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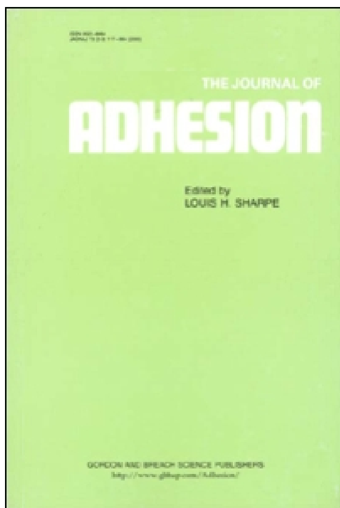

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Effects of Cure Temperature on Epoxy Resin Properties*

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An experimental study was undertaken to determine the effects of incomplete resin cure on the dynamic moduli and tensile strengths of two commercial amine-cured epoxy adhesives. Depending on the value of $T_{g\infty} - T_{cure}$, a resin may glass before complete cross-linking occurs leaving the system in a nearly-stable undercured state. The level of unreacted epoxy in the glass state was determined by FTIR, and the effects on dynamic mechanical properties and tensile bond strengths measured.

KEY WORDS Effects of cure temperature; FTIR cure kinetics; kinetic rate law; undercured glassed adhesives; dynamic mechanical properties of undercured adhesives; temperature-adhesive tensile strength behavior.

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INTRODUCTION

Many properties of epoxy resins are determined by the temperature at which they are cured. In some commercial applications adhesives are cured at ambient temperatures because it is impractical or unsafe to cure at elevated temperatures. For cure temperatures, T_c, less than the ultimate glass transition temperature of the completely cross-linked resin, *i.e.*, $T_c < T_{g\infty}$, the network will increase to a certain degree of cross-linking and then glass, or vitrify.[1–7] In the glass state the cross-linking reaction slows dramatically.[6,8] The resin then has a glass transition temperature, T_g, less than $T_{g\infty}$.

Many mechanical properties of resins in this glassed and undercured state are close to those of the fully cured state,[3,10] and chemical,[2,11] thermal,[12,13] or dynamic mechanical analyses[2,15,16] are the only way to distinguish them. Properties that are similar include various moduli, hardness and tensile and shear bond strengths

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measured at T_g or below.[3,10] In some cases observed by Sancaktar[17,18] and others[16] a "bell" shaped response of resin property *vs.* cure temperature has been observed for glassy resins, particularly for tensile strength, dynamic flex modulus, dynamic shear modulus, and fracture energy. The work reported here studied the effect of cure temperature on the degree on undercure as measured by unreacted epoxy in the glass, the dynamic mechanical properties of undercured resins, and the consequences of the undercure on the temperature dependence of tensile bond strengths.

EXPERIMENTAL

Two commercial amine cured epoxy adhesives with different properties were used in this study, Hysol's EA-956 and EA-946. These adhesives are widely used in the aerospace industry. EA-956 is a high strength, short working time (~0.5 hour at ambient), brittle adhesive with strain at failure of ~3%, while EA-946 is a medium strength adhesive with high strain capability and a working time of ~5 hours. EA-946 is based on DGEBA and epoxidized dimer acid cured with a mixture of aromatic amines. EA-956 is based on triglycidyl p-amino phenol cured with an aliphatic polyamine. Both resins consisted of two parts, an epoxy and amine, and were prepared in the recommended proportions[14] and cured at various temperatures: 4.4°C (40°F), 23.9°C (75°F), 37.8°C (100°F), 93.3°C (200°F).

The FTIR spectra were taken with a Nicolet Model DX-20 Spectrometer. The specimens were cured between two 3 mm CaF_2 plates in a Wilmad variable temperature cell with a Love Model 51-860 temperature controller. The temperature accuracy is about ±1°C. For the long duration runs of several thousand hours, the cells were stored in a desiccator between testing intervals.

The dynamic mechanical spectra were taken with a Rheometrics Model 7700 Spectrometer operating in a torsion mode using $0.5 \times 2.0 \times 0.1$ inch ($12.7 \times 25.4 \times 2.54$ mm) resin bars. Typical strains were 0.3%, and the sweep frequency was 1 Hz. Heating rates were 5°C/minute with a five-minute soak time between temperature changes.

The temperature/tensile adhesion measurements were performed using standard 1.25 inch (31.75 mm) D6AC steel tensile buttons pulled in a Satec 60k high load instrument.[19] The thicknesses of the bond specimens were about 0.001 inch (0.025 mm). The temperature was determined with thermocouples attached at several points along the periphery of the adhesive in the specimen. The experiments were performed by placing a constant tensile load on the specimen and increasing the temperature until the bond failed. Typical initial loads for EA-956 were 7000–8000 lbs (31.1–35.6 kN), and for EA-946, 4000–5000 lbs (17.8–22.2 kN). The experiment was repeated with a new specimen with the static load reduced by 500 pounds (2.22 kN), again noting the failure temperature. This was repeated until failure did not occur. In this way a failure load *vs.* temperature curve was constructed. This particular method was devised because the conventional method of determining tensile-temperature response of bonded specimens is unsatisfactory for undercured adhesives, since the cure reaction continues when one attempts to equilibrate the specimens at an elevated temperature.

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RESULTS AND DISCUSSION

1. FTIR Cure Studies

Adhesive cure was monitored with FTIR using the epoxy band at 915 cm^{-1} ratioed to the 1510 cm^{-1} aromatic C—C band,[11,20] and the assumption is that the epoxy concentration is proportional to this ratio. Figure 1 shows the cure curves for EA-956 adhesive at 4.4°, 23.9°, 37.8°, and 93.3°C in the time range 0–300 hours, and the fraction epoxy remaining is R(t) = Epoxy(t)/Epoxy(t = 0). The FTIR data show that the reaction rapidly goes to completion at 93.3°C which is corroborated by the dynamic mechanical results discussed below. At temperatures below this the reaction proceeds until vitrification, and the rate of reaction slows dramatically. The plateau gives a measure of the level of unreacted epoxy in the resin.

