The Dependence of Fracture Properties on Cure Temperature in a DGEBA/DDS Epoxy System

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SYNOPSIS

The glass transition temperature (T_g), water- and solvent-absorption characteristics, fracture toughness, and tensile properties of a diglycidyl ether of bisphenol-A (DGEBA)-based epoxy resin (Epikote 8283) cured with an aromatic amine curing agent, 4,4'-diaminodiphenyl sulfone (DDS), were studied as a function of cure temperature and cure cycle (one-step or two-step cure). The glass transition temperature (which depends on the extent of cure) shows a linear increase with increasing cure temperature and levels off toward the cure temperature of 200°C. Water and solvent uptake tended to increase with increasing cure temperature and, hence, with cross-linking level. Fracture toughness, tensile strength, strain to break, and tensile fracture energy also increased significantly with increasing final cure temperature regardless of cure cycle. In contrast, the small strain properties such as modulus, yield stress, and yield strain were not influenced greatly by cure temperature and cure cycle. From these results, we infer that the large strain properties of the resin are not inversely proportional to the cross-link density of the network as reported in many publications,[1] but, rather, that they are dependent on other structural parameters such as free volume and the flexibility of the cross-linked chains. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Brittleness still remains a major drawback of currently available epoxy resins used for engineering applications. To change this behavior, two basic solutions have been considered. One has been to reduce cross-link density of the epoxy network by the control of material or processing variables.[1-4] The alternative has been to modify the resin with secondary components such as low molecular weight liquid rubbers,[5-10] inorganic fillers,[11] or engineering thermoplastics.[12-17] The latter has generally been considered a more attractive solution in recent research.

In a modified epoxy system, the system properties are determined by two major factors: (i) the basic properties of the resin as the bulk phase (the matrix), and (ii) the microstructure resulting from the presence of the second polymeric phase. These two factors are also influenced simultaneously by processing variables such as reactant ratio and cure condition. It is believed that once the influence of these processing variables on (i) the properties of the unmodified resin and (ii) the resulting microstructure of the modified system is understood clearly it will be possible to find out conditions that will maximize the toughening effect in modified epoxy systems. In this study, the cure temperature, which is one important variable, was changed systematically over a wide range to investigate its effect on the epoxy properties. The influence of the cure cycle was studied separately through the use of different cure cycles. The dependence of microstructure and properties on cure temperature and cure cycle in a modified epoxy system will be described in a following paper. Hopefully, these two studies can indicate an optimum cure condition for maximum fracture properties in a modified epoxy system and further our understanding of the correlations of the microstructural parameters to final fracture properties of the modified system.

EXPERIMENTAL

An intimate mixture of a diglycidyl ether of bis-phenol-A (DGEBA) epoxy resin (Epikote 8283, Shell Chemicals) and an amine curing agent, 4,4'-diaminodiphenyl sulfone (DDS, Anchor Chemicals), in a stoichiometric ratio was prepared under vacuum. In this procedure, the calculated amounts of the resin and the DDS monomers were placed in a 500 mL round-bottomed flask and then connected to a rotating evaporator with an adjustable vacuum box. To minimize curing during the mixing process, the heating time was reduced to 30 min, starting from a temperature of 80°C and finishing at 120°C, using a silicone oil bath. The flask was rotated at a constant speed during the process. When the temperature reached 120°C, the mixture became a clear transparent solution. It was allowed to remain at that temperature until free from bubbles and then poured into preheated Teflon molds before being placed in an air oven for curing. This mixing procedure has two advantages over the conventional procedure in which the mixing is carried out in air. One is that moisture from the environment cannot be absorbed into the mixture, and any moisture initially present in the reactants is removed by the vacuum conditions (a number of publications have reported the detrimental effect of moisture on the properties of epoxy resins[18]). The other advantage is that a separate degassing process is not needed. The cured epoxy blocks and plaques were $120 \times 12 \times 16$ mm and $180 \times 150 \times 5$ mm, respectively.

