Factors influencing the glass transition of DGEBA–anhydride epoxy resins

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A number of chemical and physical factors influence the glass transition behaviour of anhydride-cured diglycidyl ether of bisphenol A (DGEBA) type epoxy resins. Several of these were investigated using differential scanning calorimetry to assess the nature of the glass transition, the transition temperature and the glass- and liquid-phase specific heats. The influence of molecular weight and chemical functionality, cooling rate and silica fillers were investigated for unreacted epoxy prepolymers. Two anhydride-cured systems were also considered and the influence of cure with and without silica fillers and the effect of phase separation and cooling rate were investigated.

Keywords Epoxy resin; glass transition; physical factors; chemical factors; differential scanning calorimetry

INTRODUCTION

Amorphous polymers and their composites exhibit a reversible glass-to-rubber transition which occurs over a temperature range that is determined by structural relaxation in the material. Although a discrete transition does not exist it is possible to define a glass transition temperature T_g which is both determined by and characterizes the structural or configurational state of the metastable glass. This 'structure' influences properties, the internal stress state, the long-term structural stability and hence the performance of components fabricated from amorphous polymers. It is therefore important to understand the nature of the glass transition and the factors which influence it.

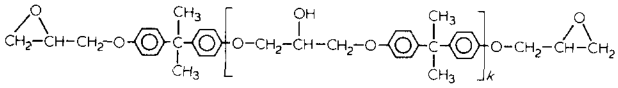
These factors may have a chemical or physical origin. The former include the nature of the polymer chain, its molecular weight[1,2], chain interactions (e.g. hydrogen bonding), specific polymer–filler effects and, for crosslinked polymers, the nature of the network and the degree of crosslinking[3,4]. Physical effects include the thermal and mechanical history and non-chemical filler effects[5,6].

Many of these factors are considered in this paper for a class of epoxy resins commonly used in the electrical power industry. Three prepolymer epoxy resins, two anhydride-cured systems and two types of silica filler were investigated using differential scanning calorimetry (d.s.c.). Unreacted, reacting and fully cured combinations were considered and emphasis was placed on separating chemical from physical effects.

MATERIALS

The principal materials considered were the Ciba-Geigy CT200–HT901 and CY207–HT903 systems. CT200 and CY207 are diglycidyl ether of bisphenol A (DGEBA) type prepolymer resins. The HT components are anhydride curing agents where HT901 is phthalic anhydride and HT903 is a mixture of phthalic and tetrahydrophthalic anhydrides.

The diepoxide prepolymers have the following chemical structure:



(I)

$$M_k = 340 + 284k \qquad (1)$$

CT200 and CY207 contain diepoxide oligomers up to $k = 12$ with different molecular weight distributions. Chemical characterization[7] indicates that CT200 contains comparable $k = 0$ to 4 mass fractions whereas CY207 contains a dominating $k = 0$ fraction accounting for up to 70% by mass of the resin if impure end-group fractions are included. These polymers were supplemented with the Epikote 828 DGEBA resin which has a higher epoxide group content. The hydroxyl and epoxide group concentrations and the number average $\bar{M}_n$ and weight average $\bar{M}_w$ molecular weights are shown in *Table 1*.

The silica flour fillers were Hoben Davies Z300 and Z300T. Both are α-quartz and have a platelet form with specific surface areas in the region of 4000 $cm^2 g^{-1}$ and density around 2.63 $g cm^{-3}$. Particulate sizes are in the range 1 μm to 150 μm as determined by test sieving, electron microscopy and Quantimet observations. The mass fraction distribution peaks around 50 μm. The fillers are obtained by dry milling and the particle surfaces are amorphous. The treated material Z300T is heated to 950°C which allows recrystallization to improve the defect character of the surface and probably reduces the number of free silanol groups (Si–O–H). In all cases where fillers were used they were oven dried and stored dry prior

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Table 1 Functional group concentrations and average molecular weights of DGEBA prepolymers

DGEBA resin	Epoxide	Hydroxyl	$\bar{M}_n$*	$\bar{M}_w$†
CT200	2.3–2.5	2.1–2.2	833	1105
CY207	4.5	0.7–1.2	444	624
Ep. 828	5.3	–	377	–

* Assessed from $\bar{M}_n$ = 2000/epoxide content (mol kg^{-1})[8,9]

