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Influence of post-curing and temperature effects on bulk density, glass transition and stress–strain behaviour of imidazole-cured epoxy network

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The effects of post-curing and temperature on the glass transition, bulk density and stress–strain behaviour in the glassy and rubbery state of 2-ethyl-4-methyl imidazole-cured epoxy network have been evaluated by differential scanning calorimetry (DSC), water displacement and tensile testing. The glass transition temperature, T_g, was found to increase with increasing post-cure temperature and the size of the base line shift in the glass transition region on the DSC thermogram can serve as an indicator of the extent of cure. At room temperature, the decrease in bulk density with increasing extent of cure may be attributed to the additional cross-linking, adding molecular constraints to the thermal constraints. Thus, a higher free volume at T_g can be expected to remain in the glassy state as the sample is slowly cooled through the glass transition temperature. In the investigation on the temperature dependence of the tensile mechanical properties, a fracture envelope was obtained. The tensile strength, Young's modulus and ultimate elongation in the glassy and rubbery state are discussed in detail.

1. Introduction

The curing process of a thermosetting epoxy resin includes several chemical reactions leading the system to gelation and vitrification. It might be expected that the extent of the curing reaction would influence the final network structure and hence the bulk properties of the cured epoxy network. In practice, many important changes take place in the network system after gelation as the reaction continues. Although at the gel point about 70% of the reaction has been completed, the network system formed results in a sample which is very brittle. Subsequent post-curing at an elevated temperature is necessary to obtain extensive cross-linking of the system; this will affect the final physical properties. In order to achieve the optimum properties of the epoxy network it is necessary to understand the post-curing and temperature effects which will bring about the properties of material in an optimum condition for service.

Generally, ease of compounding, long pot life, low viscosity, high distortion temperature and economic curing schedule have been required for curing agents used for manufacture practice purpose. The imidazole derivatives have offered these excellent prospects for curing epoxy resins in an entirely different manner from the aromatic and aliphatic amines [1]. They are added to an epoxy resin in small nonstoichiometric amounts that have been empirically determined to give the best properties. From these points of view and also because of the simplified chemistry of the resulting network, an imidazole curing agent was selected in this study.

2. Experimental procedure

2.1. Materials and preparation

A commercial grade of diglycidyl ether of bisphenol A (DGEBA), DER 332, was used. The curing agent was 2-ethyl-4-methyl imidazole (EMI-24). The EMI-24 is a Lewis base which operates as a catalyst by initiating a self-perpetuating anionic polymerization. This catalytic curing agent was effective when used in very small concentrations. Only 3 p.h.r. of this reagent is required to gel epichlorohydrin-bisphenol A type epoxy resins at 70 °C [2, 3]. The DGEBA and EMI-24 components were mechanically mixed by a stirrer at a temperature of 60 °C in order to melt any crystals present in the DGEBA epoxy resin [4]. The cure schedule was 4 h in a preheated air oven at a temperature of 70 °C followed by post-curing at the various higher temperatures for 2 h.

2.2. Thermal analysis

Differential scanning calorimetry (DSC) was used to investigate the glass transition of epoxy networks. A DuPont 1090 thermal analyser equipped with a 910 differential scanning calorimeter and a 1091 disc memory was employed. A heating rate of 20 °C min^{-1} was used. For calculation of the glass transition temperature, data analysis was carried out with computer

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software provided by DuPont Instruments Inc. The temperatures at the extrapolated onset, inflection and end points were printed on the transition analysis report. The inflection temperature is somewhat dependent on the sample size. The extrapolated onset temperature is, in general, the most reproducible. Therefore, the extrapolated onset temperature is reported as the glass transition temperature throughout this study.

2.3. Density measurements

Chang *et al.* [5] determined the bulk density of an epoxy system cured with diaminodiphenyl sulphone (DDS) using the density gradient technique and found that the bulk density of the epoxy network increased linearly with the extent of cure. However, this result is the reverse of that reported by Enns and Gillham [6] who found that the bulk density of the sample decreased with increasing extent of cure; they used the same density technique and curing agent as Chang *et al.*

In attempts to clarify the contradictions, the water displacement method, as described in ASTM standard D792-66, was employed in this portion of study. The value of bulk density was determined as a function of increasing post-cure temperature (i.e. increasing extent of cure) on samples slowly cooled from the post-cure temperature to room temperature.

2.4. Tensile properties test

In order to avoid complications due to contamination with release agents, which were used by many previous workers, and damage to the edges of the specimens if they are machined to the correct shape by using a tensile specimen template, a Teflon mould was designed.

