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The Temperature-Dependence of Some Mechanical Properties of a Cured Epoxy Resin System

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The tensile mechanical properties and fracture toughness of a Bisphenol-A type difunctional epoxy resin, cured with different amounts of metaphenylene diamine, using two cure cycles, were determined over a range of temperature. The tensile modulus in the glassy state was seen to be predominantly related to intermolecular packing, while in the rubbery state crosslink density was the important factor. Yielding appeared to be due to an increase in free volume as a result of dilatation during the tensile test and was related to a critical shear stress. The large strain properties like tensile strength, elongation-to-break, and toughness showed a more complex dependence on chemical structure, molecular architecture, intermolecular packing, and crosslink density. The roles played by the relaxation processes in determining mechanical properties are highlighted.

INTRODUCTION

The mechanical properties of crosslinked, amorphous polymers are expected to depend on their chemical structure and molecular architecture on the one hand, and the free volume and crosslink density and their distributions on the other. In rubbers, which are lightly crosslinked amorphous polymers made by crosslinking large molecules, it has been shown (1, 2) that with an increase in crosslink density, the free volume decreases with a resultant increase in stiffness. The tensile strength first increases with increasing degree of crosslinking but then decreases at very high degrees of crosslinking. This decrease has been attributed to the nonuniformity of load distribution at high degrees of cross-linking (3), apparently due to a wide distribution of spacing between crosslinks. The elongation-to-break of a rubber decreases as the degree of crosslinking increases. The situation is more complex for cured epoxy resins which are highly crosslinked, glassy, amorphous solids prepared from chemical reaction between epoxy resin molecules, generally monomeric to oligomeric in size, with curing agent molecules which are also

relatively small. There have been a number of studies on changing the crosslink densities of these systems by stoichiometric variations (4-11), i.e., by using different amounts of the curing agent. These have resulted in conflicting results which will be briefly summarized later in this section. Chang, *et al* have stated (12) that to get an unambiguous understanding of the effect of crosslink density on mechanical properties, it is preferable to vary the cure time rather than stoichiometry. Using a suitable system, they varied crosslink density by varying the cure time and showed that an increase in crosslink density tightens the network of the epoxy system as it does in the case of rubber. As a result the free volume is reduced, and there is an improvement in mechanical properties. When stoichiometry is varied, the highest crosslink density is generally obtained in the stoichiometric composition. However, the structures of the various compositions are different as they contain different amounts of the resin and the curing agent. While some authors have reported that the elastic modulus is independent of stoichiometry (4, 5), others have observed a minimum at stoichiometry (6, 7). Ultimate tensile strength has been reported to be insensitive to stoichiometry (5) but in other studies a minimum (6) or a maximum (4) have been observed at stoichiometry. Similarly, elongation-at-break has

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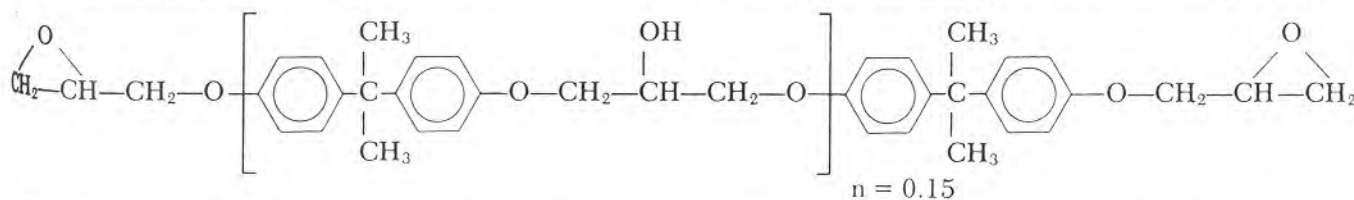
been reported to be insensitive to stoichiometry (4, 5) or to show a maximum at stoichiometry (6, 10). These various conflicting observations suggest that there is no direct correlation between the room temperature mechanical properties and the crosslink density of these samples. There is thus an obvious need to understand the physical basis of the dependence of mechanical properties of such systems having different chemical compositions. It would obviously be an advantage if the temperature-dependence of mechanical properties is studied.

In the present work, a difunctional, Bisphenol-A type epoxy resin was cured with different amounts of metaphenylene diamine (mPDA) using two cure cycles. The tensile mechanical properties were determined over a range of temperature on a tensile tester. The toughness was measured using a compact tension specimen. The dynamic mechanical properties of these samples had been measured and reported earlier (13). The results of the present investigation show that: (i) at the higher temperatures, the mechanical properties are dominated by crosslink density; high crosslink density gives high modulus, high strength and low elongation, and (ii) at lower temperatures (a) the low-strain properties like modulus and yield point are normally governed by free volume or intermolecular packing. Close packing of the molecules results in high modulus and high yield stress, and (b) the large strain properties like tensile strength, elongation-at-break and toughness are dependent on the chemical structure, molecular architecture, free volume, and crosslink density. The roles of relaxation processes in determining these properties are also highlighted.

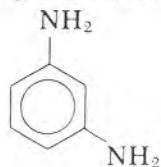
EXPERIMENTAL

Sample Preparation

The epoxy resin used was Epon 828 (Shell), which is based on diglycidyl ether of Bisphenol-A and has the following chemical structure:



The curing agent used was metaphenylene diamine having the following chemical structure:



The curing agent concentration for the stoichiometric composition, i.e., one in which the epoxy: amine ratio is 1:1, is calculated to be 14.5 parts by weight per hundred parts of the resin (phr) for this system. In the present investigation samples were prepared containing 7.5, 10, 14.5, 20, and 25 phr of mPDA using the following procedure. The resin

and the curing agent were heated in separate containers in an oven set at 75°C until the mPDA melted. They were then mixed by stirring, and the stirred mixture was vacuum-degassed for seven minutes before being poured into flexible silicone rubber molds to form tensile dogbone coupons and rectangular rheometric bars. The curing cycle used was 75°C for two hours followed by 125°C for two hours. These samples will be designated as "standard cure". Another set of samples was prepared by postcuring the standard-cure samples at 175°C for six hours in an inert gas environment; these will be referred to as the "postcured" samples.

Infrared Studies

Infrared studies were made in the near IR region on 1 mm thick discs and in the intermediate IR region on thin films cast between two cesium iodide windows.

Differential Scanning Calorimetry

DSC scans were made at 10°C/min and the glass transition temperature was obtained from these scans.

Specific Volume

The density at room temperature was determined in a sodium bromide-distilled water density gradient column. The coefficient of linear thermal expansion, α , was measured on flat discs of about 1 mm thickness and 3 mm diameter from room temperature to above glass transition temperature at a heating rate of 10°C per minute on a thermomechanical analyzer (TMA) interfaced to a computer. Since α is very small and assuming that the sample is isotropic, the density at temperature T (ρ_T) is given by

$$\rho_T = \rho_{Tr} / [1 + 3\alpha(T - T_r)]$$

where ρ_{Tr} is the density at room temperature (T_r).

The specific volume at temperature T , $1/\rho_T$, was thus obtained. The measurement of thermal expansion coefficient by the TMA requires great care (14). A number of measurements were made to ensure consistency of results.