† Calculated from the experimental molecular weight distribution

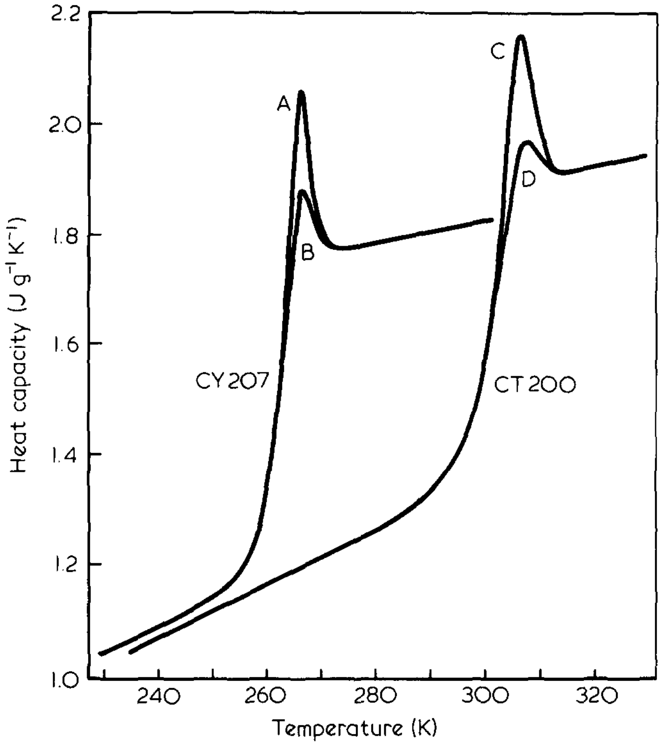


Figure 1 **Prepolymer glass transition $C_p(T)$ curves for different heating and cooling rates. CY207: +5 Knmin^{-1}, (A) −1.25 K min^{-1}, (B) −5 K min^{-1}. CT200: +10 K min^{-1}, (C) −2.5 K min^{-1}, (D) −20 K min^{-1}**

to mixing to minimize the influence of adsorbed water.

The resins and hardeners were prepared as described previously[7]. The resin:hardener mass ratios were the same for unfilled and filled materials. The latter had resin:hardener:filler mass ratios of 100:30:200 for the CT200 system and 100:60:246 for the CY207 system. These give the same organic/inorganic mass ratio for both systems. Cure of the CT200 systems took place at 398K. A two-part cure was used for the CY207 systems and included a gelation phase at 353K followed by a postcure at 393K. Mixing of the epoxy prepolymer and the anhydride was undertaken in the liquid phase to avoid reaction inhomogeneity. In the filled case the filler was premixed with the prepolymer and further degassed before adding the liquid anhydride. After a prescribed cure time individual samples were removed, allowed to cool to room temperature and then stored at 270K prior to d.s.c. analysis.

GLASS TRANSITION DETERMINATIONS

Differential scanning calorimetry was performed on a Perkin–Elmer DSC2. Data analysis followed the sample-reference-baseline method described by Richardson[10]. The resulting C_p *versus* temperature plot was integrated to produce an enthalpy plot which defined the glass transition temperature as the intersection of the curves for the glass and rubber phases[11]. This enthalpic definition of T_g is equivalent to that obtained through specific volume and it gives a value which is dependent only on thermal history and not on heating rate. Such a definition overcomes paradoxical T_g results which inevitably occur when the C_p inflection or midpoint are used; this can create errors as large as +10K when endothermic type relaxation peaks in C_p occur.

Flat samples (10–20 mg) were run as-received and rerun after cooling at rates from 0.625 to 40 K min^{-1}. The heating rate was normally 20 K min^{-1} but this was reduced to 5 K min^{-1} when T_g was less than 300K. The minimum operating temperature of 220K, as set by the acetone–carbon dioxide cooling mixture used, minimized the amount of information available for the glassy phase C_p. Thus errors in the lower temperature values of T_g were greater than the normal ±1K.

PREPOLYMER GLASS TRANSITION

Prepolymer alone

The C_p behaviour of CT200 and CY207 through the glass transition is illustrated in *Figure 1* for different thermal histories. Relaxation endotherms are present and their magnitudes depend on the difference in the heating and cooling rates. The effect of cooling rate is shown in *Figure 2* for the three prepolymers. T_g decreases by 2.5K

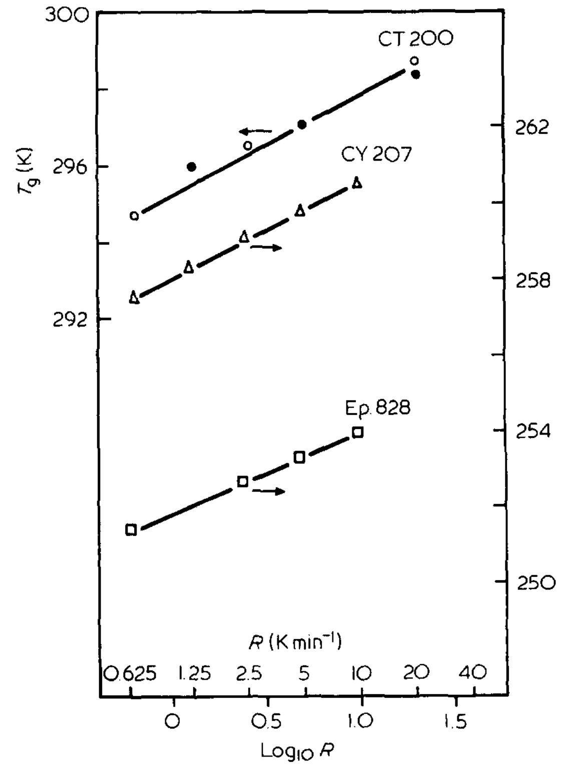


Figure 2 **Effect of glass formation cooling rate on the prepolymer T_g values. Different symbols indicate different resin batches**

Table 2 Glass transition temperatures of CT200 and CY207 prepolymers with and without Z300 and Z300T fillers

Combination	CT200 T_g (K)*	CY207 T_g (K)*
Prepolymer† only	297.0	260.6
+ Z300T	298.5	259.3
+ Z300	299.2	260.3

* The T_g values pertain to a glass formation cooling rate of 5 K min^{-1} and the typical error is ±1 K

† The prepolymer $C_p = A + BT$ coefficients for the liquid and glassy states are:

	A (J g^{-1} K^{-1})	$B \times 10^{-3}$ (J g^{-1} K^{-2})
CT200 liquid	1.255 ± 0.022	2.10 ± 0.007
glass	−0.045 ± 0.012	4.60 ± 0.009
CY207 liquid	1.244 ± 0.004	1.906 ± 0.003
glass	−0.16 ± 0.03	5.17 ± 0.09

Table 3 Comparison of calculated and experimental specific heats (J g^{-1} K^{-1}) of prepolymer–filler (1:2 by weight) mixtures in the glassy and liquid phases. Two temperature points were chosen for reliability

		C_p for Z300		C_p for Z300T	
	T (K)	Calc.	Expt.	Calc.	Expt.
CY207					
glass	230	0.755	0.745	0.751	0.745
	250	0.815	0.805	0.813	0.805
rubber	270	1.048	1.036	1.045	1.039
	300	1.106	1.096	1.100	1.099
CT200					
glass	240	0.779	0.759	0.775	0.773
	280	0.892	0.873	0.89	0.887
rubber	320	1.164	1.134	1.157	1.151
	350	1.218	1.186	1.209	1.205

per decade decrease in cooling rate. For a cooling rate of 5 K min^{-1} the T_g value is inversely related to molecular weight according to:

$$T_g = 333.4 - 3.12 \times 10^4 \bar{M}_n^{-1} \tag{2}$$

This relationship, originally proposed by Fox and Flory[1] was also found for epoxy prepolymers by Aleman[12]. Using a first C_p-inflection definition of T_g (but an unspecified cooling rate) he obtained the coefficients 377.5 and 6×10^4. Within experimental error the glass- and rubber-phase C_p values away from the transition are independent of the glass formation cooling rate. Linear $C_p(T)$ relationships were obtained for these regions and the coefficients for the CT200 and CY207 prepolymers are given in the footnotes to *Table 2*.

Filler effect

Silanol groups at silica surfaces are potential hydrogen-bonding sites for DGEBA prepolymer hydroxyl and epoxide groups. These may contribute to a chemical filler effect and a significant effect for the prepolymers could provide an insight into the subsequent behaviour of the cured networks. To test specific heat additivity, the silica $C_p(T)$ relationships were determined. Polynomial fitting of the data gave:

for Z300:

$$C_p = 5.454 \times 10^{-3} + 3.276 \times 10^{-3}T - 2.555 \times 10^{-6}T^2 \quad \text{J g}^{-1}\,\text{K}^{-1} \tag{3}$$

for Z300T:

$$C_p = 2.386 \times 10^{-3} + 3.223 \times 10^{-3}T - 2.545 \times 10^{-6}T^2 \quad \text{J g}^{-1}\,\text{K}^{-1} \tag{4}$$

The marginally higher values for Z300 are consistent with the higher amorphous fraction expected.

The four combinations of prepolymers and fillers were compounded in the mass ratio 1 to 2. The results are shown in *Table 2*. In the CY207 case the T_g variations are within the experimental error. There is a small increase in T_g when CT200 is filled and the increase is largest with the untreated Z300 filler which has the largest number of free silanol groups. The additivity of prepolymer and filler specific heat can be seen from the results of *Table 3* which compares calculated and experimental values at two temperature points in the glassy and liquid phases. The agreement is acceptable.

UNFILLED RESIN GLASS TRANSITION DURING CURE

Overall behaviour

The T_g determinations of partially cured materials require care. Identical thermal histories are essential; these were imposed by cooling from above T_g at a specified rate (5 or 40 K min^{-1}) prior to the determination of the glass transition temperature. In every case the maximum temperature of the d.s.c. runs was limited to prevent further reaction but sufficient to determine the rubber-phase $C_p(T)$ and to ensure the correct cooling rate at T_g.

Figure 3 illustrates the effect of cure on the glass transition behaviour of the CT200–HT901 system. The T_g changes and the complementary C_p difference between the glassy and rubber phases at T_g ($\Delta C_p(T_g)$) are shown in *Figure 4*. Reproducibility between different preparations is good. Only the postcure part of the curing of the CY207–HT903 system was studied because previous work[7] had shown that less extensive changes occur in the gelation phase. The cure behaviour of T_g and $\Delta C_p(T_g)$ for this system are shown in *Figure 5*. The overall behaviour is similar to the CT200 case but the magnitudes of change and the rates of change are very different.

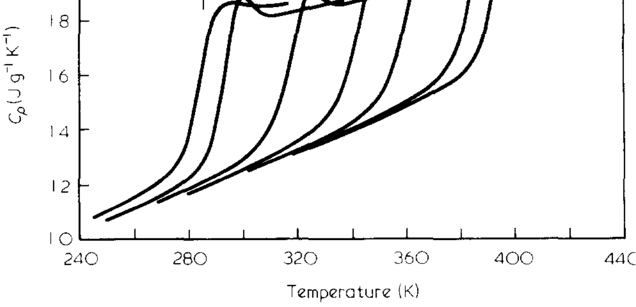


Figure 3 The effect of reaction on the glass transition of unfilled CT200–HT901 cured at 398K for the times indicated