The Teflon mould was assembled in two steps. First, a 15 cm × 15 cm × 0.32 cm highly polished Teflon spacer with four dumb-bell shaped openings and two similar Teflon sheets were pinned together using five Teflon alignment pins. This assembly was then sealed around the three closed edges by wrapping 2×10^{-3} in (~ 0.05 mm) thick aluminium foil around it. A 2.5 cm wide aluminium foil was formed to a 45° bevel along the open edge to provide a full-length funnel. Finally, the assembled Teflon mould was backed by two glass plates and clamped together using six heavy-duty binder clips. The mould is easily assembled and dismantled. The dumb-bell shaped opening spacer can be reused many times.

All stress–strain tests were performed on a Material Test System equipped with 436 control unit, 406 controller, 410 digital function generator and 409 temperature controller. The measurements were made according to ASTM D638 type IV, with a gauge length of 25 mm and a crosshead speed of 5 mm min^{-1}.

3. Results and discussion

3.1. Effect of post-curing

3.1.1. Glass transition behaviour

The DSC thermograms for EMI-24 cured epoxy network as-cured and post-cured at 110, 130 and 150 °C are presented in Figs 1–4, respectively. These DSC thermograms all show a distinct glass transition. The magnitude of the sigmoidal base-line change decreased with increasing post-cure temperature. This indicated that the degree of cross-linking in thermoset networks affects the magnitude of the base-line change

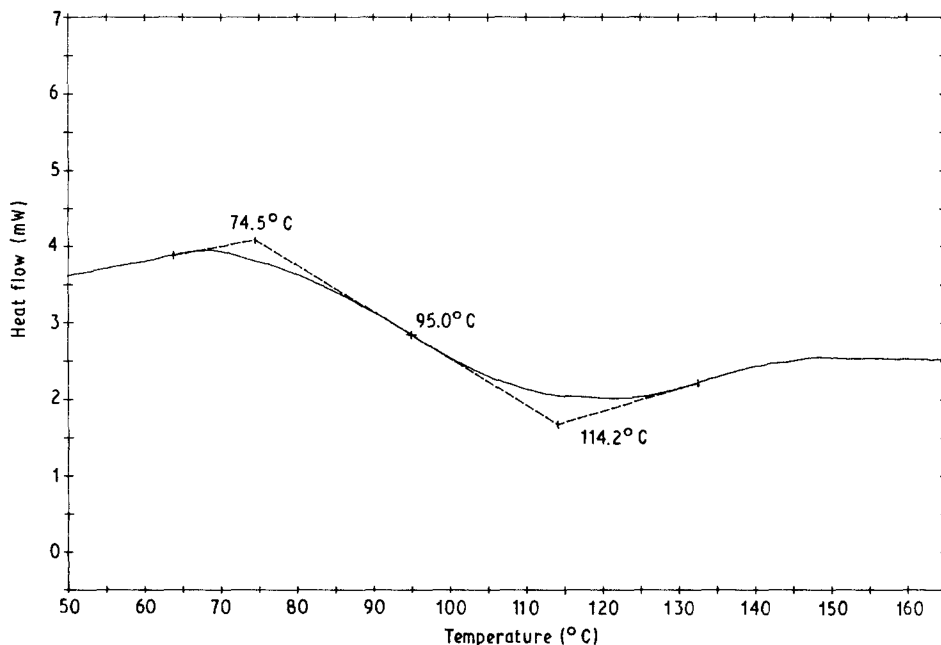

Figure 1 DSC thermogram of non-post-cured epoxy network.

