated here, but the relationship between the E_g and specific volume at room temperature ($\bar{v}_{rt} = 1/\rho_{rt}$) is shown in Figure 7. The relationship between the T_g^i and density is given in Figure 8, and the relationship between the E_g and T_g^i is given in Figure 9.

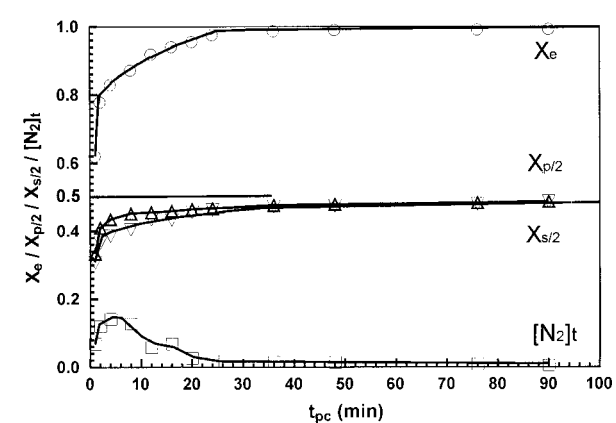


Figure 5 The extent of the reaction of amine and epoxy groups with postcure versus postcure time.

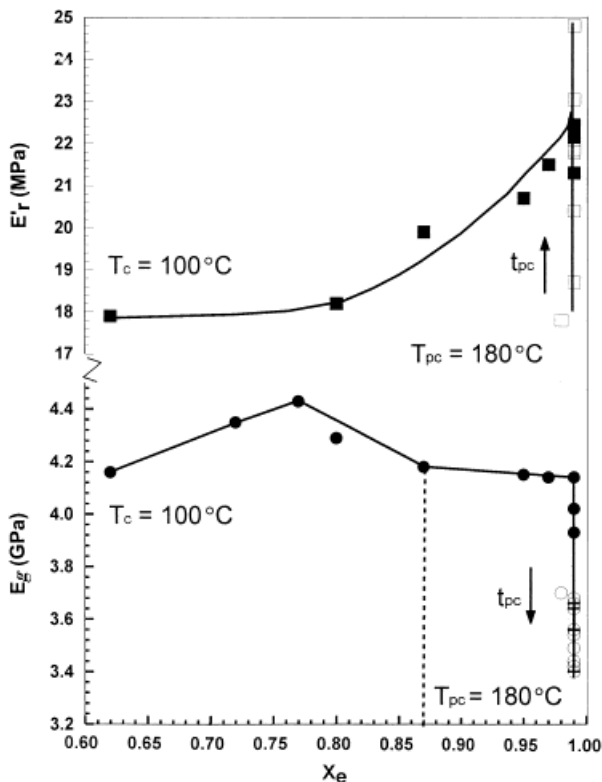


Figure 6 The lower curve is the glassy modulus (E_g) versus the extent of the reaction (X_e). The upper curve is the rubbery modulus (E_r) versus the X_e . The arrows indicate increasing postcure time.

DISCUSSION

Glassy Modulus as Function of Cure Treatment

In this series of experiments the composition was kept constant with a slight excess of hardener,

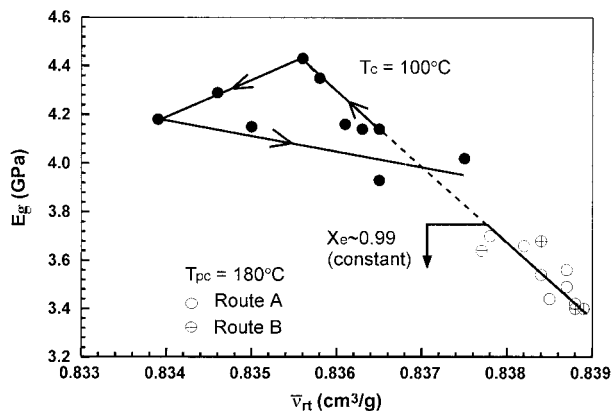


Figure 7 The glassy modulus (E_g) versus the specific volume at room temperature (v_{rt}^- , 22°C). The arrows indicate increasing cure time.

