Strain softening in an epoxy resin

K. W. THOMSON, L. J. BROUTMAN
Department of Metallurgical and Materials Engineering, Illinois Institute of Technology, Chicago, Illinois 60616, USA

Post-yield behaviour, particularly strain softening, has been studied here for an epoxy resin to examine the effects of postcuring and plasticization by water and a non-volatile diluent dibutylphtalate. The significance of necking was examined by conducting compression tests (at room temperature) as well as tensile tests. In the case of tensile tests, elevated temperatures were used in order to achieve yielding. The amount of strain softening was found to be reduced by postcuring or by the addition of a plasticizer. In the case of postcuring, little change in yield stress occurred, whereas, with plasticizers, a reduction in yield stress does occur.

1. Introduction

The microscopic processes involved in the plastic deformation of polymers are less understood than in the case of metals. In particular, the phenomenon of strain softening has no universally accepted explanation. This effect is widely observed in polymeric materials as a drop in load (for constant elongation rate) following the initial yielding stage [1].

Several theories for plastic deformation in polymers have been proposed. Robertson [2] suggested that shear stress introduces a bias in the preferred conformation of backbone chains. Flexing of the bonds produces a local rise in free volume permitting deformation. Bauwens [3] has shown that the process may be described in terms of activation of chain segments by stress.

Strain softening appears to be connected with the growth of shear bands through the material [4, 5]. Once a small sheared region has nucleated and grown to a critical size, it may continue to expand, allowing further strain at a lower stress. Localized shear bands have been observed using polarized light to examine compressed specimens of various polymers [6].

Strain softening has been observed for a number of epoxy resin systems [6–9] and has been shown to be influenced by the degree of postcuring [10]. Diffuse shear bands have been observed in some cases [6, 11], but have not always been observed in epoxies which exhibited strain softening [7]. The yield process in these materials apparently does not involve any severe disruption of primary bonds. This has been inferred from the similarity to yield in glassy thermoplastics [7] and from measurements of the cross-link density within yielded regions [11].

In this study, strain softening has been investigated in an epoxy resin to examine the effects of postcuring and plasticization by water or a non-volatile diluent. The yield stress and modulus of the material have previously been examined in some detail and the glass transition temperatures (T_g) were determined from the modulus data [12]. The glass transition temperatures were defined from the midpoint of the transition from the glassy to rubbery state.

Since a load drop may arise from necking in a tensile specimen when the true stress is increasing [1] some consideration of the testing geometry is necessary. Thus, the significance of necking was assessed by conducting uniaxial compression tests in addition to tensile tests. Compression tests could be carried out at room temperature since brittle fracture was effectively suppressed. Elevated temperatures were required in tensile tests to obtain sufficient ductility for the yield behaviour to be observed.

2. Experimental procedure

The epoxy resin was Epon 828 (Shell Chemical Co.) which was cured with metaphenylenediamine (*m*PDA) in the ratio 14 phr. In some cases dibutylphtalate (DBP) was added to the resin before

curing to act as a plasticizing agent. Various curing schedules were used but in all cases the mixed epoxy was gelled at room temperature for at least 20 h and then cured for 2 h at 80° C in an air-circulation oven. The cured resin was released from the mould and postcured if required.

Details of the fabrication of the tensile specimens have been reported elsewhere [12]. They were cut from cast plates approximately 2 mm thick, surface ground to a uniform thickness of 0.89 ± 0.03 mm, and machined to shape. The gauge section was approximately 36 mm long and 5.3 ± 0.2 mm wide.

Tensile tests were performed on an Instron TT-D testing machine equipped with an environmental chamber and extensometers. A cross-head speed of 0.05 in. min^{-1} * was used which gives a nominal strain rate of 6×10^{-4} sec^{-1}.

Compression specimens were fabricated by pouring the epoxy into a silicon rubber mould to produce cylindrical castings of 19.5 mm diameter. The end faces were machined to give a length of 22.0 mm.

Uniaxial compression tests were also performed on the Instron testing machine using a cross-head speed of 0.02 in. min^{-1} † for a nominal strain rate of 4.5×10^{-4} sec^{-1}. All compression tests were carried out at room temperature. The end faces of the specimens were lubricated with molybdenum disulphide grease. Uniform deformation occurred at least up to the yield point but non-uniform behaviour often produced barrelling in the post-yield region, particularly in the unplasticized material.

The maximum load obtained during the compression tests was about 4500 kg. Since this load was expected to cause significant deflection in the loading system and no extensometer was used, the compression of the specimen has been plotted in terms of the nominal cross-head displacement rather than the strain.