Further reaction in the glass state is extremely slow,[6,8] and the unreacted epoxy can remain in the glass for very long periods. The EA-956 adhesive was monitored at 23.9°C for 3500 hours (~5 months), and the unreacted epoxy levels were reduced from 0.25 to 0.18. From a practical standpoint, any effects of undercure on bond strength and other properties of an adhesively-bonded structure will, therefore, remain for considerable periods.

Figure 2 illustrates the effect of step increases in temperature on the epoxide level and, as expected, the level of unreacted epoxy decays to a value corresponding to the temperature.[8] From the data generated on EA-956 adhesive it is possible to show the effect of cure temperature on the fraction of unreacted epoxy in the resin. Figure 3 illustrates this with a plot of unreacted epoxy level *vs.* ($T_{g\infty} - T_c$). The data

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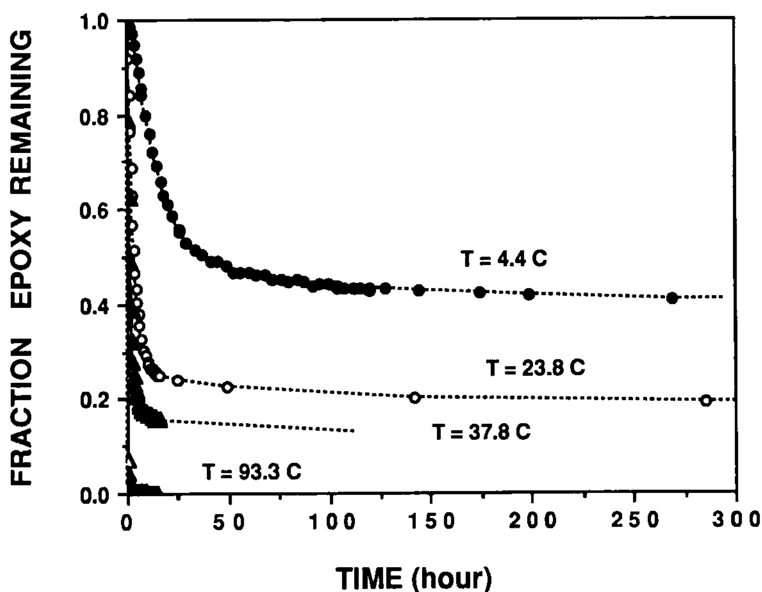

FIGURE 1 Cure curves for EA-956 adhesive at different temperatures determined by FTIR. The effect of glassing on reducing the rates is clearly seen.

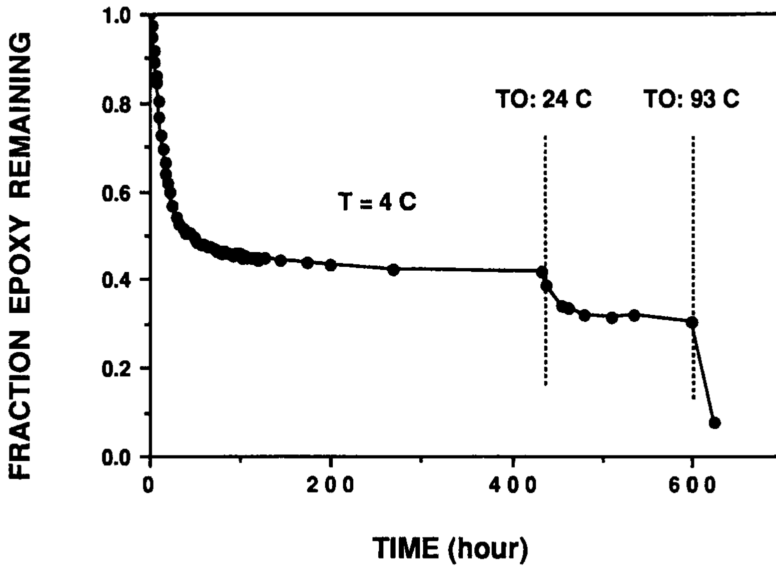

FIGURE 2 Stepwise increases in the temperature of EA-956 resin in the glass state permits the cure reaction to resume and the unreacted epoxy levels off at a new value.

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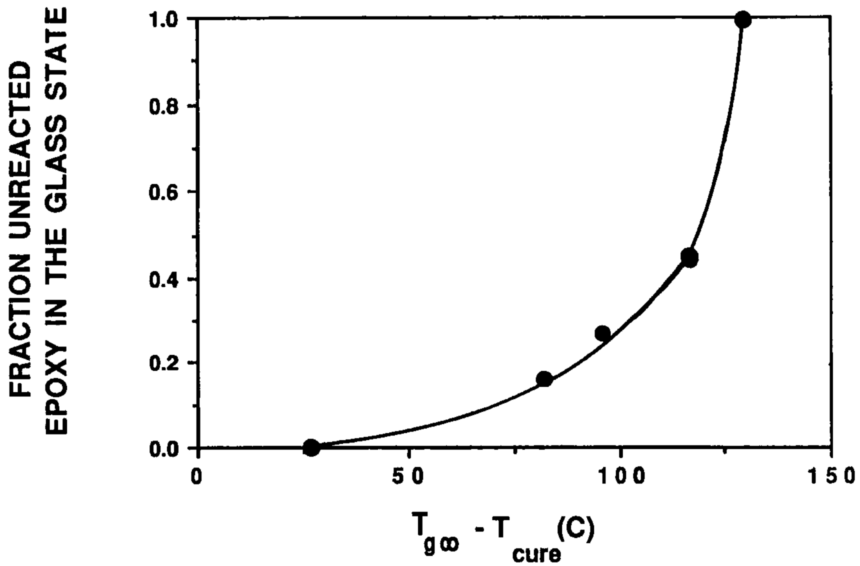

FIGURE 3 The level of unreacted epoxy depends on the temperature difference $T_{g\infty} - T_{cure}$.

show that this is a steep curve and small changes in cure temperature can make large changes in the level of undercure.