Tensile Mechanical Measurements

Three types of tensile tests were made. In the first test strain gages were glued to the tensile dogbone coupons and the rheometric bars, and the load-elongation curves were recorded at room temperature at a constant loading rate of 1 lb/sec. Since the gage response is linear only at low strains, the load-elongation curves were obtained up to strains

of about two percent, and from the initial parts of these curves, the elastic modulus was calculated. Thus, though the strain rate varies during the experiment, it will not change significantly during the limited strain range studied. Also the loading rate used gave strain rates close to those used in the other two tests. This test gave highly reproducible results, and at least two measurements were made for each sample.

The second tensile test was done on another tensile tester (Material Test System or MTS). Using a small environmental chamber, the load-elongation curves were recorded for the standard cure tensile dogbone coupons over a wide temperature range at a strain rate of about two percent per minute. In calculating the strain from the crosshead displacement, the gage length of the sample was taken as the length of the parallel portion of the dogbone (1.1"). Since the shoulders of the dogbone will also undergo limited deformation and since the machine compliance would also contribute to the deformation, this strain is designated as the "apparent strain".

Finally, tensile measurements were made on the Instron tensile testing machine over a wide temperature range at a strain rate of about two percent per minute. At room temperature extensions were monitored with the help of an extensometer and, therefore, like the strain gage test, the strains will be the true strains of the specimen. At other temperatures the extensions were measured from crosshead displacement. In these cases the strain was calculated by taking the gage length as the length of the specimen between the grips (1.395") instead of the length of the parallel portion of the dogbone (1.1"). This procedure had been found by experience to give strains closer to those given by the extensometer. At least four dogbone samples were tested at each temperature. Due to instrumental and time constraints, the sample was not taken to the breaking point if it continued to stretch beyond ten percent or so. In such cases the tensile strength was taken as the stress at which the sample continued to stretch. The initial modulus was calculated by drawing a tangent at the initial part of the load-elongation curve.

Toughness Measurements

Notched compact tension (CT) specimens with fresh razor blade cuts were tested in tension on the MTS, and the load required to propagate the crack was monitored as a function of time. From this the parameter k_Q was computed which has been shown (15) to be a measure of the sample toughness.

Dynamic Mechanical Measurements

The dynamic mechanical spectra were recorded on a Rheometrics Mechanical Spectrometer (RMS) at four frequencies and have been discussed in detail elsewhere (13). From the rubbery modulus (modulus above T_g), G' , the molecular weight between crosslinks, M_c , was calculated using the fol-

lowing approximate expression (16):

$$\log_{10} G' = 7 + \frac{293 \rho}{M_c}$$

where ρ is the density.

RESULTS AND DISCUSSION

General Characterization

The glass transition temperatures of the various samples, as obtained from the peak positions of $\tan \delta$ on the RMS at a frequency of 0.016 Hz are shown in Fig. 1a and from the DSC in Fig. 1b. The values of molecular weight between crosslinks, M_c , calculated from the rubbery torsional modulus, are shown in Fig. 2. As expected, the stoichiometric sample has low M_c or high crosslink density and a high T_g ; on either side of stoichiometry, both crosslink density and T_g decrease. Postcuring results in a considerable increase in the crosslink density and

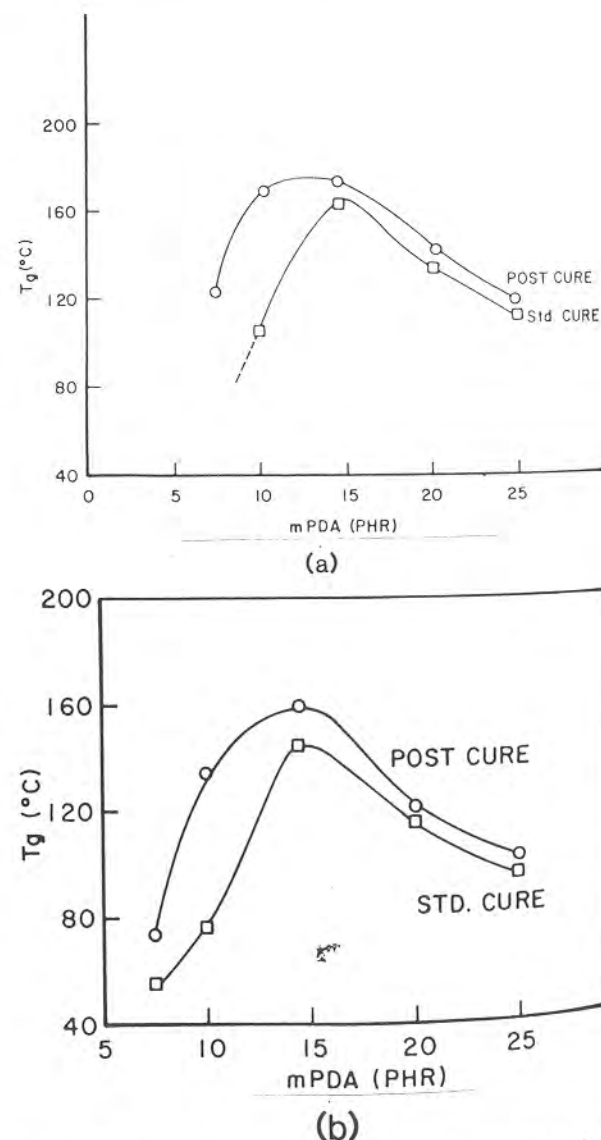


Fig. 1. The dependence of glass transition temperature (T_g) on curing agent concentration from (a) peak position of $\tan \delta$, and (b) DSC.

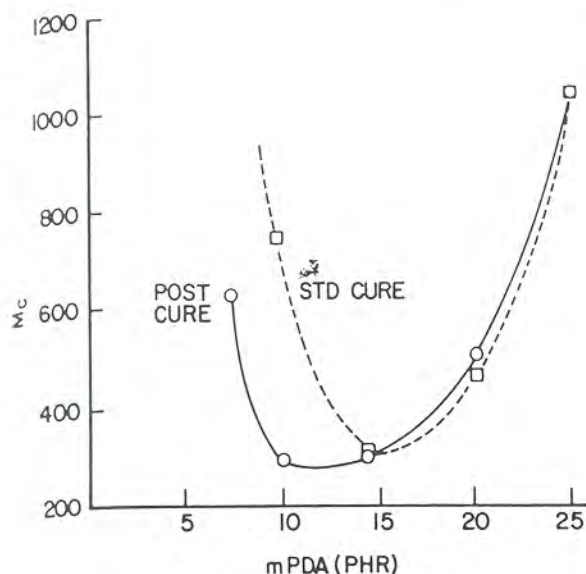


Fig. 2. The dependence of molecular weight between crosslinks (M_c) on curing agent concentration.