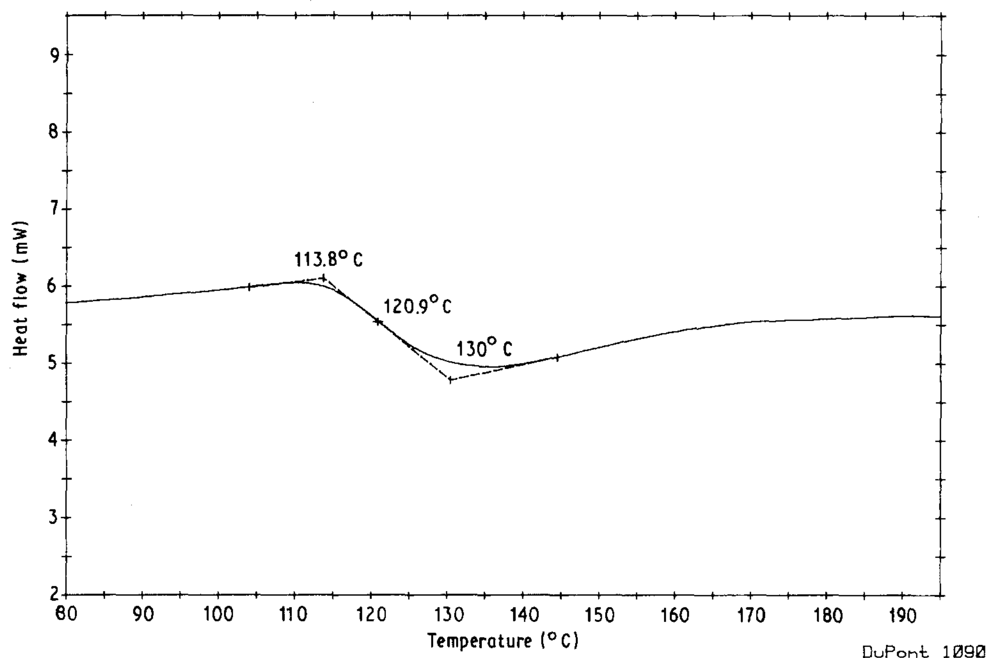

Figure 2 DSC thermogram of epoxy network post-cured at 110 °C.

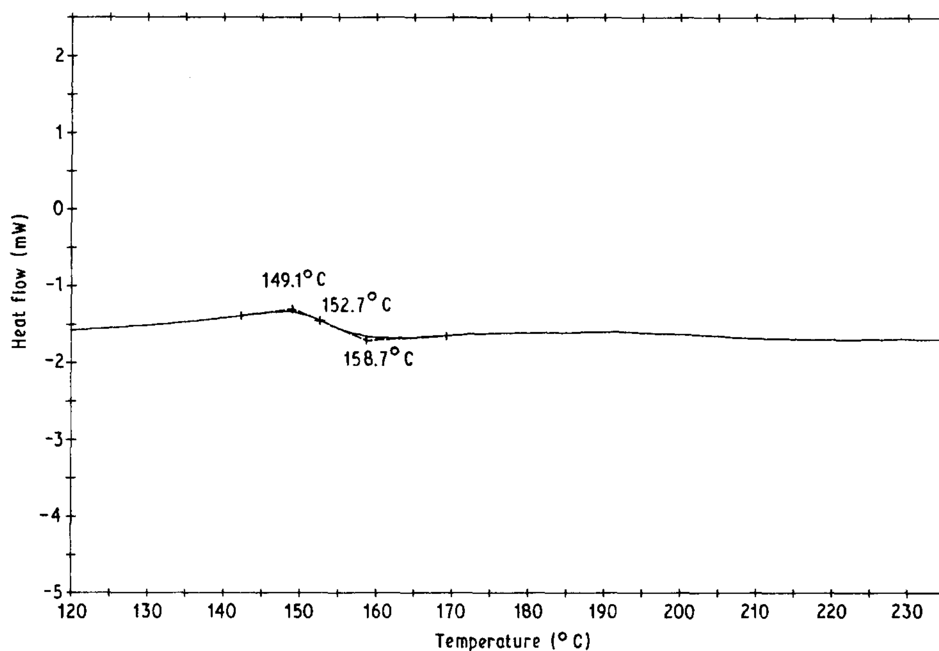

Figure 3 DSC thermogram of epoxy network post-cured at 130 °C.

in the temperature range of the glass transition. The non-post-cured sample has a lower degree of cross-linking, thus shows a larger step and broader transition region, as seen in Fig. 1. On the other hand, the sample post-cured at 150 °C exhibits a nearly indistinguishable transition region, as shown in Fig. 4. This, we suggest, is due to the T_g molecular motion being restricted by the high degree of cross-linking. This observation suggests that the size of the glass transition base-line shift can provide information about the extent of cure of an epoxy system.