Figure 4 shows the FTIR kinetic curves for EA-946 adhesive to 150 hours at various temperatures, 4.4°, 23.8°, and 93.3°C. Within experimental error there is no indication of glassing and the reaction appears to go to completion even at 4.4°C. This is consistent with the dynamic mechanical data given below. Figure 5 compares the kinetic curves for EA-956 and EA-946 adhesives at 4.4° and 23.9°C, and shows that the rates of epoxy depletion are similar up until EA-956 begins to glass. EA-946 acquires strength consistent with the level of cross-link density developed. This suggests that the difference between long and short working time adhesives is not necessarily dependent on rates of chemical reactions, but on whether or not the resin glasses at the temperature of cure.

The cure of both resins adequately follows a first order rate law, (Figure 6) at least in the non-glass region.[5] The EA-946 cure shows first order kinetics to an extent of 80% of the reaction and EA-956 up to the onset of vitrification. The activation energies were determined as 65.7 kJ/mole for EA-956 and 44.3 kJ/mole for EA-946. Table I summarizes the results, and Figure 7 shows the Arrhenius plots. These are in the range of values usually reported for amine-cured epoxy adhesives.[2,12]

The first order kinetics observed for these adhesives appears at variance with the mixed second-third (autocatalytic) order kinetic rate law normally written for amine-epoxy cure,[12,13,21,22] although examples exist of simpler rate laws observed.[23,24]

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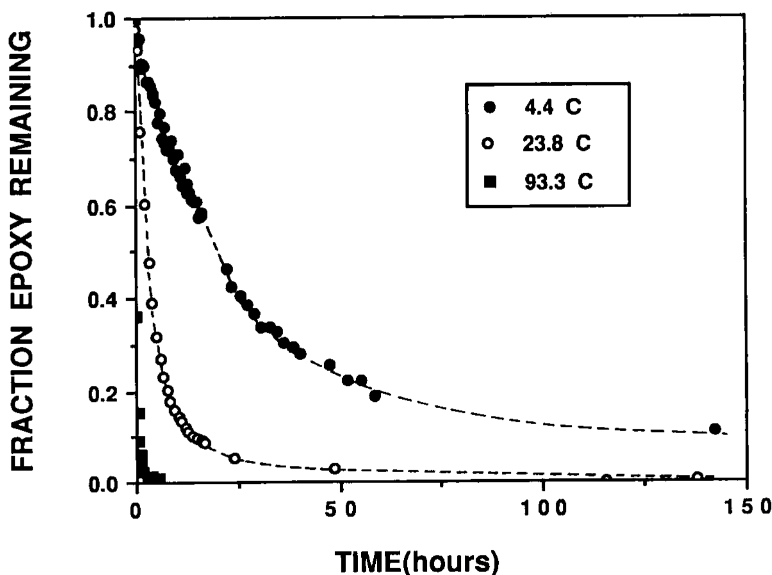

FIGURE 4 Cure curves for EA-946 epoxy adhesive determined by FTIR at different temperatures. There is no indication of incomplete cure due to vitrification.

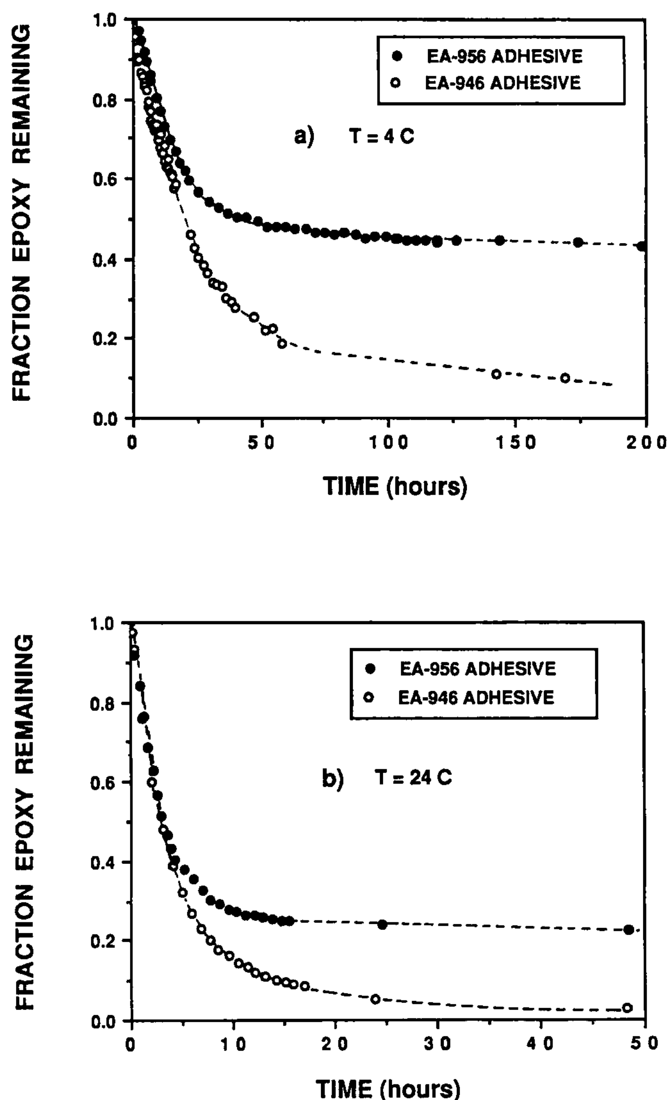

FIGURE 5 FTIR kinetic plots of EA-956 and EA-946 adhesives at a) 4.4°C and b) 23.8°C showing that the rates for the chemical reactions are similar before vitrification sets in.