Some specimens were plasticized with water by immersing them at 70° C. Tensile specimens reached saturation within 14 days immersion time and the maximum water content was about 3% by weight. Their behaviour was compared with specimens annealed in air for the same time at 70° C. Compression specimens immersed in water took much longer to approach saturation. They were tested after 163 days of immersion when

their water content was about 2.6%. Their behaviour was compared with specimens which were annealed in air at 70° C for the same time.

In general, the tensile or uniaxial compression stress—strain curves showed either a stress maximum followed by strain softening or a yielding stage followed by deformation at constant or slightly increasing stress. The maximum stress ($\sigma_{y,max}$) and the minimum post yield stress ($\sigma_{y,min}$) are defined in Fig. 1 (inset).

3. Results
3.1. Effect of postcuring
The effect of postcuring on the post-yield behaviour is clearly demonstrated by the results of uniaxial compression tests on the unplasticized epoxy system (Fig. 1). The maximum stress in the yield region ($\sigma_{y,max}$) is almost independent of the postcure temperature. The strain at which $\sigma_{y,max}$ occurs increases with postcure temperature reflecting a decrease in the average modulus. The post-yield behaviour shows considerable variation with the minimum stress in the post-yield region ($\sigma_{y,min}$) increasing with postcure temperature until the strain-softening effect dissapears for the 150° C postcured material. Similar results were also obtained in tests on specimens cured with methylene dianiline (35 phr).

Uniaxial compression tests on specimens of the 828/mPDA system plasticized with 25 phr DBP showed strain softening only in material cured at 80° C without postcuring. The rate of strain hardening increased as the postcure temperature was increased (Fig. 2). $\sigma_{y,max}$ was not constant but also increased with postcure temperature to the testing temperature for this material.

There was some difficulty in duplicating these results in tensile tests. At temperatures well below the glass transition, the tensile specimens invariably failed by brittle fracture at or before $\sigma_{y,max}$. Hence it was necessary to use elevated temperatures to achieve sufficient plasticity to observe post-yield behaviour. This introduces the problem of comparing stress—strain curves at different temperatures for materials with different glass transition temperatures.

The stress—strain curves for the unplasticized material cured at 80° C only and tested at various temperatures (Fig. 3) may be compared with curves for the 150° C postcured material (Fig. 4).
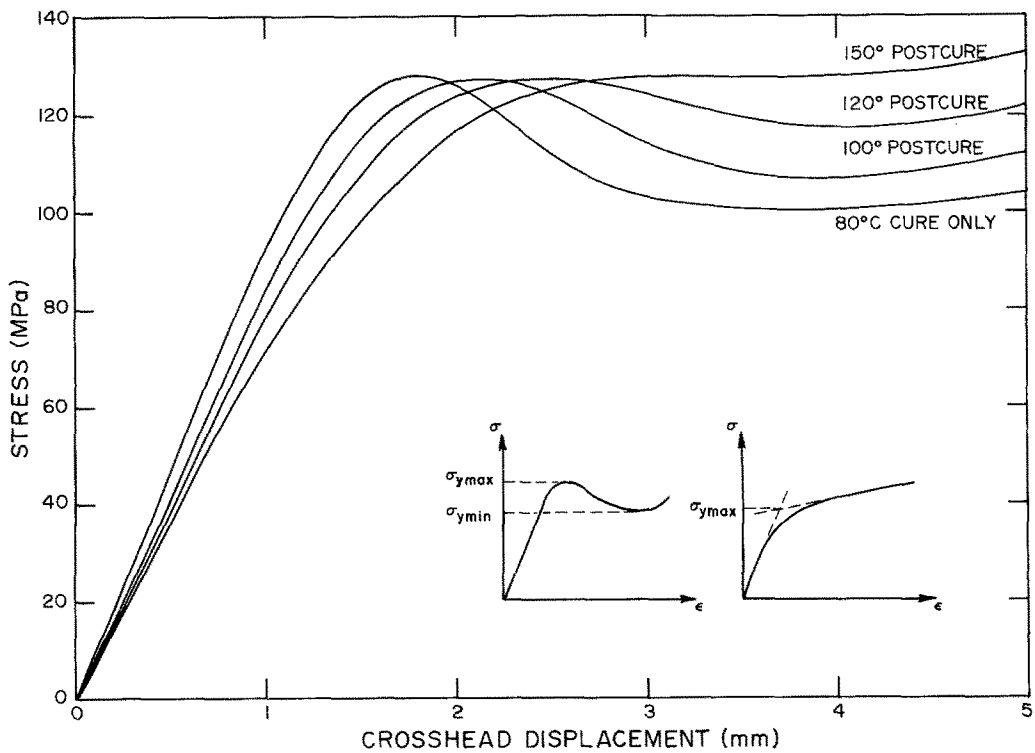
*0.0212 mm sec^{-1}.
†0.0085 mm sec^{-1}.