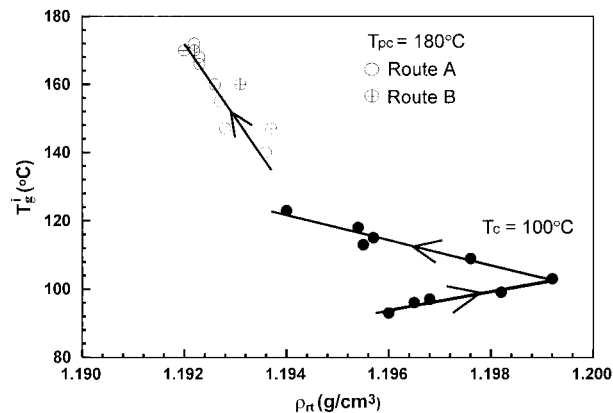


Figure 8 The glass-transition temperature (T_g^i) versus the density at room temperature (ρ_{rt}). The arrows indicate the increasing cure/postcure times (see Tables I, II).

which is the epoxy-hardener ratio (E/A) that is often used for the cure of bisphenol A diglycidyl ether (BADGE) type resins with DDM. In practice it is usual for the composition to be fixed, which means the E/A ratio is constant, and then the variable is the cure schedule. Also, a common practice is to use stepped cures with the resin held at constant temperature for a specific time and the temperature raised in a sequence of time steps. Thus, the cure and postcure temperatures and times have to be determined to attain a specific balance of properties. The two cure treatments used were the variable t_c with a constant T_c of 100°C and a variable t_{pc} at a constant T_{pc} of 180°C following an initial cure at 100°C for a t_c of 30 min. The changes in the glassy modulus are shown in Figure 1 where $t'_c = t_c - 30$ min to allow

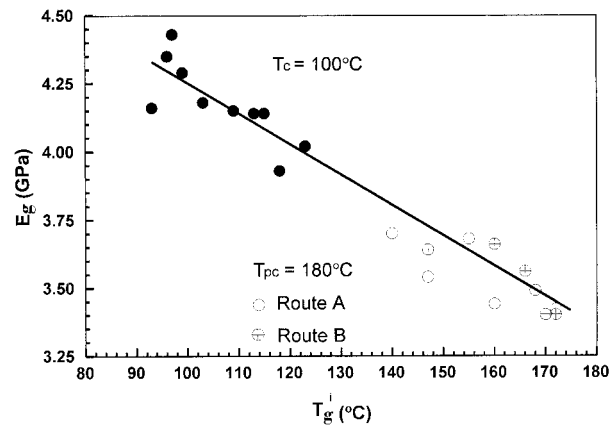


Figure 9 The glassy modulus (E_g) versus the glass-transition temperature (T_g^i).

a common time axis for a cure at T_c and T_{pc} of 100 and 180°C, respectively. This sequence would embrace the usual cure practice with determination of the glassy modulus and other properties as a function of the cure and postcure times.