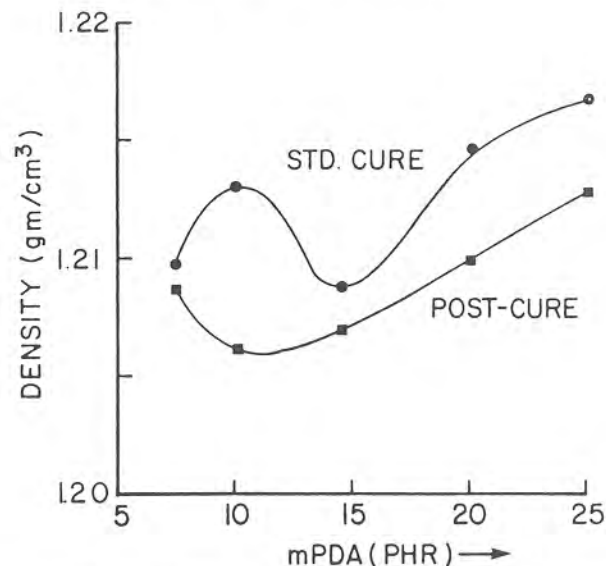


Fig. 3. The variation of room temperature density with curing agent concentration.

the T_g of the epoxy-rich samples, but the effect on the other samples is very slight. It may also be noted that the DSC T_g 's are lower than the T_g 's obtained from the dynamic mechanical studies.

Infrared Results

Infrared studies showed that the 7.5 and 10 phr "standard cure" samples contained a considerable amount of unreacted epoxy groups while the 20 and 25 phr samples had unreacted amines. The stoichiometric sample (14.5 phr) also contained small amounts of unreacted epoxy and amine groups. On postcuring, the 10 phr sample showed the most dramatic reduction of unreacted epoxy groups followed by the 7.5 phr sample. The stoichiometric sample now had no detectable unreacted groups. There was little change in the 20 and 25 phr samples. In the epoxy-rich samples, further crosslinking had apparently occurred by reaction between the epoxy and the hydroxyl groups. Since 175°C is close to the maximum curing temperature ($T_{c\infty}$) of the stoichiometric sample (17), the postcuring apparently results in more fully cured samples whose chemistry would be expected to remain essentially unchanged during the thermal and mechanical measurements.

Molecular Packing

The room temperature density data are shown in Fig. 3. It is seen that the sample having the highest crosslink density and T_g in the standard-cure series (14.5 phr) has the lowest density. On postcuring the densities of all the standard-cure samples decrease, the largest decrease being for the 10 phr sample which also shows maximum increase in T_g .

The data on coefficient of linear thermal expansion below (α_g) and above (α_L) T_g is shown in Fig. 4 as a function of stoichiometry. Above T_g , the stoichiometric sample has the lowest thermal expansion apparently due to a tight network. The densities of

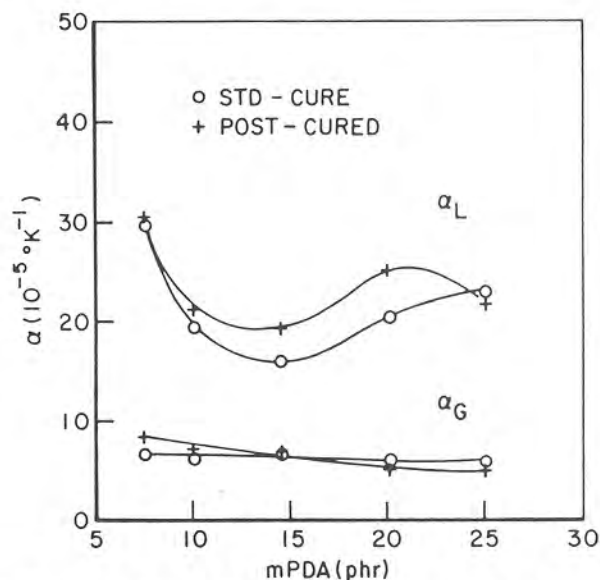


Fig. 4. The coefficient of linear thermal expansion below (α_g) and above (α_L) T_g .

the standard and postcured samples of different stoichiometry, calculated as indicated earlier, are shown as functions of temperature in Figs. 5 and 6 respectively. In making these calculations, the T_g 's obtained from differential scanning calorimetry were used, and it was assumed that it is a sharp transition. It may be noted that at room temperature, the highest crosslinked samples have low densities compared to the other samples, while at higher temperatures, they have relatively higher densities. As discussed in detail elsewhere (13), this is because the room temperature conformation of the molecules in the various samples corresponds in fact to the conformation they had at their respective glass transition temperatures. Thus in samples with high T_g , which is far away from room temperature, there is a relatively higher fractional

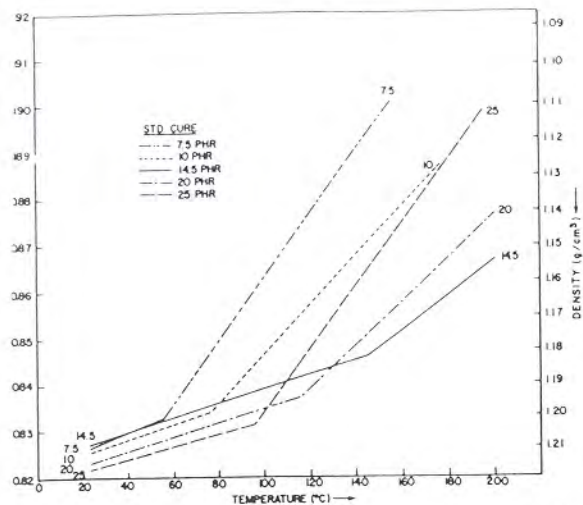


Fig. 5. The dependence of density on temperature for the standard-cure samples.

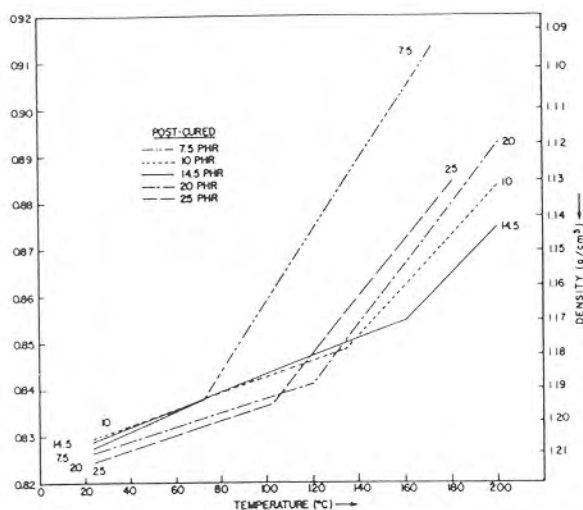


Fig. 6. The dependence of density on temperature for the post-cured samples.

the volume at room temperature and as a result the intermolecular distances are relatively high.

The Stress-Strain Curves

The average stress-strain curves for the standard-cure and postcured samples obtained from tensile tests on the Instron at room temperature and 120°C are shown in Figs. 7 and 8, respectively. In both sets of samples, the stoichiometric sample with the highest crosslink density has the lowest modulus at room temperature and the highest modulus at 120°C. This suggests a correlation of the tensile modulus with molecular packing as measured by density. It is also seen that at room temperature, the 7.5 and 10 phr samples, which contain an excess of epoxy molecules, have very low breaking extensions. The dependence of the mechanical parameters on structure will now be discussed.