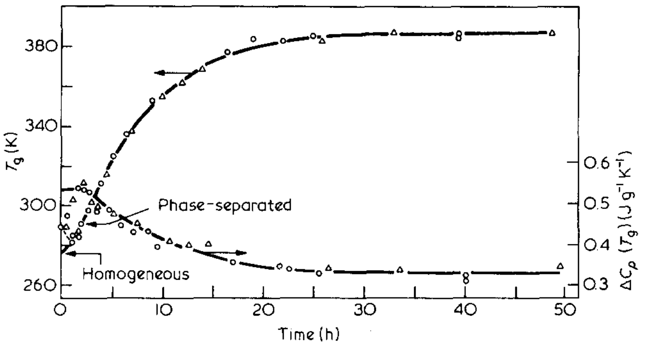


Figure 4 T_g and $\Delta C_p(T_g)$ variation during reaction at 398K of unfilled CT200–HT901. Different symbols indicate different preparations

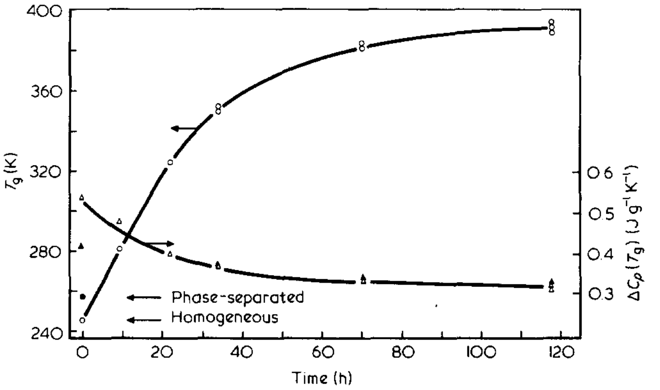


Figure 5 T_g and $\Delta C_p(T_g)$ variation during the postcure reaction of CY207–HT903 at 393K following 20 h reaction at 353K

In both systems the glass- and rubber-phase specific heats decrease with increasing reaction as illustrated in *Figure 6* for C_p(300K). This occurs as a result of a net C_p decrease of the whole transition with no significant change in either the glass or rubber phase $C_p(T)$ slopes. *Figure 3* illustrates this point. As cure progresses, the glass transition moves up the converging glass- and rubber-phase linear regions which in turn are decreasing in absolute C_p with time. This is considered a consequence of network formation which involves a net decrease in both chain mobility and vibrational contributions to C_p.

Phase separation

Stored CT200 specimens exhibit a minimum in T_g in the first hour of reaction and CY207 specimens at the beginning of postcure may exhibit a higher T_g than that expected. This effect could be produced by unreacted anhydride crystallizing from solution and decreasing the plasticization of the mixture.

Two extreme cases of anhydride mixing can be envisaged:

(i) all the anhydride is present as a microcrystalline phase with a crystalline C_p^c contribution;

(ii) the anhydride is in solution with a liquid phase C_p^l contribution.

To test this, the anhydride's crystalline and liquid phase $C_p(T)$ relationships were determined:

HT901:

$$C_p^c = 0.096 + 3.35 \times 10^{-3}T \quad \text{J g}^{-1}\,\text{K}^{-1} \tag{5}$$

$$C_p^l = 0.848 + 2.05 \times 10^{-3}T \quad \text{J g}^{-1}\,\text{K}^{-1} \tag{6}$$

HT903:

$$C_p^c = 0.039 + 3.69 \times 10^{-3}T \quad \text{J g}^{-1}\,\text{K}^{-1} \tag{7}$$

$$C_p^l = 0.996 + 1.96 \times 10^{-3}T \quad \text{J g}^{-1}\,\text{K}^{-1} \tag{8}$$

Crystalline mixtures were obtained by mixing required proportions of finely powdered anhydride into the prepolymers, with some assisted gentle heating. These phase-separated mixtures were then repeat scanned to just above their T_g's and then heated for a short period to allow the anhydride to go into solution, rather than react significantly. For each resin system the $C_p(T)$ relationships for each prepolymer–anhydride combination can be calculated using mass fraction additivity and the individual component $C_p(T)$ expressions. These include:

(i) combination of a glassy prepolymer with a crystalline C_p^{gc} or liquid C_p^{gl} anhydride phase;

(ii) combination of a liquid prepolymer with a crystalline C_p^{lc} or a liquid C_p^{ll} anhydride phase.

However, in the C_p^{gl} case a glassy anhydride specific heat is more appropriate. This could not be determined but since in general[13] $C_p^g \simeq C_p^c$ we may set $C_p^{gc} \simeq C_p^{gl} \equiv C_p^g$. The C_p^{lc}, C_p^{ll} and C_p^g relationships were assessed from equations (5) to (8) and prepolymer relationships similar to those in the footnotes to *Table 2*. The coefficients obtained for a number of cases are shown in *Table 4*.

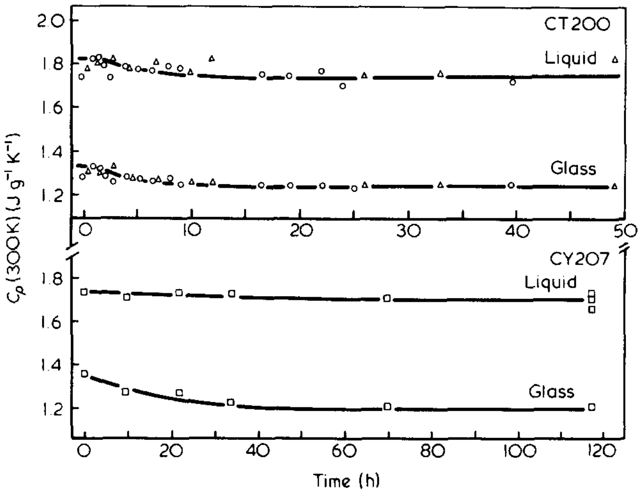


Figure 6 Variation of the glass and rubber phase specific heat at 300K during reaction of CT200–HT901 and CY207–HT903

