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# Studies of cure schedule and final property relationships of a commercial epoxy resin using modified imidazole curing agents

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A commercial epoxy prepolymer (MY750) was cured with novel modified imidazole curing agents under both isothermal and dynamic scanning conditions. The thermal behaviour of the formulated mixtures was investigated using differential scanning calorimetry and thermogravimetric analysis, and glass transition temperature ($T_g$) values derived for polymers resulting from both cure schedules. $T_g$ values and the thermal stability of polymers arising from the isothermal cure schedules were generally higher than those for the corresponding dynamic cure. For samples cured by the dynamic curing process, a lower heating rate resulted in higher $T_g$ values and superior thermal stability. The same findings were obtained for samples cured by the isothermal curing process when the relatively low initial cure temperatures were optimal. The results of this study indicate that the initial and post-cure conditions may affect the final properties, and support the view that both the initial and post-cure schedules are of critical importance in governing the nature of the early network formation and the final network structure. © 1998 Elsevier Science Ltd. All rights reserved.

**(Keywords: epoxy resins; imidazole curing agents; thermal properties)**

## INTRODUCTION

Epoxy resins are of considerable technological importance, as they form the continuous phase that binds together many lightweight, tough composite materials. There are many factors governing the physicomechanical properties of the final resin. For example, it has long been recognized that the chemical nature of the curing agent can have a significant influence on the gel-time and the physical properties of the epoxy, largely because it determines both the morphology and cross-link density of the growing network. The strength and toughness of the epoxy, for instance, can be be markedly affected by small changes in the curing agent. For example, some imidazoles are highly effective, fast curing agents[1] and are added to commercial epoxy systems to catalyse the homopolymerization of epoxide groups (in a polyetherification mechanism) to yield a thermoset network. However, unmodified imidazoles have low stability when mixed with epoxies (cure occurs slowly at room temperature), making them unsuitable for use in one-pot compositions, and therefore much work has been carried out into stabilizing imidazoles for use as latent epoxy curing agents.

One approach involves the preparation of transition metal–imidazole complexes[2,3], some of which which exhibit very good solubility in common epoxides[3], good stability at room temperature[4] and a rapid cure at elevated temperatures[5,6]. The kinetics of the curing reaction based on this system have been studied by high-temperature *in situ* $^1$H n.m.r. coupled with other spectroscopic techniques[5,7], showing that the polymerization occurs through consecutive first-order propagation steps. It has been observed for this system that the mechanism of the network formation and the magnitude of final properties, e.g. glass transition temperature ($T_g$), of the cured resin show great temperature dependence. However, this is at odds with the common understanding of the development of $T_g$, in which the final state of cross-linking of the thermoset network can be reached by post-curing at a temperature above the ultimate glass transition temperature, regardless of the initial thermal cure history[8,9]. These effects occur at post-curing temperatures that are below thermal degradation. The implication is that the mechanism of the polymerization and the final structure of the cured material are identical for a particular formulation, although some workers have found a relation between thermal history and final properties of cured systems. Meyer *et al.*[10] studied the influence of the thermal history on mechanical properties of a bisphenol A diglycidyl ether (BADGE)–diaminodiphenylsulfone (DDS) system using dynamic mechanical thermal analysis (d.m.t.a.), while Chang[11] found strong dependence between the thermal history and ultimate $T_g$ of a BADGE-2-ethyl-4-methylimidazole (EMI) system using differential scanning calorimetry (d.s.c.).

To date, little systematic work has been carried out to determine the importance of the thermal history in determining the nature of the network architecture and final resin properties. In this work, d.s.c. and thermogravimetric analysis (t.g.a.) have been used to gain some insight into the relations between physicomechanical properties and thermal history of an epoxy prepolymer cured using a range of imidazole derivatives. The structures of the curing agents are shown in *Figure 1*; the unmodified imidazole adduct is denoted I and the corresponding copper(II) complex denoted II. The preparative routes for these curing agents are described elsewhere[6]. A similar approach has also been

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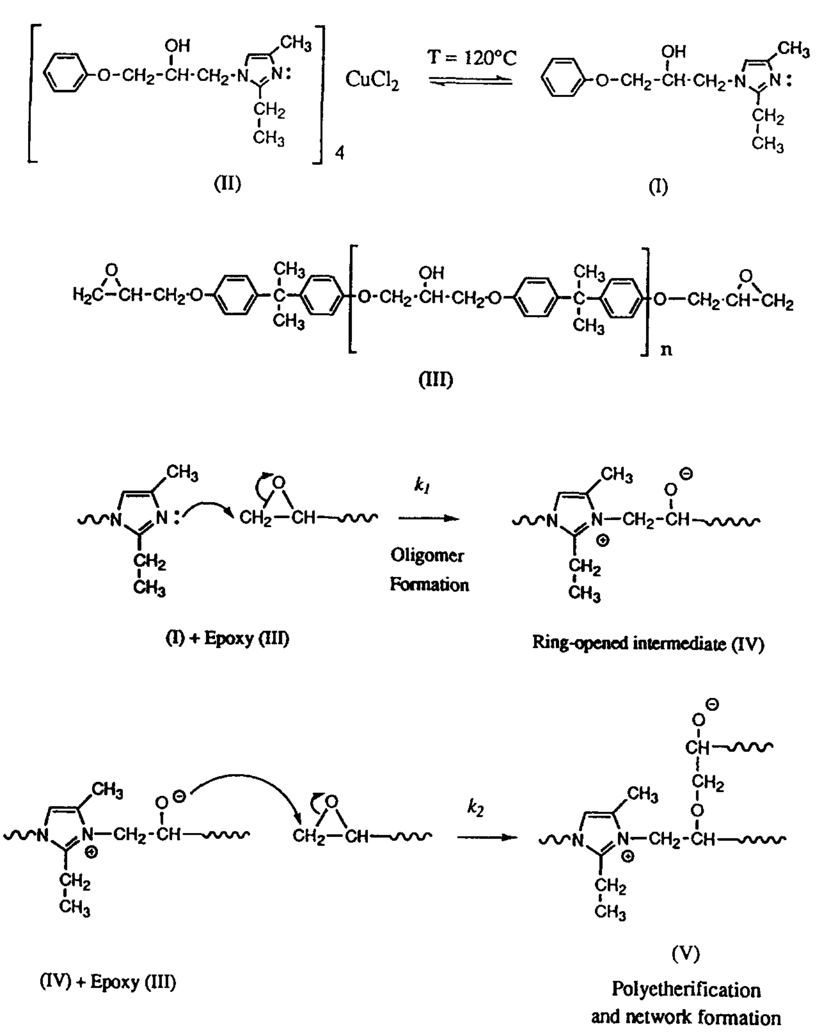