The Modulus

The initial modulus data at room temperature, as obtained from tensile measurements on strain-gaged samples, is shown in Fig. 9. The similarity of

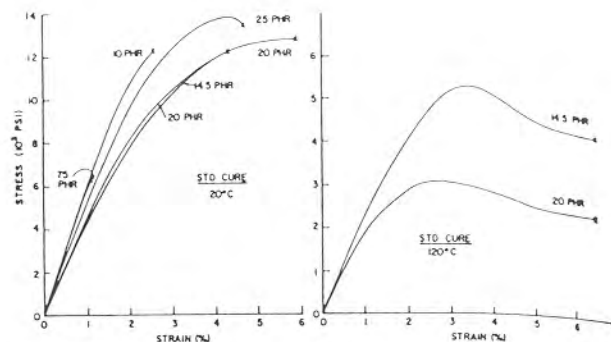


Fig. 7. The stress-strain curves for the standard-cure samples at (a) room temperature and (b) 120°C.

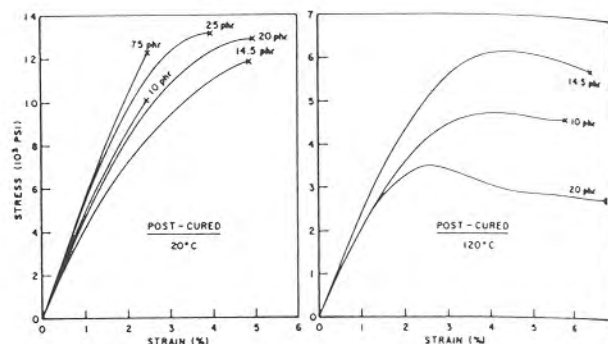


Fig. 8. The stress-strain curves for the postcured samples at (a) room temperature and (b) 120°C.

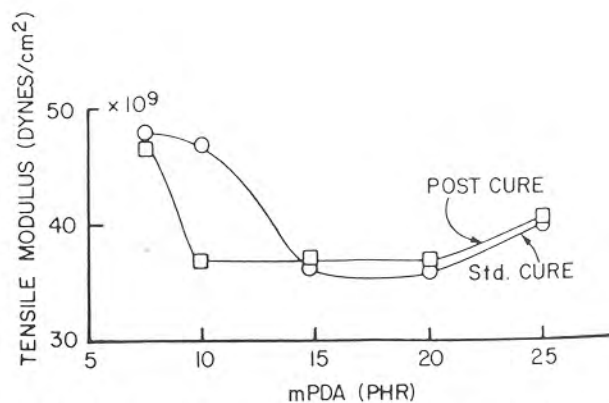


Fig. 9. The room temperature elastic modulus obtained from tensile tests of strain-gaged specimens.

this data with the density data (Fig. 3) is noteworthy and suggests that density and therefore intermolecular packing is a predominant factor in determining modulus at room temperature. In the glassy state, the stiffness relates to changes in the stored elastic energy on deformation which are associated with small displacements. This view is reinforced on examination of the β peak data summarized in Fig. 10. It is noteworthy that on postcuring, the epoxy rich samples show a much larger β -peak and also a marked reduction in tensile modulus. This indicates that the room temperature modulus is influenced by the relaxations occurring during the β -transition. It may be worth stating that the relaxation time for this mechanism will be very short at room temperature, and the effect will therefore be more appar-

ent in a high speed test.

When the data are examined in detail, however, there are some features which suggest that other factors in addition to intermolecular packing could also play a role. For example, in both the standard-cure and postcured samples, the 7.5 phr sample has the highest modulus but not the highest density. Also, while on postcuring the density decreases for all the samples, the modulus does not. An explanation of these observations would require a detailed knowledge of their molecular structure and architecture. The higher rigidity of the 7.5 phr sample, for example, is most likely because of the considerable steric hindrance offered by the unreacted epoxy molecules in the glassy state. In the amine-rich samples, the added mobility on postcuring, apparently due to the relatively large intermolecular separation, is reflected in density but not in modulus. A likely reason for this could be that while density is an average property of the total sample, modulus would be expected to be more sensitive to the morphology of the sample as it would be affected to a great extent by the more compliant, less crosslinked phase.

In a tensile test accurate measurement of the rubbery modulus presents many difficulties. At the

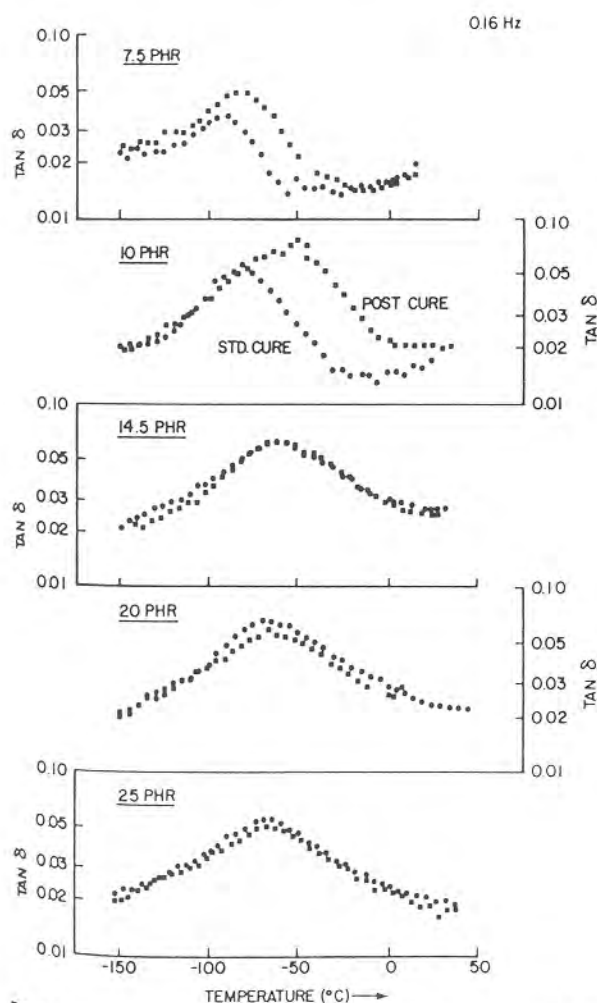


Fig. 10. The β -peak of samples of different stoichiometries at 0.16 Hz.

high temperatures of measurement, the loads are low and the sample slips from the grips. However, measurement of torsional modulus on rectangular rheobars in the Rheometrics mechanical spectrometer gives reasonably accurate data and is shown for the two sets of samples in Fig. 11. The modulus now shows excellent correlation with crosslink density (Fig. 2); in fact it is used as a measure of the crosslink density. Above T_g , the molecular chains gave considerable flexibility, and the rubberlike elastic deformations are associated with changes in molecular conformation; the intermolecular forces are no longer operative and molecular architecture would not be expected to play an important part. The relatively high modulus of the highly crosslinked samples thus arises from the greater constraints to mobility because of the pinning of the molecules at the crosslink sites which are more numerous at or close to stoichiometry.

The initial moduli calculated from the initial slope of the load-elongation curves obtained from the Instron measurements are shown in Fig. 12 as a function of the curing agent content. It is noteworthy that the room-temperature data are similar to the strain-gage modulus data, and the points made to explain the earlier data are therefore relevant in this case also. As temperature increases, the lower T_g polymers (7.5 and 25 phr) show greater reduction in modulus than the high T_g samples, as expected. The correlation with density data is apparent.

The room-temperature initial modulus is shown as a function of T_g in Fig. 13. The high T_g samples have the lowest moduli, thus suggesting that the intermolecular spacing is large in these samples. This lends support to the earlier model which postulated that during the curing of the sample, more free volume is trapped in the high T_g samples as they are cooled to room temperature.

