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Yielding behaviour in model epoxy thermosets — I. Effect of strain rate and composition

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Yielding behaviour was investigated in two series of epoxy networks where the molecular architecture (crosslink density) was varied without any significant chemical changes in the structure. The DGEBA-based networks cured with aromatic amines had higher yield stresses than related networks cured with aliphatic amines, due to differences in the rigidity of the backbone. In each series, the yield stress was also found to rise with increased crosslinking. This may be caused by the increased constraint of the crosslinks on the molecular segments involved in the yielding process. The Eyring equation was found to satisfactorily describe the dependence of the yield stress on the strain rate. Surprisingly, the calculated volume of the flow unit was independent of both the crosslink density and the nature of the amine. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: yielding; yield stress; strain rate)

INTRODUCTION

The properties of crosslinked polymers often depend, in a complex way, on the molecular architecture or topology of the network as well as on the chemical composition. Because changes in crosslink density invariably produce a change in the chemistry of the system, it is usually difficult to separate the two effects. The smallest change in chemistry which results in crosslinking may be considered to be the replacement of two hydrogen atoms on the polymer chain with a covalent crosslinking bond[1]. Systems which are crosslinked in this manner have been previously used to study the effect of crosslinking on the glass transition temperature[1], the rubbery modulus[2] and the fracture toughness of filled thermoset polymers[3]. Here, we use the same method of systematically varying the crosslink density with minimal compositional change to establish the factors affecting the stress–strain and yield behaviour of epoxy networks.

Thermosetting resins such as epoxy resins are used extensively for their high performance properties in applications such as aerospace composites. This selection is based on their high glass transition temperatures which results from the highly crosslinked network structure. Unfortunately the corresponding lack of molecular mobility leads to a tendency towards brittleness and so methods of improving the toughness of the matrix are being sought. In the region surrounding a crack tip in a polymer solid, the intensification of the stresses results in localized deformation by yielding, microcracking or crazing[4]. In particular, if yielding can be enhanced in preference to crack propagation, then a tougher polymer will result. Thus, yielding can be a key mechanism controlling the toughness of polymeric materials. The significance of the magnitude of the yield stress to determining the fracture behaviour is illustrated in *Figure 1*. If the yield stress of the material is high then the stress intensification by the crack tip produces only a small plastic zone around the crack and little plastic energy is dissipated during crack propagation. Alternatively, when the yield stress is low, the plastic zone is enlarged and as a result of the considerable plastic energy dissipated during crack growth, higher toughness is observed.

While models for yielding in linear thermoplastic polymers exist[5], the three-dimensional connectivity of networks means that the yielding process in thermosets is not as well understood and a better understanding of the phenomenon may lead to an improvement in the toughness in these materials, possibly by designing materials with lower yield stresses but without compromising the modulus and the glass transition temperature (T_g). Therefore, the objectives of this research are to study the stress–strain behaviour of a model series of epoxy thermoset resins and to analyse the influence of the network structure and crosslink density on the yield behaviour. The dependence of yielding on temperature for these systems will be published elsewhere[6].

EXPERIMENTAL

The epoxy resin, the diglycidyl ether of bisphenol-A (DGEBA), was supplied by Ciba Geigy, Australia as a viscous resin, Araldite F. The average epoxy concentration of this resin is reported to be 5.35 mol/kg, corresponding to an average molecular weight of 374 g/mol for a diepoxy monomer. The aliphatic curing agents, butylamine (BA, MW = 73 g/mol, supplied by Merck) and its dimeric analogue, diamino-octane (DAO, MW = 144 g/mol, supplied by Aldrich), along with the aromatic curing agents, aniline (An, MW = 93 g/mol, supplied by Unilab) and the dimeric analogue, diaminodiphenyl methane (DDM,

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MW = 198 g/mol, supplied by Aldrich) were of standard laboratory grade and were dried with 4 Å molecular sieves before use. The structures of the monomers are shown in *Figure 2*.

The DGEBA epoxy was cured with the amine mixtures BA/DAO or An/DDM using stoichiometric ratios of aminohydrogen and epoxide groups. Ratios of the monofunctional amines, BA or An, to difunctional amines, DAO or DDM, are expressed as the ratio of active hydrogens on each amine. Thus a 50/50 ratio is a 2:1 molar ratio of monofunctional to difunctional amine. However, since the molecular weight of the difunctional amine is approximately twice that of the monofunctional amine, a 50/50 ratio of aminohydrogen units is approximately equivalent to a 50/50 weight ratio.

Since the DAO (MP = 50°C) and DDM (MP = 85°C) are solids at room temperature, these amines were melted at 60 and 90°C, respectively, and then combined with the other pre-heated components. Mass balances where monitored so that any evaporation by the volatile BA or An amines could be corrected. Following thorough mixing the epoxies were poured into PTFE moulds. The specimens prepared with 100% An were too brittle to test (presumably because slight imbalances in stoichiometry produced a low molecular weight polymer) and so the low crosslink density analogue of DGEBA/DDM was prepared from a 95/5 ratio of An to DDM.