Table 4 $C_p = A + BT$ (J g^{-1} K^{-1}) coefficients for homogeneous, phase-separated and fully reacted prepolymer–anhydride mixtures in the glass and liquid phases

	CY207:HT903 (100:60)		CT200:HT901 (100:30)	
Condition	*A*	*B* x 10^{-3}	*A*	*B* x 10^{-3}
Unreacted				
C_p^g	–0.05	4.49	–0.004	4.31
C_p^{lc}	0.761	2.69	0.977	2.42
C_p^{ll}	1.12	2.04	1.151	2.12
*Reacted**				
Glass phase	–0.033	4.1	–0.112	4.51
Rubber phase	1.141	1.94	1.043	2.35

* The coefficients quoted are representative means whose errors are variable. The values quoted give C_p values with errors of typically ±2%

Comparison of the experimental and calculated $C_p(T)$ behaviour for the CY207 system is shown in *Figure 7*. The homogeneous mixture fits the calculated C_p^{ll} and C_p^g curves well but the phase-separated mixture is less successful above the glass transition; this is probably due to partial dissolution which would account for the low T_g obtained. Similar results were obtained for the CT200 system. In the CY207 system the T_g of the homogeneous mixture is about 20K below that of the pure prepolymer whereas in the CT200 system it is 10K lower. The lowering in T_g is proportional to the anhydride mass fraction. This analysis and the observation of crystallites by polarizing optical microscopy confirms that the anomalous behaviour at the beginning of cure arises from phase separation.

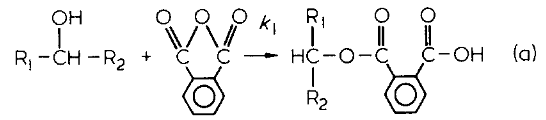
CURE KINETICS

Reaction mechanism

Previous infra-red studies of the cure kinetics of the resin systems considered here[7] generated detailed information on the chemical changes occurring during cure and they confirmed the reaction scheme proposed by Fisch and Hofmann[14]. This scheme may be represented simply by the following reactions where phthalic anhydride is considered.

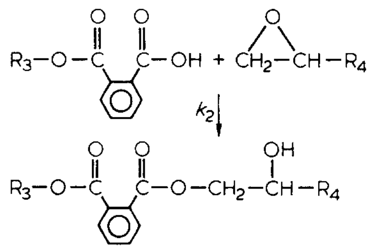
Addition esterification

monoester formation:



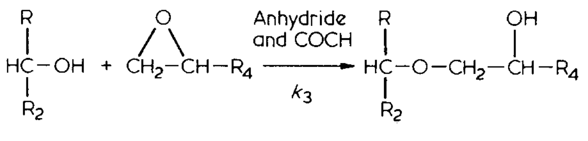
(a)

diester formation:



(b)

Addition etherification



(c)

The importance of the availability of free hydroxyl groups in promoting reaction (a) is clear. Also, the subsequent availability of carboxylic acid groups in promoting reactions (b) and (c) ensures that the course of network formation, including the competition between addition esterification and addition etherification, is largely controlled by the initial availability of reactive hydroxyl groups. The influences of these reactions on the glass transition are considered below.

Kinetic analysis

Comparison of the glass transition temperature cure behaviour with that observed chemically using i.r. spectroscopy[7] may be undertaken by defining a T_g extent-of-change parameter:

$$P(t) = [T_g(t) - T_g(0)]/[T_g(\infty) - T_g(0)] \qquad (9)$$

In the CT200–HT901 case an extrapolated $T_g(0) = 269$K is obtained. This is 3K lower than the experimental homogeneous mixture T_g and its use does not significantly alter the results. In the CY207–HT903 case the behaviour in the postcure period only is considered and no extrapolation to zero time was required.

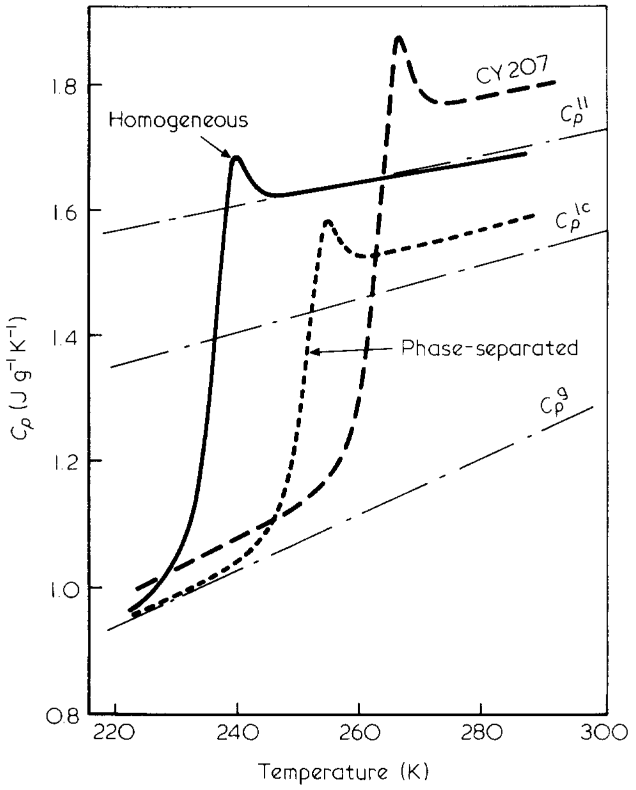


Figure 7 **Comparison of the CY207–HT903 homogeneous and phase-separated glass transition behaviour and the experimental C_p values with the calculated values: C_p^s = homogeneous glass phase, C_p^{lc} = prepolymer liquid phase and crystalline anhydride phase, C_f^{ll} = prepolymer and anhydride homogeneous liquid phase. Heating and cooling rates, +5/−5 K min^{-1}**