The cure conditions employed in this study were mostly isothermal, single-step cures ranging in set temperatures from 160 to 240°C; the cure time was standardized at 6 h. This length of time has been reported as sufficient to vitrify the resin even at the lowest cure temperature of 160°C.[19] Some samples were also cured in a two-step program to provide a comparison with the simple one-step cure. A sum-mary of the two step program is shown in Table 1.

Specimens for thermal and mechanical testing were machined from the cured resin blocks or plaques. Samples of 18–25 mg were used to measure the glass transition temperatures (T_g's) on a Mettler differential scanning calorimeter (DSC) at a heating rate of 10°C/min. The T_g's were also measured by a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) run at a frequency of 3 Hz and a heating rate of 2°C/min. Bulk densities were measured at room temperature (19°C) using hydrostatic weighing techniques.[20] When we measured the sample weight in water, the sample surfaces were rubbed with wet tissue prior to immersion in order to prevent the formation of bubbles. The penetration of water into the sample was minimized by taking readings within 5 sec. Water and solvent uptake were measured gravimetrically after immersing the samples in liquid at 80°C for 14 days (water) and at room temperature for 30 days (solvent).

All the mechanical tests were carried out on a testing machine (Instron 4505) at room temperature and at least five samples were tested for each cure condition. The fracture toughness tests were carried out at a cross-head speed of 1.0 mm/min. Small compact tension specimens ($15.8 \times 15.2 \times 10$ mm) were precracked by inserting a thin razor blade into the machined notch and impacting with a small hammer. In order to prevent crack blunting, a fresh razor blade was used for each specimen. This is one of the standard techniques to produce sharp cracks. The flexural modulus was measured on rectangular specimens of $50 \times 10 \times 2.4$ mm in a three-point bending mode at the same crosshead speed as used in the compact tension tests; the span to depth ratio was 16 : 1. Tensile properties were determined on dumbbell-shaped specimens, at a crosshead speed of 5 mm/min. The extension was measured with the help of an extensometer attached to the specimen. A gauge length of 25 mm was used for these tests.

Table I Physical and Mechanical Properties Changes for a DGEBA/DDS System Cured by a Two-step Cycle

Cure Schedules	T_g (°C)		G_{1c} (J/m^2)	Flexural Modulus (GPa)
	(a)	(b)		
140°C · 2 h/180°C · 2 h	171	188	98	3.25
140°C · 3 h/200°C · 3 h	199	212	174	2.95
120°C · 6 h/200°C · 15 h	210	222	174	2.95

[a] Measured by DSC.
[b] Measured by DMTA.

RESULTS AND DISCUSSION

Glass Transition Temperature

The most direct method of determining glass transition temperature is by dilatometric measurements of volume as a function of temperature under near equilibrium conditions.[21] Two other commonly used techniques, DSC and DMTA, also give indication of glass transition temperatures, shifted to slightly higher values due to kinetic effects. Figure 1 shows the data of the glass transition temperature (T_g) obtained from DSC and DMTA measurements for the various samples prepared using the one-step cure. The two different T_g's increase linearly in a similar manner with increasing cure temperature, and then tend to level off from the cure temperature of 200°C, approaching their maximum glass transition temperatures, $T_{g\infty}$ (207°C for DSC and 217°C for DMTA). Since the cure time is fixed at 6 h for all samples, the variations in T_g observed here can be taken as a consequence of (i) the extent of cure resulting from varying the cure temperature, or (ii) network topology and the associated free volume, or (iii) both of the effects combined. At this point, it will be necessary to review structural variation under different cure temperatures in order to identify the influence of the network structure on the glass transition temperature. The glass transition temperature of a polymer is heavily dependent on its molecular weight and increases proportionally with increasing molecular weight.[22] The equivalent statement for a crosslinked network is to say that the glass transi-

tion temperature is strongly dependent on cross-linking density.[22]

