

Effects of Cure Treatment on Glass Transition Temperatures for a BADGE–DDM Epoxy Resin

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SYNOPSIS

The extent of cure for epoxy resin (BADGE) with a small excess of amine hardener (DDM, 4 w/o) was determined by assay of the epoxy groups using near infrared spectroscopy. The effect of cure time at 100°C and postcure time at 180°C has been investigated. For the lower temperature cures the room temperature density, ρ_{rt} , increased with time, reaching a maximum at $X_e = 0.87$, and then decreased with extended cure times. For postcure, there was a monotonic decrease in ρ_{rt} that was unrelated to the extent of cure. There was an approximate linear relationship between glass transition temperature and $\ln(t)$, which increased even when essentially all of the epoxy groups had reacted, that is $X_e \sim 0.99$. © 1996 John Wiley & Sons, Inc.

The importance of the specification of the operational definition of glass transition temperatures is clearly established by comparison of different methods of determining glass transition temperatures.

For isothermal cures, there were broad $\tan \delta$ loss peaks, while for postcure, there was a large reduction in size of the loss peak at extended times. This suggests that there is a change in network structure that is not related to the extent of reaction of epoxy groups, because $X_e \sim 0.99$ after 30 min at 180°C.

INTRODUCTION

The attainment of optimum mechanical performance from thermosetting resins requires control of the cure process. The operational variables are the structure of the prepolymers, the functionality of the curing agent or hardener, the stoichiometry of the reactive groups, and the cure treatment, with specification of the thermal history of the resin after

the start of mixing the prepolymer with hardener. General reviews are those of Nielsen¹ and Prime,² who discuss the most important thermosetting resins such as epoxies, phenolics, and unsaturated polyesters. Gillham^{3,4} introduced a time–temperature transformation (TTT) diagram to provide a basis for the specification of the cure of thermosetting resins. More recently, Wang and Gillham⁵ introduced a T_g -temperature–property (T_g TP) diagram to represent the structural changes that occur during cure to the glass transition temperature, T_g , that increases due to the cure processes. An outline of the structural changes that occur during cure of a thermosetting resin is given by Ellis⁶ in a recent discussion of TTT diagrams, together with a slightly modified CTP diagram in which the structure is related to a cure parameter, C , which is defined by $C = (T_g - T_{g0}) / (T_g - T_{g\infty})$, where T_{g0} is the glass transition temperature of the initially uncured system and $T_{g\infty}$ that of a fully cured resin. T_g is the glass transition temperature that depends on the thermal treatment of the resin–hardener mixture. The difficulties of defining a glass transition temperature unambiguously were mentioned and not explored, but will be discussed in detail in the present article. Epoxy resins have many important industrial applications, such as coatings, adhesives, and resin

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matrices, for advanced composites. There are several monographs⁷⁻⁹ in which the chemistry and technology of epoxy resins is discussed in detail. The importance of various factors that affect the T_g of an epoxy network has been evaluated by Chang,¹⁰ who suggests that the orders of magnitude (in °C) of the influence is approximately:

Degree of cure	200
Catalyst concentration	> 50
Network structure/curing history	> 50
Purity of monomer	10
Physical ageing (reversible)	10

These estimates were based on a DGEBA resin cured with a catalyst that promotes the homopolymerisation of epoxy groups to form ether linkages. Chang¹⁰ suggests that a probable highest limit for T_g of about 190°C as the degree of cure increases with thermal treatment of the resin.

With cure involving reaction of epoxy groups with amine hydrogen atoms there is a reduction in the volume occupied by the system and the free volume decreases, and there is also increased "resistance" to conformational changes. When the structure of the cured resin is varied by increasing the molecular weight of the prepolymer and the cure treatment kept constant, the major effect on the glass transition temperature will be due to changes in free volume as cure progresses, and as was shown previously,¹¹ $T_g = T_g(\bar{M}_n^{-1})$ is a linear function. This relationship was recently confirmed by Vakil and Martin.¹²

An alternative approach¹³ was the study of the affect of the epoxy-amine ratio (Epon 828 plus PACM-20) on the glass transition temperature. A maximum T_g of about 170°C was attained with the stoichiometric ratio of epoxy to amine groups. Also, the effect of the "flexibility" of the diamine hardener has also been evaluated.¹⁴

The overall aim of the present work is to improve understanding of the role of thermal treatments on the properties of a cured epoxy resin and, hence, to be able to specify cure treatments for specific applications. A constant composition of the resin-hardener (BADGE plus DDM) has been investigated with an isothermal cure at $T_c = 100^\circ\text{C}$ and postcure at $T_{pc} = 180^\circ\text{C}$ for a range of cure and postcure times, t_c and t_{pc} . Measurement of the conversion of epoxy groups, room temperature density, and glass transition temperatures and the effects of the thermal treatment on these properties are reported and detailed correlations presented. It is shown that it is

important to specify an unambiguous operational definition of the glass transition temperature, and the differences between alternative definitions are quantified. We have found a limiting glass transition temperature for BADGE cured with DDM of 178–189°C following a postcure at 180°C for 7 h. The exact value of T_g will depend on the method of measurement, which will be explored in detail following presentation of our results. This limiting glass transition temperature is close to that suggested by Chang¹⁰ mentioned earlier.

EXPERIMENTAL MEASUREMENTS

Preparation of Specimens

The resin, Shell 828, was mixed with 27 phr (parts per hundred of resin) hardener, DDM, at 100°C with batch weights of resin of 400 ± 0.1 and hardener of 108 ± 0.1 g and cast between sheet molds (see below). With this ratio of hardener (4 w/o excess DDM) there is an excess of amine hydrogens to epoxy groups that ensures that essentially all of the epoxy groups react during cure. Two materials were used for the molds, glass and mild steel plates; the former was used for cures at $T_c = 100^\circ\text{C}$ and the latter for postcures at $T_{pc} = 180^\circ\text{C}$. The plates were degreased and cleaned before coating with "Freekote 44" (Rotec Chemicals Ltd) release agent, which was "baked on" at 95°C. The mixed resin and hardener were poured on to a plate and another plate placed on top. The plates were separated by a spacer so that sheets either 4.5 or 1.5 mm thick could be produced. After carefully filling the cavity between the plates they were then clamped together and four thermocouples were inserted to monitor the cure temperature. The molds were placed in an air-circulating oven at the required cure or postcure temperature. After specific cure times, t_c , the glass mold was removed from the oven and allowed to cool to room temperature. Postcured samples were cured in the metal molds at $T_{pc} = 180^\circ\text{C}$, and some samples were cooled slowly and others rapidly quenched to -18°C as noted appropriately when the results are reported. Two postcure routes were used: route A—the resin was cured at $T_c = 100^\circ\text{C}$ for $t_c = 30$ min and then postcured immediately; route B—the sheets were allowed to cool to room temperature, "rested" for 3 days at 22°C, and then postcured at $T_{pc} = 180^\circ\text{C}$. Cure and postcure times t_c and t_{pc} are reported as equivalent times for the thermal treatments. The error in these reported times are larger

for shorter cure times but negligible for longer cures, $t_c, t_{pc} > 60$ min. Specimens for measurement of their viscoelastic properties were cut from the molded sheets to fit into the DMTA apparatus. These specimens were either $4 \times 4 \times 4.5$ or $40 \times 10 \times 1.5$ mm.