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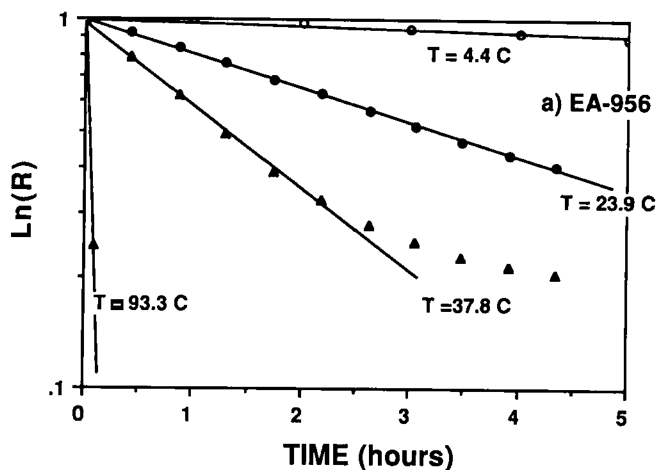
Much of the data generated on epoxy cure kinetics comes from laboratory studies where the compositions of the reactants are known and controlled. Kinetic studies of commercial adhesives are less clear since the complete compositions are generally not known. The two commercial adhesives of this study are fast reactors, as Figure 5 shows that ~50% of the epoxy has reacted in less than 5 hours at ambient temperature. This suggests that the adhesives are catalyzed or have considerable ROH content to accelerate the rates.

It has been our experience, however, that first order rate laws are frequently observed for commercial adhesives. We do not have a mechanistic explanation for the first order kinetics, but we have observed many cases using a variety of analytical methods including FTIR, NMR, GPC, and DSC. Jozavi and Sancaktar[25] have shown that the cure of Metlbond 1113 adhesive could successfully be modelled with a first order rate law. Further studies are warranted to understand the mechanism of cure in these systems since they are used extensively in industry.



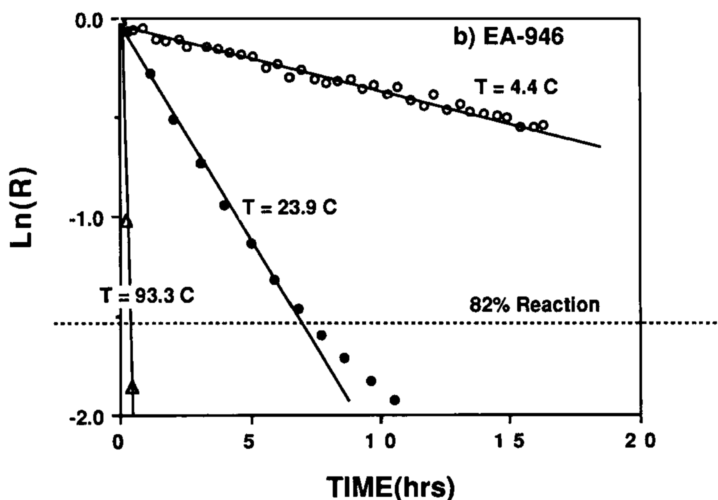


FIGURE 6 First order plots of EA-956 and EA-946 FTIR cure data in the non-glassed region.

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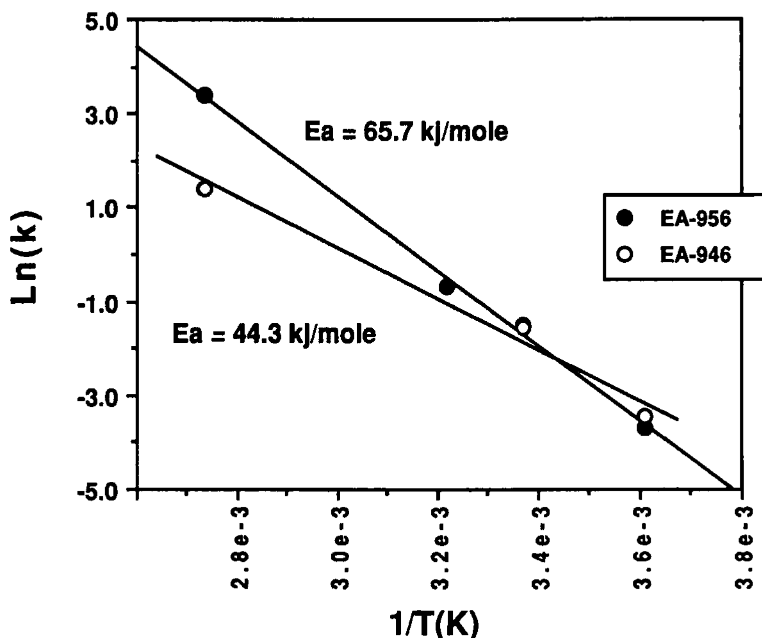

FIGURE 7 Arrhenius plots for the two adhesives.

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TABLE I
Summary of FTIR results

Resin	$T_{g\infty}$ (C)	Cure temperature	Unreacted epoxide	k(hr^{-1})	Ea (kJ/mole)
EA-956	120	4.4	0.45	0.025	65.7* (71.0**)
		23.8	0.25	0.22	
		37.8	0.16	0.51	
		93.3	0.0	29.7	
EA-946	10	4.4	0.0	0.032	44.3* (48.9***)
		23.8	0.0	0.21	
		93.3	0.0	4.09	

*FTIR data from the 1st order region
**Dynamic viscosity data
***DSC data

2. Dynamic Mechanical Results

As mentioned earlier, it is difficult to determine if a resin system in its glass state is fully cured solely from simple mechanical tests. The FTIR measurements discussed above are one way to determine this, and the use of dynamic mechanical measurements is another. Figure 8 shows the dynamic mechanical storage moduli, G′, of a series of EA-956 adhesives cured at various temperatures, and the data are summarized in Table II. The T_gs were taken as the maxima in the G″ curves.