Figure 1 Uniaxial compression stress–strain curves after postcuring at various temperatures and (inset) definition of $\sigma_{y,max}$ and $\sigma_{y,min}$.
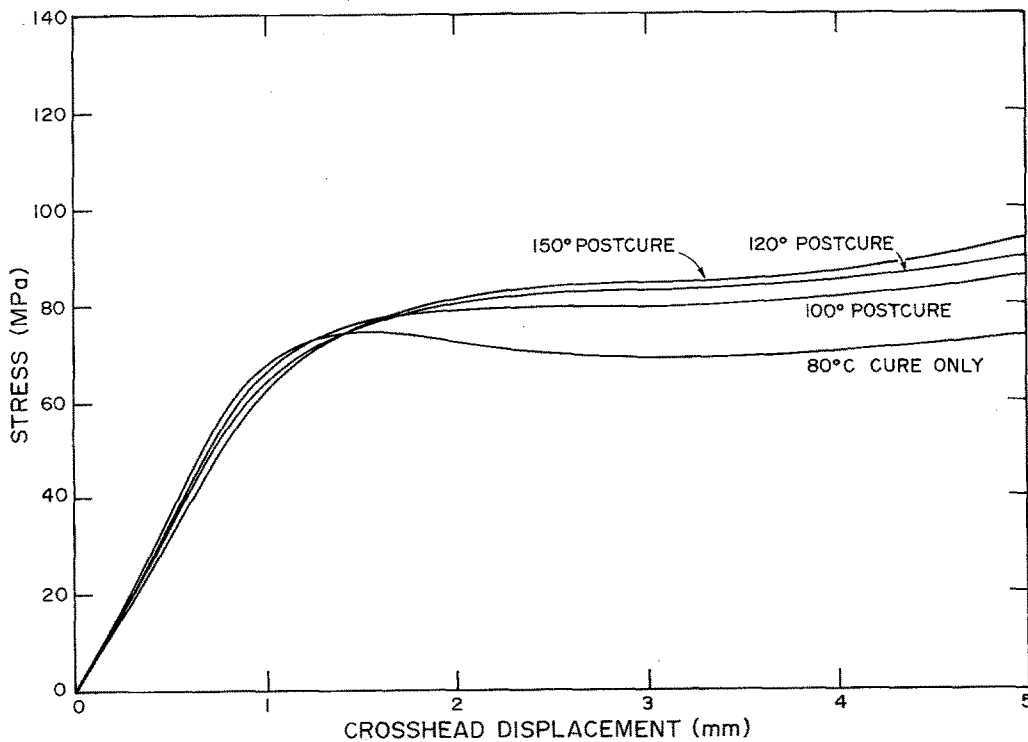