DMTA Measurements

The complex Young's modulus E^* of the cured resins were measured using a Polymer Laboratories DMTA¹⁵ over the temperature range 20 to 220°C in an air environment with constant displacement. Some measurements were at a fixed frequency of 1 Hz with a temperature scan of 4°C/min, that is, $dT/dt = q = 4^\circ\text{C}/\text{min}$. Other measurements were carried out in the multifrequency mode with a temperature scan of 2°C/min. The frequencies were 0.33, 1, 3, and 10 Hz or 1, 3, 10, and 30 Hz. Three or four samples for each cure/postcure condition were measured. Data acquisition was via a Hewlett Packard HP900 with Polymer Laboratories software.¹⁵ Changes in the storage modulus with cure times and postcure are illustrated in Figure 1. It should be noted that the glass-to-rubber transition for the shorter cure times at $T_c = 100^\circ\text{C}$ are broadened by further cure occurring when the temperatures rise above the original cure temperature. The operational definitions of the glass transition temperature of the cured resins are illustrated schematically in Figure 2. For Figure 2(a) and (c), measurements were made with a constant displacement and a constant frequency of 1 Hz and $q = 4^\circ\text{C}/\text{min}$. For the multifrequency mode measurements, Figure 2(b), a constant displacement was also used, but with $q = 2^\circ\text{C}/\text{min}$. The significance of these oper-

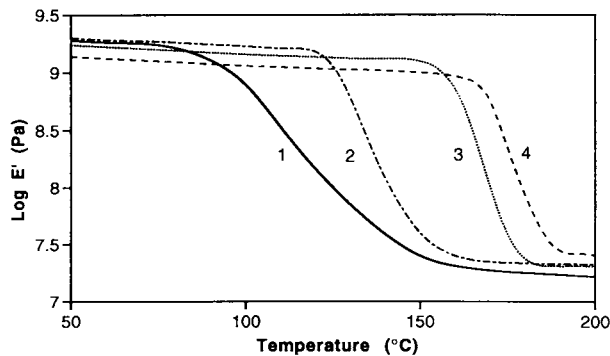


Figure 1 DMTA measurements of the storage modulus with cure treatments: 1 and 2 $T_c = 100^\circ\text{C}$, 3 and 4 $T_{pc} = 180^\circ\text{C}$; 1 $t_c = 60$ min, 2 $t_c = 750$ min; 3 $t_c = 30$ min plus $t_{pc} = 60$ min; 4 $t_c = 30$ min plus $t_{pc} = 360$ min. Measurements at a frequency of 1 Hz and $q = 4^\circ\text{C}/\text{min}$.

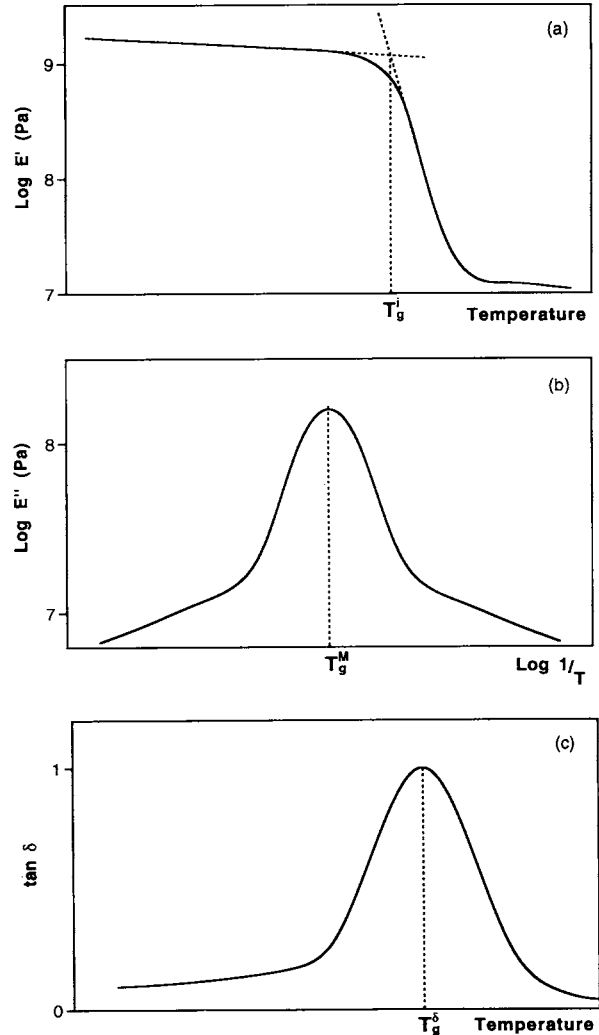


Figure 2 Schematic representations of DMTA measurements of the viscoelastic properties of cured resins. The glass transition temperatures T_g^z are defined by the constructions shown (a) T_g^i , (b) T_g^M , and (c) T_g^s .

ational definitions will be discussed in detail following presentation of our results.

Measurement of Density

The room temperature density was determined by weighing samples in air and immersed in water. The samples $25 \times 25 \times 1.5$ mm were machined from the cast sheets of cured epoxy resin that were prepared for measurement of dynamic mechanical properties (DMTA). The edges were smoothed with silicon carbide paper (280, 400, and, finally, 800 grade) to ensure that air bubbles would not be trapped when the weight of the samples immersed in distilled water

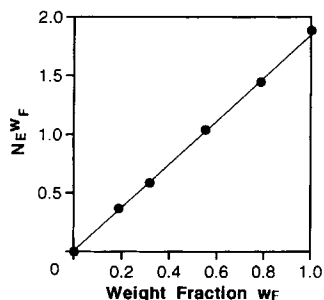


Figure 3 Calibration plot for estimation of the concentration of epoxy groups from the intensity of near infrared absorption. For details, see Determination and the Extent of Reaction.

were measured. A correction was applied to compensate for the weight of the partially immersed suspending wire. The apparent weight of samples immersed in water were measured to ± 0.0002 g and in air to ± 0.0001 g, with 8 to 12 different test specimens measured.