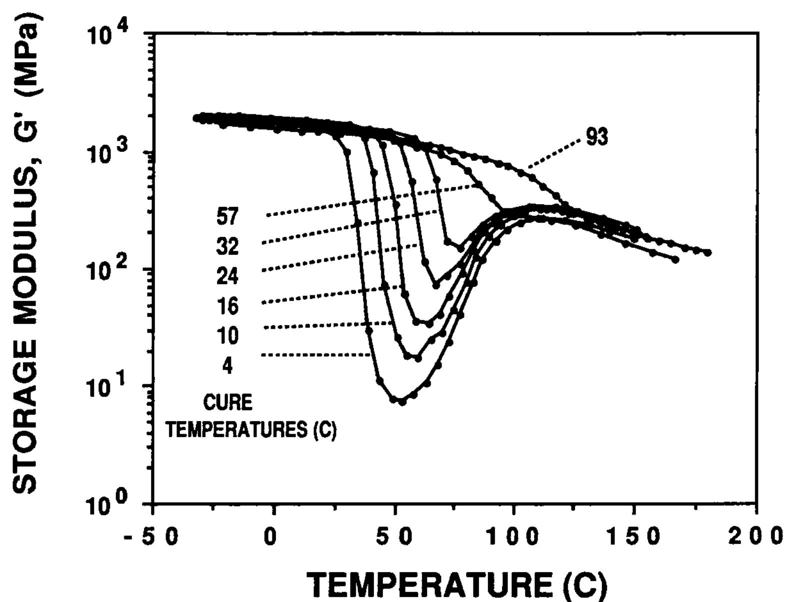

FIGURE 8 Dynamic mechanical storage moduli, G′, for EA-956 adhesive cured at various temperatures.

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TABLE II
Glass transition temperatures of EA-956 resin

Cure temperature (C)	T_g (C)	Extent of reaction
4	33	0.55
10	42	—
16	51	—
24	57	0.75
38	67	0.84
57	85	—
93	120	1.0

As expected from the FTIR cure studies, the resins cured at temperatures below $T_{g\infty}$ are undercured and the network is not completely formed.[2] The general shape of the dynamic mechanical traces can be understood as follows: the reduced level of cross-linking lowers the glass temperature from $T_{g\infty}$ by an amount dependent on the level of undercure. When the temperature is increased above T_g the undercured resin is in an incompletely cross-linked elastomeric state with low modulus, hence the considerable drop in G′ at $T>T_g$. Also at $T>T_g$ the cross-linking reaction commences and G′ rises toward its fully-cured value. The magnitude of the drop in G′ at $T>T_g$ also mirrors the degree of undercure, and is a significant factor in adhesive strength.

Figures 8 and 11 show little variation of dynamic storage modulus, G′, as a function of cure temperature at $T<T_g$, whereas at $T>T_g$ some differences were noted but were on the order of the reproducibility of the experiments. It may be that at cures >100°C there would be a reduction in moduli analogous to that observed by other workers.[16–18]

The effect of cure temperature (specifically, $T_{g\infty}-T_c$) on resin T_g is shown in Figure 9 for EA-956 adhesive.[26] Except at high undercure levels, the response is reasonably linear over the range. The glass transition temperature for the unreacted resin was measured as −2°C.

Pascault and Williams[27] and others[2,5,6,28,29] discuss the relation between T_g and extent of reaction, X, in terms of an expression:

$$\frac{T_g-T_{go}}{T_{g\infty}-T_{go}}=\frac{\lambda X}{1-(1-\lambda)X} \tag{1}$$

where T_{go} = the glass transition temperature of the unreacted resin (−2°C)
and λ is related to polymer chain mobilities (or heat capacities) with a value between 0 and 1.

Figure 10 shows a plot of this equation with an experimentally fitted value of λ = 0.33 and data from Table II, and the agreement supports the validity of the expression for computing shifts in T_g with varying extents of reaction. This value of λ is in the range observed by other workers.

Figure 11 shows similar dynamic mechanical traces for EA-946 adhesive cured at

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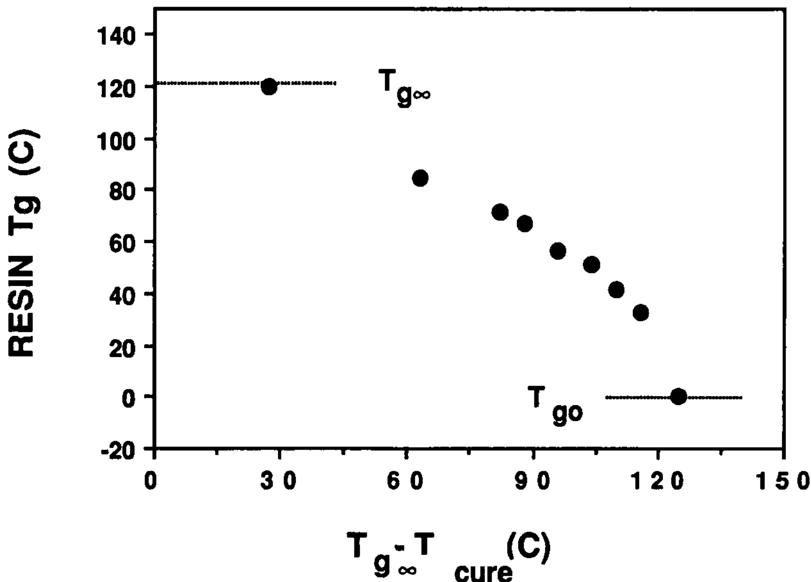

FIGURE 9 EA-956 resin T_g (from G″) as a function of cure temperature showing the effect of resin undercure.