Figure 2 Uniaxial compression stress–strain curves for material with 25DBP after postcuring at various temperatures.
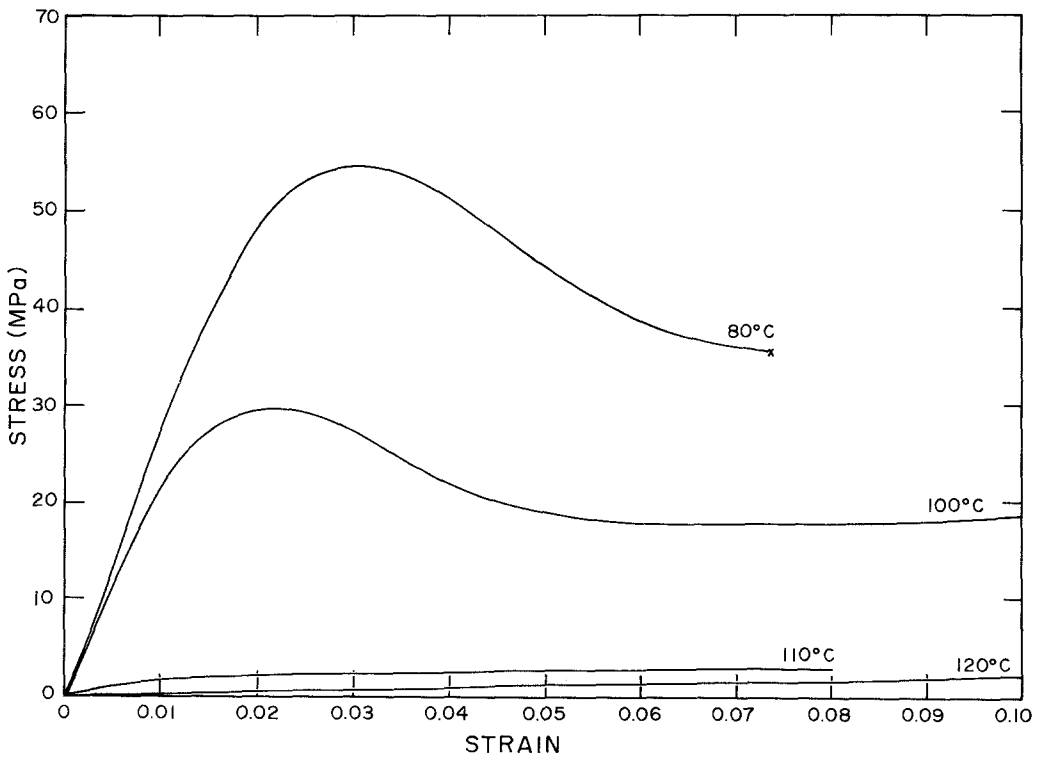
Figure 3 Tensile stress–strain curves at various testing temperatures for material cured at 80° C and annealed in air at 70° C for 14 days.
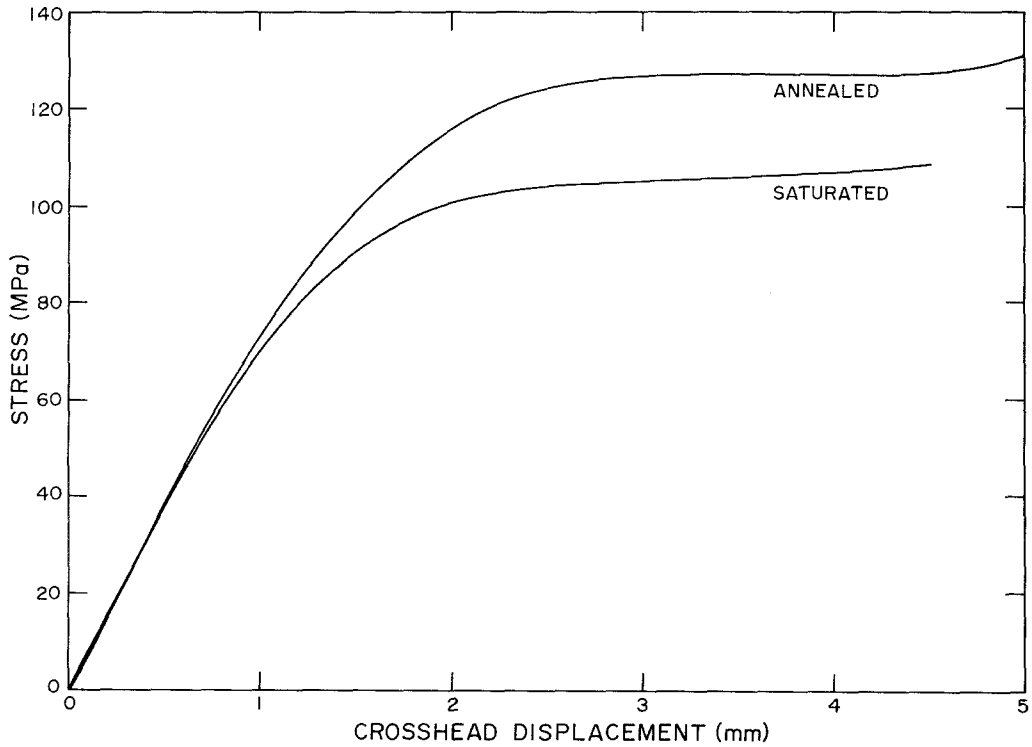

Figure 4 Tensile stress–strain curves at various testing temperatures for material postcured at 150° C and annealed in air at 70° C for 14 days.

These specimens were annealed in air at 70° C for 14 days before testing. The glass transition temperatures for these materials are 110 and 154° C, respectively [12]. The results suggest that the magnitude of the post yield drop is smaller in the 150° C postcured material.

Strain softening was observed for the 150° C postcured material when tested in tension (Fig. 4) but not in compression (Fig. 1). This effect may be explained by the different test temperatures if the amount of strain softening is shown to decrease as the test temperature is lowered below the glass transition. This could explain the reduction in strain softening as the glass transition temperature was increased by raising the postcure temperature (Fig. 1). However, there is little evidence from the tensile tests to support this view. Compression tests at elevated temperatures would clarify this point. Necking may also be involved since it would allow a load drop for higher strain-hardening rates in tension than would be required to cause a load drop in compression. Necking was observed in tensile tests where a load drop accompanied failure.

3.2. Effect of DBP

The addition of 5 phr DBP to the Epon 828 before curing with mPDA removed any trace of strain softening in tensile tests on the 150° C postcured material (Fig. 5). Even at temperatures approaching the glass transition temperature (137° C) the stress remained virtually constant in the post-yield region. Tensile tests on material containing 19, 15 or 20 phr DBP showed similar behaviour although the glass transition temperatures were lower.