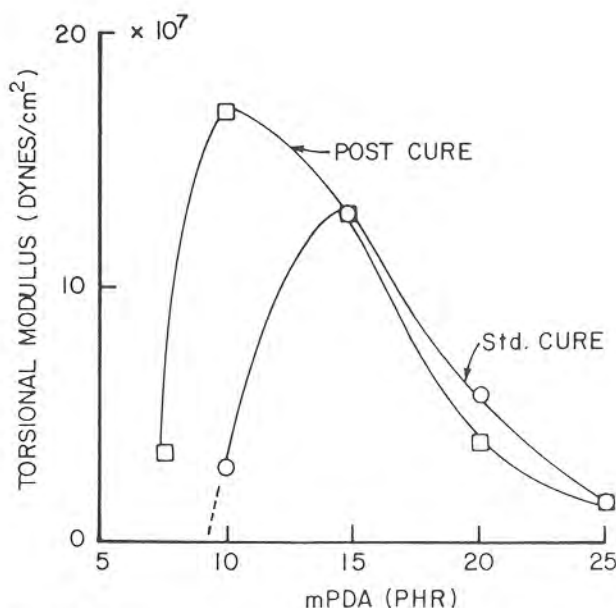


Fig. 11. The torsional modulus above T_g as a function of curing agent concentration.

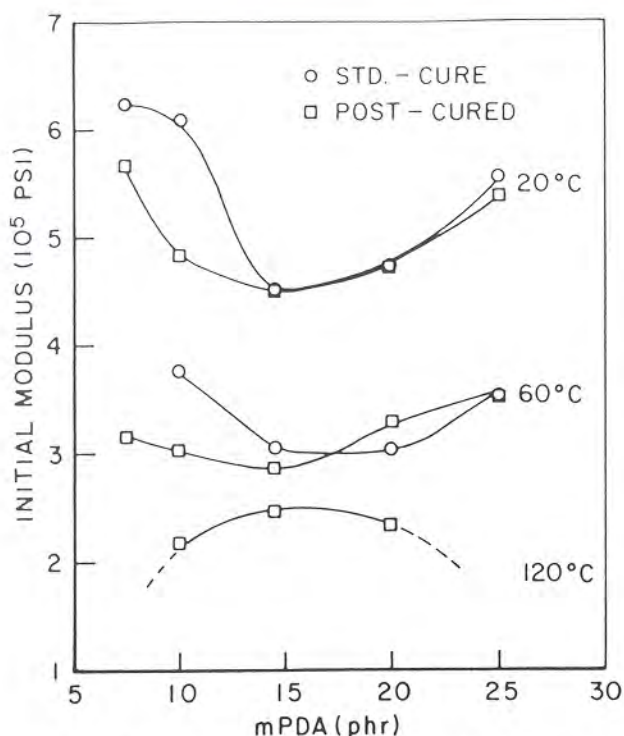


Fig. 12. The dependence of initial modulus at three temperatures on curing agent concentration.

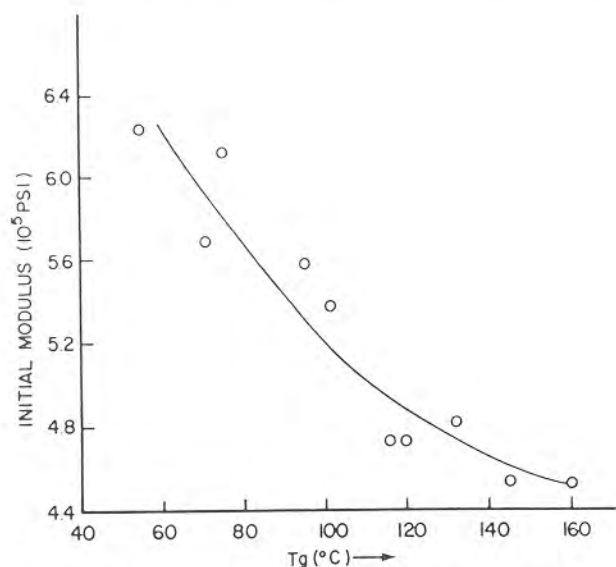


Fig. 13. The room temperature initial modulus as a function of sample T_g .

The Yield Behavior

The load-elongation characteristics of the samples, as obtained from studies conducted on the Instron tensile tester, gave useful information on their yield behavior. First, it was seen that the temperature-dependence of yield stress showed remarkable similarity to the temperature-dependence of torsional modulus; and second, the yield strains decreased with increasing temperature. However, the Instron tests were made over a limited temperature range and at large intervals of temperature,

and only very limited data on yield was obtained from these tests.

For two samples, viz. standard-cure 20 and 25 phr, which showed distinct yield behavior over a wide temperature range, the load-elongation studies were made over a wider temperature range and at smaller intervals of temperature on another tensile tester (MTS). Since yield occurs only up to or below T_g , thermal history will not be expected to significantly affect the sample structure. As stated earlier, only uncorrected strains were obtained in the present case and are therefore designated "apparent strain" in the figure.

The yield stress data for the 20 and 25 phr standard-cure samples are shown in Figs. 14a and b, respectively. The shear modulus (G') data obtained from the RMS is also included in these figures. In plotting shear modulus vs. $(T - T_g)$, the T_g values were those obtained from the maxima of $\tan \delta$ (Fig. 1). The yield stress is plotted taking two T_g values, the first is the same as that used for plotting shear modulus, viz. that based on the dynamic data and the second was the DSC T_g which, for the two samples under consideration, is approximately 20°C lower than the T_g obtained from the $\tan \delta$ peak. There are two important reasons why the DSC T_g is more appropriate for the tensile data. First, the time factor is larger in the tensile test than in the dynamic test; and second, as the sample is stretched, its free volume can increase and thus lower T_g . This second point will be discussed later in this section. The ratio of yield stress to shear modulus is nearly constant at between 0.06 to 0.07 for the temperatures studied. Gent (18) has suggested that yield occurs at a critical shear stress which is a constant fraction of the modulus of rigidity. Thus the yield process in these samples appears to be related to the attainment of a critical shear stress. Such an observation has been made for another cured epoxy resin system also which was tested in compression (11).

The stress-strain curves presented earlier in Fig. 7 show that the material initially responds elastically and the Young's modulus remains practically constant in the range of small strains of 1 to 2 percent. Since the Poisson's ratio, ν , is typically assumed to be 0.35, the sample is constrained from contracting laterally and the body dilates under tension. Since the total strain is less than 10 percent, the relative dilatation $\Delta V/V$ due to tensile strain, ϵ , can be approximated to (19, 20):

$$\frac{\Delta V}{V} = \epsilon(1 - 2\nu)$$

If all the volume change is assumed to result in an increase in free volume, the yield occurs at a critical strain, ϵ_c , given by (2, 11, 19):

$$\epsilon_c = \frac{\Delta\alpha(T_g - T)}{(1 - 2\nu)}$$

where $\Delta\alpha$ is the difference between the glass and rubber coefficients of volumetric expansion.

The plots of ϵ_c vs. $(T - T_g)$ are shown in Fig. 15.