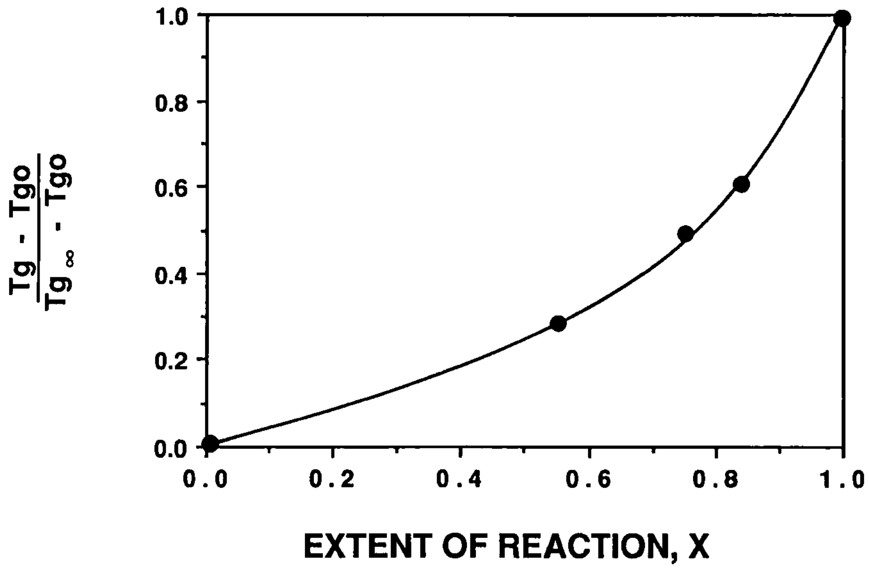

FIGURE 10 Plot of Equation 1 with EA-956 data fitted with a value of $\lambda = 0.33$.

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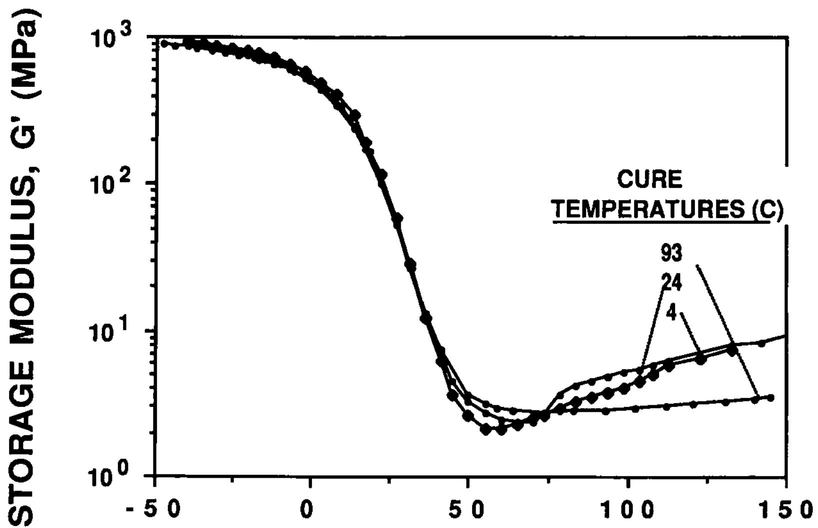
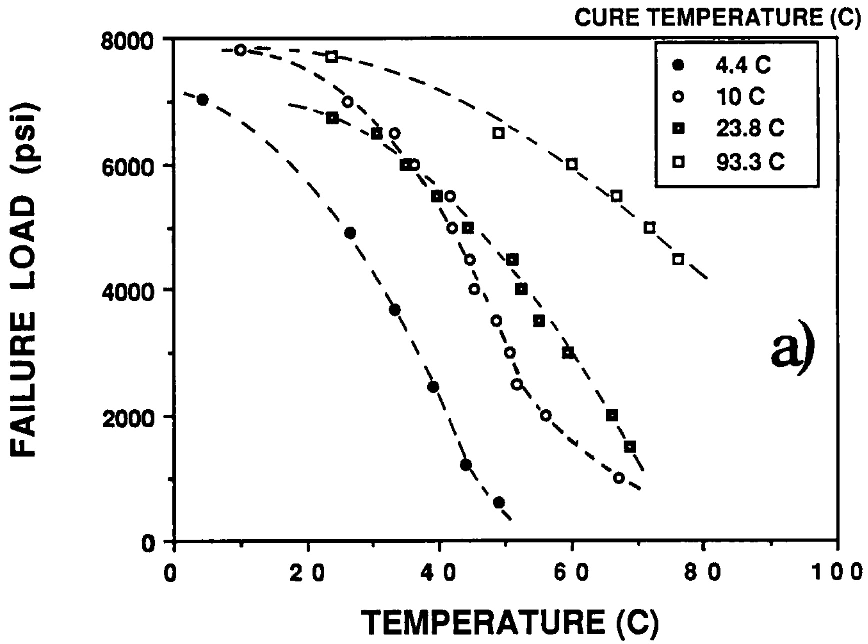


FIGURE 11 Dynamic mechanical storage moduli, G′, for EA-946 adhesive cured at various temperatures.