Table I shows the effect of post-curing on the glass transition temperature. The glass transition temperature for the epoxy network post-cured at 200 °C was not detected by the DSC technique. This may be due to an extremely high degree of cross-linking at 200 °C; the glass transition may either disappear or it may be shifted to such a high temperature that the network decomposes before reaching T_g. Presumably it is the former because, as shown below, our samples approach a limiting T_g of ~177 °C. It is well known that the glass transition temperature in thermosetting

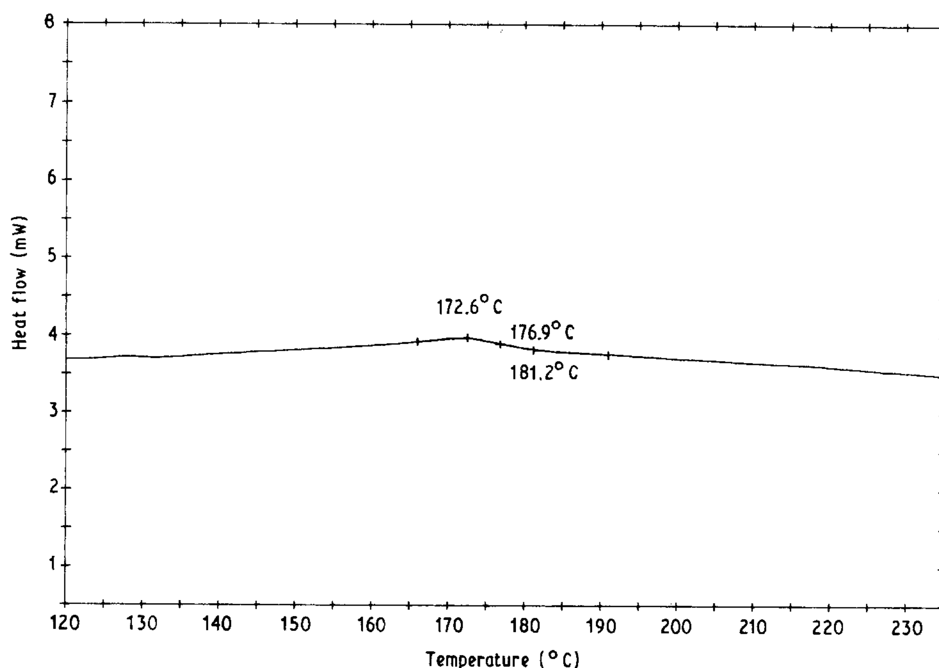

Figure 4 DSC thermogram of epoxy network post-cured at 150 °C.

TABLE I Effect of post-curing on glass transition temperature and bulk density

Post-cure temperature (°C)	T_g (°C)	Density (g cm^{-3})
NP[a]	75	1.2010
110	114	1.1948
130	149	1.1895
150	172	1.1841
170	177	1.1830
200	Absent	1.1828

[a] NP: nonpost-cured, sample only cured at 70 °C for 4 h.

polymers progressively increases during the curing reaction. As T_g reaches the cure temperature the curing reaction stops, because large-scale molecular motions and diffusion cease at temperatures below T_g. As seen in Table 1, the T_g is higher than the cure temperature, this may be due to the curing reaction being exothermic and thus increasing the actual temperature of the sample during post-cure.

A plot of glass transition temperature versus post-cure temperature is shown in Fig. 5. For low post-cure temperatures the glass transition temperature linearly increases with post-cure temperature, i.e. from 114 °C for a sample post-cured at 110 °C, to 172 °C for a sample post-cured at 150 °C. At higher post-cure temperatures (> 150 °C), the increase in T_g decreases and a constant value of about 177 °C is reached for a sample post-cured at 170 °C. This trend is in good agreement with studies on other epoxy systems [5–7]. Because the T_g reflects the extent of mobility of polymer chains it can provide an insight into the cured epoxy network structure and an estimate of the cross-link density. Therefore, in our EMI-24 cured epoxy system, the T_g of 177 °C for the sample post-cured at 170 °C may serve as an indicator of a nearly completely cured epoxy network.

3.1.2. Bulk density

As listed in Table I, the room-temperature density decreases with increasing extent of cure; the standard as-cured sample has the highest density while the sample with the highest post-cure temperature has the lowest density. A plot of density as a function of post-cure temperature is shown in Fig. 6. The downward pattern is just the reverse of Fig. 5, the density initially

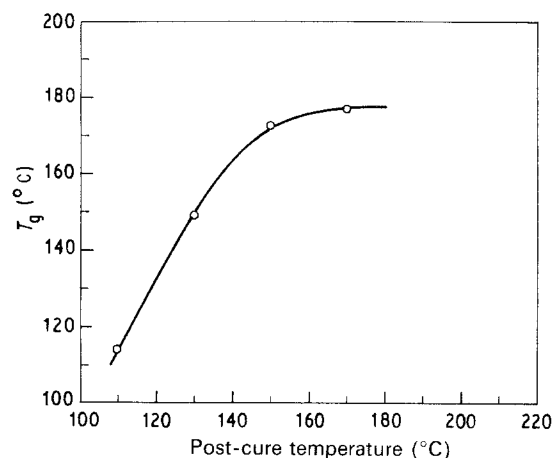

Figure 5 Glass transition temperature as a function of post-cure temperature for EMI-24-cured epoxy network.