For cure at a T_c of 100°C there was a sharp maximum in the E_g at about a t'_c of 45 min, which is more clearly seen in Figure 2 with the expanded t'_c scale. Following the sharp maximum there was a gradual decrease in the E_g with extended cure time, even though there could be little change in the extent of reaction, because $X_e \approx 0.99$ when the t'_c was 180 min. The changes in the X_e and amine hydrogens are reported and discussed in the following section. For postcures there was an essentially monotonic decrease in the E_g with postcure time and there could not be any further epoxy-amine reactions because all epoxy groups were consumed after a t_{pc} of 30 min (see Table II). Also, it may be noted that rapid quenching had a minimal effect on the glassy modulus of the postcured resins. Thus, the effective structure is essentially independent of the annealing processes. The changes in the E_g with cure paralleled the changes in the room temperature density of these samples reported recently,¹³ which is discussed in a later section. For this series of experiments with a slight excess of amine groups, which ensured that all of the epoxy groups reacted, and because $R = 0.96$, the minimum extent of reaction for gelation was $p = 0.586$, which was slightly greater than the 0.577 required when $R = 1$. From Figure 1 it can be seen that the extent of reaction for the shortest cure time ($t_c = 1 \text{ h} = t'_c = 30 \text{ min}$) was 0.62, which showed that this sample must have contained an important weight fraction of sol. This was the minimum extent of reaction that allowed the samples to be prepared for measurement of the glassy modulus.

Conversion of Reactive Groups

The concentrations of the epoxy and amine hydrogen groups were measured as described earlier. It is convenient to express these concentrations in terms of the conversions for epoxy, primary, and secondary amines as X_e , X_p , and X_s , respectively. In Figure 3 the X_e is plotted versus the t_c . The conversion of primary amine hydrogens is reported as $X_p/2$ because the initial ratio of epoxy to primary amines is ≈ 2 .

Figure 3 shows that the rates of conversion initially increased with the time of cure because

these curves are convex to the time axis. For longer cure times the $X_e \rightarrow 1$ and $X_p/2 \rightarrow 0.5$, which were their limiting values for complete reaction of the epoxy and primary amine functional groups. The kinetics of amine cure reactions was reviewed in detail¹⁶ and it would be inappropriate to give a detailed analysis of these results because our primary purpose was to report and discuss the effects of cure treatment on the properties of the cured resin. The important result to note is that for long cure times at 100°C the conversion of epoxy groups approached unity ($X_e \rightarrow 1.0$). There was the normal problem that as the conversion approaches unity the assay becomes relatively less accurate. However, it is possible to observe vestigial epoxy IR absorption even when the concentration of epoxy groups is too low for accurate assay. For the cure times longer than 400 min there was very little evidence of the presence of epoxy groups, and it was similar for $X_p/2$. Hence, it may be concluded that essentially all reactive groups have reacted for long cure times at 100°C, which was a t_c of $\geq 6 \text{ h}$. It may also be noted (Fig. 3) that the concentration of unreacted secondary amine groups initially increased and then fell to essentially zero at long cure times.

The stoichiometric equivalence of the reactions between amine and epoxy groups is shown in Figure 4 in which the extent of the amine reaction is plotted versus X_e . It would appear that the X_H was initially slightly in excess of the X_e for short cure times and the reverse was the case for long cure times. These deviations were small and further analysis is required to confirm their significance. However, the essentially complete conversion of the epoxy and amine groups was further confirmed. A similar conclusion followed from the results for postcure at a T_{pc} of 180°C given in Figure 5.

Affects of Conversion on Elastic Moduli

Glassy Modulus for 100°C Cure Temperature

The changes in the glassy modulus with the extent of conversion are shown in Figure 6. For a cure at a T_c of 100°C the effect of cure on the glassy modulus was small but an increase and decrease were observed, which illustrated why there are reports that both effects were observed as noted in the Introduction. For $0.6 < X_e < 0.75$ the glassy modulus increased linearly by about 7.5%, and for $X_e > 0.75$ there was an essentially linear decrease of about 7.5%. The accuracy of these modulus measurements was sufficient for

this effect to be real, although the changes in the glassy modulus were small. There were other property changes that paralleled those for the glassy modulus for resins with extents of conversion within the range of $0.6 < X_e < 0.87$, which is discussed later.