Determination of the Extent of Reaction

Because the extent of reaction is defined by

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

where $[E]_o$ and $[E]_t$ are the concentrations of epoxy groups initially, $t_c = 0$, and after reaction time t_c , it is clear that to determine the extent of reaction, X_e , it is necessary to measure the concentrations of epoxy groups at different cure times. Methods of estimating X_e have been discussed by Ellis,¹⁶ and the most direct methods for the assay of the concentrations of epoxy groups are based on measurement of the infrared absorption of the resin. Although the spectral region of 3 to 15 μm has been used effectively,¹⁷ more recently the overtone region 1.3 to 2.3 μm has been exploited,¹⁸ and the advantages of use of the near infrared region have been discussed.¹⁹

The absorption bands in the overtone infrared region have been assigned,²⁰ and the "normalized" intensity of the epoxy absorption at 2.205 μm has been used to measure the concentration of epoxy groups. The normalized intensity, N_E , was calculated using the intensity of the aromatic —CH absorption band at 1.668 μm ; with

$$N_E = \frac{A_E(2.205)}{A_R(1.668)}$$

where A_E is the epoxy and A_R is the reference absorption. The intensity of the aromatic —CH absorption is unaffected by consumption of the epoxy groups. The absorptions were determined using the usual "baseline" methods. The resin samples were contained within specially constructed glass cells with a flexible gasket seal, which could be located within the spectrometer for recording the spectra.

To confirm the accuracy of the normalization of the intensity of the epoxy absorption band a set of solutions of the resin in carbon tetrachloride were prepared. The carbon tetrachloride did not have a significant absorption band in the region of either the epoxy or reference peaks. The product of the normalized absorption with the weight fraction (w_F) of resin in the solution is plotted vs. the weight fraction of resin in the solution in Figure 3, which is linear confirming the accuracy of measurement of N_E . When the resin is mixed with an aromatic amine hardener, not only is there a dilution of the resin but there is also a contribution to the aromatic —CH absorption. Both these effects are accommodated by use of the calibration in Figure 3 with allowance for an increase of the reference band intensity by the ratio of hardener to resin.

EXPERIMENTAL RESULTS

The densities of the cured resins measured at room temperature ($T_{rt} = 22^\circ\text{C}$) are plotted vs. equivalent

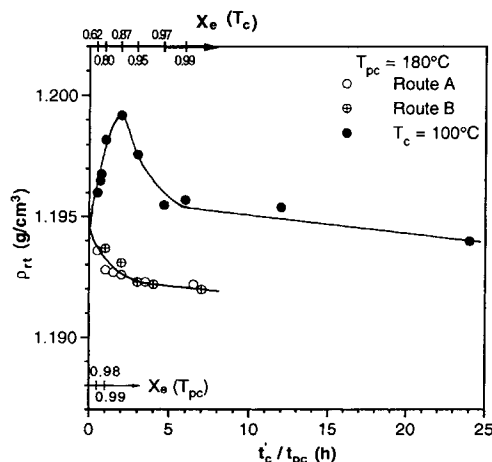


Figure 4 Room temperature density of resins as a function of cure/postcure time. $t'_c (= t_c - 30 \text{ min})$ is a common time axis with t_{pc} . For details of postcure, see Preparation of Specimens.

cure time t'_c and postcure time t_{pc} in Figure 4. Prior to postcure the resins were initially cured at 100°C, i.e., $T_c = 100^\circ\text{C}$, $t_c = 30$ min, and then postcured at 180°C as described in the experimental section. The use of equivalent cure time t'_c allows both the results for resins cured at 100°C and also postcured to be plotted on a common time axis. Also, shown in Figure 4 are the extents of reaction, X_e , determined from the intensity of the epoxy peak in the near infrared spectrum by the procedure outlined previously.

The changes in T_g^i with both cure time and postcure are shown in Figure 5. The method of determining T_g^i from DMTA measurements was described in the DMTA Measurements section, together with its operational definition. For cure at $T_c = 100^\circ\text{C}$, the glass transition temperature increases to a limiting value of 124°C, which is 24°C higher than the cure temperature. The limiting value of T_g^i was determined from a plot of T_g^i vs. $1/t_c$, which is linear for $0 < 1/t_c < 5 \times 10^{-3} \text{ min}^{-1}$, as shown in Figure 5. The linear equation that fits the data in that range is

$$T_g^i = 123.66 - 3.209 \times 1/t_c$$

with $r = -0.978$, $r^2 = 0.956$.

It should also be noted that T_g^i increases even when there is little change in the residual concentration of epoxy groups. Thus, when $X_e \sim 0.97$, the glass transition temperature is 113°C, and when $X_e \sim 0.99$, it is $T_g^i = 115$ and increases to about 124°C without possible further increase in X_e .

With postcure, T_g^i increases considerably, as is shown in Figure 5, with most of this increase occurring after essentially all of the epoxy groups had reacted. The highest value of $T_g^i = 172^\circ\text{C}$, less than the estimated limiting value of 177.5°C, which is only slightly less than the postcure temperature. This limiting value for T_g^i was also determined by a plot of T_g^i vs. $1/t_{pc}$ and is also shown in Figure 5 with a linear relationship of

$$T_g^i = 177.47 - 2.06 \times 1/t_{pc}; \quad r = 0.992, \quad r^2 = 0.984$$

The estimates of T_g^Σ as defined in Figure 2, determined from DMTA measurements, are given in Figure 6 plotted vs. $\ln(t_c)$, which is a convenient variable because it is often necessary to include data with both short and long cure times. Although such plots are empirical, they can be very useful for the representation of data, especially for the selection of "practical" cure times, and the parameters for

the linear equations are given in Table I. Similar plots T_g^Σ vs. $\ln(t_{pc})$ are given in Figure 7. Also, shown in Figures 6 and 7 are the extents of consumption of epoxy groups, that is X_e . Both $T_{g\ell}^\Sigma$ for cure at 100°C and $T_{g\infty}^\Sigma$ for postcure at 180°C estimated from plots of TT_g^Σ vs. either $1/t_c$ or $1/t_{pc}$ are shown on Figures 6 and 7, and $T_{g\ell}^\Sigma$ estimates are included in Table I.

The change in the $\tan \delta$ peak with both cure time and postcure is given in Figure 8.