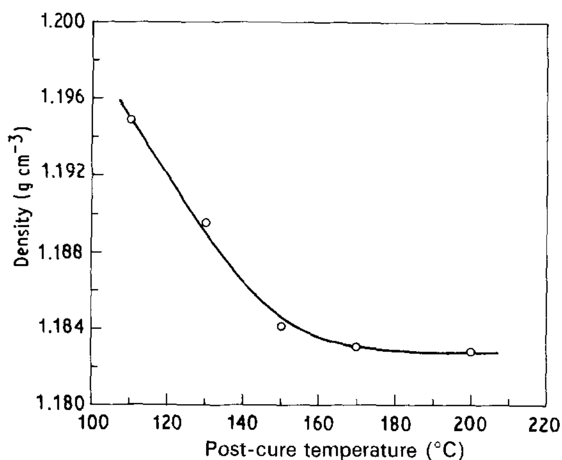

Figure 6 Bulk density as a function of post-cure temperature for EMI-24-cured epoxy network.

linearly decreasing sharply with increasing post-cure temperature up to 150 °C, and then decreasing at a lower rate to approach a constant value for the sample post-cured at about 170 °C. This thus confirms that the post-cure temperature of 170 °C may serve as an indicator of a nearly completely cured epoxy network. This is rather surprising, because one would intuitively expect that the bulk density would increase with increasing T_g (i.e. lower free volume) due to increased post-cure temperature. To explain this apparently anomalous behaviour, Wu [8] suggested that the decrease in the room-temperature density with increasing post-cure temperature (i.e. increasing cross-link density) is due to the combined cross-linking and thermal constraints which result in a higher T_g than due to thermal constraint only, and, therefore, a higher free volume in the glassy state as the sample is slowly cooled through the glass transition temperature.

3.1.3. Stress–strain behaviour

The effect of cross-link density on the room-temperature tensile mechanical properties of epoxy networks has been studied over a period of at least 20 years [9–13]. The results that have been reported in the literature, however, still exhibit many discrepancies. Possibly this could be traced to the fact that the tensile mechanical properties at room-temperature (glassy state) are determined primarily by the strength of intermolecular forces and not by the strength of the covalent bonds of the network chain. Hence the tensile mechanical properties are independent of the degree of cross-linking at room temperature as we concluded in the previous study on the effect of stirring [8]. Thus, in this study of the effect of post-curing, the determination of tensile mechanical properties was carried out at high temperature, at 210 °C, in the rubbery state. In order to reduce further curing, the measurement was done rapidly, the specimen being given 5 min in the temperature-control chamber for equilibration prior to deformation.

Plots of tensile strength, σ, Young's modulus, E, and ultimate elongation, ε, as functions of post-cure

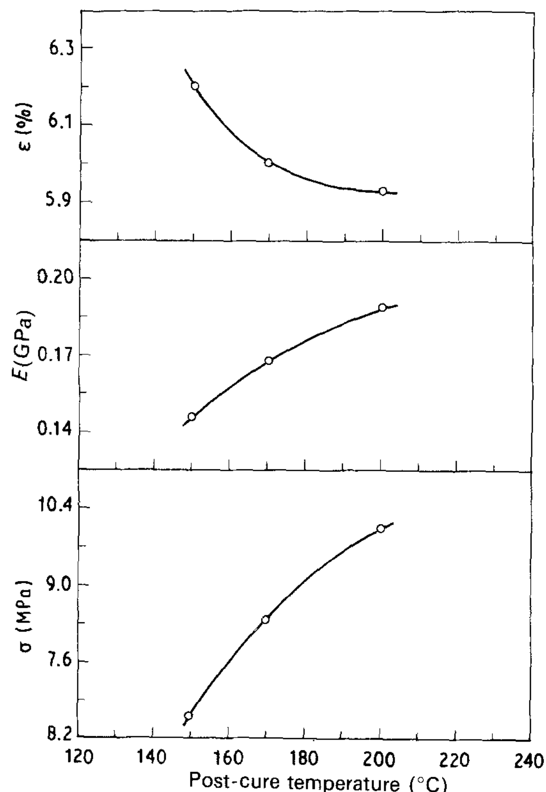

Figure 7 Tensile mechanical properties in the rubbery state as a function of post-cure temperature for EMI-24-cured epoxy network.

temperature is shown in Fig. 7. It is observed that the tensile strength and Young's modulus increased with increasing post-cure temperature while the ultimate elongation, inversely, decreased. The increase of tensile strength and Young's modulus with increasing post-cure temperature were expected because the higher post-cure temperature is intuitively expected to result in an increase in cross-link density and, as a consequence, increases strength and stiffness. Moreover, the more densely cross-linked the system, in which segmental motion is thus much restricted, results in a lower ultimate elongation.