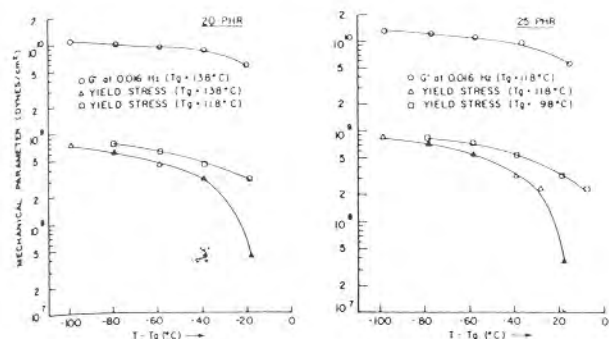


Fig. 14. The variation of torsional modulus and yield stress of standard-cure samples on $(T-T_g)$. (a) 20 phr, (b) 25 phr.

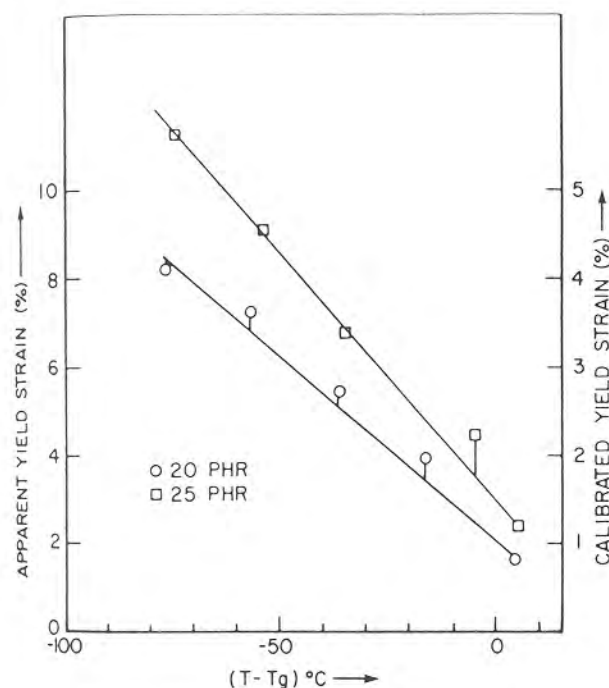


Fig. 15. The variation of yield strain with $(T-T_g)$.

where the T_g 's used were taken from the DSC data (Fig. 1b). As stated earlier, the apparent yield strains are uncorrected strains. These were corrected by calibrating the extensions obtained on the MTS with the extensometer-monitored extensions obtained on the Instron on similar specimens. The calibrated yield strains are also included in Fig. 15. From the slopes of the lines, the $\Delta\alpha$ values for the 20 and 25 phr samples obtained by use of the calibrated values of strain and taking $\nu = 0.35$ are found to be 12.75×10^{-5} and $16.8 \times 10^{-5} \text{ } ^\circ\text{K}^{-1}$, respectively. These compare reasonably well with the measured value of $\Delta\alpha$ of 12.6×10^{-5} and $22.1 \times 10^{-5} \text{ } ^\circ\text{K}^{-1}$, respectively, for the two samples. This analysis based on limited data suggests that an increase in free volume with tensile deformation is a likely mechanism for yield in these materials. A similar observation has been made for another cured epoxy resin system tested in compression (11). That a small increase in volume does take place in these two samples on tensile deformation was verified from density measurements on deformed and undeformed portions of the same spec-

imen. The samples were stretched at room temperature and the deformed sample for density measurement was taken from the "necked" part of the dogbone. In both cases the densities showed small drops, viz. from 1.2116 to 1.2114 g/cm^3 for the 20 phr sample and from 1.2145 to 1.2140 g/cm^3 for the 25 phr sample. Thus it would appear that an increase in free volume could be a possible factor in the yielding of these samples.

Tensile Strength

In a uniaxial tensile test, the whole cross-section of the specimen and all the flaws in the material are subjected to uniform stress and therefore failure should occur at the largest flaw. Thus tensile strength is quite representative of the material's strength.

The temperature-dependence of the tensile strength of post-cured samples is shown in Fig. 16 and for comparison the corresponding dynamic data is shown in Fig. 17. The similarity between tensile strength and torsional modulus and their dependence on relaxation processes is noteworthy.

The stoichiometric-dependence of tensile strength at 20, 60, and 120°C is shown in Fig. 18 for the standard-cure and postcured samples. When compared with the corresponding data for modulus (Fig. 11), the most noteworthy difference between the two results is in the case of the epoxy-rich samples: while their moduli are relatively high compared to the other samples, their tensile strengths are relatively low. However, as in the case of modulus, the tensile strength of the epoxy-rich samples are affected by postcuring to a much greater extent than the other samples. It was earlier seen that on postcuring, an additional crosslinking mechanism becomes operative, and since it involves the unreacted epoxy groups, the changes are greatest in the epoxy-rich samples whose crosslink density and T_g increase appreciably. Due to the relatively large increase in T_g on postcuring, there is a considerable reduction in density, particularly in the case of the 10 phr sample. Thus the changes in tensile strength will reflect these changes in structure, molecular architecture, crosslink density, and intermolecular packing.

It may be recalled that a small strain mechanical property like the elastic modulus shows the predominant influence of intermolecular packing in the glasslike state because the resistance to initial deformation arises from the intermolecular forces. Once this resistance to initial deformation is overcome, the sample either deforms by yielding or may show a brittle fracture. It was seen that intermolecular packing or free volume still plays an important role in yielding. As deformation continues it would be expected that factors like molecular architecture and the length of the molecule between crosslink would also become important. Thus while in the case of elastic modulus, crosslink density plays a important part only when the sample is in the rubberlike state, in the case of tensile strength, could affect the room temperature results also.

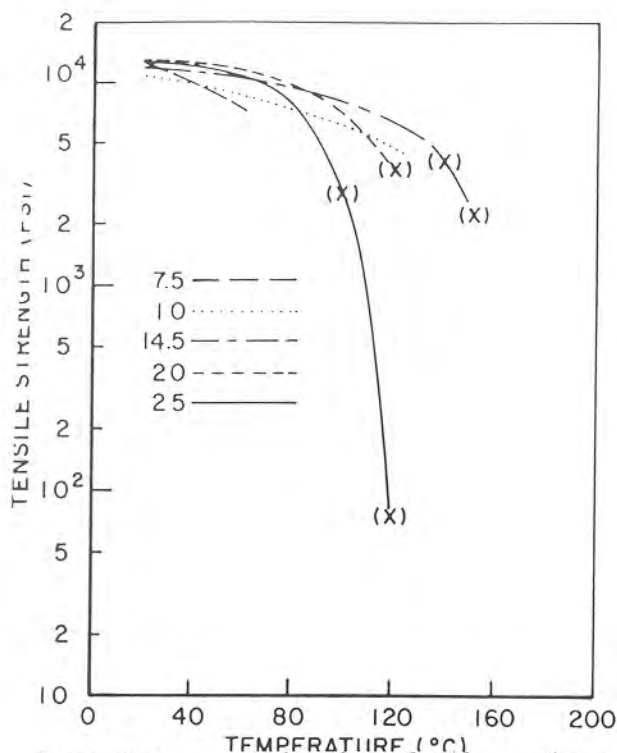


Fig. 16. The temperature-dependence of tensile strength on post-cured samples. The symbol (x) represents the flow stress as in these cases the samples were not taken to fracture