DISCUSSION

Density Changes with Cure

The room temperature density, ρ_{rt} , of the cured resin as a function of equivalent cure time, t'_c , is given in Figure 4 ($t'_c = t_c - 30$ min). Only for solid resins, that is, when $X_e > X_{e,gel}$, could the room temperature density be measured conveniently, where $X_{e,gel}$ is the extent of reaction at the gel point. Hence, for all the measurements given in Figure 4 $X_e > 0.6$, and for long cure times $X_e \rightarrow 1$. For this range of extent of cure, $0.6 < X_e < 1.0$, the room temperature density changes by about 0.5%, with a maximum at $t'_c = 120$ min. The accuracy of the density measurements is about 0.05%, that is, 1/10th of the range of the values given in Figure 4, and, hence, there is a significant effect on density of cure time of t_c , at constant cure temperatures ($T_c = 100^\circ\text{C}$). Cizmecioglu, Gupta, and Fedors²¹ have discussed the change in density with cure and report a monotonic increase in ρ_{rt} with cure time with a range in density of about 0.8%, which is somewhat larger than the maximum increase that we observe. Also, they find a linear relationship between ρ_{rt} and the extent of reaction; however, this linear relationship is unexpected. Because ρ_{rt} must be related to the specific volume at the cure temperature T_c , i.e., $\bar{v}(T_c, t_c)$, but also with an allowance for the contraction on cooling from T_c to room temperature T_{rt} . This allowance will depend on the glass transition temperature of the curing resin, $T_g(t_c)$, and the difference between $T_g(t_c)$ and T_c ; thus, the relationship between ρ_{rt} and t_c will in general not be simple, as, in fact, we have found (Fig. 4). However, we note that the extent of conversion, X_e , of the linear relationship reported by Cizmecioglu, Gupta, and Fedors is essentially the same as that for the present measurements $0.4 < X_e < 1.0$ compared with $0.6 < X_e < 1.0$.

Pang and Gillham²² carried out a detailed study of the changes in the densities, ρ_{rt} , with cure time

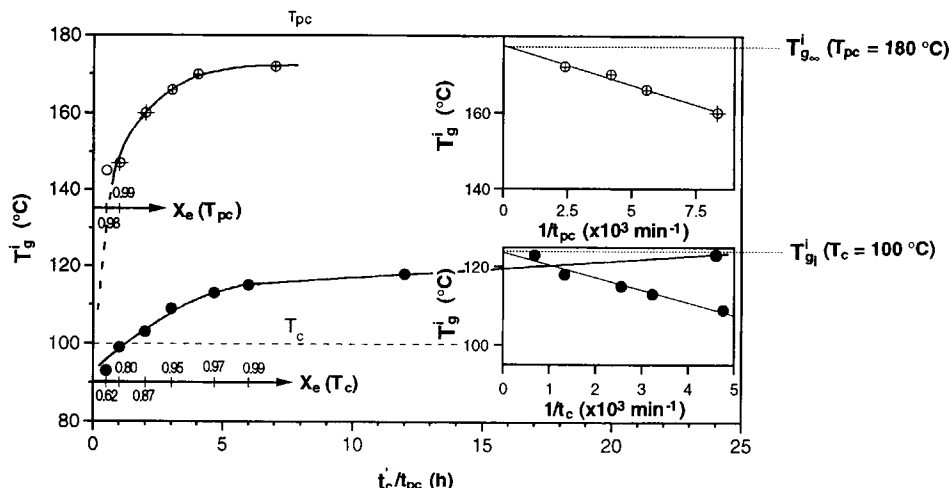


Figure 5 Glass transition temperature T_g^i as a function of cure/postcure time. Abscissas: main graph t' or t_{pc} ; insets $1/t_c$ or $1/t_{pc}$. (●) Resins cured at $T_c = 100^\circ\text{C}$. Post-cured resins $T_{pc} = 180^\circ\text{C}$: (○) Route A, (⊕) Route B, (⊕) Routes A and B.

over a range of curing temperatures, T_c , with subsequently both fast and also slow cooling from T_c to room temperature. For their lowest cure temperature, $T_c = 80^\circ\text{C}$, with both fast and slow cooling they found ρ_{rt} increased monotonically with cure time, t_c . However, with higher T_c (120–180°C) the density, ρ_{rt} , decreases monotonically with t_c also for both fast and slow cooling. For $T_c = 100^\circ\text{C}$ with fast cooling, ρ_{rt} increases monotonically while with slow cooling ρ_{rt} is initially independent of t_c and then decreases. Thus, the behavior that we report for a

BADGE resin cured with DDM also occurs with other epoxy resins and curing agents, and the results reported by Pang and Gillham²² have a greater generality than they proposed. It is one of our aims to show that the changes in room temperature density with extent of cure at constant cure temperature are not anomalous, as would appear to be the case for the title of Pang and Gillham's article²² (Anomalous Behaviour of Cured Epoxy Resins). From Figure 4 it can be seen that for prolonged cure times ($t_c > 6$ h) at constant $T_c = 100^\circ\text{C}$ there is a small decrease in ρ_{rt} , which is unrelated to the extent of conversion because $X_e \sim 0.99$ for $t_c = 6$ h. There is a maximum in the room temperature densities, $\rho_{rt} = 1.199$, when $t_c = 120$ min and $X_e = 0.87$. Also, the glass transition temperature for this extent of cure is $T_g^i = 103^\circ\text{C}$, which is only slightly higher than $T_c = 100^\circ\text{C}$.

Not only is the room temperature density reduced with a prolonged cure at a relatively low cure temperature, $T_c = 100^\circ\text{C}$, but with a postcure at 180°C the density, ρ_{rt} , is considerably lower than for the resins cured at $T_c = 100^\circ\text{C}$ (see Fig. 4). For postcure at $T_{pc} = 180^\circ\text{C}$ following an initial cure of $t_c = 30$ min at $T_c = 100^\circ\text{C}$, there is a monotonic decrease in ρ_{rt} with t_{pc} that is also unrelated to the extent of cure because $X_e \sim 0.99$ when $t_{pc} = 30$ min. It should be noted that there is little difference in ρ_{rt} for postcure routes A and B. Thus, there are structural differences in the cured resins that are not simply a function of the extent of conversion of epoxy groups. These structural differences also affect the glass

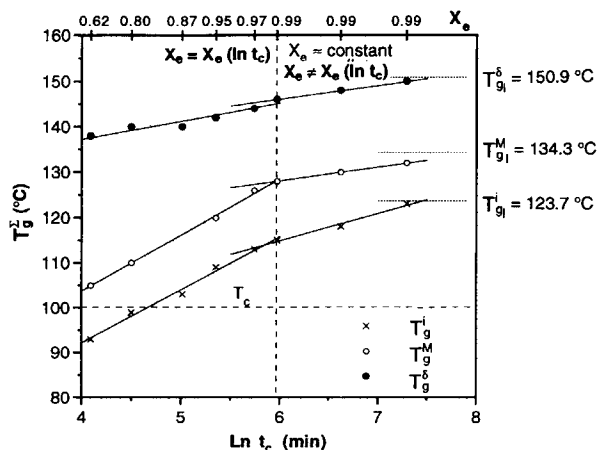


Figure 6 Glass transition temperatures T_g^z vs. $\ln t_c$ for resins cured at $T_c = 100^\circ\text{C}$. For definitions of T_g^z see Figure 2. T_{gt}^z was determined from extrapolation of T_g^z vs. $1/t_c$ plots to $1/t_c \rightarrow 0$ (see Fig. 5 inset).