Thus, for a cure at 100°C the structural changes were significant because the glass-transition temperature increased with extended cure, which is also discussed later. It should be noted that the range of values for E_g were within those expected for thermosetting and thermoplastics below their glass-transition temperatures. Although epoxy resins are generally *somewhat* viscoelastic, even below their T_g values, for these samples the rate of strain had a minimal effect on the measured value of the E_g for constant displacement rates from 0.5 to 10 mm/min. This was because the major factor determining the glassy modulus was the intermolecular force field between network chains as discussed by Tobolsky.¹⁷ Kaelble et al.⁸ applied this theory to estimate the glassy modulus of epoxy resins, and aspects of these calculations are discussed later.

It can be appreciated that these changes in the E_g for a cure at 100°C were not directly related to the network structure because the rubbery modulus increased monotonically with the extent of reaction as shown in Figure 6. Often the network structure parameter, which is the average molecular weight of network chains (\bar{M}_c), is calculated from the rubbery modulus.⁸ There are difficulties with such calculations with cured thermosetting resins because the network chains are short. The rubbery modulus is subsequently discussed; however, with cure at 100°C the average length of the network chains decreased with the increase in cure time.

Glassy Modulus for 180°C Postcure Temperature

For postcures at 180°C there was little change in the X_e , which is constant at approximately 0.99. In Figure 1 and Table II it can be seen that the E_g was decreased by about 10% with postcure and it was previously noted that there was a decrease in the E_g with extended cure at 100°C , even when $X_e \approx 0.99$ (Fig. 6). There was total decrease in the E_g of about 18%, including cure at a T_c of 100 and postcure at a T_{pc} of 180°C . This again confirmed that there were structural changes with extended cure and postcure of this DDM/epoxy system that were not directly associated with the reactions between amine hydrogens and epoxy groups.

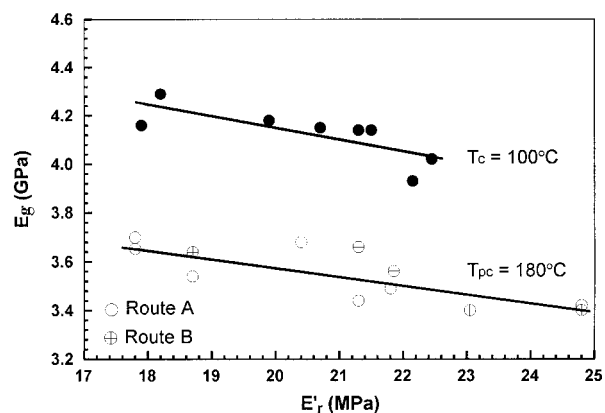


Figure 10 The glassy modulus (E_g) versus the rubbery modulus (E_r).

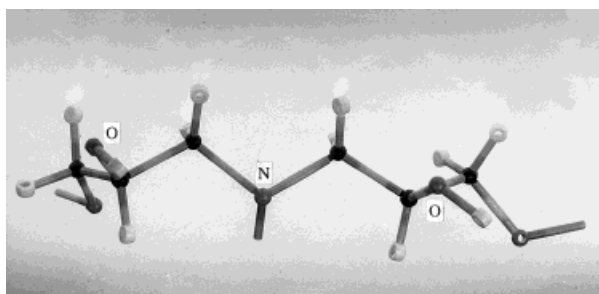
These structural changes affected the glass-transition temperatures as reported previously¹³ and the glassy modulus in the present results.

Similarly, there were changes in the network structure with postcure not related to X_e as can be seen from Figure 6 because the E_r increased with postcure time while the $X_e \approx 0.99$ was constant. Thus, not only was the network structure important but also the junction flexibility, which for a "tight" network affects the apparent concentration of network chains. Also, the density or specific volume of the resin affects the glassy elastic modulus. The relationships between the E_g and the room temperature density are discussed in the next section.