**Figure 1** Structures of the compounds used and the proposed mechanism of epoxy cure involving the metal–imidazole complexes

applied to the cure of epoxy resins using aromatic metal–diamine complexes[12].

## EXPERIMENTAL

### *Materials*

The commercial epoxy prepolymer MY750 (the structure is nominally represented by III in *Figure 1*) was donated by Ciba-Geigy (UK), Duxford, Cambridgeshire. Phenyl glycidyl ether (PGE), EMI and copper(II) chloride were obtained from Aldrich Chemical Company; AnalaR grade $CDCl_3$ was obtained from Fisons. Purities were determined using $^1H$ n.m.r. (except for $CuCl_2$, for which elemental analysis was used) at 298 K using a Bruker AC-300 high-field FT n.m.r. spectrometer operating at 300.15 MHz. The compounds analysed correctly and were used as-received.

### *Sample preparation*

The preparative routes to the 1:1 adduct of phenyl glycidyl ether and 2-ethyl-4-methylimidazole (PGE–EMI) (I) and the corresponding metal complex $Cu(PGE\text{–}EMI)_4Cl_2$ (II) are described elsewhere[6]. Compositions of 5 and 6.64 wt% of I and 5.6 and 7.5 wt% of the complex II (in molar equivalence to the adduct) in MY750 were made, respectively. The adducts were dispersed directly in the resin, whereas the complexes were dissolved in dichloromethane before mixing (the solvent being removed under vacuum at 30°C for 4 h).

### *Equipment*

Differential scanning calorimetry (d.s.c.) was performed both isothermally and at various heating rates (1, 5, 10, 15 and 20 K $min^{-1}$) under nitrogen (30 $cm^3 min^{-1}$) using a Shimadzu DSC-50 calorimeter interfaced with a Shimadzu TA-501 thermal analyser. Samples (8 ± 2 mg) were run in sealed aluminium pans. Thermogravimetric analysis (t.g.a.) measurements were made both isothermally and dynamically at various heating rates (1, 5, 10, 15 and 20 K $min^{-1}$) under nitrogen (30 $cm^3 min^{-1}$) using a Shimadzu TGA-50 calorimeter interfaced with a Shimadzu TA-501 thermal analyser. Samples (6 ± 1 mg) were run in an open aluminium pan. $^1H$ n.m.r. spectra were obtained at 298 K using a Bruker AC-300 high-field FT NMR spectrometer operating at 300.15 MHz; samples were dissolved in $CDCl_3$.

### *D.s.c. data treatment*

*Heat of reaction ($\Delta H$).* The degree of cure is usually obtained by integrating the exothermic peak area of a heat flow curve (*Figure 2*) and comparing this value with the maximum heat of cure, as the sample is scanned to a desired maximum temperature that will effect full cure but is lower than the degradation temperature. However, the values of conversion derived from this treatment are not very reliable because the 'maximum heat' of cure can never be truly realized, since the reaction usually stops at a certain stage of cure. This is mainly due to topological constraints in a highly cross-linked network, which may

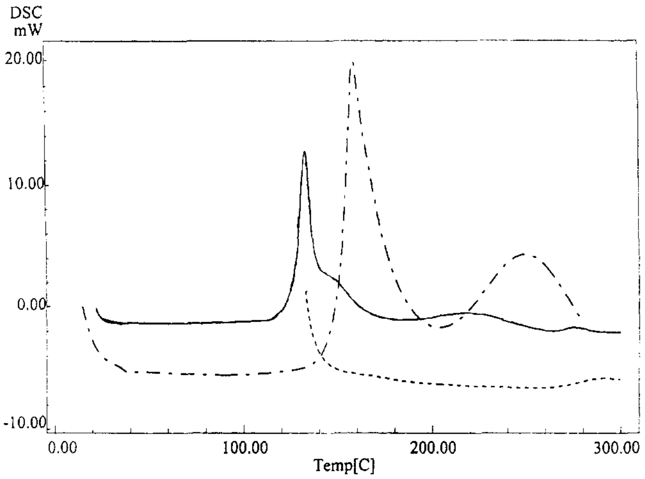

**Figure 2** D.s.c. thermograms of a mixture of a blend of epoxy (III) and curing agent (I) (6.64 wt%) (under nitrogen). Scanning rate (K $\min^{-1}$): ——, 5; – · –, 20; – – –, 20 (rescan)