3.2. Temperature dependence of tensile mechanical properties

It is well known that temperature has a significant effect on the mechanical properties of polymers. In order to make optimum use of epoxy networks as structural materials it is important to know how the tensile mechanical properties of this EMI-24-cured epoxy system are influenced by temperature. In this portion of the study the samples were cured at 70 °C for 4 h and then 2 h at 170 ° for post-curing.

Fig. 8 shows the variation of stress–strain behaviour with temperature at constant strain rate. The rupture points can be connected to construct a fracture envelope, as proposed by Smith [14] for cross-linked elastomers. Much practical information on the ultimate properties of a network can be obtained from consideration of its fracture envelope. It is obvious from the figure that the epoxy network exhibited a

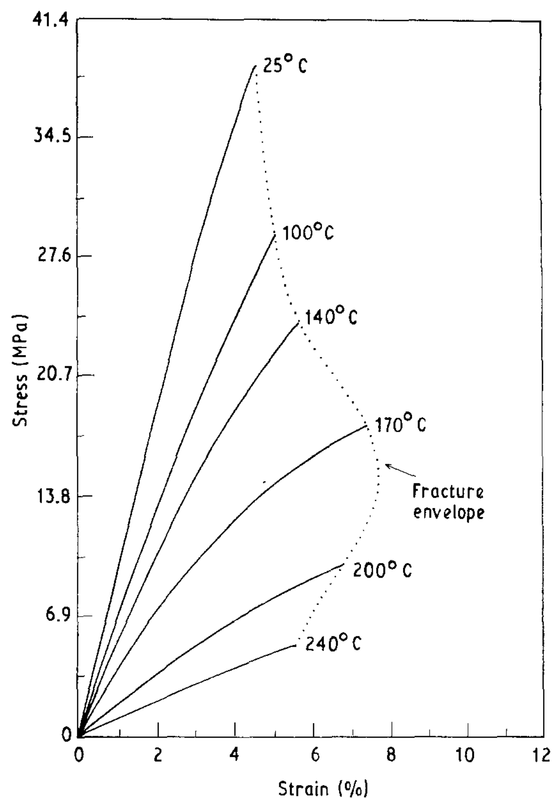

Figure 8 The stress–strain behaviour of EMI-24-cured epoxy network at different temperatures.

"brittle–ductile" transition behaviour. As the temperature is increased the rupture point moves clockwise around the envelope, the stress at break decreasing continuously while the strain at fracture first increases up to the glass transition temperature of ~177 °C during the transition from brittle to ductile behaviour, and then decreases again as the material enters the rubbery state region.

A plot of the effect of temperature on tensile strength for the EMI-24 cured epoxy network is shown in Fig. 9. It appears that the tensile strength decreases markedly with increasing temperature up to the glass transition temperature; just beyond T_g, as defined here, the tensile strength decreases even more rapidly, and then tends to level off and reach a constant value as the material enters the rubbery region.

A similar trend is observed for the Young's modulus as a function of temperature, as shown in Fig. 10. This is a typical curve of viscoelastic behaviour for cross-linked amorphous polymers. Based on another report [15], it is apparent that the modulus drop will be shifted to higher temperature and will plateau at a higher level above T_g with increasing cross-link density, but that cross-link density has very little effect on the modulus below T_g.

Fig. 11 shows the effect of temperature on the ultimate elongation. It is interesting to note that the ultimate elongation exhibits a maximum at the glass transition temperature. A similar trend was also shown by Shimbo *et al.* [15]. They also showed that the ultimate elongation is strongly affected by the cross-link density at temperatures above T_g, but that there is little effect in the room-temperature range. This is consistent with our previous conclusion that the room-temperature tensile mechanical properties are independent of cross-link density.