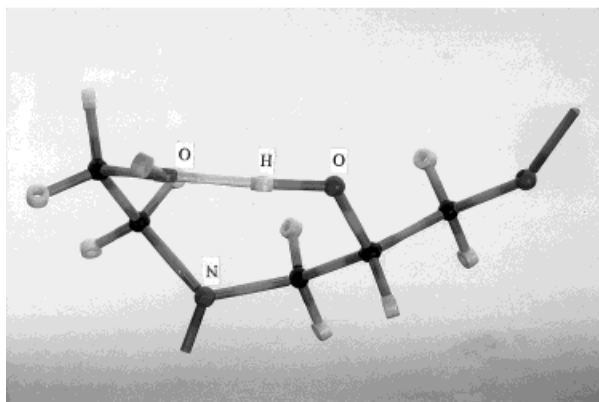
Relationships between Glassy Modulus and Network Structure

The parameter representing the network structure is the rubbery modulus. The conventional calculation of \bar{M}_c , the number-average molecular weight between junction points, is not reported. The reasons for not converting E_r to \bar{M}_c were outlined previously. However, the relationship between \bar{M}_c and E_r normally used is linear, apart from a correction for chain ends. That correction is usually regarded as negligible for tight networks; thus, for the present purposes there would be no advantage in converting E_r to \bar{M}_c , although calculation of \bar{M}_c from our E_r measurements yielded acceptable values of \bar{M}_c . These effects are discussed in the Conclusions section.

From Figure 10 it can be seen that there were two inverse, approximately linear, relationships between the E_g and E_r ; also, the tighter the network, the lower the value of the E_g . Because there



(a)



(b)

Figure 11 Structure I: (a) an extended conformation and (b) H-bonded ring.

are two separate relationships that depend on the cure conditions, it must be concluded that the structure formed at a T_c of 100°C was different from that formed at a T_{pc} of 180°C.

These results showed that calculation of the network structure from a chemical model is unsatisfactory. Although formally correct, the method proposed by Macosko and Miller¹⁸ is not satisfactory when the flexibility of the junction points change. For rubbery networks with long network chains this effect is unimportant. However, for tight networks the flexibility of junctions affects the rubbery modulus.

There are several interactions that may affect the flexibility of the junctions, for instance, hydrogen bonding of the hydroxyl groups, as shown in structure I in Figure 11. The concentration of hydrogen bonded groups is temperature dependent.¹⁹ Banks and Ellis showed that the presence of water facilitates the opening of such an eight-membered ring, and hence a low concentration of water causes a large decrease in the glass transition temperature of the resin.²⁰

With prolonged postcure at 180°C it is possible that water was eliminated from structure I with

the formation of a substituted morpholine ring (II) as shown in Figure 12.

A similar ring closure by elimination of water was the mechanism for the cure of polyamic acid (material H) proposed by Venditti and Gillham.²¹ It would be helpful if a search for the presence of structure II confirmed its presence. The formation of substituted morpholine rings would account for the changes in properties without any further reaction between amine and epoxy groups. There may be other reactions that decreased the flexibility of the network junctions.

Glass-Transition Temperature as Measure of Resin Structure: Relationships between Glassy Modulus and Glass Transition Temperature

The methods of determining the structure of network polymers was discussed by Nielsen.⁶ It would appear that the most sensitive parameter is the glass-transition temperature. More recently Wang and Gillham²² used the change in T_g to provide a parameter to specify the extent of cure of resins, and that proposal was discussed by Ellis.²³ Ellis and colleagues pointed out that an operational definition of T_g is required because a full specification of the glass-transition requires four or maybe five parameters.¹³ However, it is useful to have a single parameter and our choice was T_g^i , which was discussed in detail recently.¹³ The T_g^i is the most useful single parameter because it models the relationship between the cooperative rearrangement of chain segments and the temperature dependence of such molecular motion. Thus, it is sensitive to the flexibility of the junctions as discussed earlier.