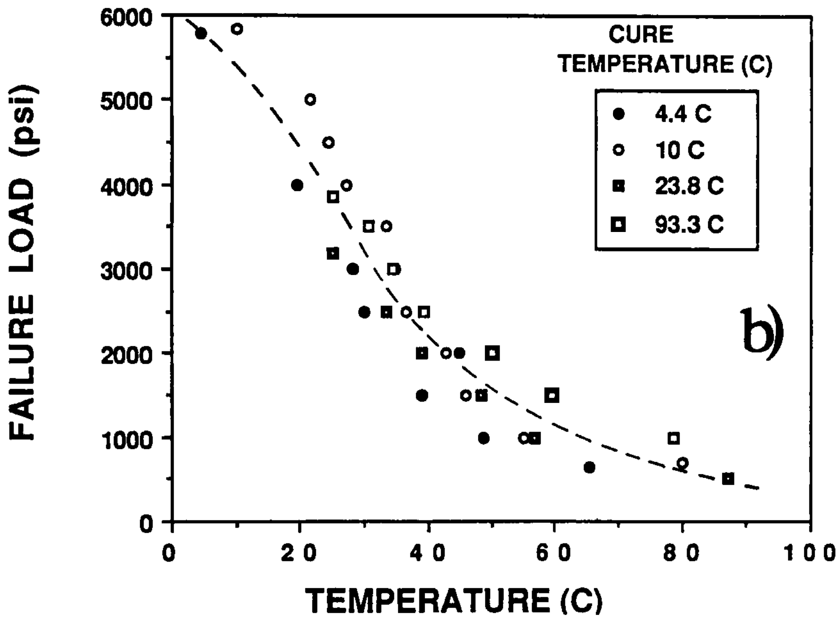


FIGURE 12 Tensile adhesion failure load *vs*. temperature for a) EA-956 cured at 4.4°, 10°, 23.8°, and 93.3°C, and b) EA-946 cured at 4.4°, 23.8°, and 93.3°C.

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different temperatures. As expected from the FTIR cure data there are no indications of undercure in the spectra. The increases in G′ at $T>T_g$ appear to be related to a high temperature cross-linking reaction, as the rubbery modulus has been observed to increase irreversibly on high temperature aging of this adhesive.

3. Tensile Bond Strength-Temperature Results

For various reasons, many bonded structures require that the adhesive be cured at temperatures below $T_{g\infty}$. From the above results it is clear that some adhesives will glass before complete cross-linking occurs, and they can remain in that state for long periods of time. The dynamic mechanical results show that T_g may be dramatically reduced, and the modulus at temperatures slightly above T_g will be very low compared with the completely cross-linked resin. These results suggest that tensile strength of an undercured adhesive and, therefore, adhesive bond strengths, may be very sensitive to slight increases in temperature. This may be important in applications where an adhesively-bonded structure experiences a sudden increase in temperature while under load.

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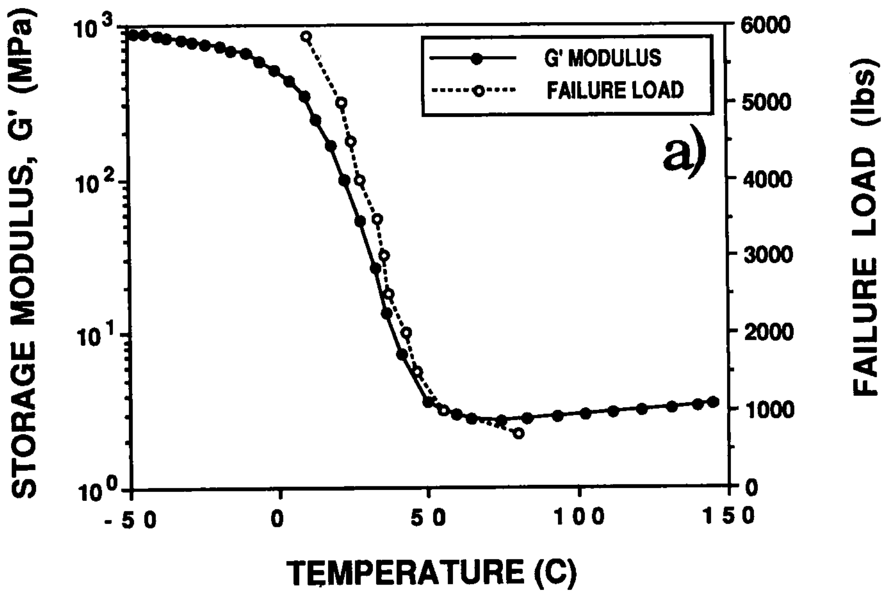
Since the cure reaction commences when $T>T_g$, the usual method of measuring the temperature dependence of bond strength cannot be used as it requires a thermal equilibration step. The tensile experiments were performed by placing a standard tensile bond specimen under a constant load and increasing the temperature until it failed. The static loads were decreased on subsequent specimens by 500 pounds (2.22 kN) until the bond did not fail. Figure 12a shows the data obtained for EA-956 adhesively-bonded specimens cured at 4.4°, 10°, 23.8°, and 93.3°C. The first point of interest is that the bond strengths are not significantly affected by the undercure as long as the resin is in the glass state and below T_g. The second significant point from the data is, as expected, that the temperature sensitivities of the adhesives are very much greater for the systems with significant undercuring. When comparing the ambient-cured (23.9°C) with the completely-cured (93.3°C) the data predict that the ambient-cured bond will fail at 1550 psi (10.69 MPa) if the temperature is raised to 70°C, whereas the fully-cured bond has about 5500 psi (37.92 MPa) capability when it is heated to 70°C. The situation is even more dramatic when looking at the 4.4°C cured bond. It will fail at loads <300 psi (2.07 MPa) when heated to ~50°C.

Similar studies with EA-946 adhesive are shown in Figure 12b and, as expected, there is no significant effect of cure temperature on the responses. The reduction in bond strength is due to system passing through $T_{g\infty}$.

In some cases the failure load *vs.* temperature response follows the change in dynamic storage modulus at the glass transition, as illustrated in Figure 13 for EA-946 and 4.4°C-cured EA-956 adhesives. In other systems the reduction in load capability occurs at temperatures considerably below T_g. The fully-cured EA-956 illustrates this in Figure 14. It appears that the failure load capability correlates with a lower temperature transition in the glass state. We have observed other examples where adhesives exhibiting a transition below T_g fail in that temperature region and not at T_g.