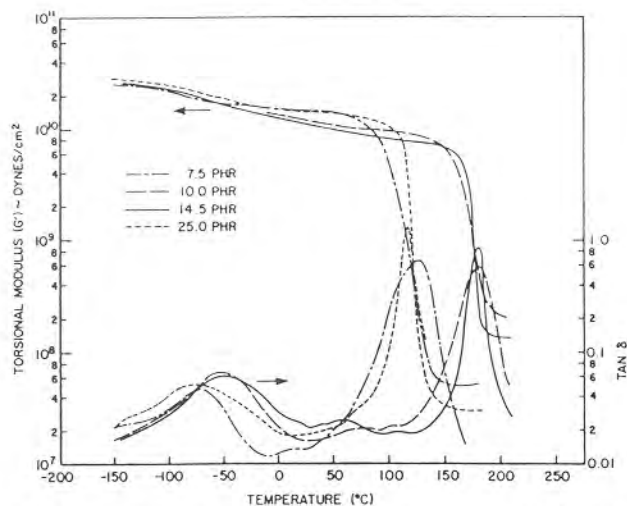


Fig. 17. The dynamic spectrum for the postcured sample at 0.016 Hz.

It was earlier seen by infrared spectroscopy that the 7.5 phr standard-cure sample has a very large number of unreacted epoxy groups. Also the crosslink density of this sample is very low and, as pointed out by Bell (21), the overall molecular weight of the sample would also be low. The steric hindrance due to the pendant epoxy molecules, which are connected to the network only on one end, does give the sample high stiffness but as the sample is stretched further, the low overall molecular weight is not able to support large stresses and it breaks in a brittle manner at low extensions. When the sample is postcured, there is considerable

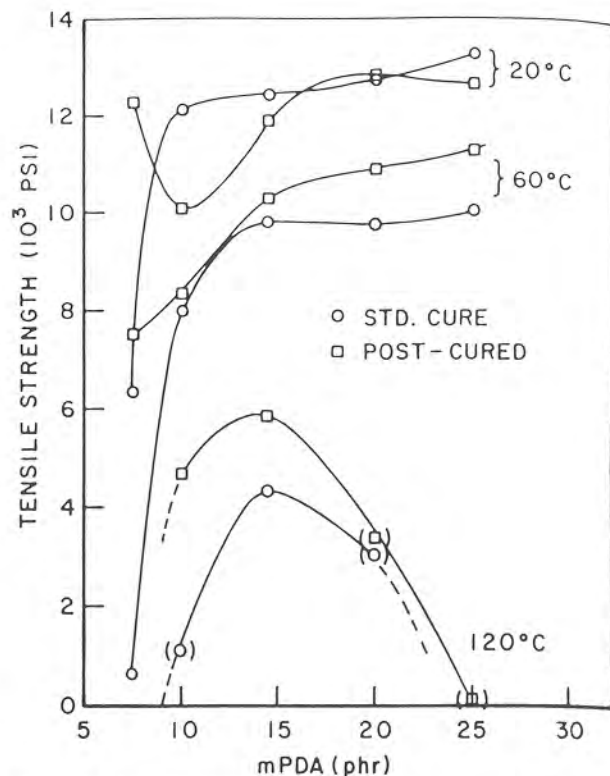


Fig. 18. The dependence of tensile strength on curing agent concentration at three temperatures. The brackets () represent flow stress as the sample was not taken to fracture.

further crosslinking and the tensile strength increases. These samples have low T_g and, therefore with increase of temperature, there is a rapid decrease in strength. The 10 phr samples also show a lower strength compared to the other samples. But the effect of postcuring is complex in the case of this sample. The room temperature tensile strength decreases on postcuring thus indicating that an increase in free volume plays a more important role than the increase in crosslink density in this case. It may also be noted that at 60°C, unlike the modulus, the tensile strength of the postcured samples is higher than the corresponding standard-cure samples. This suggests that the higher T_g of the postcured samples reduces the temperature-dependence of their tensile strength, a conclusion supported by the 120°C data. It may also be noted that with increase in temperature, the low T_g samples show much greater fall in strength than the high T_g samples.

It has been pointed out (10) that network perfection can influence the mechanical properties of a cured epoxy resin. The epoxy rich samples with dangling epoxy molecules will have an imperfect network, and the dynamic spectra presented earlier (Fig. 17) did show a very broad α -peak for these samples. This imperfect network will result in non-uniform stress distribution and will be conducive to a brittle failure in the glassy state. However, with increase in temperature, the pendant molecules will soon become mobile and give ductility to the sample, as is observed to be the case.

The tensile strength above T_g has not been accu-

rately measured due to experimental difficulties. However, approximate measurement on the MTS show that above T_g the stoichiometric sample has the highest strength and that the strength decreases on either side of stoichiometry. This suggests that in the rubberlike state, crosslink density is the predominant factor determining strength.

Elongation-to-Break

The data on elongation-to-break at 20 and 60°C are shown as a function of stoichiometry in Fig. 19. The stoichiometric variation in elongation-to-break at room temperature is from a minimum of 1.1 percent to a maximum of 6.2 percent for the standard-cure samples and 2.4 percent to 5 percent for the postcured samples, i.e., a factor of between 2 to greater than 5. On the other hand, the room temperature modulus and tensile strength show a much smaller dependence on stoichiometry. The epoxy excess samples, which apparently have a very irregular network, show very low elongation-to-break. With increasing amine content, the elongation-to-break increases and then decreases slightly. Morgan, *et al* observed (10) that the stoichiometric sample had the maximum elongation-to-break in the epoxy system studied by them, and this was attributed to uniform stress distribution in this sample. The present results as well as those of Kim, *et al* (6) show that the network gives maximum extension at an amine content slightly higher than stoichiometric. With increase in temperature the low T_g samples show rapid increase in elongation-to-break while the high T_g samples show less increase.

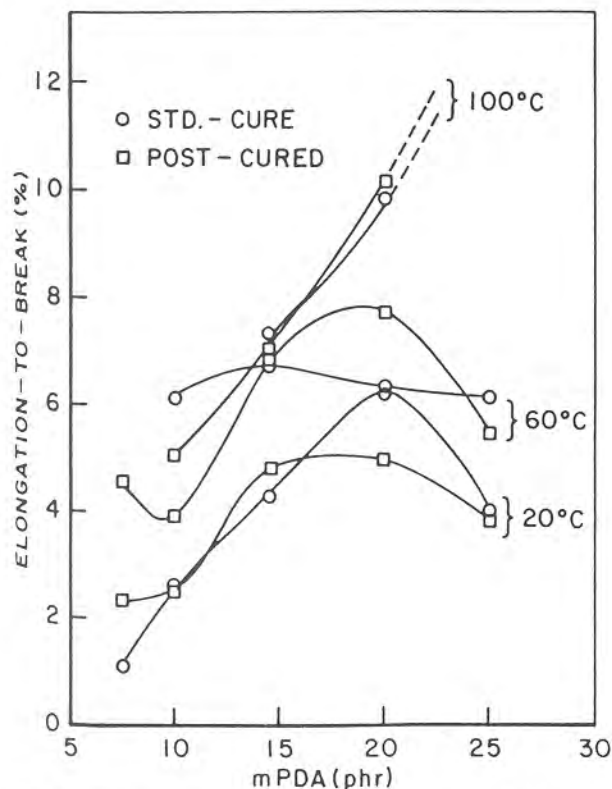


Fig. 19. The dependence of elongation-to-break on curing agent concentration.