In a DGEBA/DDS epoxy system, the molecular weight of the network increases mainly through linear polymerization between epoxy and primary amine; in contrast, the branching reactions occur between epoxy and secondary amine and by side reactions such as etherification.[23] It has been reported that the etherification reactions do not occur to a significant extent in a DGEBA/DDS system in the absence of a catalyst.[23,24] The linear polymerization reactions largely precede the branching reactions because the primary amine is more reactive than is the secondary amine.[25] We have assumed that in the range of cure temperatures from 160 to 240°C, and within the allocated time of 6 h employed in this study, the linear polymerization reaction has reached its maximum extent in all samples. However, the extent of the branching reaction will have a more critical dependence on cure temperature; it will be limited at 160°C and will increase with increasing cure temperature. Therefore, the cross-link density of the final network will vary with the extent of the branching reaction and, hence, the cure temperature, at a fixed time. In order to estimate the structural variation of the epoxy network, the average molecular weight between crosslinks for cured resin can be calculated from the corresponding T_g according to the following empirical equation.[26]

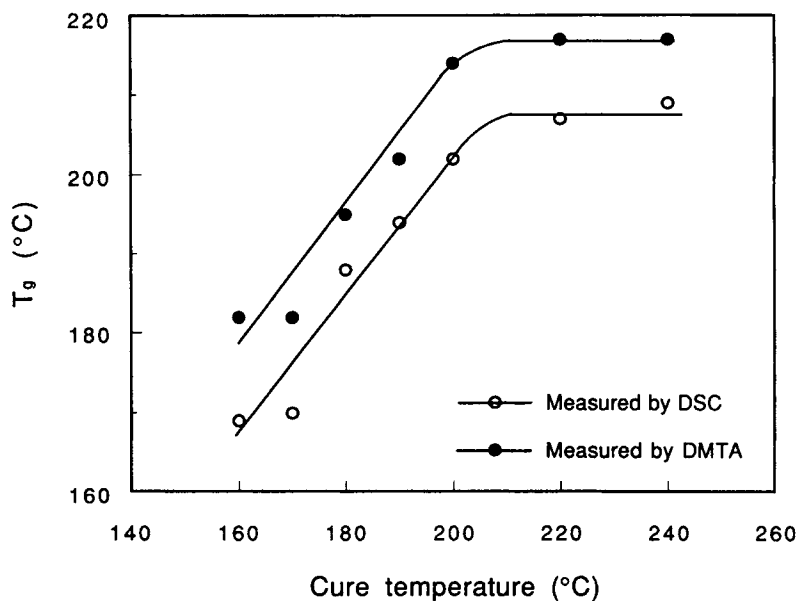$$M_c = \frac{39,000}{T_g - T_{go}} \qquad (1)$$

Figure 1 Glass transition temperature vs. cure temperature for the DGEBA/DDS epoxy system.

where T_{go} is the glass transition temperature of the uncrosslinked resin. T_{go} for our resin system was $-6°C$ in our DSC measurement. Consequently, one point of view is that the variation of the glass transition temperature observed in this study may be attributed to the variation of crosslink density of the networks. Therefore a sample cured at higher temperature has a higher crosslink density and therefore a correspondingly lower value of M_c.

An alternative view is to assume that the extent of reaction is the same, i.e. all bonds are made in all samples (independent of cure temperature), but the conformations and configurations of individual bonds and molecules are different, requiring different occupied and free volumes, and therefore leading to different bulk densities. The results of bulk density measurements, shown in Fig. 2, are consistent with this view. Consideration of the network chains leads to the observation that such changes in free volume can be due to (i) rotation of the benzene rings in the epoxy resin and DDS, and configurational changes of the $-O-CH_2CHOH-CH_2-N-$links. In the latter case there are four bonds with bond angles around $110°$ allowing for trans and gauche conformations. The higher the temperature of curing the higher the probability of the molecules to be in configurations characterised by excess free energy. We suggest that both of these effects are responsible for lowering the bulk density of the samples cured at higher temperatures, as observed in Fig. 2.

The results in Fig. 1 and Fig. 2 contain apparently conflicting results, i.e. samples cured at $220°C$, of lower bulk density, exhibit higher T_g than samples

cured at $160°C$, with higher density but lower T_g. To resolve this conflict it must be concluded that T_g is more significantly influenced by the crosslinking density than any free volume effects.