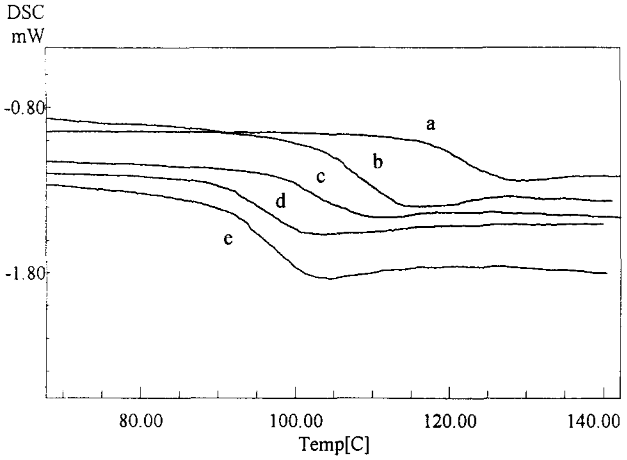

**Figure 3** Glass transition ($T_g$) region from d.s.c. for epoxy (III) and curing agent (II) (7.5 wt%) (under nitrogen). Cure scanning rate (K $\min^{-1}$): (a) 1; (b) 5; (c) 10; (d) 15; (e) 20

prevent a considerable amount of functional groups from further reaction during the latter stages of cure. The heat of the cure reaction for this system has already been studied[6] and hence the heat of reaction serves mainly as a means of monitoring the approximate extent of cure.

*Glass transition temperature* ($T_g$). The glass transition temperature ($T_g$) denotes the region over which an amorphous polymer loses its glass-like properties and assumes those more commonly associated with a rubber. $T_g$ is a second-order thermodynamic response and it involves a temperature zone within which long-range molecular motion and greater rotational freedom occur. The exact determination of $T_g$ is still disputed; in this work it was obtained as the intercept of the two tangents of the heat-flow temperature curve before and during the transition temperature. This $T_g$ determination was made by using the analysis software of a Shimadzu TA-501 thermal analyser. $T_g$ of a cross-linked system may be somewhat ill-defined. The macroscopic glass transition phenomena generally occur over a relatively wide range of temperature, not only because of a distribution of molecular weight and segmental lengths between the cross-linking points, but also because of distributions of unreacted functional groups and monomers which tend to be 'arrested' in the rigid network. Unlike d.m.t.a., there is a considerable uncertainty in the assignment of $T_g$ (*Figure 3*) using d.s.c., since there is inaccuracy associated with the measurement of heat capacity over a wide temperature range and also in separating spontaneous relaxation from the vibrational contributions. Although the onset of the glass transition is quite diffuse for the present system, it ends quite sharply at the onset of the rubbery region (*Figure 3*) and it can be seen that $T_g$'s of lower magnitude show greater glass transition thermal response than those of higher magnitude. *Figure 3* shows the effect of cure scanning rate on the magnitude of $T_g$. All $T_g$'s were obtained at a standard d.s.c. scan rate of 10 K $\min^{-1}$.

## RESULTS AND DISCUSSION

A comprehensive thermal analysis was carried out by varying the thermal cure histories using both dynamic and isothermal processes over a wide range of time–temperature conditions. In many cases it is in practice very difficult to determine the final stage of post-cure during the latter stages of cure, the thermal response is small since the reaction is rather slow (due to the low concentration of unreacted functional groups) in the cross-linked rubbery or glassy state. On the other hand, a small amount of reaction during these latter stages can greatly increase $T_g$ since these reactions result directly in cross-linking. However, in some cases the measured $T_g$ unexpectedly decreased with an apparent increasing conversion. Hence the choice of the maximum temperature for scanning and isothermal post-cure is critical, since one side effect, isothermal ageing, may cause degradation, possibly leading to a reduction in the observed value of $T_g$. For these epoxy resin systems, the observed cured $T_g$ is also a function of the stoichiometry of the curing agent, as differing amounts of imidazole derivatives result in different cross-link densities in the polymer network. For example, it has been found that for the BADGE–EMI system, 3–5 wt% EMI produces the optimal $T_g$[11,13]. A reduced EMI content would result in a more linear structure, while higher EMI contents may result in increased adduct in the cured resin, yielding a lower $T_g$. Therefore in this study, formulations containing 5 and 6.64 wt% (1) and 5.6 and 7.5 wt% (2) (in molar equivalence) were made so as to obtain a system with the highest possible $T_g$. To avoid a bewildering array of measurements, data are presented separately, initially as dynamic and isothermal cure processes and subsequently as dynamic and isothermal post-cure to effect 'full' cure. Before discussion of the data from the d.s.c. experiments, the t.g.a. data for a range of cure schedules are presented.

### *Assessing the effect of the cure schedule using t.g.a.*

These experiments were undertaken to assess the possible effects of degradation on the polymers of the cure schedules (both isothermal and dynamic). In each case the formulated mixture (containing a curing agent and the epoxy prepolymer, III, was heated in the t.g.a. furnace in as close an approximation to the actual cure conditions as possible. Both dynamic and isothermal studies were performed to parallel the cure schedules in the d.s.c., to assess the extent of degradation experienced by the mixtures during cure. In the dynamic experiment, sample mixtures were heated from ambient temperature to 300°C at 1, 5, 10, 15 or 20 K $\min^{-1}$ to effect cure and the weight differential was measured after the cure schedule was complete. In all cases

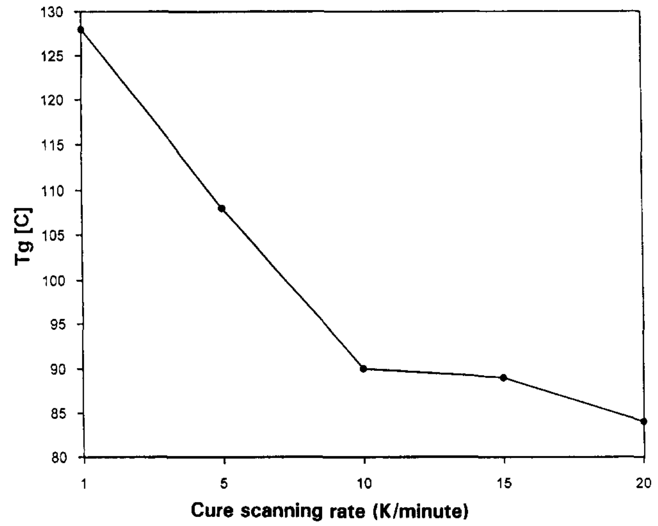

**Figure 4** Glass transition temperature ($T_g$) of a formulation of epoxy (III) and curing agent I (6.64 wt%) versus cure scanning rate from d.s.c.