In crosslinked rubbers, the elongation-at-break can decrease with increasing temperature (22). For a cured epoxy resin system also such a decrease at high temperatures has been reported (23). For the standard-cure samples, the MTS measurements showed similar effects. The crosshead displacement which is a measure of the apparent elongation-to-break is shown (Fig. 20) as a function of temperature for the 14.5 and 25 phr samples. In the glassy state, the network has low extensibility. In the viscoelastic state there is increased ductility. In the rubbery state, the intermolecular forces are absent, and the samples behave as fluids with the crosslinks acting as the pinning points. The material is not able to support high loads and breaks down at low stresses which develop at low extensions. The maximum extension which occurs around T_g shows good correlation with M_c ; the higher the value of M_c , the more is the network extensibility in the high temperature range, as expected.

Toughness

The room-temperature toughness data, obtained in terms of k_Q from mode I deformation of a compact tension specimen containing a crack, are shown in Fig. 21. In both standard-cure and postcured samples, the toughness first increases with curing agent concentration and then decreases. The epoxy rich samples, which have low extension-to-break, have low toughness.

The trends shown by toughness and elongation-to-break are similar and suggest a correlation between these two parameters. It is noteworthy that like elongation-to-break, the toughness also shows much higher variations within each set of samples compared to the variations shown by other mechanical parameters like modulus and tensile strength. To ensure consistency, the K_Q tests were repeated a number of times on the standard-cure samples. Though the absolute values differed for various sets of measurements, the trends were similar, and there

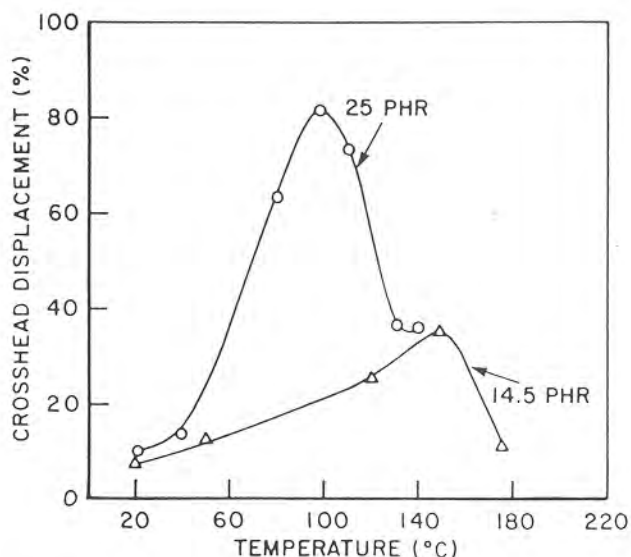


Fig. 20. The temperature-dependence of apparent elongation-to-break of two standard-cure samples.

was a maximum in K_Q for the 20 phr sample. Since reproducibility of results is not high, comparison between the standard-cure and postcured sets of samples will not be advisable though comparison within each set of samples would appear to be justified.

The room temperature impact properties have been shown to correlate with the β -relaxation (24). The present data do not show a clear-cut correlation between toughness and the β -relaxation. In the postcured samples, for example, the 10 phr sample has a fairly well-pronounced β -peak (Fig. 9) but its toughness is still low (Fig. 21).

For the stoichiometric sample the toughness was studied as a function of temperature, and the correlation with extension-to-break is again observed, as shown in Fig. 22.

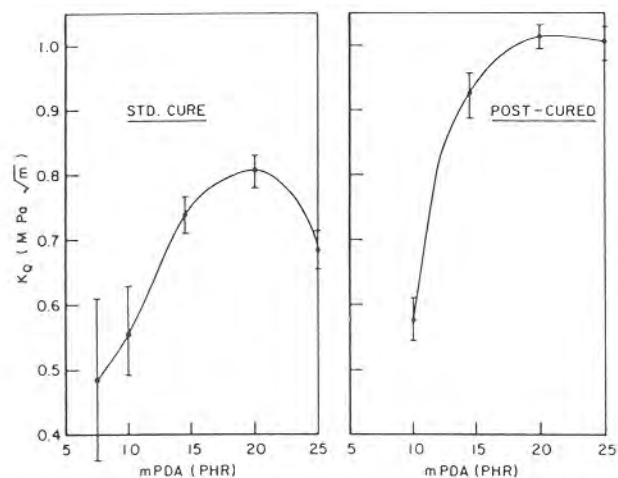


Fig. 21. The dependence of room-temperature toughness of (a) standard-cure and (b) postcured samples on curing agent concentration.

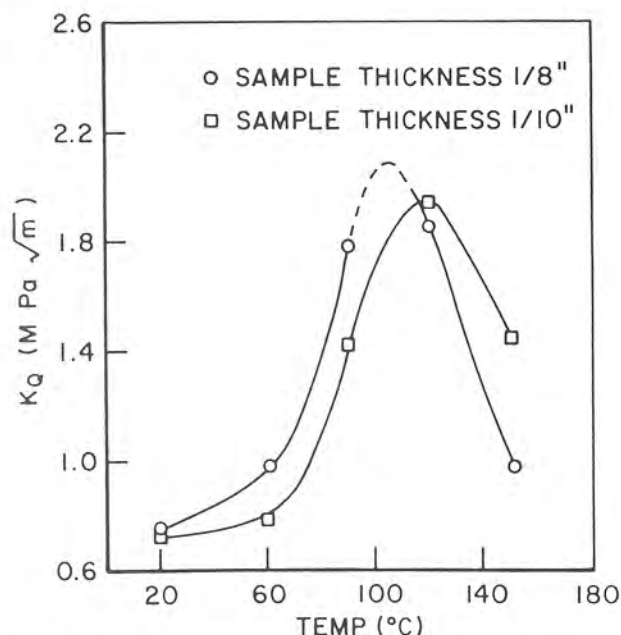


Fig. 22. The temperature-dependence of the toughness of stoichiometric samples.

CONCLUSION

The mechanical properties of crosslinked epoxy networks, cured with varying amounts of curing agent and subjected to two curing cycles, have been studied over a range of temperatures and show the following features.

Small-Strain Properties

In the glassy state, the small-strain properties like stiffness and yield point, show some influence of molecular architecture but are predominantly related to the intermolecular distances as reflected in their densities. Crosslink density does not appear to be important. The effect of stoichiometry on these parameters is rather small. As temperature increases the samples with low T_g show a relatively larger decrease in these parameters. In the rubberlike state, the stiffness is predominantly governed by crosslink density and showed a much wider variation within each set of samples.

Large-Strain Properties

In the glassy state, the large-strain properties like strength, elongation-to-break, and toughness are affected by intermolecular packing, molecular architecture, and molecular weight between crosslinks. The overall molecular weight is also important. The regularity and perfection of the network also plays an important part. Toughness appears to show good correlation with elongation-to-break. As temperature increases the samples with low T_g show a relatively large change in these parameters. In the rubberlike state, crosslink density appears to be the important factor.

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