Comparison of the uniaxial compression results for the unplasticized specimens (Fig. 1) and for specimens containing 25 phr DBP (Fig. 2) confirms that the addition of the plasticizer reduces the amount of strain softening. In both tension and compression, the addition of DBP also appears to reduce $\sigma_{y, max}$ at temperatures a corresponding amount below the glass transition temperature.

3.3. Effect of water

Saturation of the 150° C postcured polymer with water has the effect of lowering the glass transition temperature as with the addition of DBP and other plasticizers [12]. The results from tensile tests on saturated specimens (Fig. 6) show that the post-yield behaviour is also similar to that observed for DBP plasticized specimens with the disappearance of all traces of strain softening. The results in Fig. 6 may be compared to the results in Fig. 4
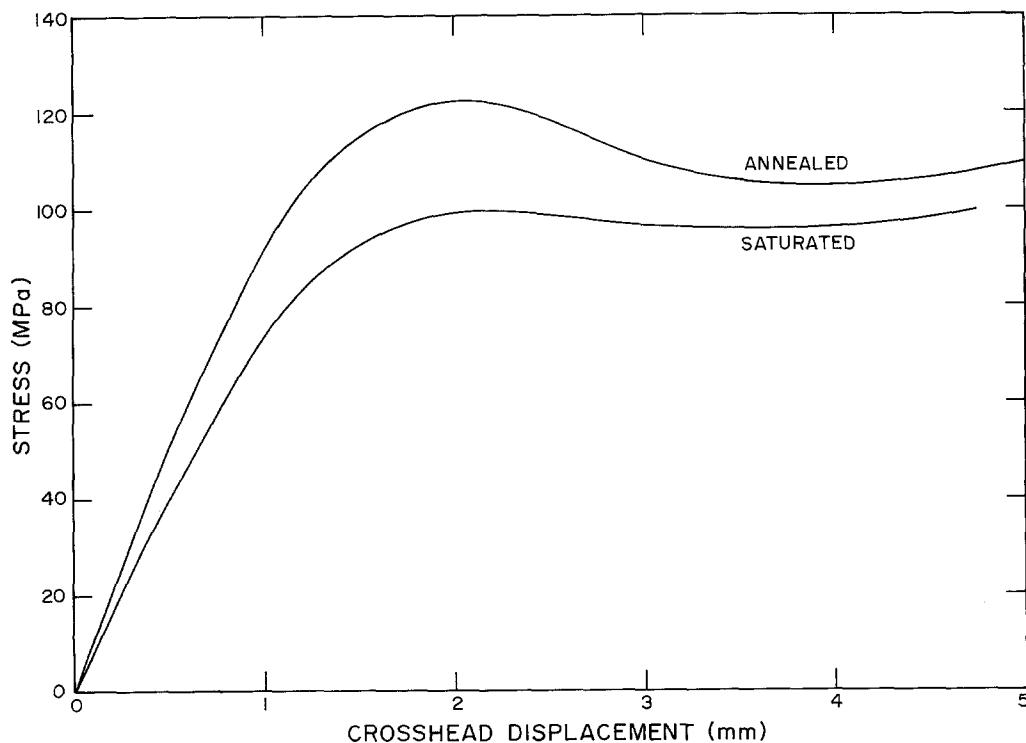

Figure 5 Tensile stress–strain curves at various testing temperatures for material with 5 phr DBP.
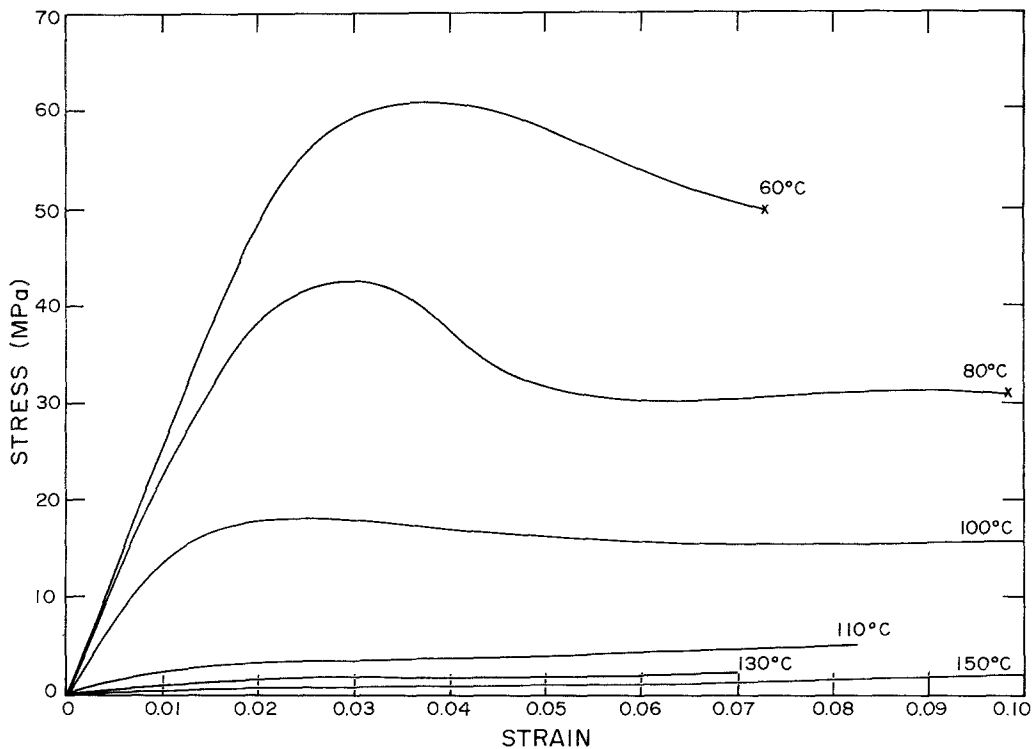
Figure 6 Tensile stress–strain curves at various testing temperatures for material postcured at 150° C and saturated in water at 70° C for 14 days.