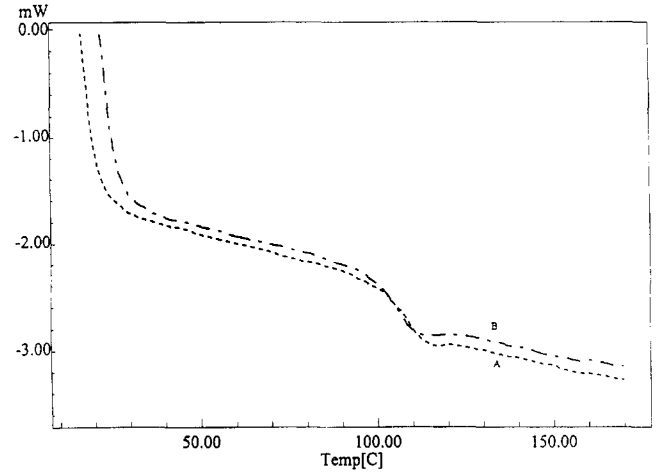

**Figure 5** Plots of glass transition temperature ($T_g$) of a formulation of epoxy (III) and curing agent I (6.64 wt%) from d.s.c.: A, after a cure schedule of 25–300°C at 20 K $min^{-1}$; B, after rescan at 20 K $min^{-1}$

the prepolymer formulations exhibited no significant weight loss (i.e. ~0.5%) during the cure schedules, and indeed this negligible loss may be due to the loss of volatile matter rather than degradation. In the isothermal study samples were analysed under a nitrogen atmosphere and were subjected to the following heating programme: 10 K $min^{-1}$ ambient temperature to a preselected isothermal cure temperature ranging from 100 to 160°C and dwell times ranging from 12 to 32 h depending on the preselected temperature. A further final post-cure (between 140 and 160°C depending on the reactivity of the curing agent system as determined by d.s.c. and discussed below) was applied until no further increase in $T_g$ was observed in the d.s.c. experiments. The weight loss is generally smaller than in the dynamic process (to 300°C) because the resin is very stable at these temperatures (175°C).

### *D.s.c. experiments*

*Dynamic cure process.* Samples were cured under nitrogen by heating at a range of cure scanning rates from room temperature to 300°C followed by a room-temperature quench. No post-cure treatment was required since it was believed that the cure could be completed by scanning the sample to such high temperatures and no further increase in $T_g$ could be achieved by any further treatment. In all cases the scanned sample was allowed to cool to room temperature slowly and was then rescanned to determine $T_g$. The results are shown as $T_g$ against the cure scanning rate for each particular sample (*Figure 4*, *Table 1*). Both adduct- and complex-cured epoxy systems behaved in a similar fashion (i.e. higher $T_g$ was produced as a result of a slow cure process). In the most extreme cases (at cure scan rates of 1 and 20 K $min^{-1}$) the difference amounted to ~45°C—a significant variation. Two factors that might have been considered are as follows. At high heating rate (e.g. 20 K $min^{-1}$) there is inevitably a temperature lag between the 'measured' temperature and that of the sample. Furthermore, in the slow scans the total cure time is significantly longer: at 5 K $min^{-1}$ it is four times that at 20 K $min^{-1}$ over the same temperature range, allowing more reaction and the production of a higher $T_g$ (*Figure 4*, *Table 1*). However, this supposition was not supported by further analyses. From the data shown in *Figure 2* it can be seen that at a cure scanning rate of 20 K $min^{-1}$ the exothermic peak is not finished by 280°C (this is in marked contrast to the thermogram obtained at a cure scanning rate of 5 K $min^{-1}$). Furthermore, after rescanning the same material to compensate for the relatively short overall cure time, a residual exotherm was revealed, indicating that the material had still not reached full cure during the fast cure process. However, rather than an increasing, the final $T_g$ decreased after this treatment (*Figure 5*). For complex-cured systems this phenomenon was even more significant (*Table 1*). This kind of negative effect of dynamic post-cure was also found in the sample initially cured by the isothermal process, as shown in the next section. These observations suggest that $T_g$ values are not always proportional to conversion, because the architectural and conformational structure is more influential. In the light of these data it is more likely that the complex effect of the initial and post-cure conditions on the final network structure is crucial. The same measurements were carried out on an aged complex mixture (which had been refrigerated for 15 months at ~0°C). The resulting $T_g$'s were found to be marginally lower (e.g. 3°C) than that of the freshly prepared samples (*Table 1*), which is in agreement with Chang's findings[11].