Figure 8 illustrates kinetic first- and half-order plots of CT200–HT901 and CY207–HT903 respectively. In both cases the overall behaviour is neither first nor half-order. However, first-order behaviour during the first part of the change can be seen which in the CT200–HT901 case extends to a P value of about 0.85 and about 0.92 in the CY207–HT903 case with time bases different by a factor of 4. An initial rate constant of about 4.2×10^{-5} s^{-1} and 1.1×10^{-5} s^{-1} is obtained for the CT200 and CY207 systems respectively. This T_g cure behaviour may be compared with that observed for the formation of ester and ether groupings characteristic of the reactions described earlier.

In both resin systems aromatic ester formation proceeded with first-order kinetics more rapidly than ether formation which exhibited half-order kinetics overall[7]. A comparison of effective first-order rate constants is made in *Table 5*. This confirms that in both systems the glass transition change closely parallels the etherification reaction. This connection is discussed further below.

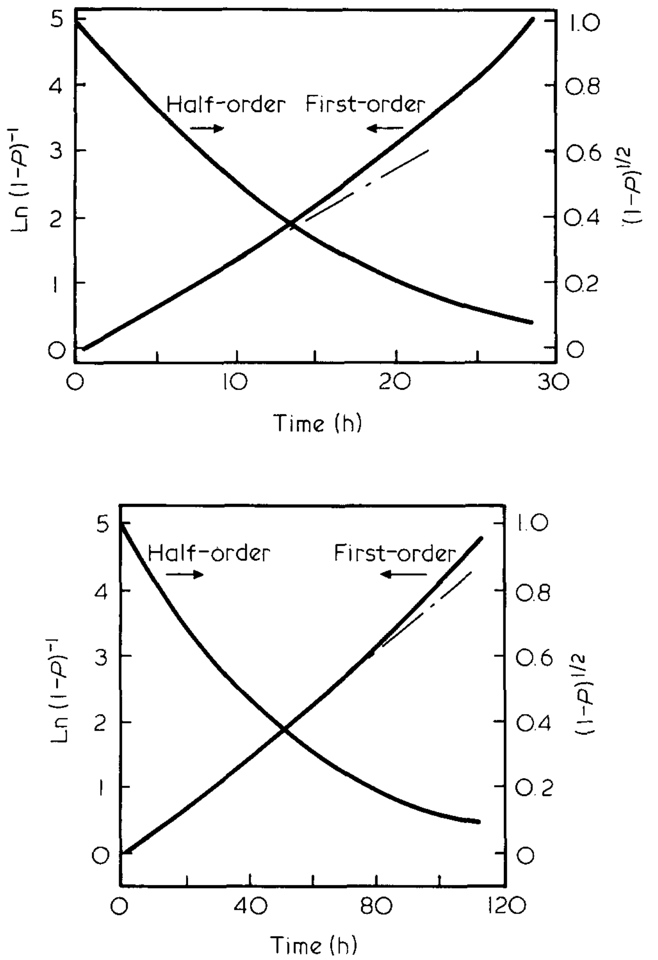


Figure 8 Kinetic plots of the extent-of-change parameter (P) for first-order $\ln(1-P)^{-1}$ and half-order $(1-P)^{1/2}$ reaction behaviour of (a) CT200–HT901 and (b) CY207–HT903. Functional forms derived in ref.7

Table 5 Comparison of T_g and chemical group first-order rate constants for the crosslinking reaction of CT200–HT901 and CY207–HT903

Parameter	CT200–HT901 $k \times 10^{-5}$ (s^{-1})	CY207–HT903 $k \times 10^{-5}$ (s^{-1})
T_g*	4.2	1.1
Anhydride	8.6	2.9
Aromatic Ester	6.5	4
Ether*	5†	1.05‡

* First-order behaviour only applicable during initial phase of the reaction
† First-order behaviour up to $P = 0.5$
‡ First-order behaviour up to $P = 0.45$

FULLY REACTED MATERIALS

In principal a filled or unfilled material will appear fully reacted when either all of its potentially reactive groups are consumed or the material reaches a constant chemical or physical state. The latter may occur in the absence of complete chemical reaction if the reaction temperature is lower than some ultimate glass transition temperature for the system in question. In this case a T_g equivalent to the reaction temperature is obtained, because low network mobility severely impedes further reaction.