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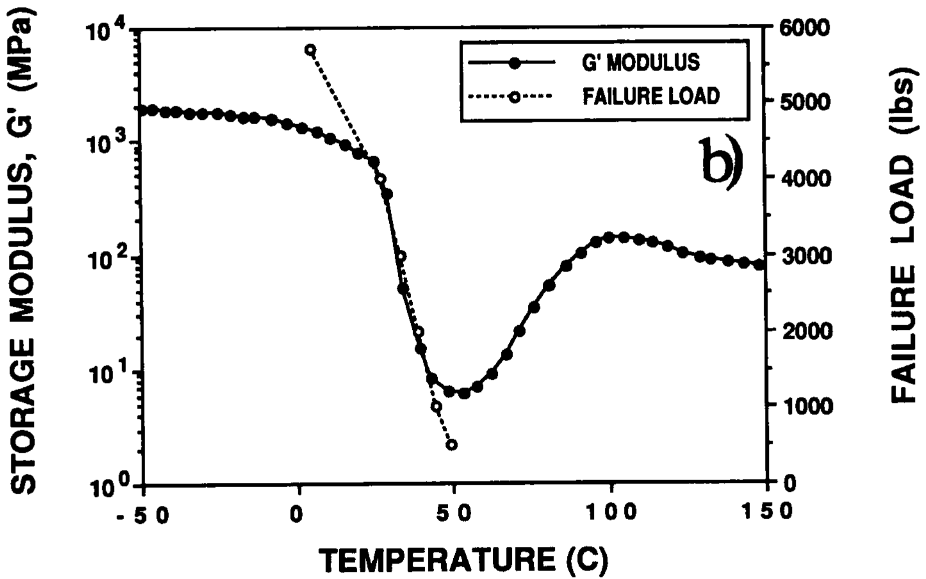
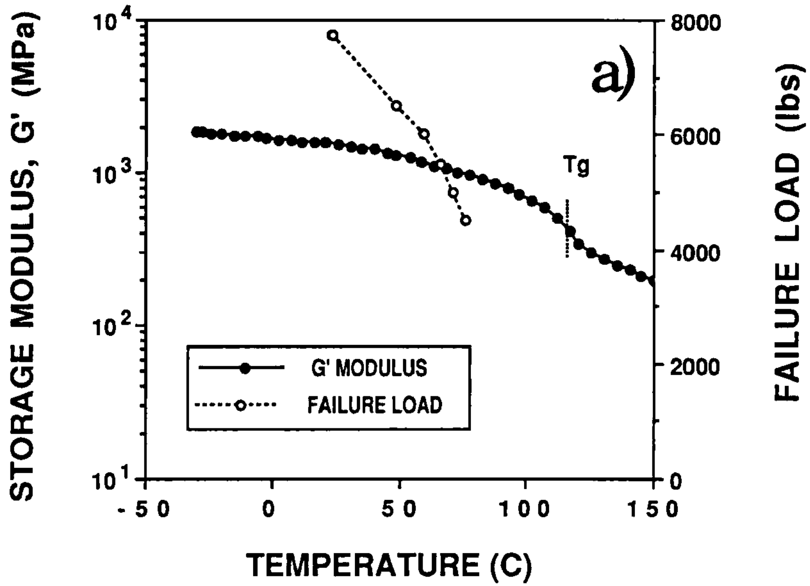


FIGURE 13 Dynamic storage modulus and tensile failure load *vs.* temperature for a) EA-946 adhesive, and b) EA-956 cured at 4.4°C.



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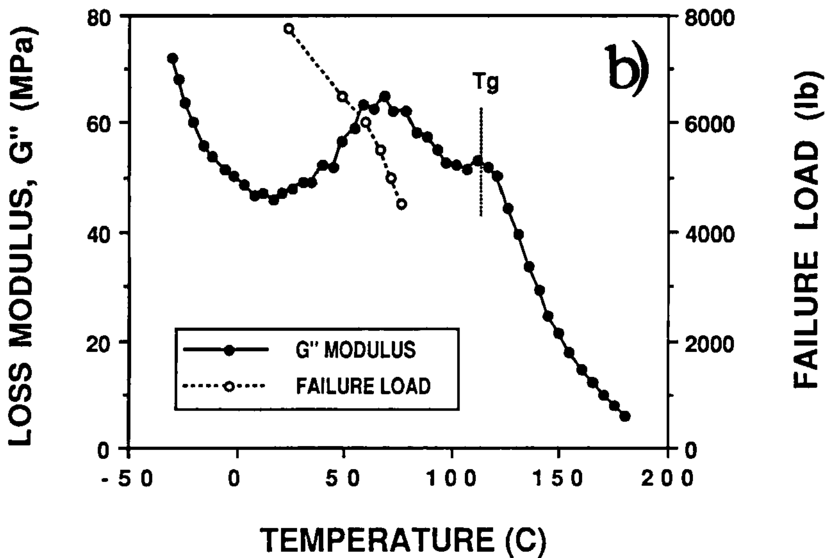

FIGURE 14 Dynamic moduli and failure load *vs.* temperature for EA-956 adhesive cured at 93.3°C; a) storage modulus, G′; b) loss modulus, G″.

CONCLUSIONS

The purpose of this study was to determine the effects of incomplete cure of glassed epoxy resins on their mechanical properties and tensile bond strengths. The degree of undercure, as measured by the level of unreacted epoxy, was observed to depend on $T_{g\infty} - T_{cure}$. Resin T_gs determined by dynamic mechanical measurements were related to the degree of undercure. The temperature dependence of tensile bond strength was also shown to be a sensitive function of undercure with reductions in strength as great as 15× observed.

Acknowledgement

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