*Isothermal cure process.* From the dynamic experiments there was already some indication of the cure temperatures required to achieve the final cured glass transition temperature ($T_{gf}$) of ~128°C for the systems under dynamic conditions. With this guidance, adduct-containing mixtures were cured by holding the calorimeter isothermally at 100, 110, 120, 130, 140 or 160°C and $T_g$ was measured during the course of cure. As expected, in all cases $T_g$ increased with the curing time to a plateau (*Figure 6* shows a typical example). No further reaction occurred at this cure temperature ($T_c$) (although the reaction was not complete) and the maximum $T_g$ was 121°C (after 32 h at a $T_c$ of 100°C) and 143°C (after 10 h at a $T_c$ of 140°C) for adduct-cured resins. The complex mixtures behaved somewhat differently, in that if the cure temperature was insufficient to effect dissociation of the complex (e.g. $< 120$°C), then the polyetherification reaction could not proceed to vitrification. For example, after subjecting a complex-containing mixture to 100°C for 16 h, a maximum $T_g$ of ~64°C was recorded. To obtain the maximum degree of cure, a post-cure at a higher temperature is required. The choice of temperature

**Table 1** Combined physical data for epoxy resin (III) cured with imidazole curing agents

| Curing agent | | $T_{gf}$ | Temperature (°C) at weight loss (%)[b] | | | | | | Onset of degradation | Char yield |
|---|---|---|---|---|---|---|---|---|---|---|
| (content, wt%) | Cure schedule | (°C)[a] | 1 | 5 | 10 | 20 | 40 | 60 | (°C)[c] | (wt%)[d] |
| I (6.64) | 25–300°C, 1 K min$^{-1}$ | 128 | 366 | 388 | 403 | 416 | 428 | 437 | 408 | 85 |
| I (6.64) | 25–300°C, 5 K min$^{-1}$ | 108 | 352 | 379 | 397 | 413 | 427 | 436 | 411 | 83 |
| I (6.64) | 25–300°C, 10 K min$^{-1}$ | 90 | 345 | 375 | 391 | 407 | 424 | 434 | 404 | 83 |
| I (6.64) | 25–300°C, 15 K min$^{-1}$ | 89 | 342 | 375 | 389 | 407 | 423 | 434 | 402 | 84 |
| I (6.64) | 25–300°C, 20 K min$^{-1}$ | 84 | 334 | 370 | 386 | 404 | 422 | 433 | 401 | 85 |
| | + 25–300°C, 20 K min$^{-1}$ | 80 | | | | | | | | |
| II (7.50) | 25–300°C, 1 K min$^{-1}$ | 116 (115)[e] | 351 | 375 | 388 | 402 | 420 | 431 | 397 | 81 |
| II (7.50) | 25–300°C, 5 K min$^{-1}$ | 103 (101)[e] | 336 | 365 | 377 | 394 | 416 | 430 | 386 | 80 |
| II (7.50) | 25–300°C, 10 K min$^{-1}$ | 98 (95)[e] | 331 | 363 | 377 | 397 | 418 | 434 | 395 | 75 |
| II (7.50) | 25–300°C, 15 K min$^{-1}$ | 90 (90)[e] | 326 | 358 | 372 | 394 | 415 | 431 | 388 | 77 |
| II (7.50) | 25–300°C, 20 K min$^{-1}$ | 91 (90)[e] | 319 | 356 | 371 | 390 | 414 | 429 | 385 | 81 |
| | + 25–300°C, 20 K min$^{-1}$ | 85 | | | | | | | | |
| II (7.50) | 16 h, 160°C | 135 | 337 | 369 | 386 | 407 | 423 | 434 | 401 | 80 |
| II (7.50) | 16 h, 120°C | 92[f] | | | | | | | | |
| | + 8 h, 160°C[f] | 140 | 354 | 376 | 388 | 403 | 422 | 433 | 402 | 80 |
| II (7.50) | 16 h, 100°C | 64[f] | | | | | | | | |
| | + 4 h, 120°C[f] | 104[f] | | | | | | | | |
| | + 4 h, 140°C[f] | 129[f] | | | | | | | | |
| | + 4 h, 160°C[f] | 146 | 351 | 376 | 392 | 410 | 425 | 436 | 404 | 79 |

[a] Final $T_g$ after sample fully cured (measured at 10 K min$^{-1}$)
[b] Measurements from ambient to 500°C at 10 K min$^{-1}$
[c] From intersection of tangents from weight loss data
[d] From residual mass at 500°C
[e] $T_g$ value of 'aged' sample (after storing at ~0°C for 15 months)
[f] $T_g$ value after partial cure (as indicated in column 2)

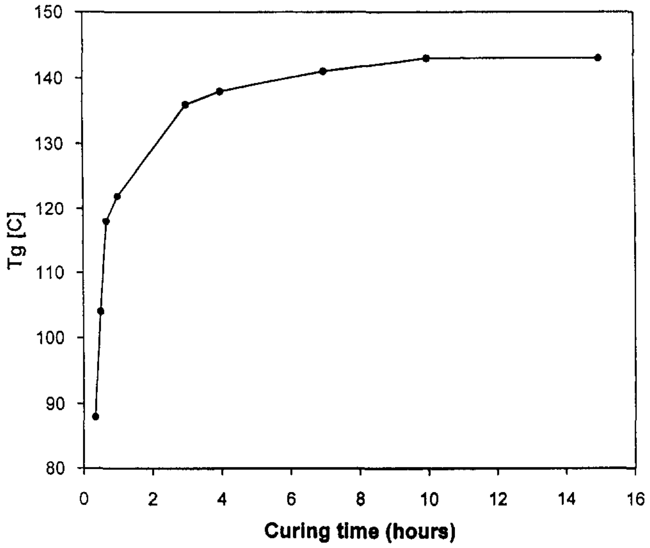

**Figure 6** Glass transition temperature ($T_g$) versus reaction time of a formulation of epoxy (III) and curing agent I (6.64 wt%) during isothermal cure at 140°C