Table 6 Comparison of fully cured T_g values of filled and unfilled resins for a glass formation cooling rate of 5 K min^{-1}

System and history	T_g (K)*	T_g range (K)
CT200–HT901†	386 ± 2	372 to 389
CT200–HT901–Z300†	385 ± 1	365 to 386
CT200–HT901–Z300T†	384 ± 1	366 to 386
CY207–HT903		
(a) 20 h at 353K + 117 h at 393K	390 ± 2	
(b) as (a) but cooled from 420K after 1st d.s.c. run	399 ± 1	388 to 400
(c) as (a) + 24 h at 403K	403 ± 1	
(d) as (c) + 18 h at 430K	408 ± 1	
CY207–HT903–Z300		
as (b) above	398	397 to 402
as (c) above	401	
CY207–HT903–Z300T		
as (b) above	398	397 to 402
as (c) above	401	

* Most representative value
† Cured at 398K for 50 h; subsequent heating above 398K produces no significant increase in T_g

Filled–unfilled comparisons

These comparisons centre on the effect of filler on T_g and specific heat additivity. *Table 6* compares the magnitude and range of T_g values observed for both systems. This indicates that no significant filler effect on T_g exists in the nominally fully cured materials. Anomalies in T_g appear greater in the CT200 systems which also achieve maximum T_g values which are not limited by the reaction temperature. Conversely, the CY207 systems are more consistent but are limited by the reaction temperatures applied.

The assessment of specific heat additivity in the glass and rubber temperature regions requires the corresponding unfilled resin $C_p(T)$ relationships. These are summarized in *Table 4*. Statistically it is difficult to establish a difference in the glass-phase $C_p(T)$ coefficients; any differences are small. The calculated and experimental specific heat values in the glass and rubber phases were compared. Agreement in the CT200 case was excellent but it was poorer in the CY207 case.

In the unreacted prepolymers it was shown that, for every decade change in cooling rate, T_g changed by about 2.5K. In the crosslinked networks the polymer structural relaxation behaviour during glass formation is expected to be slower and a smaller cooling rate effect should result. The effect of cooling rate for the fully cured and filled materials was determined by obtaining a series of T_g values for 5 K min^{-1} and 40 K min^{-1} cooling rates on a collection of independent samples (up to 8). The results are listed below:

CT200–HT901	2.0 ± 0.7 K/decade
CY207–HT903	2.1 ± 0.7 K/decade
Filled epoxies	2.0 ± 0.6 K/decade

Within the errors quoted, a decrease in T_g of about 2K for every decade change in cooling rate is obtained. However, the large errors indicated are significantly reduced when linear regression of data covering several cooling rates down to −2.43K/day is carried out, whereas the mean remains the same.

Chemical comparisons

It was shown above that kinetically a correlation was found between the T_g change and ether group formation.

Previous work[7] also identified a number of key chemical differences between the nominally fully cured materials. Whereas both systems contain similar aromatic ester contents, the branched ether and carboxylic acid contents are significantly higher in the CY207 system. An absence of residual carboxylic acid groups near the completion of reaction implies that most diester crosslinks (cf. reaction (b)) have already formed leaving no room for further esterification. This is the case in the CT200 system where no significant postcure changes in T_g are observed whereas in CY207 significant changes are observed on heating above the original reaction temperature (cf. *Table 6*).

The ultimate T_g value of the CY207 system is higher than that of the CT200 system and dynamic mechanical measurements[15] indicate a higher Young's and shear modulus in the rubber phase of CY207–HT903 in comparison with CT200–HT901. For shear modulus, values of 6.2 MN/m^2 and 12.5 MN/m^2 are obtained for the CT200 and CY207 systems respectively at 435K; the temperatures of the mechanical loss peaks are similar to the d.s.c. T_g values reported here. From the kinetic theory of rubber elasticity the shear modulus (G) is given by:

$$G \simeq RT\rho/\bar{M}_c \qquad (10)$$

where R is the Universal gas constant, ρ the density and $\bar{M}_c$ is the number average molecular weight between crosslinks. However, for highly crosslinked systems, such as epoxy resins, equation (10) has been found[16,17] to predict too low a value for $\bar{M}_c$. Neilsen[16] proposed an empirical equation:

$$\log_{10} G \simeq 7.0 + \frac{293\rho}{M_c} \quad \text{dyn cm}^{-2} \qquad (11)$$

which was found to hold well for epoxy resins.

The nominally fully cured densities of the CT200 and CY207 systems are 1.22 g cm^{-3} and 1.24 g cm^{-3}; the resulting molecular weight between crosslinks (M_c) for the systems are 450 and 330 respectively. Following Fox and Loshaek[3], Reitsch *et al.*[4] suggested for crosslinked networks that:

$$T_g = T_{g\infty} + K/M_c$$

The two resin systems considered give a $T_{g\infty}$ value of 350K and a K value of 1.6×10^4. It is interesting that the $T_{g\infty}$ values for the linear prepolymers (equation (2)) and the networks differ by only 17K.

These results confirm the influence of crosslink density on T_g and the correlation of T_g with the branched ether content of the resins. The M_c values determined are close to the theoretical values expected for the individual networks based on the molecular weight between functional groups in the DGEBA oligomers.

DISCUSSION

This work has sought to assess those chemical and physical factors which influence the nature of the glass transition in anhydride-cured DGEBA epoxy resins. In common with other linear glassy polymers T_g was found to be inversely related to the prepolymer molecular weight. However, in $k=0$ diepoxide oligomers each repeat unit contains a free hydroxyl group and their concentration increases as the average molecular weight of the prepolymer increases. This increase was shown to favour greater molecular aggregation through interchain hydrogen bonding[18,19]. By light scattering[18] these aggregates are thermally unstable but persist up to normal processing temperatures and will certainly be present at the glass transition. This hydrogen bonding must cause chain immobilization and influence T_g. However, two-phase glass transitions are not observed so a discrete hydrogen-bonded phase probably does not exist in the glassy state. Similarly, the presence of silica fillers has little or no influence on the glass transition of either the prepolymers or their cured networks. The small effect observed in the CT200 prepolymer probably originates from DGEBA–silica surface hydrogen bonding.