which are from specimens annealed in air at the same temperature and for the same time as the saturated specimens were immersed in water.

Immersion of the 80° C postcured material has been shown to produce an increase in the glass transition temperature which appears to be associated with further cross-linking [12]. Nevertheless, the tensile stress–strain curves for saturated specimens (Fig. 7) show that the post-yield drop is smaller than it is for the annealed material (Fig. 3).

The reduction in the amount of strain softening is confirmed by uniaxial compression tests at room temperature. Figs 8 and 9 show the behaviour of 150° C postcured and 80° C cured specimens, respectively. Specimens immersed in water at 70° C for 163 days are compared to specimens which were annealed in air at the same temperature for about the same time. The 80° C cured material shows a lower $\sigma_{y,max}$ and a comparatively small load drop after immersion in water. The 150° C postcured material shows no load drop in either case but the strain-hardening rate may be slightly greater after immersion and $\sigma_{y,max}$ is lower.

4. Discussion
The effect of postcuring, adding DBP or saturation

with water was, in all cases, to reduce or eliminate the post-yield load drop. Where there is no load drop, such as in the case of the 150° C postcured material in compression, there was some evidence for an increase in the strain-hardening rate when the material was plasticized with DBP or water.

Postcuring appeared to have little effect on $\sigma_{y,max}$ as defined in Fig. 1 (inset), provided the testing temperature was well below the glass transition temperature. This was demonstrated for uniaxial compression tests at room temperature on the unplasticized material. These results are in agreement with previous work using Epon 828 resin cured with TETA (triethylenetetramine)[10].

Plasticization with DBP or water appeared to have the same effect on the yield behaviour. In both cases the post-yield load drop was reduced and $\sigma_{y,max}$ was lower. This was clearly evident in the compression results from specimens immersed in water (Figs 8 and 9) and from DBP plasticized specimens (Fig. 2 compared to Fig. 1). Comparison of tensile results at corresponding temperatures below the glass transition temperatures (Figs 3 to 7) suggests that $\sigma_{y,max}$ also decreases in tension when the material is plasticized with DBP or water.
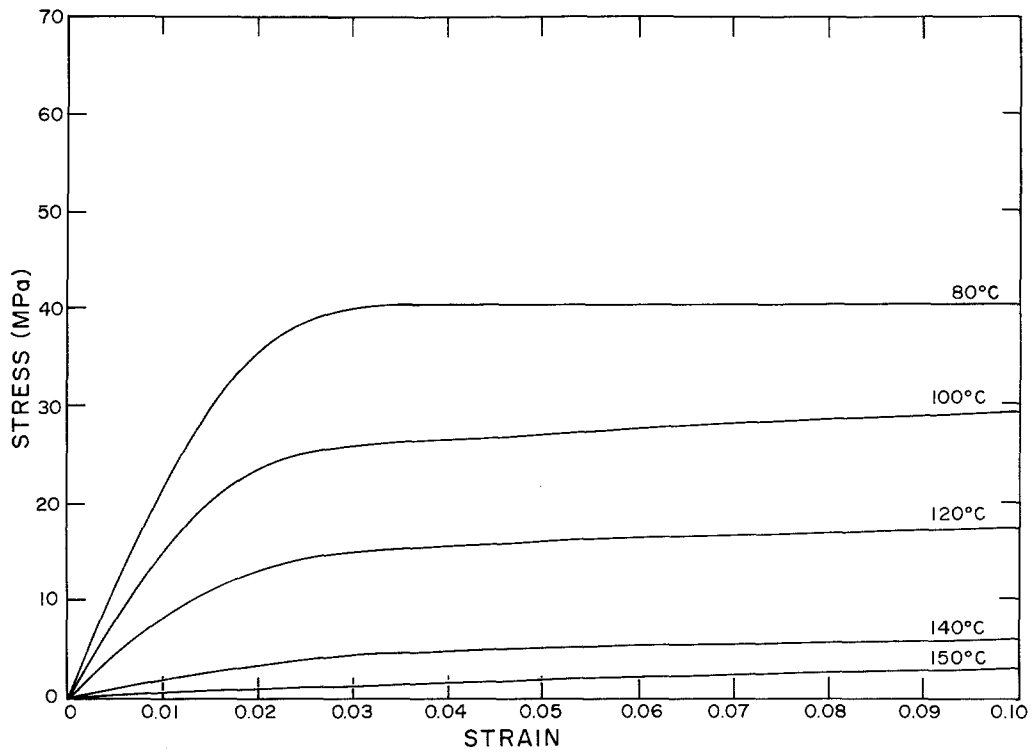
2705