Table I Empirical Parameters for Linear Equations for $T_g^\Sigma = A + B \ln(t_c)$

Range X_e	Parameter	T_g^i	T_g^M	T_g^δ
$0.6 < X_e \leq 0.99$	A	45.38	54.22	121.75
	B	11.73	12.39	3.90
	r	0.996	0.999	0.958
	r^2	0.991	0.998	0.918
$X_e \sim \text{constant} \sim 0.99$	A	78.46	109.92	127.92
	B	6.07	3.03	3.03
	r	0.991	0.999	0.999
	r^2	0.982	0.999	0.999
$T_{gt} \text{ }^\circ\text{C}$	—	123.7	134.3	150.9

transition temperatures of the cured resins, as will be discussed subsequently.

The room temperature density will be determined not only by the structure of the cured resin but also by the rate of cooling from the curing or postcuring temperature. We have not investigated the effect of cooling rate systematically but with rapid quenching to -18°C and subsequently slow warming to room temperature the density is even lower, that is 1.189. With such rapid quenching contraction of the resin is inhibited when its temperature is less than $T_g(t_c)$, and, hence, the room temperature density is low.

Further analysis of these room temperature densities as a function of cure treatment will be given after consideration of the effects of such cure schedules on the glass transition temperatures of the resins. From the data given in Figure 4 it is clear that for cure of a BADGE-type epoxy resin with DDM there are structural changes at long cure times or

high postcure temperatures that occur after essentially all of the epoxy groups have reacted.

Glass Transition Temperatures

The increases of T_g^i with time for both cure at $T_c = 100^\circ\text{C}$ and $T_{pc} = 180^\circ\text{C}$ are shown in Figure 5, and it can be seen that with a postcure at an elevated temperature there is a considerable increase in T_g^i .

For cure at a constant temperature the increasing glass transition temperature equals T_c when $t'c \sim 70$ min and $X_e \sim 0.82$ and with prolonged cure T_g approaches a limit T_{gc}^i ($T_c = 100^\circ\text{C}$) of 124°C , which was estimated from a plot of $T_g^i(t_c)$ vs. $1/t_c$ with extrapolation to $1/t_c = 0$ (inset Fig. 5), and will be discussed later. However, it can be appreciated that T_g^i exceeds $T_c = 100^\circ\text{C}$ by about 24°C . Even after the reaction of epoxy groups is essentially complete $X_e \sim 0.99$ ($t' = 360$ min) T_g^i increases by about 10°C .

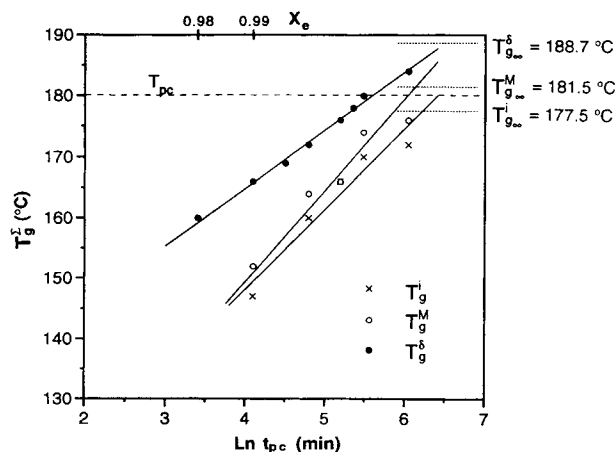


Figure 7 Glass transition temperatures T_g^Σ vs. $\ln t_{pc}$ for resins postcured at $T_{pc} = 180^\circ\text{C}$. For definitions of T_g^Σ , see Figure 2. $T_{g\infty}^\Sigma$ was determined from extrapolation of T_g^Σ vs. $1/t_{pc}$ plots to $1/t_{pc} \rightarrow 0$ (see Fig. 5 inset).

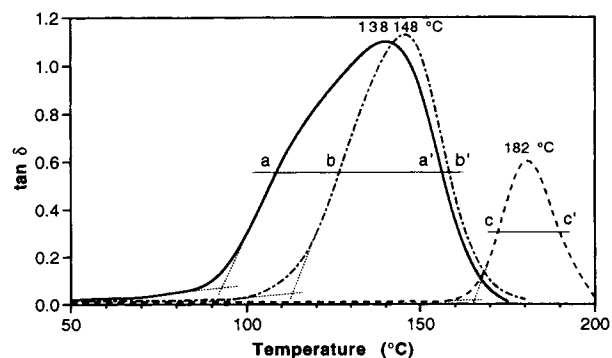


Figure 8 DMTA measurement of $\tan \delta$ vs. temperature for resins cured at (a) and (b) $T_c = 100^\circ\text{C}$ and (c) $T_{pc} = 180^\circ\text{C}$. (a) $t_c = 60$ min; (b) $t_c = 750$ min; (c) $t_c = 30$ min plus $t_{pc} = 390$ min. Measurements at a frequency of 1 Hz and $q = 4^\circ\text{C}/\text{min}$.

With postcure, X_e increases from 0.62 to ~ 0.99 for $t_{pc} = 60$ min when $T_g^i = 146^\circ\text{C}$, which is considerably higher ($\sim 20^\circ\text{C}$) than $T_{g\ell}^i$ ($T_c = 100^\circ\text{C}$). For longer postcure times T_g^i continues to increase, although all of the epoxy groups have reacted (i.e., when $t_{pc} = 60$ min). The limiting value of the glass transition temperature is less than T_{pc} , that is, $T_{g\infty}$ ($T_{pc} = 180^\circ\text{C}$) = 177.5°C and is estimated by the same method as $T_{g\ell}^i$ ($T_c = 100^\circ\text{C}$) (see Fig. 5). Because the glass transition temperature is a function of both the structure of the cured resin and the thermal history of the sample, it would not be expected that a simple relationship should exist relating T_g to either t_c or t_{pc} .