Water- and Solvent-absorption Characteristics

Water and solvent resistance is considered an extremely important property for those epoxy resins that are used in structural applications and has attracted many studies.[18,27,28] The water-absorption characteristics of epoxy resins have also been used as an indicator of the degree of structural packing of the epoxy network.[24,27,29,30] This approach has been based on the following water-absorption mechanism: At the early stage of the absorption process, the water molecules occupy the free volume entrapped in the cross-linked network. At a later stage, some of the water molecules remaining in the free volume disrupt the polar groups such as hydroxyls, attached to the network, and become hydrogen-bonded water. The former water is called bulk, unbound water and the latter is termed bound water. Therefore, the epoxy network that has a larger free volume and/ or more polar groups can absorb more water. The water and solvent uptake figures obtained in this study are shown in Figure 3. Both increase with increasing cure temperature, although the slope for solvent uptake is greater than that for water. This result implies that the highly cross-linked systems, cured at high temperatures, contain greater free volume and/or more polar groups. This can be explained as follows: In addition to the $-OH$ groups
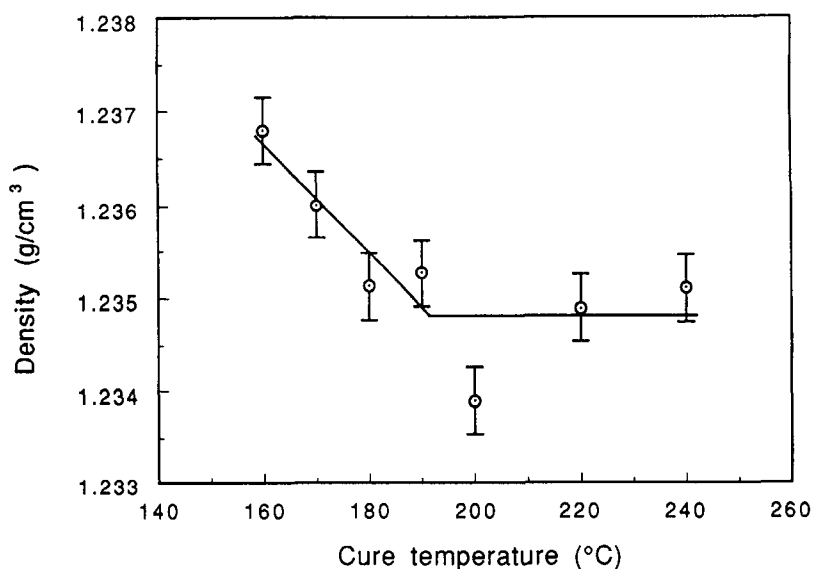

Figure 2 Bulk density vs. cure temperature for the DGEBA/DDS system.
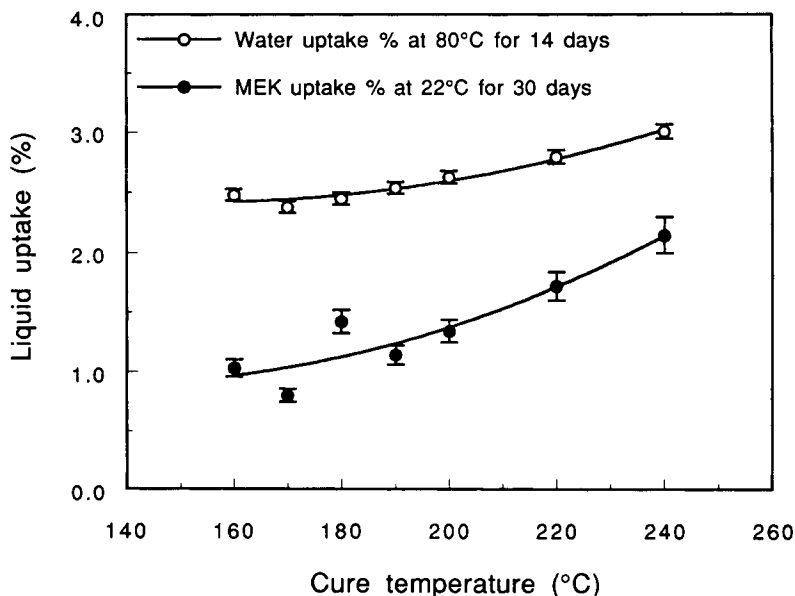
Figure 3   Water and solvent absorption vs. cure temperature for the DGEBA/DDS system.