The advantages of correlating the properties with the glass-transition temperature is well il-

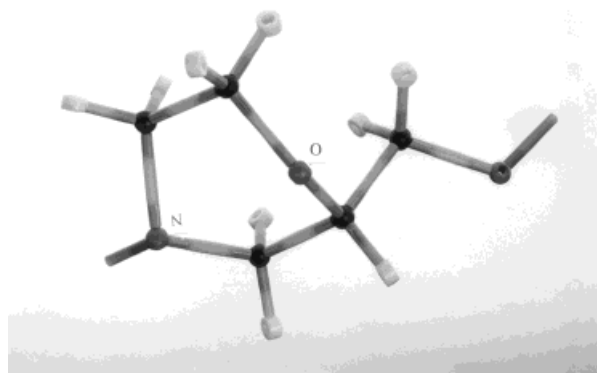


Figure 12 Structure II: the formation of a substituted morpholine ring.

illustrated by the present data (Fig. 9), which shows that there was a linear relationship between the E_g and T_g^i . There was a single relationship that correlated data for a cure at a T_c of 100°C and a T_{pc} of 180°C. The inverse linear relationship is clearly shown in Figure 9, but this is not unique; for other systems the relationship may be more complicated. For instance, an analysis of the data of Palmese and McCullough²⁴ showed that the relationship between the E_g and T_g depended on the ratio of epoxy to amine groups in the initial resin hardener mixture.

The linear relationship with increasing T_g^i with a decrease in the density of the cured resins is shown in Figure 8, which includes the resins cured at a T_c of 100°C for long cure times and those postcured at a T_{pc} of 180°C. However, for shorter cure times at a T_c of 100°C there was a separate branch where the relation between T_g^i and ρ_{rt} with E_g increased with density. The resins for these shorter cure times coincided with those shown in Figure 2 and for $0.6 < X_e < 0.87$ shown in Figure 6. Thus, the linear branch for shorter cure times was also the region where there was a linear decrease in the specific volume, which was directly related to the extent of reaction as shown previously.¹³ In that article (see Fig. 11) there was a sharp discontinuity at $X_e = 0.87$, which was the same as the discontinuity found for the relationship between T_g^i and ρ_{rt} .

CONCLUSIONS

The present work showed that the extent of conversion of epoxy groups cured with DDM could attain essentially 100% (Fig. 3), which is in agreement with the observations of Mijovic and coworkers²⁵ and is also endorsed by Wise et al.²⁶ It was initially surprising that all the epoxy groups were consumed at a cure temperature of 100°C because with the onset of glass formation the cure reactions become diffusion controlled and limited.²⁷ However, Mijovic et al.²⁵ found that very high conversions were attained with DDM, even for cures at 100°C (see their fig. 7). The rate of conversion of epoxy groups for a cure at 100°C was similar but not exactly the same as those reported by Mijovic et al.²⁵ and Wise et al.²⁶ and a detailed analytical comparison will be presented in the future.²⁷ There is an added advantage with the present measurements because the extent of reaction of the amine groups was also measured.

There was an increase in the glass-transition temperature with postcure at 180°C that was not due to the reactions of the epoxy and amine groups (Fig. 13). It is important to note that there were other reactions that may have occurred as the glassy state was approached. The reaction proposed for the formation of a morpholine ring II could occur even in the glassy state because the reactive groups were in close proximity and even hydrogen bonded (I) prior to the elimination of a molecule of water.

For cure at 100°C the limiting T_g was 124°C, which is approximately that found by Wise and coworkers²⁶ (see their fig. 15) who also show that the T_g is a function of the cure temperature. With long postcures at 180°C a somewhat higher limiting T_g of 178°C was attained¹³ compared to the 170°C of Wise et al.²⁶