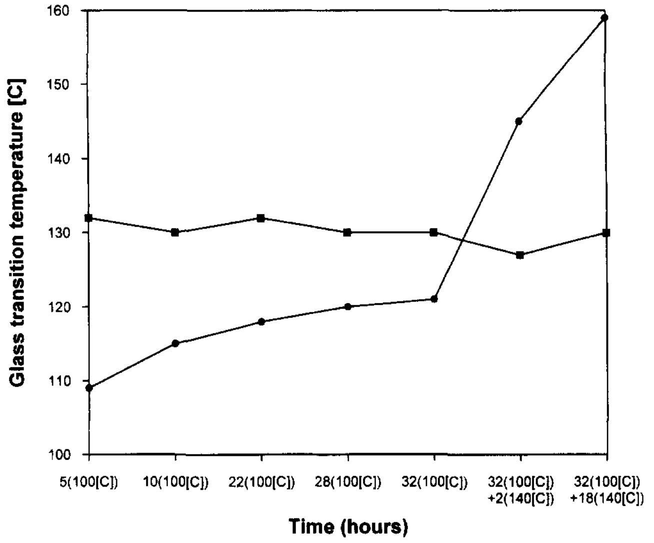

**Figure 8** Glass transition temperature ($T_g$) as a function of cure schedule: •, $T_g$ versus isothermal cure time; ■, $T_{gu}$ versus isothermal cure time after dynamic scan post-cure (25–300°C at 10 K min$^{-1}$)

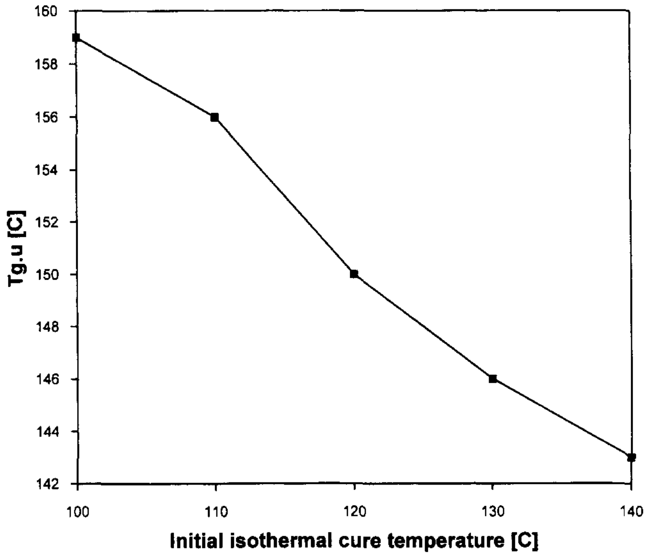

**Figure 7** Final glass transition temperature ($T_{gf}$) of a formulation of epoxy (III) and curing agent I (6.64 wt%) versus initial isothermal cure temperature from d.s.c.

at which this is carried out is important, as excessive temperatures may lead inevitably to degradation of the polymer during the cure process. The adduct-containing samples were then subjected to an isothermal post-cure at 140°C (160°C in the case of complex-containing mixtures) until no further increase in $T_g$ was observed (*Table 1*). *Figure 7* shows the final $T_g$ (after post-cure at 140°C) of adduct systems cured initially at different isothermal temperatures. It can be seen that lower initial cure temperatures produce higher final $T_{gf}$ values. However, this lower initial cure temperature window has a limited range which may be associated with viscosity. It has been reported[11] that if the initial curing temperature is too low (e.g. by ageing samples at room temperature for 6 months, followed by full curing at high temperature), then the ultimate $T_g$ obtained is low. This is also shown in our dynamic analyses and on aged samples (*Table 1*).

By comparison with those obtained from the dynamic scanning curing process, the final $T_g$'s from isothermal initial and post-cure processes are much higher. It having been found that a relatively low-temperature, isothermal initial cure can potentially produce a higher final $T_g$ than that from a dynamic cure process, the effect of dynamic post cure was then examined and compared with isothermal post-cure on samples of epoxy III cured with I, 6.64 wt%. At different stages during a cure schedule (involving an initial isothermal cure at 100°C and a post-cure at 140°C), dynamic scan post-cure at a heating rate of 10 K min$^{-1}$ from ambient to 300°C was applied. The results are presented in *Figure 8*, in which the $T_g$ of samples is plotted against isothermal cure time together with the $T_{gf}$ value from subsequent dynamic scanning post-cure. In this case, the $T_{gf}$ values are nearly identical (~130°C) regardless of the previous $T_g$ values obtained before this post-cure, particularly in the later cases, for which the measured $T_{gf}$ values were even lower than the $T_g$ values obtained after isothermal post-cure (but before this dynamic post-cure treatment). This dynamic scan treatment may result in the ultimate conversion for this polymer system, but may also change the final network structure by allowing it to relax and explore more conformational space. Although the curing reaction is irreversible, allowing no possibility of segmental rearrangement during post-cure, the treatment by increasing the sample temperature quickly to 300°C (which is much higher than $T_g$) may produce a distorted network or cause some decomposition, consequently reducing $T_g$. This confirms that the findings of 'erasable' thermal history[13] are observable only under limited circumstances.