attached to the backbone of the oligomeric epoxy monomer, more —OH groups are produced by ring opening during the cure. As a result, the number of —OH groups in the cross-linked network increases in proportion to its cross-link density. But the implication in our work that the highly cross-linked system would have greater free volume in a glassy state (below T_g) can be considered an anomalous result. This has been reported elsewhere where the cross-linking density of the network was controlled by varying the reactant ratio or cure time.[19,30,31] These research workers also found a decreasing room-temperature density with increasing cross-link density and further concluded that the lower density for the highly cross-linked system is responsible for the lower modulus observed. Our results agree with the above conclusions.

Fracture Toughness

Figure 4 shows the measured fracture toughness, G_{Ic}, of the samples cured at different temperatures. Each value is the average of at least five measurements. The strong dependence of fracture toughness on cure temperature can be seen. At cure temperatures over 200°C, the toughness values tend to level off. The maximum value of 221 J/m² for the sample cured at 220°C shows a large increase compared to the value of 96 J/m² for the sample cured at 160°C. This tendency was also observed earlier in T_g, although its dependence on cure temperature was not

as strong. Here we can derive an important proportional relationship between the fracture toughness and the cross-link density. This proportional relationship of fracture toughness with cross-link density is quite unusual and contrary to most reported results obtained under conditions of varying reactant ratio or varying molecular weight of epoxy prepolymers.[3,32] The workers reported that the crack initiation fracture toughness values increased with M_c. This different result obtained by us using slightly different parameters implies that the cross-link density is not always a strong determining factor for fracture toughness but that the other structural parameters such as free volume (discussed earlier), chain flexibility, and the degree of intermolecular packing are more likely to be responsible. The other noteworthy item is that the fracture toughness tends to reach its maximum at the cure temperature of 200°C and does not vary with further increase in cure temperature up to 240°C, which shows that the degradation has not progressed significantly in the samples cured at the higher temperatures even though the color of the cured bars was slightly changed to semitransparent light black.

Tensile Properties

Load-elongation Curves

The shape of the load-elongation curves are influenced by the specimen size as well as by the material
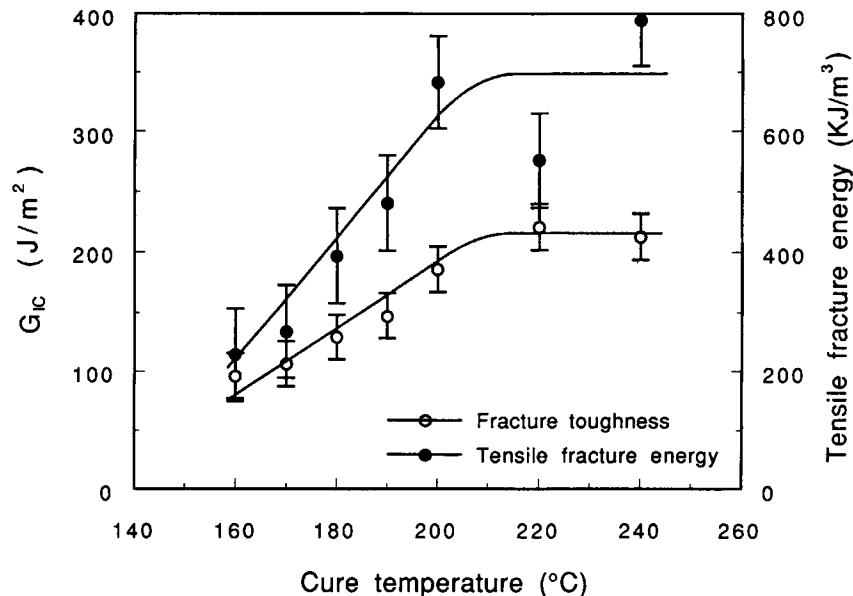
Figure 4 Fracture toughness and tensile fracture energy vs. cure temperature for the DGEBA/DDS system.