With the possible formation of a morpholine ring II there is no corresponding decrease in specific volume that occurs with the reaction of epoxy and amine groups. Thus, there are apparent anomalies in the change of density with cure. There was a minimum in the specific volume versus glass-transition temperature (Fig. 14) for a cure at a T_c of 100°C, which is similar to the minimum observed by Vindetti and Gillham.²¹ However, with postcure at a T_{pc} of 180°C there was only a slight increase in the specific volume with the T_g . Thus, although there was a general dependence of the glass-transition temperature on the free volume,²⁸ the flexibility of the network chains was important,²⁹ as was that of the network junctions, with the formation of hydrogen bonds and possibly the formation of morpholine rings. Thus, calculation of

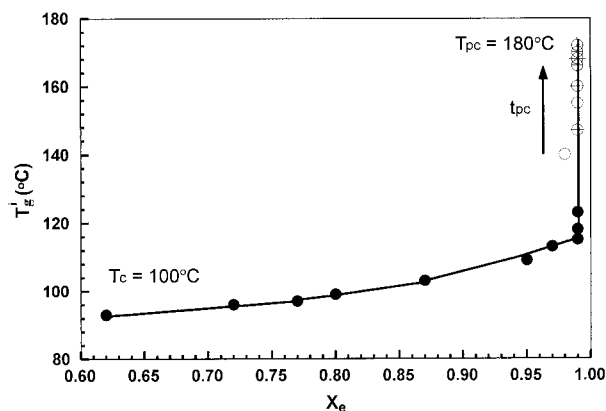


Figure 13 The glass-transition temperature (T_g^i) versus the extent of reaction of the epoxy groups (X_e). The arrow indicates increasing postcure time.

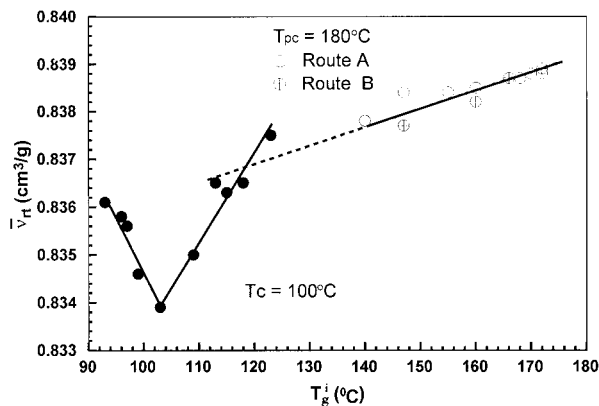


Figure 14 The specific volume at room temperature (\bar{v}_{rt}) versus the glass-transition temperature (T_g^i). The T_g^i increases with the cure time and extent of epoxy conversion for a cure at 100°C (see Table I). The T_g^i increases with postcure time but is independent of the epoxy conversion (see Table II).

the rubbery network structure from measurements of the rubbery modulus was not as straightforward as often presented. Similarly, the calculation of \bar{M}_c from the extent of the chemical reaction was correct only when the restrictions of the probability theory for formation of networks applied¹⁸ and there were no affects from the changes in the flexibility of the network junctions.

The calculation of a value for \bar{M}_c for an epoxy resin network from measurements of the E'_r using the following equation is simplistic:

$$E'_r = \gamma N k T = \frac{\gamma \rho R T}{\bar{M}_c} \quad (1)$$

where N is the number of network chains per unit volume; γ is a numerical factor, the precise value depending on the detailed structure of the network; ρ is the density; and \bar{M}_c is the mean molecular weight of the network chains. Use of eq. (1) implies that all of the polymer is incorporated into the network without any free chain ends. Such a condition only applies when the extents of conversion are high at $X_e > 0.9$ or even higher, depending on the quantitative applicability of the relationships given by Macosko and Miller.¹⁸ Network structures are discussed by Mark,³⁰ who illustrates the complications that may arise. This equation is only applicable to essentially ideal networks where the only contribution to the elastic stored energy function is entropic. Even for elastomeric

networks with long network chains the enthalpic contribution may be significant, (approximately 20% or more).³⁰ Use of eq. (1) directly ignores such internal energy changes.