Figure 7 Tensile stress–strain curves at various testing temperatures for material cured at 80° C and saturated in water at 70° C for 14 days.
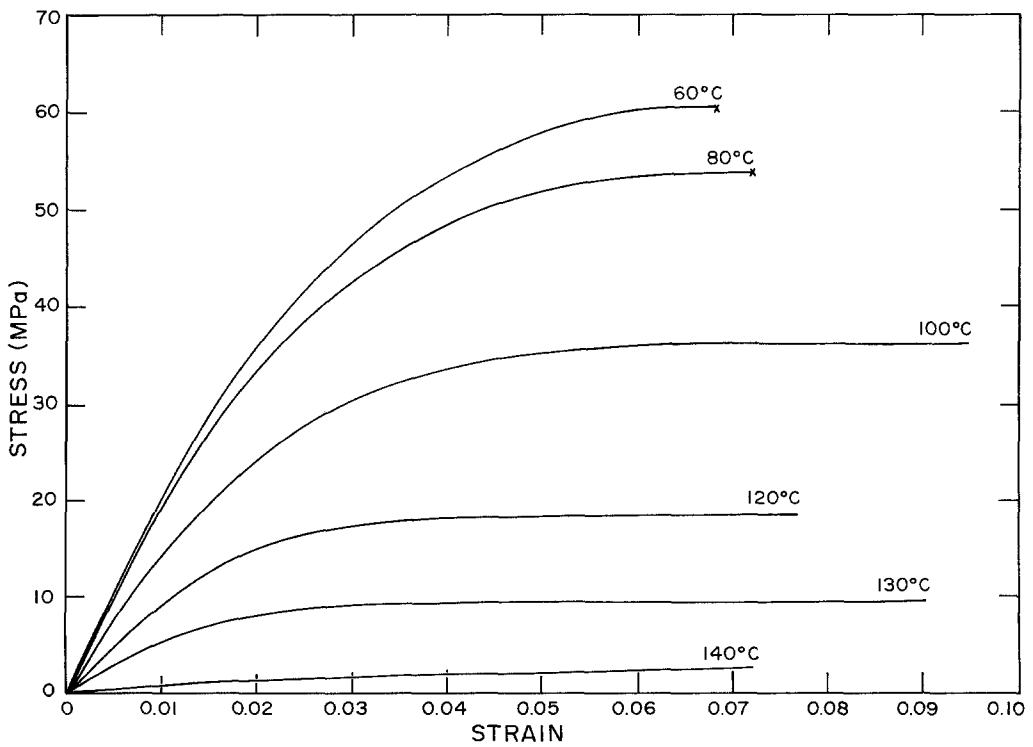