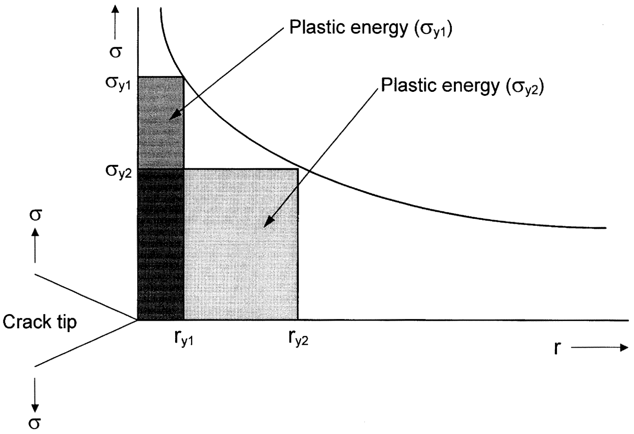

Figure 1 Schematic of tensile stress as a function of distance from the crack tip in a state of plane stress. For a material with yield stress σ_{y2}, the radius of the plastically yielded zone r_{y2} is greater than for the material with a higher yield stress σ_{y1} and hence the volume of the plastically deformed material and the fracture energy is greater. A similar conclusion applies to the more complex stress state in plane strain (adapted from Ref.[4])

The curing behaviour of the samples was investigated on *ca.* 10 mg samples with a Perkin–Elmer DSC-7 Differential Scanning Calorimeter in scanning mode, at a scan rate of 5°C/min. Following this curing run, the samples were re-scanned to measure the fully cured glass transition temperatures.

On the basis of the DSC studies, the DGEBA/BA/DAO systems were cured at 50°C for 12 h and then post-cured at 120°C (which is above the ultimate glass transition temperature in all cases) for the same period so that they were fully cured. Similarly, the DGEBA/An/DDM systems were initially cured at 70°C for 12 h and then post-cured at 160°C (which is in the vicinity of or above the ultimate T_g) for a further 12 h before cooling in the mould to room temperature.

For highly crosslinked epoxies tested in tension, the tensile yield stress is often greater than the fracture stress and the material will have a tendency to undergo brittle failure before it can exhibit macroscopic yielding. To avoid this problem, compression testing was used as a means of determining the yield characteristics. For uniaxial compression experiments, cylindrical samples were cured in 10 mm diameter PTFE moulds as described above and were machined to 16 mm length. Compression testing of these cylinders was performed between machined parallel steel platens on an Instron 4505 tensile tester using a variety of crosshead speeds at 22 ± 1°C. No lubricant was used between the surfaces. Rectangular bars, 20 mm × 10 mm × 4 mm, were also tested in a plane-strain compression test[7] at 22 ± 1°C. The specimen was placed cross-wise between two 3.2 mm wide parallel steel rails such that the ratio of sample width (10 mm) to die width (3.2 mm) was sufficient to ensure that the constraint exhibited by the unstressed material on each side of the die maintained plane-strain conditions[7]. As with the uniaxial compression testing, no lubricant was used between the surfaces.

For the uniaxial compression testing, at least two replicate samples were tested at each nominal strain rate from 6.25×10^{-4} to $62.5\ \mathrm{min}^{-1}$ (crosshead speeds were between 0.01 and 1000 mm/min) and the maximum error was ± 3 MPa. For the plane-strain compression test, specimens were tested in duplicate at a nominal strain rate of $0.0625\ \mathrm{min}^{-1}$ (crosshead speed of 0.25 mm/min) and the maximum error was ± 5 MPa. The yield point was taken as the point where the load passed through a maximum or at the obvious 'knee' in the load–displacement