All estimates of T_g^Σ are above T_c , except for T_g^i , with the two shortest cure times as shown in plots of T_g^Σ vs. $\ln t_c$ for the present data given in Figure 6, which also illustrates the differences between the estimates of T_g^i , T_g^M , and T_g^δ . To show the affect of cure time on glass transition temperatures, Gillham and co-workers^{22,23} have plotted T_g vs. $\ln t_c$. Some of their plots are sigmoidal, but ours are approximately linear, but are better represented by two linear equations as shown in Figure 6 and Table I. The data of Matsuoka^{24,25} has been replotted in Figure 9, and the behavior is similar to ours except that for the present data the increase in T_g^Σ occurs without a concurrent increase in X_e ($X_e \sim 0.99$), while that of Matsuoka does increase somewhat, i.e., from $X_e \sim 0.92$ to 0.95. Of course, it should be noted that the curing system used by Matsuoka and co-workers is very different from DDM.

Thus, because T_g^Σ increases even when $X_e \sim 0.99$, there must be structural changes that are unrelated to the consumption of epoxy groups. Plots of T_g^Σ vs. $\ln t_c$, which are linear, should not be extrapolated beyond the data available and do not provide a method for the estimation of $T_{g\ell}^i$, that is, the limiting glass transition for "full" or extended cure. Values of $T_{g\ell}^i$ were determined from plots of $T_{g\ell}^i$ vs. $1/t_c$ similar to that shown for T_g^i in Figure 5, and much higher glass transition temperatures can be attained by postcuring at an elevated temperature. From the data given in Figure 6 it can be appreciated that "full" cure is not achieved when $X_e \rightarrow 1$ (i.e., 0.99 ± 0.01), because T_g^Σ increases with prolonged cure time as previously noted when $X_e \sim 0.99$ and has to remain approximately constant for prolonged cure times.

Linear relationships are also approximate empirical functions for T_g^Σ vs. $\ln(t_{pc})$, as shown in Figure 7, which also shows that $T_g^i < T_g^M < T_g^\delta$. It is important that with postcure the glass transition

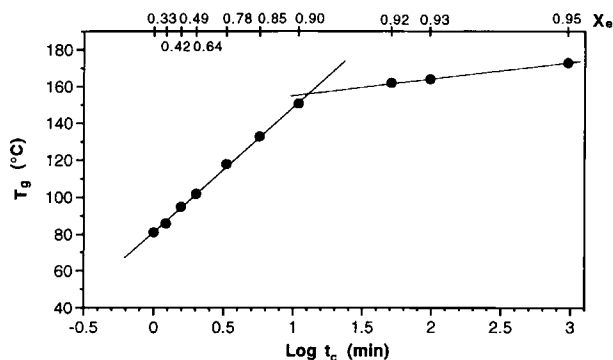


Figure 9 Glass transition temperature T_g vs. $\log t_c$ for Matsuoka's data^{24,25} for the cure of a novolac epoxy system at 140°C . T_g was determined by DSC after quenching and then reheating each sample from 25°C .

temperatures are significantly higher than for resins cured at $T_c = 100^\circ\text{C}$. Thus, T_g^δ ($T_{pc} = 180^\circ\text{C}$) with $X_e = 0.98$ is 160°C , while T_g^δ ($T_c = 100^\circ\text{C}$) with $X_e = 0.97$ and 0.99 are 145 and 146°C , respectively. Thus, the glass transition temperature is higher for the postcured samples even when the extent of reaction, that is, conversion of epoxy groups is essentially the same. With prolonged postcure T_g increases without further possible increase in the consumption of epoxy groups, i.e., when $X_e \sim 1$ ($X_e \cong 0.99$) and, hence, there must be structural changes not associated with the chemical reaction between epoxy and amine groups.

There may be large differences between glass transition temperatures estimated by alternative procedures, for instance the difference between T_g^δ and T_g^i is 43°C for resins cured for 60 min at $T_c = 100^\circ\text{C}$. For the whole range of cures studied including postcures, both T_g^δ and T_g^M are plotted vs. T_g^i in Figure 10. The differences between both T_g^δ and T_g^M decreases as T_g^i increases, which is partially due to the glass transition becoming sharper as cure progresses.

The relationships between both T_g^δ and T_g^M with T_g^i are approximately linear, as shown in Figure 10. For T_g^M vs. T_g^i , a single linear function adequately includes both cure at $T_c = 100^\circ\text{C}$ and postcure at $T_{pc} = 180^\circ\text{C}$. However, for T_g^δ , a somewhat better fit is obtained by fitting linear functions to the cured and postcured data separately. The slopes of all the functions are less than unity, with T_g^δ vs. T_g^i having the lower slope. The convergence of these estimates of the glass transition temperature is due not only to the transition becoming sharper with cure as observed above but also T_g^δ will be influenced by the continued cure that may occur when the DMTA

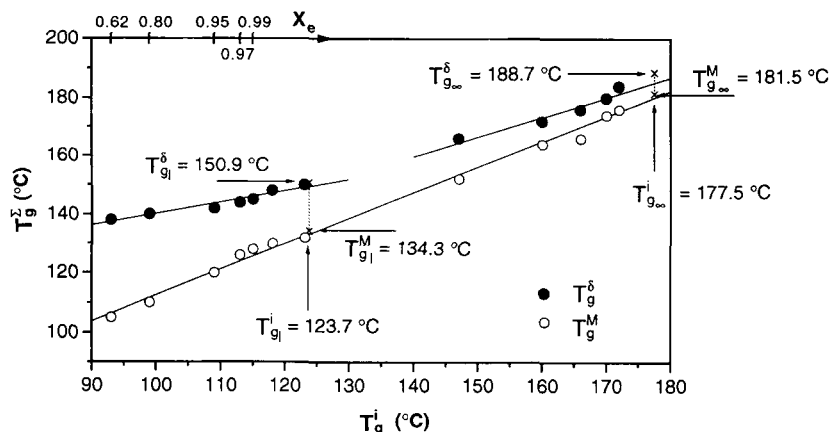


Figure 10 T_g^M and T_g^δ vs. T_g^i for resins cured at $T_c = 100^\circ\text{C}$ and postcured at $T_{pc} = 180^\circ\text{C}$. For cures: $90 < T_g^i \leq 124^\circ\text{C} \equiv T_{g1}^i$; for postcures: $140 < T_g^i \leq 178^\circ\text{C} \equiv T_{g\infty}^i$.

measurement temperature increases above the glass transition temperature.