### *Thermal stability of the cured epoxy resins*

T.g.a. experiments were performed under nitrogen on each cured resin sample to assess the thermal stability of the polymer. In each case the mixture was scanned at a heating rate of 10 K min$^{-1}$ from ambient temperature to 500°C after the final $T_g$ was measured by d.s.c. These data were represented as plots of residual weight versus temperature (*Figure 9*); all plots displayed a similar profile, indicating no significant differences in thermal stability from polymers cured using the dynamic cure schedules

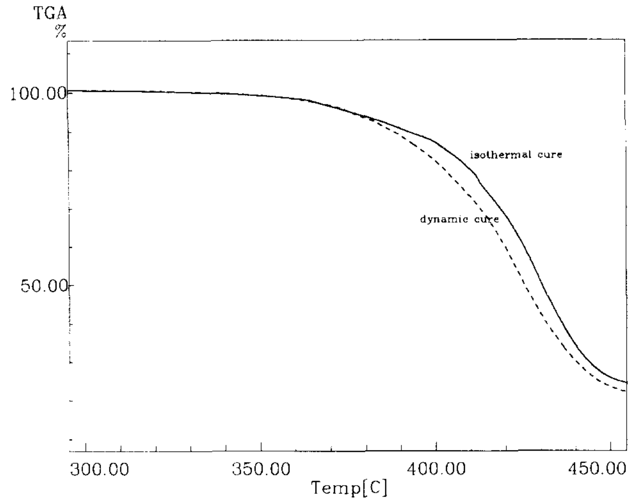

**Figure 9** T.g.a. plots of cured mixtures of epoxy (III) and curing agent (I) (6.64 wt%) after dynamic and isothermal cure schedules (t.g.a. under nitrogen at a heating rate of 10 K min$^{-1}$)

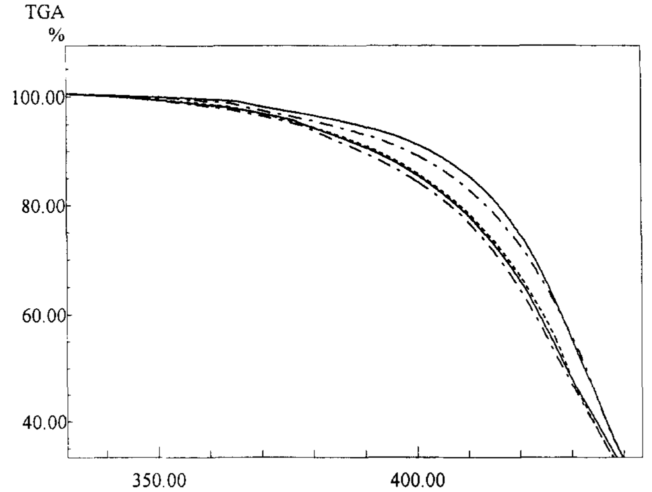

**Figure 10** Expansion of t.g.a. plots (of region showing onset of degradation) of cured mixtures of epoxy (III) and curing agent (I) (6.64 wt%) after a variety of cure schedules (t.g.a. under nitrogen at a heating rate of 10 K min$^{-1}$). Cure scanning rate (K min$^{-1}$): — - -, 20; ——, 15; - - -, 10; —— - ——, 5; — — —, 1

(*Table 1*). Even in the worst case no significant degradation (i.e. a weight loss exceeding 1%) was observed up to 319°C. Although some discrepancies were observed in the order of stability, in general those samples cured using a slower scanning rate were found to be more stable on subsequent rescan of the cured resin (i.e., as expected, the onset of the initial weight loss appeared at higher temperatures for samples with higher values of $T_g$, *Figure 10*). All plots from polymer samples cured isothermally displayed a similar profile to the t.g.a. data from samples cured using the dynamic cure schedules (*Figure 9*), indicating no significant differences in the mechanism of degradation. However, it can be seen that those samples cured using a scanning schedule were found to be less stable on subsequent rescan of the cured resin than those polymers cured using a comparable isothermal programme. The overall trend is that, as expected, samples exhibiting a higher $T_{gf}$ display superior thermal stability for both dynamically and isothermally cured resins. These data appear to support the suggestion from the d.s.c. experiments that the significant difference in the curing schedules favours one polymerization mechanism over another.

The combined dynamic and isothermal d.s.c. results suggest that for the same formulations of BADGE and imidazole derivatives, the final $T_{gf}$ is determined not only by the degree of cure but also by the thermal history during cure. The overall result shows that samples cured at high temperatures or at a high cure scanning rate gave lower values of $T_{gf}$. This suggests that the final network structure, and by implication the network formation process, is strongly dependent on the thermal curing history (in which the final $T_g$ may range from 84°C to 160°C). Chang[11] studied the relation between thermal history and $T_g$ in a BADGE–EMI system by d.s.c., using mainly isothermal cure cycles, and found a similar trend, i.e. that higher initial cure temperatures resulted in a lower ultimate $T_g$. By d.m.t.a. analyses of a BADGE–DDS system, Meyer *et al.*[10] found that there was a temperature region (140–180°C) in which the final $T_g$ is unaffected by initial cure temperature, but that the final $T_g$ was reduced above and below this region. It was considered that high initial cure temperatures might lead to the formation of a more inhomogeneous network. In an earlier study on processing property relationships in graphite/epoxy composites, Mijovic[13] found that different thermal histories prior to post-cure had an effect on the properties of the composites. However, that effect was 'erased' by the subsequent post-cure temperature. Although this may be true over a certain range of variation in cure history, the final $T_g$ may depend on both initial and post-cure conditions. The overall time–temperature–property relationships revealed by the present study suggest that the reaction at an early stage of cure (and implicitly the architecture of the network) may occur in different ways if the cure temperature is varied.