The derivation of eq. (1) imposes restrictions on the network structure which are not satisfied by epoxy networks. A study many years ago³¹ used the concepts of $\bar{M}_{c,phys}$ for the ideal network that would yield estimates of the rubbery modulus from relationships such as eq. (1). However, the network formed by chemical reactions is not ideal and calculations based on the extent of conversion yield a chemical estimate of network structure designated as $\bar{M}_{c,chem}$. The relationship between $\bar{M}_{c,phys}$ and $\bar{M}_{c,chem}$ depends on the detailed structure of the network and the specific chemistry involved in its formation. Fuller details of the theory of elastomeric networks are readily available.^{30,32}

From inspection of Figure 6 it can be appreciated that for a cure at a T_c of 100°C the E'_r increases monotonically with the extent of reaction for $X_e < 0.99$. However, with postcure the E'_r is essentially independent of the extent of reaction. This is because changes of the structure of the resin with postcure do not involve the conversion of epoxy groups. Also, with reactions, such as the formation of a possible morpholine ring II at the network junctions, the effective number of network chains is reduced because a more rigid structure is formed. Thus, with a simplistic interpretation using eq. (1), the rubbery modulus is also reduced. The E'_r should increase with the temperature so postcured samples with high T_g^i would have an even lower value of E'_r if corrected to a reference temperature. Hence, we did not correct for the temperature effect because of this and other uncertainties. The changes in the structure of this epoxy resin with postcure were not due to the physical aging effects investigated by Maddox and Gillham³³ but were instead due to the formation of H-bonded structures such as I or chemical reactions of which the formation of II is only one suggestion.

The use of the near IR absorption can now be agreed upon as the most satisfactory method to monitor the extent of reaction of the epoxy groups. However, at present the most sensitive measure of the molecular structure of highly crosslinked networks is their glass-transition temperature. Gillham reported on many studies that show the advantages of monitoring the cure of thermosetting systems by measuring their

glass-transition temperatures. The only caution that we would add is that an operational definition of the glass transition must be specified. Figure 9 shows that the glass-transition temperature can be used as an efficient measure of the structure of these cured epoxy resins. There is a clear dependence of the glassy modulus on the glass-transition temperature.

The glassy modulus must be a function that represents intermolecular forces and very localized reorientation of segments of either the network chains or their junctions. The latter is determined by the type of hardener and the extent of reaction of their functional groups with epoxy groups plus any other reactions that affect the flexibility of the junctions. The localized reorientation of the bisphenol A unit was discussed in detail by Luise and Yannas in terms of their strophon theory.³⁴ Unfortunately, this does not appear to be extended to highly crosslinked resins. It is important to note that the displacement of the atoms of the polymer in the glassy state was very small. For rubberlike elastic behavior there must be extensive reorientation of polymer segments so that the entropy term makes a significant contribution to the free energy of deformation, hence the differences in the relationships (Fig. 10) between the E_g and E_r' for the resins cured at a T_c of 100°C and those postcured at 180°C.

A very general theory for the elastic modulus of polymers that is determined only by intermolecular forces was proposed by Tobolsky¹⁷ and was used by Kaelble et al.⁸ to give an estimate of the glassy modulus of epoxy resins of 3.1–4.0 GPa. The present results were of the same order as these but slightly higher, which may have been due to difficulties in estimating the solubility parameter. However, it was not possible to explain the relationship shown in Figure 9 simply in terms of intermolecular forces.

The inverse relationship between the E_g and T_g shown in Figure 9 was found in other systems but is not universal. For instance, the analysis of the data of Palmese and McCullough²⁴ showed that it was not correct for resins cured with an excess of epoxy groups but did apply for those cured with the stoichiometric concentration and an excess of amine.

However, it is clear from the present results that the glass-transition temperature of a cured resin is the parameter that most accurately represents the state of cure of a resin and also allows

the specification of a full cure and the degree of cure.

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