4. Conclusions

By controlling the effect of post-curing, EMI-24-cured epoxy networks with a wide range of cross-link density (or extent of cure) have been formed. The glass

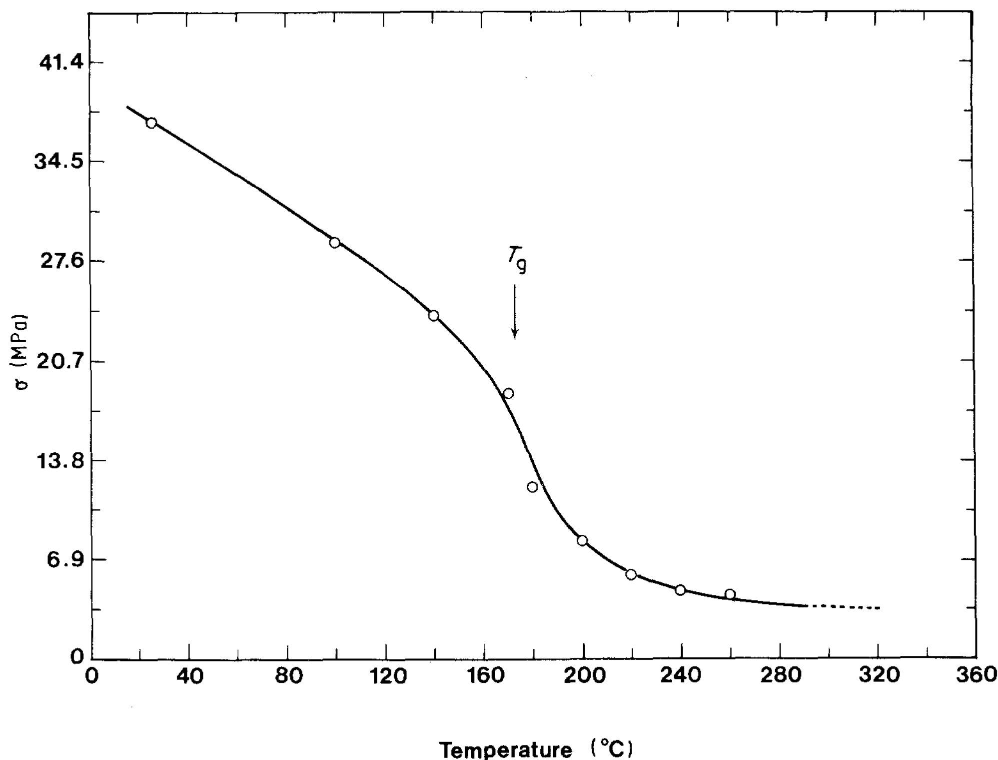

Figure 9 Temperature dependence of tensile strength for EMI-24-cured epoxy network.

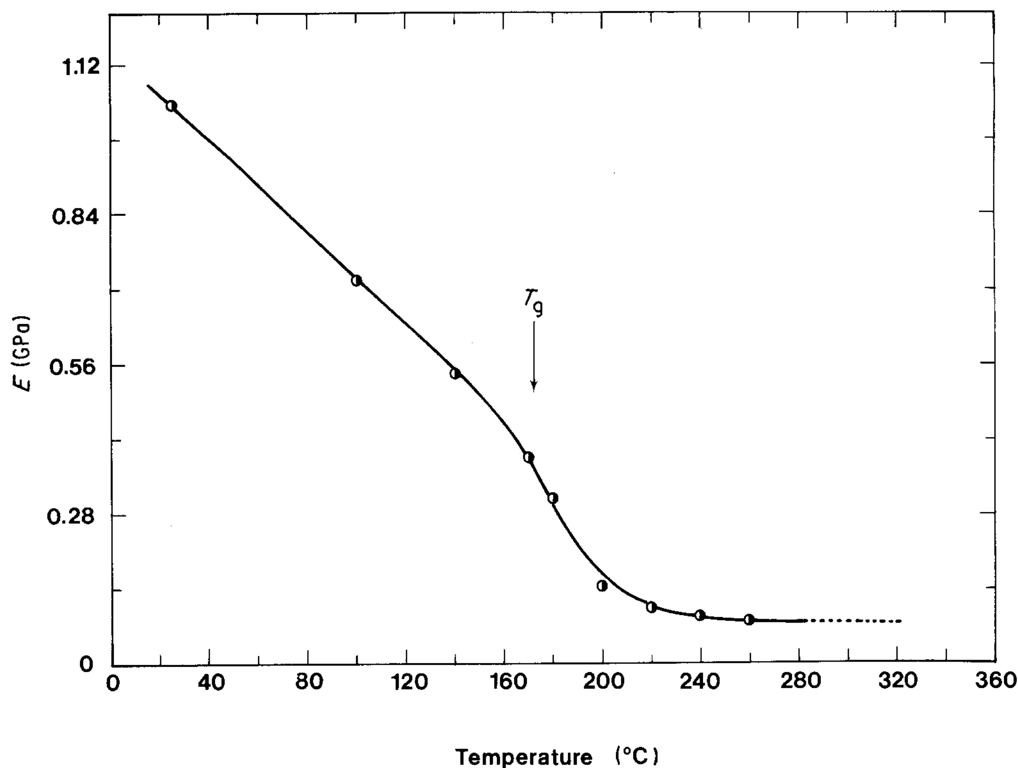

Figure 10 Temperature dependence of Young's modulus for EMI-24-cured epoxy network.