The increase in the glass transition temperature with cure is at least partially due to a decrease in free volume, which is related to the increase in density with cure for $0.6 \leq X_e \leq 1.0$, which was discussed previously (see Fig. 4). Also, there will be more and more restriction of permitted modes of molecular motion as cure progresses, for instance, the conversion of tri to tetra junction points. Much of the increase in glass transition temperature with cure at $T_c = 100^\circ\text{C}$ must be due to such reactions because there is an increase in T_g^i of about 15°C for X_e increasing from 0.95 to 0.99 (Fig. 5) (10°C increase after $X_e \sim 0.99$). With postcure T_g^i increases by about 30°C after all of the epoxy groups have reacted. From the density data (Fig. 4), it may be inferred that there are only small decreases in free volume; therefore, with postcure other reactions occur other than consumption of epoxy groups, which decreases the possible modes and extent of molecular motion permitted. These "chemical" structural changes are not due to the onset of physical aging, which is due to time dependent relaxation processes that involve molecular conformation rearrangements.

The differences between T_g^i , T_g^M , and T_g^δ reported here highlight the importance of specifying the appropriate definition of glass transition temperatures. To fully specify the glass-rubber transition will require at least four parameters, that is, for instance, E_g , E_r , an inflexion temperature, and a slope constant.^{26,27} However, for most studies a temperature that can be identified with the onset of main chain molecular motion is the most important parameter. This temperature may be specified by T_g^i but with

qualification regarding the thermal history of the sample and also the rate of temperature increase required to identify T_g^i .

Molecular motion is permitted as the temperature is increased through the glass transition, and the more extensive such motion, the larger will be the $\tan \delta$ loss peak. Such motion is discussed by Matsuoka and Quan.²⁸ For cures at 100°C , there is a broad loss peak, which is shown in Figure 8. The loss peak for the resin cured for 60 min will be somewhat broadened due to chemical reactions that can occur as the temperature is raised above T_g^i so that molecular motion permits reactive groups to move into mutually reactive positions. However, it may be noted that extrapolations of the baseline and rising side of the loss peak intersect at 93°C , which is identical with T_g^i defined in Figure 2. This is further evidence that at this is a minimum temperature for molecular motion involving chain segment rotations to be permitted. Other types of molecular motion, such as rotation of the methyl groups of the Bisphenol A unit, require very low temperatures to be "frozen," as shown by NMR studies by Banks and Ellis.^{11,29} A model for possible crankshaft motion of a unit adjacent to a network junction point, that is, next to the reacted nitrogen atom derived from DDM, was proposed previously. Also, the role of hydrogen bonding inhibiting such motion at temperature below the glass transition temperature was proposed by Banks and Ellis.³⁰

The increase in T_g^δ with prolonged cure at $T_c = 100^\circ\text{C}$ is shown in Figure 8, and the loss peak is broad. The broadening of the loss peak for a shorter cure time is illustrated by comparison of aa' with bb' drawn at half the $\tan \delta$ peak height. It is also of interest to note that the extrapolation (Fig. 8) to

determine the "onset" of molecular motion is 114°C compared with $T_g^i = 118^\circ\text{C}$, estimated by the method shown in Figure 2(a). Because $t_c = 12$ h is a very long cure at $T_c = 100^\circ\text{C}$, it is clear that even after this extensive cure there are large loss processes occurring through the glass transition region.

The very much smaller loss peaks for postcured samples is also illustrated Figure 8, and the onset of the glass transition occurs at 167°C compared with $T_g^i = 172^\circ\text{C}$, so perhaps this method is somewhat more sensitive for the "onset" of molecular motion than measurements of $\log E'$ vs. T . This is a small difference, but may be worth further investigation. However, the most important observation is the large reduction in the size of the loss peak with long postcure times. For such resins the molecular motion adjacent to the junction point will be inhibited.

Volumetric Effects of Cure Treatment

For a resin curing at a temperature, T_c , the volume may either increase or decrease when the reacted groups occupy a different volume to the unreacted groups. Bailey,³¹ who was interested in the expansion of spirocarbonates during polymerization, has also calculated the shrinkage during both addition and ring-opening polymerizations. For instance, the calculated shrinkage for the ring-opening polymerization of epoxy groups present in ethylene oxide and styrene oxide are 23 and 9%, respectively. For the cure of an epoxy resin with amine hardeners there is a decrease in volume, but from our results (Fig. 4), as well as others such as Pang and Gillham,²² it can be appreciated that although the room density, ρ_{rt} , of a cured resin is higher than that of the initial mixture of resin plus hardener the function $\rho_{rt} = \rho_{rt}(t_c)$ does not increase monotonically. It is also remarkable that the room temperature density of the postcured resins ($T_{pc} = 180^\circ\text{C}$) are considerably lower than the resins cured at constant temperature $T_c = 100^\circ\text{C}$ (see Fig. 4). For reasons that will become apparent, the appropriate variable for representation of the change of density with cure is a plot of its reciprocal, \bar{v} , the specific volume vs. extent of reaction, and this is shown in Figure 11. For constant temperature cure at $T_c = 100^\circ\text{C}$, there is a minimum in the specific volume when $X_e = 0.87$ and $T_g^i \sim T_c = 100^\circ\text{C}$. Also, the specific volume of postcured samples increase with postcure time even though the reaction of epoxy groups is essentially complete, which is also illustrated in Figure 11. Such volumetric changes may appear to be anomalous,²²

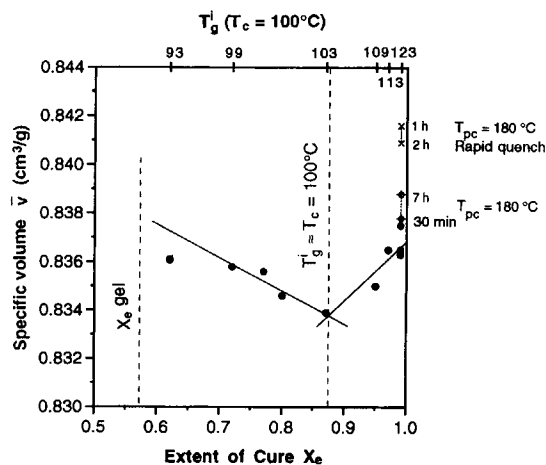


Figure 11 Specific volume at room temperature versus extent of reaction: (●) $T_c = 100^\circ\text{C}$; (⊕, ×) postcured samples for t_{pc} indicated.

but here we will attempt to rationalize such changes in terms of the volume decreases due to the reaction of epoxy groups.