During reaction up to the point of physical gelation anhydride phase separation is possible in unfilled and filled materials and occurs as a recrystallized component in the material. This acts to increase the T_g of the mixture by removing plasticizing anhydride molecules. The T_g increase will not exceed the T_g of the pure prepolymer or the partially reacted network and no positive or negative filler effect is observed.

During cure the T_g and $\Delta C_p(T_g)$ respectively increase and decrease as reaction proceeds. This is consistent with the transition being confined between solid and rubber phase $C_p(T)$ curves which remain invariant with respect to each other. However, in both systems studied the absolute values of C_p in both the solid and rubber phases decrease slightly as a consequence of network formation. This indicates that the basic C_p value is set by the constituents in the first instance, rather than by their chemical state during reaction. As network formation proceeds, vibrational and rotational degrees of freedom are lost and a small reduction in C_p occurs.

The overall kinetic behaviour of the T_g change observed during cure does not strictly parallel particular chemical groups. However, the first 80–90% of the change in both systems exhibits rate constants comparable to those observed for branched ether crosslink formation. Also, in the higher epoxide/hydroxyl group ratio resin (i.e. CY207–HT903) a higher ether group content is accompanied by a high T_g. However, from torsional pendulum analysis this higher T_g also reflects a lower molecular weight between crosslink sites as expected for a largely $k=0$ prepolymer resin system. Earlier work[19] based on light scattering observations of the CT200–HT901 system showed that during cure the density more closely paralleled the esterification reactions whereas the longitudinal modulus paralleled the etherification reactions. More detailed light scattering work to be reported confirms these physical property–chemical group correlations in both the CT200–HT901 and the CY207–HT903 systems.

These results indicate the importance of the etherification reaction (c) in determining the bulk connective properties of these epoxy networks. However, the progress and competition of both the esterification and etherification reactions are coupled through the anhydride ring opening reaction (a) which acts as a sink for available free hydroxyl groups. The availability of these groups is determined by their initial concentration and the propensity of the system to hydrogen-bond either intermolecularly or to filler surfaces. The scope for variable behaviour and end-properties is therefore inherent in the system and close control of several factors is important particularly in the higher hydroxyl-group-containing systems. This may explain the greater variability in ultimate T_g's observed in the CT200–HT901 materials prepared here.

Thermal history is important in influencing the magnitude of T_g and hence the structural and configurational state of the polymer matrix. The unreacted prepolymers exhibit changes in T_g of 2.5K per decade change in cooling rate whereas the filled and unfilled reacted networks exhibit values close to 2K per decade change in cooling rate. These values reflect the ease with which the materials can relax towards their equilibrium state. The smaller value obtained in the reacted networks is consistent with the system exhibiting a more hindered relaxation. In this case, the different resins and their filled counterparts exhibit the same cooling rate effect, which implies that the relaxation times are insensitive to the detailed chemical state of the material and the presence of fillers. These and other structural relaxation topics will be the subject of future publications.

This work has shown that many factors influence the glass transition in epoxy resin prepolymers and their cured networks. Many of these factors are present or claimed to exist in other polymeric systems but in many cases ambiguous methods of analysis, uncertain thermal history and incomplete chemical or structural information prevent a fuller understanding being obtained.

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REFERENCES

1 Fox, T. G. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
2 Fedors, R. F. *Polymer* 1979, **20**, 1055
3 Fox, T. G. and Loshaek, S. *J. Polym. Sci.* 1955, **15**, 371
4 Rietsch, F., Daveloose, D. and Froelich, D. *Polymer* 1976, **17**, 859
5 Peyser, P. and Bascom, W. D. *J. Macromol. Sci., Phys. B* 1977, **13**, 597
6 Peyser, P. *Polym. Plast. Tech. Eng.* 1978, **10**, 117
7 Stevens, G. C. *J. Appl. Polym. Sci.* 1981, **26**, 4259 and 4279
8 Batzer, H. and Zahir, S. A. *J. Appl. Polym. Sci.* 1975, **19**, 585
9 Ravindranath, K. and Gandhi, K. S. *J. Appl. Polym. Sci.* 1979, **24**, 1115
10 Richardson, M. J. *J. Polym. Sci. C* 1972, **38**, 251
11 Richardson, M. J. and Savill, N. G. *Polymer* 1975, **16**, 753
12 Aleman, J. V. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 2561
13 Chang, S. S. and Bestul, A. B. *J. Chem. Phys.* 1972, **56**, 501
14 Fisch, W. and Hofmann, W. *J. Polym. Sci.* 1954, **12**, 497 (see ref. 7 for additional references)
15 Stevens, G. C. and Richardson, M. J. to be published
16 Neilsen, L. E. *J. Macromol. Sci. C* 1969, **3**, 69
17 Katz, D. and Salee, G. *J. Polym. Sci. A* 1968, **2**, 801
18 Stevens, G. C., Champion, J. V. and Liddell, P. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 327
19 Stevens, G. C., Champion, J. V., Liddell, P. and Dandride, A. *Chem. Phys. Lett.* 1980, **71**(1), 104