properties. However, the ratio of the nonlinear elongation to the breaking elongation, $(\delta_B - \delta_y)/\delta_B$, is believed to be influenced by material property alone and can be measured from the tensile load–elongation curve. Here, δ_B and δ_y are the elongations at breaking point and yield point, respectively. This ratio is expected to represent the ductility of the materials.[33] The values of the ratio calculated from

our measurements are shown in Figure 5. It can be seen that these values increase as the cure temperature increases, again reaching a plateau above 200°C. This result indicates that the epoxy becomes more ductile at the higher degree of cross-linking obtained at higher cure temperatures. Fundamentally, fracture toughness combines strength and ductility of the materials. In this respect, the in-
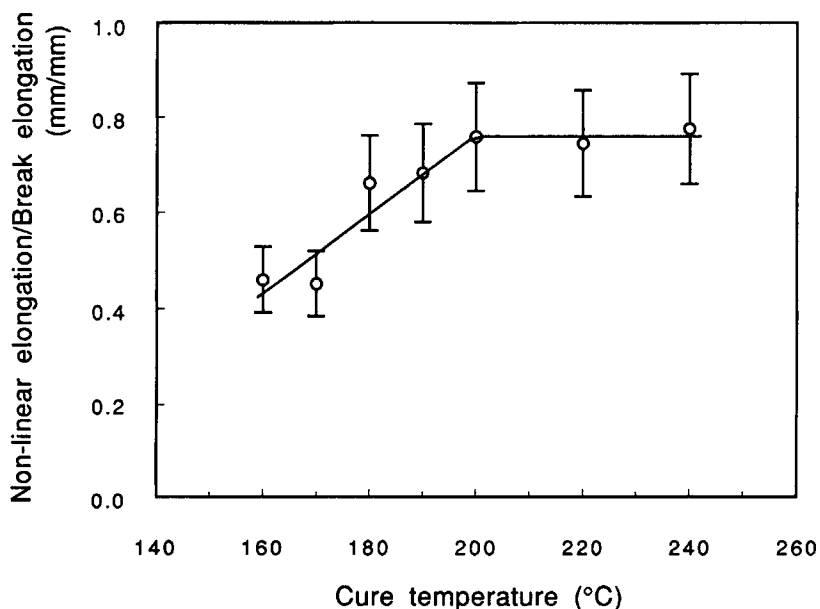

Figure 5 The ratio of nonlinear elongation to breaking elongation vs. cure temperature for the DGEBA/DDS system.
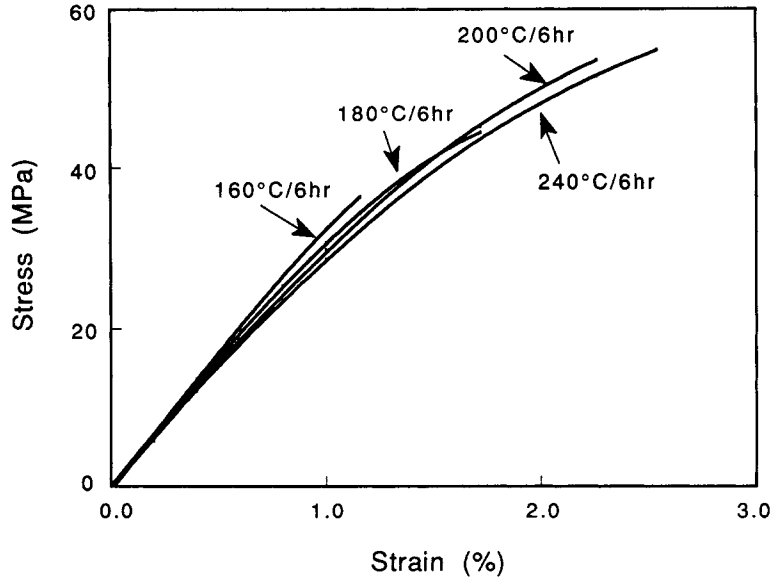
Figure 6   The representative stress–strain curves, showing the dependence of tensile behavior on cure temperature, in the DGEBA/DDS system. End of curve indicated break-point.

creasing ductility combined with cross-link density increases coincides with our observed fracture toughness results.