For an epoxy resin cured with DDS Pang and Gillham²² found that the total shrinkage (measured at room temperature) was less than 10%, and was greatest, $\rho_{rt} = 1.223$, for the lowest temperature of cure, $T_c = 80^\circ\text{C}$. At higher cure temperatures the changes in ρ_{rt} were complicated. For the present resins cured with DDM, the maximum shrinkage occurred after about 2 h at $T_c = 100^\circ\text{C}$, and the maximum density was 1.199 (Fig. 4) and then decreased with further cure.

The density of cured epoxy resins has been studied extensively, and early measurements have been reviewed by Lee and Neville³² and Nielsen,¹ and a detailed investigation is that of Fisch et al.³³ More recent work has been reviewed by Won et al.,³⁴ who also presented detailed measurements for several DGEBA epoxy systems cured with a diamine hardener and a monoamine chain extender. They summarized recent contradictory evidence that in some cases the density increases with an increased degree of crosslinking and also the reverse behavior. Qualitatively, it can be appreciated that our results given in Figure 4 illustrate *both* effects. Won et al.³⁴ also proposed model network structure from which they could calculate its van der Waal's volume and, hence, a packing density, ρ^* , which is defined by

$$\rho^* = \frac{V_w}{V} = \frac{V_w}{M/\rho}$$

where V_w is the van der Waal's volume occupied by the atoms of a structural unit with molecular weight, M (relative molar mass), and ρ is the measured density. Similar calculations have been carried out by Oleinik³⁵ and Bellenger and co-workers,³⁶ who considered epoxy ring opening and the degree of hydrogen bonding in cured resins.³⁷ Morel et al.³⁸ considered effects due to the viscoelasticity of cured resins on their packing volume.

Cizmecioglu et al.²¹ calculated the change in volume due to cure of an epoxy resin using estimates of the volume occupied by epoxy and amine groups before reaction and the volume of the reacted groups. The correct equation for their estimate is

$$\bar{v} = \bar{v}_0 - 0.016X_e$$

They found experimentally that $\frac{d\bar{v}}{dX_e}$ was somewhat larger numerically, 0.025 cm³/g. Pang and Gillham²² obtained an even larger estimate of 0.07 cm³/g. However, from the slope of the line in Figure 11 we find that $\frac{d\bar{v}}{dX_e} = -0.014$, but the decrease in volume with extent of reaction only occurs when $T_g^i \leq T_c = 100^\circ\text{C}$, as shown in Figure 11. When T_g^i exceeds T_c , there are two effects that lead to a higher specific volume at room temperature. Volumetric contraction will not occur instantaneously as the extent of reaction increases when $T_g^i > T_c$. Also, contraction when the sample temperature is reduced from T_c to room temperature will be less due to $\alpha_g < \alpha_\ell$, where α_g and α_ℓ are the thermal expansion coefficients for the glassy and the liquid states, respectively. Another factor is that contraction in the glassy state is very time dependent, whereas that in the liquid or rubbery state is very much less time dependent, that is, when $T > T_g$.

The higher specific volume of the postcured samples is readily explained in terms of the reduced expansion coefficient for the glassy state. It should be noted that the specific volume increases with postcure time without any possible increase in the extent of reaction of epoxy groups. This increase in specific volume is associated with an increase in the glass transition temperatures of the postcured samples, as shown previously. This effect is also demonstrated by the higher specific volume of rapidly quenched samples (see Fig. 11).

CONCLUDING REMARKS

From the present measurements of the extent of consumption of epoxy groups, the room temperature density and glass transition temperatures as functions of both cure time at $T_c = 100^\circ\text{C}$ and postcure time at $T_{pc} = 180^\circ\text{C}$, it is possible to draw the following conclusions.

1. There is maximum room temperature density following isothermal cure at $T_c = 100^\circ\text{C}$ when $t_c = 120$ min and decreases as the cure continues. This is due to the thermal expansion coefficient of the glassy polymer being lower than that of the rubbery state, that is when $T_c < T_g(t_c)$ for long cure times. This result confirms and extends the studies of Pang and Gillham.²²
2. There is no monotonic relationship between ρ_{rt} and the extent of reaction. The relationship between specific volume and extent of reaction derived by Cizmecioglu et al.²¹ applies for $0.6 \leq X_e \leq 0.87$. When $X_e = 0.87$, the glass transition temperature T_g^i is approximately equal to the cure temperature ($T_c = 100^\circ\text{C}$, $T_g^i = 103^\circ\text{C}$) and the relationship does not apply for higher extents of reaction, longer cure times, or postcures (see Fig. 11).
3. A comparison of the terminal glass transition temperatures obtained in this work is given in Table II together with other determinations. Chang,¹⁰ from a study of a catalyzed high-temperature cure of BADGE resins, suggests that the ultimate limit for the glass transition temperature, T_{gu} , of epoxy networks is $\sim 190^\circ\text{C}$.
4. With postcure, there is considerable reduction in the magnitude of the relaxation processes that occur through the glass transition region. This is shown by the very much smaller $\tan \delta$ loss peak for the postcured samples in Figure 8.
5. There are changes in the chemical structure of the network that occur after essentially all of the epoxy groups have reacted. There are both density changes and considerable changes in T_g for cure or postcure times when the extent of reaction has to be essentially constant, that is, $X_e \sim 0.99$. These reactions restrict the molecular motion permitted in the glass transition region and, hence, the $\tan \delta$ loss peak is smaller (Fig. 8). A search for possible chemical reactions other than epoxy-

Table II Terminal Glass Transition Temperatures of Epoxy-DDM Networks

Reference	Glass Transition Temperature (°C)			Cure Treatment
	T_g^i	T_g^M	T_g^b	
Grillet et al. ³⁹	178 ^a	—	184	$T_c = 110^\circ\text{C}$, $t_c = 3\text{ h}$ + $T_{pc} = 190^\circ\text{C}$, $t_{pc} = 3\text{ h}$ Stoichiometric composition
Cukierman et al. ¹⁴	—	184	—	2 h steps at $T < T_{\text{exotherm}}$ + 3 h at $T_{\text{exotherm}} + T_{pc}$ $= T_g + 30^\circ\text{C}$ $t_{pc} = 24\text{ h}$
Present work	$T_{g\ell}^\Sigma$	124	134	$T_c = 100^\circ\text{C}$ $t_c = 24\text{ h}$
	$T_{g\infty}^\Sigma$	178	182	$T_c = 100^\circ\text{C}$ $t_c = 30\text{ min}$ $T_{pc} = 180^\circ\text{C}$ $t_{pc} = 7\text{ h}$

^a DSC "onset" value.

amine would be rewarding in elucidating the structure of epoxy networks with high glass transition temperatures.

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