Figure 8 Uniaxial compression curves for material cured at 80° C and either immersed in water or annealed in air at 70° C for 163 days.
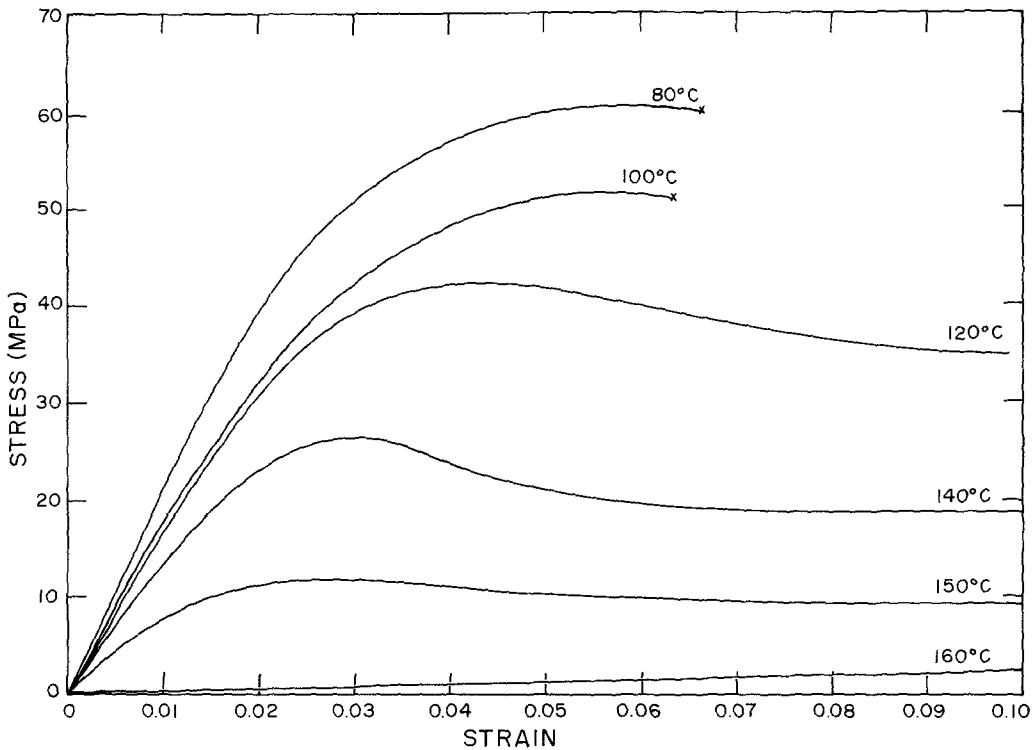
2706

Figure 9 Uniaxial compression curves for material postcured at 150° C and either immersed in water or annealed in air at 70° C for 163 days.

Current theories of plastic deformation in polymers [4, 5] suggest that strain softening is due to the growth of sheared regions which nucleate when the stress approaches $\sigma_{y,max}$. The result of postcuring was found to be a decrease in the amount of strain softening with little change in $\sigma_{y,max}$. This implies that the sheared regions may be nucleating at the same stress level but that their growth is inhibited in the postcured material, possibly due to to a higher density of cross-links. The details of this behaviour are not clear since there is evidence that few cross-links are broken during deformation [11]. The greater cross-link density may inhibit the growth of sheared regions by restricting the available conformations which can be reached without breaking primary bonds.

The presence of water or DBP reduced the amount of strain softening but also lowered $\sigma_{y,max}$. This suggests that the main effect of the plasticizer was to reduce the stress required for the nucleation of sheared regions but had little effect on their growth. The decrease in $\sigma_{y,max}$ appears to be consistent with the concept of additional free volume introduced by plasticizers [12].

Apart from the importance of strain softening in testing yield theories, it may also be of significance to the fracture properties. Cherry and Thomson [10] have suggested that $\sigma_{y,min}$ may be of greater importance in controlling the fracture behaviour than $\sigma_{y,max}$. A lower $\sigma_{y,min}$ may allow the development of a larger yielded zone and hence increase the fracture toughness at no expense to the general yield properties or modulus. The results suggest that postcuring may tend to embrittle some epoxy systems with little gain in other properties except the glass transition temperature. Plasticization may also increase toughness but with a degradation in general yield stress and glass transition temperature.

5. Conclusions

The amount of strain softening which occurs in an epoxy resin system was found to be reduced by postcuring or by the addition of a plasticizer or water. Postcuring reduced the amount of strain softening with little change in the yield stress. Addition of the plasticizer or water did cause a reduction in the yield stress.

Acknowledgement

References

1. I. M. WARD, *J. Mater. Sci.* **6** (1971) 1397.
2. R. E. ROBERTSON, *J. Chem. Phys.* **44** (1966) 3950.
3. J. C. BAUWENS, *Polymers* **21** (1980) 699.
4. P. B. BOWDEN and S. RAHA, *Phil. Mag.* **29** (1974) 149.
5. A. S. ARGON and M. I. BESSONOV, *Poly. Eng. Sci.* **17** (1977) 174.
6. P. B. BOWDEN and J. A. JUKES, *J. Mater. Sci.* **7** (1972) 52.
7. S. YAMINI and R. J. YOUNG, *ibid.* **15** (1980) 1814.
8. A. E. MOEHLANPAH, O. ISHAI and A. T. DIBENE-DETTO, *J. Appl. Polymer Sci.* **13** (1969) 1231.
9. O. ISHAI, *ibid.* **11** (1967) 1863.
10. B. W. CHERRY and K. W. THOMSON, *J. Mater. Sci.* **16** (1981) 1913.
11. I. STEG and O. ISHAI, *J. Appl. Polymer Sci.* **11** (1967) 2303.
12. K. W. THOMPSON and L. J. BROUTMAN, *Polymer Eng. Sci.* in press.