Stress–strain Curves

The averaged nominal stress–strain curves, obtained from the load-deflection curves, are plotted in Figure

6. They show that the stress increases up to a breaking point in all samples without showing a trace of work softening. There are two distinct features to be observed: One is a strongly dependent trend observed in fracture toughness. This trend is evident in the large-strain properties like tensile strength, strain to break, and tensile fracture energy as shown in Figures 4 and 7. The tensile fracture energies in
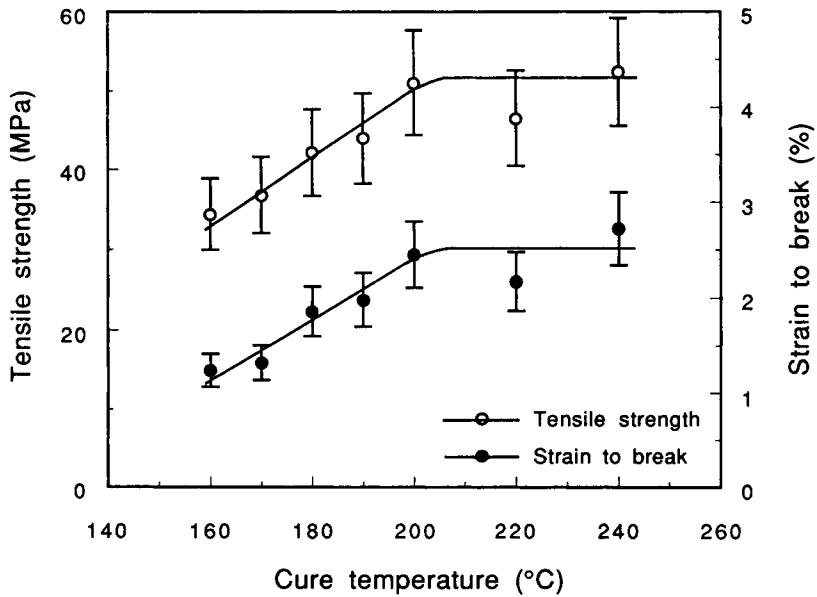

Figure 7   Tensile strength and strain to break vs. cure temperature for the DGEBA/DDS system.

Figure 4 were obtained from the area under the stress–strain curve. Dramatic increases of 52, 119, and 246% are observed, respectively, with increasing cure temperature. Gupta et al.[34] reported that the large-strain properties depend on many factors such as intermolecular packing, chemical structure, molecular architecture, and cross-link density of the network.

The other feature is a non- or weakly dependent trend in small-strain properties like tensile and flexural moduli, yield stress, and yield strain, as shown in Figures 8 and 9. The small-strain properties represent the elastic characteristics of the material. These properties only slightly decrease with increasing cure temperature and are not nearly as significant as those observed in the large-strain properties. A summary of the results discussed up to now indicates the important conclusion that the toughness (which combines strength and ductility) of the pure unmodified epoxy resin can be improved significantly by employing a high cure temperature in a one-step cure without a sacrifice in stiffness characteristics.

The Effect of Cure Cycle

Table I contains data on glass transition temperature, fracture toughness, and flexural modulus of the cured resin samples prepared in various two-step procedures. The values are quite similar to those for the samples cured in single step with the same final cure temperature. This indicates that the final

properties of the resin are not greatly dependent on cure cycle variations but are strongly dependent on the final cure temperature.

This is a significant observation from our work and it will be a useful basis for estimating the contribution of the matrix resin properties to total system properties in a modified resin system separated from the influence of microstructure variations caused by the incorporation of a modifier.

CONCLUSIONS

(i) The glass transition temperature of our DGEBA/DDS epoxy system linearly increases with increasing cure temperature to approach its $T_{g\infty}$ and then levels off from the cure temperature of 200°C. This linear dependence of glass transition temperature on cure temperature is attributed to changes in the cross-link density that is also proportional to cure temperature.

(ii) Water- and solvent-absorption characteristics are increased with increasing cure temperature. This result indicates that the free volume in the network increases as the cure temperature increases because the higher rate of cross-linking freezes in the voids.