The reaction mechanism and the kinetics of cure have already been studied in previous work[4–7]. The cure is believed to involve two distinct steps: (1) initiation via the formation of an oligomeric adduct from the imidazole derivative (I) and the epoxy (BADGE) monomer (III) (*Figure 2*); and (2) propagation arising from the consecutive etherification reactions between the reactive oligomeric adduct (IV) and successive BADGE monomers. The glass transition temperature increases with increasing cure. However, as $T_g$ is advanced, there is an increasing component of free volume, due to expansion of the network at higher reaction temperatures. These effects are associated with non-equilibrium structure during cure. Chemical effects are also likely to occur due to different reactions which depend on temperature. Taking account of physical effects, it would appear that the chemical kinetics also influence the network structure. Examination of the system by h.p.l.c. and molecular weight distributions would appear to confirm that the reaction kinetics do influence the network structure.

Earlier mechanistic studies of imidazole cure of epoxies[14] have shown that the alkoxide ($RO^-$) propagation is considered to be favoured at lower temperatures whereas the hydroxyl (OH) propagation route is active only at higher temperatures, perhaps leading to different network structures. However, purely from a consideration of the molecular structure of the epoxy monomers and oligomers, it is not obvious how the two paths (of $RO^-$ and OH polyetherification) should lead to different types of ether-linked network. However, there is a difference between these two paths if one considers the position of the alkoxide ($RO^-$) and hydroxyl (OH) groups. $RO^-$ groups are generally located at terminal positions in the intermediate which is produced by the initial attack of an $RO^-$ group on an oxirane ring at the terminus of the molecule, while the OH group is initially produced towards the middle of the BADGE oligomer (*Figure 1*). The geometrical structures resulting from these two paths may be slightly different at early stages of cure, the product from the $RO^-$ etherification may result in a more linear structure; OH etherification may result in a more branch-like structure. The influence of these two kinds of intermediate structure on the formation and final structure of the network cannot be gauged easily. The magnitude of this proposed effect may be expected to be small since the concentration of hydroxyl groups is rather low (in some cases pure BADGE with no hydroxyl groups was examined[11]) and all the procedures were carried out under moisture-free conditions in the absence of acid contaminants. However, one point which is clear from the outcome of the results of the present investigation is that this is certainly not the sole factor influencing the final structure and properties. It is accepted that in an amine–epoxy (e.g. BADGE–DDS[10]) system a large number of hydroxyl groups, which are generated from the initial reaction of amine and epoxide groups, can further react with epoxide at higher temperatures[15] to leave virtually no small amine species in the final network. This in turn results in an inhomogeneous molecular weight distribution. In view of earlier published work, and with reference to *Figure 1* which represents our visualization of the network-forming mechanism, one may speculate on the following possibilities:

(1) From the equilibrium reaction of II and I, the potential of the curing agent (I) is not fully developed during the short period of rapid heating (affecting the distribution of oligomeric (IV) and polymeric (V) species during cure).

(2) The high curing temperature and the rapid scan cure process promote fast reaction and under these conditions reactions may also occur between larger molecules, e.g. between two intermediate species (IV) rather than between intermediate (IV) and another BADGE oligomer (III). This leads to a wide distribution of molecular weights. In the synthesis of the 1:1 adduct of PGE and EMI in solution, we found that for stoichiometric (1:1) reaction, more 2:1 and 3:1 products were produced at higher temperatures. This indicates that the second and third reaction steps occur more easily at higher temperature, thus leaving a larger amount of unreacted EMI than at lower temperatures. This occurs because the PGE reacts with a 1:1 adduct to form a 2:1 adduct in a consecutive reaction, rather than with the remaining EMI at higher temperatures. The occurrence of these mechanisms results in a cross-linked system containing more residual monomer and small oligomers which may lead to different paths of molecular growth and network formation. They also yield a network containing a broader range of oligomeric lengths between branch points. Moreover, there is the possibility of non-elastically contributing species—the products of inter- or intramolecular cyclization—which are not incorporated directly into the network.

(3) From an analysis of d.s.c. data, Chang has suggested that a loose network may be formed in the highly expanded liquid at high temperatures[11].

(4) The statistics of encounter of epoxy groups at different temperatures may produce different network structures. It is generally considered that the influence of the thermal history on the network formation should be more universally observable in many cross-linked polymer systems[10]. In practice, large samples with a high heat of reaction may show less of the thermal history effect due to autocatalysis under a high rate of energy release, due to low thermal conductivities.

One or more of these factors may have a direct bearing on the nature of the network formed during cure.

It should be noted that in industrial applications, to save time and energy and to increase productivity, most processes are driven towards conditions which lead to the most rapid reaction. However, the results of the present work indicate that exposure of the epoxies to rapid heating during cure may result in a reduction of the properties of the cured epoxies[16]. The study of the network mechanism–structure–property relationships under different reaction conditions is important not only to gain an understanding of complex curing processes, but also to ensure quality control in industrial applications. Apparently it is not sufficient to determine the kinetics of cure, but also necessary to investigate further the network structure and various pathways that such thermosetting resins may take. Although the characterization of the cross-linked system in terms of architectural mechanism is extremely difficult (due to the complexity of the reaction and the insolubility of the gelled product), many techniques such as dynamic viscosity measurement, spectroscopic analysis and chromatography may be useful in providing such information during the earlier stages of cure prior to gel point. This is discussed in greater detail elsewhere[17].

## CONCLUSIONS

It is not widely appreciated that the nature of the final network structure depends so heavily on the thermal history. Conventional wisdom holds that during a cure cycle, raising the isothermal cure temperature effectively 'erases' the effects of the previous step. In this way the evolving network's $T_g$ may in turn be raised until it reaches that of the higher cure temperature and the reaction effectively ceases. The results of this study support the view that both the initial and the post-cure schedule are of critical importance in governing the nature of the final properties, while the initial curing conditions determine the architectural nature of the early network formation which may persist despite later, higher-temperature, cure steps. The post-cure conditions not only extend the degree of cure but also determine the deformation of the final network.

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