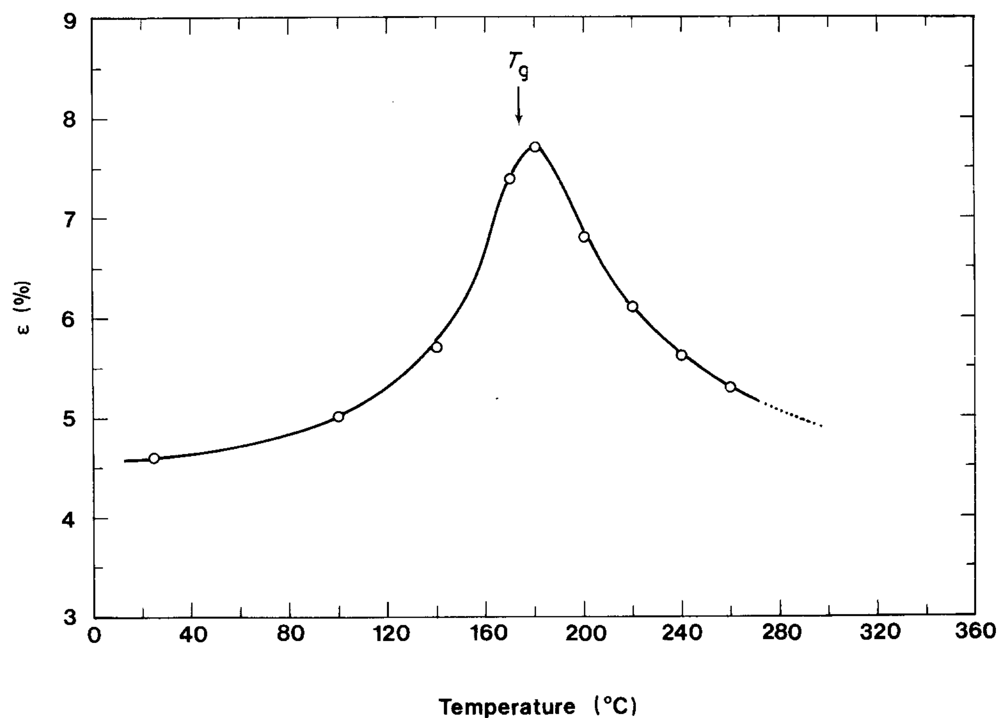

Figure 11 Temperature dependence of ultimate elongation for EMI-24-cured epoxy network.

transition behaviour, bulk density, stress–strain behaviour in the rubbery state, temperature dependence of tensile mechanical properties of these epoxy networks were investigated.

Based on the experimental results, the following conclusions were drawn.

1. The study of effect of post-curing make it clear that both the temperature and the size of the base-line shift in the glass transition region on the DSC thermogram can provide information about the extent of cure in an epoxy system.

2. The glass transition temperature, as is well known, increases with increasing post-cure temperature. The high value of T_g is attributed to the increase in cross-link density.

3. The decrease in room-temperature density as the

post-cure temperature increases (i.e. increase in cross-link density) is due to the addition of cross-linking constraints to the thermal constraints, and can be expected to result in a high free volume in the glassy state as the sample is slowly cooled through the glass transition temperature.

4. The tensile strength and Young's modulus in the rubbery state show a significant increase with increasing post-cure temperature while the ultimate elongation, inversely, decreases.

5. As is well known, temperature has a great effect on the stress–strain behaviour. In agreement with this expectation, a fracture envelope has been obtained as a function of deformation temperature which provides practical information on the ultimate properties of the EMI-24-cured epoxy network. With increase in temperature up to the glass transition temperature both the tensile strength and Young's modulus decrease; just beyond T_g there exists a rapid drop in tensile strength and Young's modulus, followed by a levelling off to reach a constant value as the material enters the rubbery state. The ultimate elongation shows a maximum at T_g as the temperature is progressively increased. It is strongly indicated that the EMI-24-cured epoxy network exhibits a brittle–ductile transition behaviour with temperature.

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