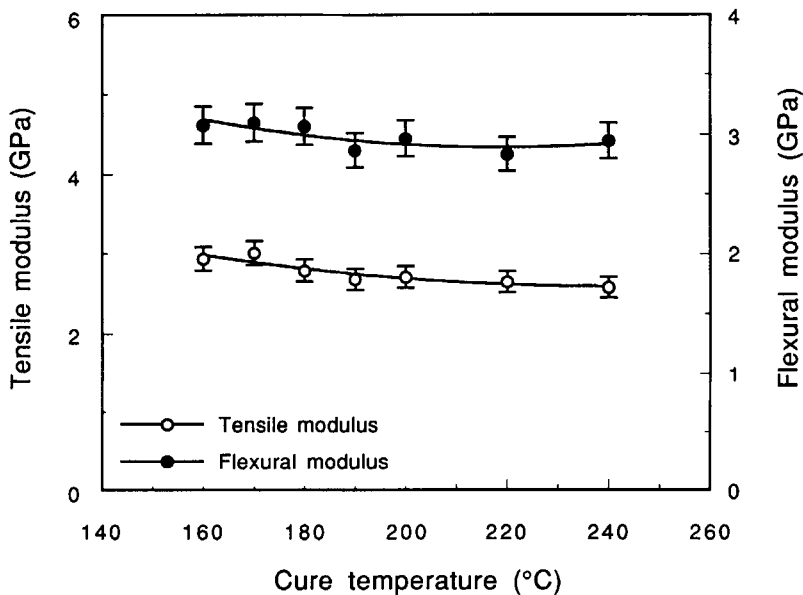(iii) The fracture toughness increases to approach a maximum value as the cure tem-

Figure 8   Tensile and flexural modulus vs. cure temperature for the DGEBA/DDS system.
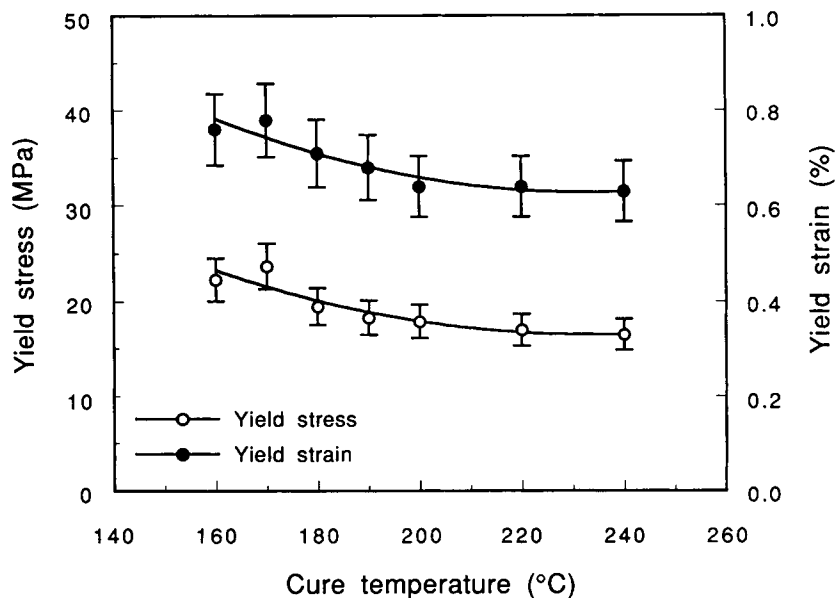
Figure 9   The stress and strain at yield point vs. cure temperature for the DGEBA/DDS system.

perature increases and then levels off. This is not consistent with other reported results and implies that the fracture toughness may not have any direct correlation with cross-link density.

(iv) The ratio of the nonlinear elongation to the breaking elongation that represents the ductility of the material shows a similar trend with cure temperature as that observed for the fracture values.

(v) The large-strain properties such as tensile strength, strain to break, and tensile fracture energy show similar dependence on cure temperature. In contrast, the small-strain properties such as modulus, yield stress, and yield strain are not greatly influenced by cure temperature.

(vi) The properties of the resin are determined by the final cure temperature, regardless of the cure cycle.

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