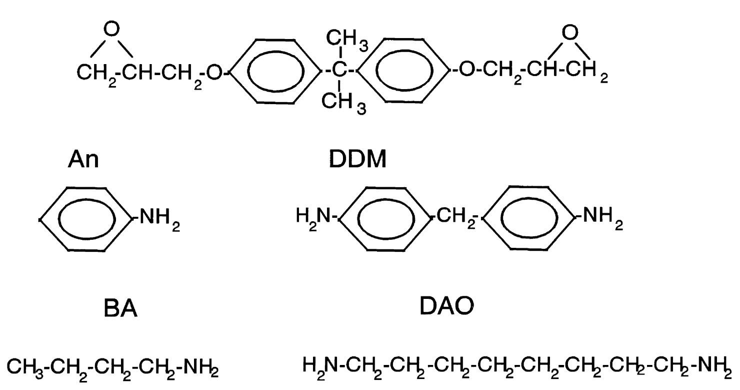

Figure 2 Structure of the monomers used

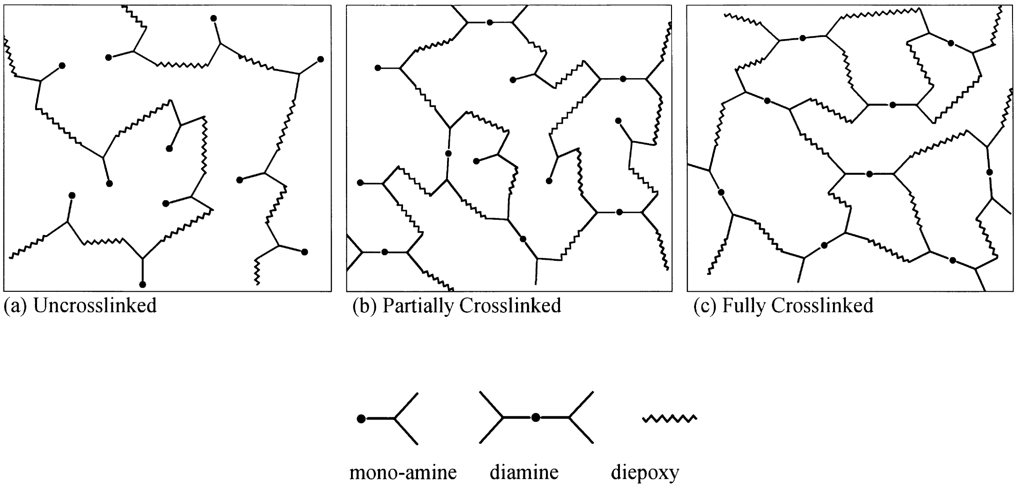

Figure 3 Schematic of the range of topologies formed with the model systems with minimal chemical differences: (a) linear polymer; (b) partially crosslinked polymer; (c) fully crosslinked polymer

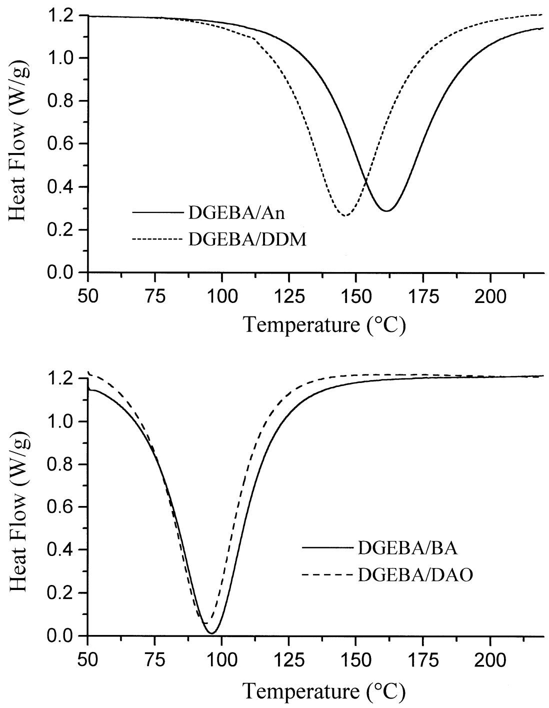

Figure 4 Scanning DSC traces for the systems DGEBA/DAO, DGEBA/BA, DGEBA/DDM and DGEBA/An. The scan rate was 5°C/min

curve if no maximum was evident. In both test geometries, the compliance of the testing rig is significant but, as it only affects the calculated strain, this factor is ignored here.

RESULTS AND DISCUSSION

Curing behaviour

Figure 3 is a schematic of the structures resulting from the reaction of DGEBA with either a monoamine (BA or An) or a diamine (DAO or DDM). Despite the chemical similarity in molecular structure between the two aliphatic amines (BA and DAO) or between the aromatic amines (An and DDM), a linear chain structure results from the copolymerization of DGEBA with monoamine (*Figure 3a*) whilst diamine curing produces a three-dimensional network (*Figure 3c*). An illustration of the chemical similarity of the two amine systems is shown by the DSC scans in *Figure 4*. The polymerization rate curve for DGEBA/BA is almost identical to that for DGEBA/DAO since the attachment of an aminoalkyl chain to the terminal carbon of butylamine would not be expected to have a significant inductive effect on the reactivity of the amine group[8]. In contrast, aniline reacts at a considerably slower rate, as would be expected from the electron withdrawing effect of the benzene ring[8]. The DDM/DGEBA system also reacts much more slowly than the aliphatic amines but due to the induction effect of the para-methylene group DDM would be expected to be more reactive than An—in fact it reacts at approximately twice the rate of An[9].

The T_g values of the epoxy resins cured with BA, DAO, An and DDM were 56, 104, 86 and 166°C resin, respectively—the resin DGEBA/95%An/5%DDM had a T_g of 97°C. As expected[9,10] the T_g increased as the crosslink density was raised for the two series and the aromatic-based amines had a higher T_g than the corresponding aliphatic analogues.

Yielding behaviour

The stress–strain curve for a typical sample is shown in *Figure 5* along with a sequence of photographs of the compression specimen at the various stages indicated. After the initial linear region, the stress passes through a pronounced maximum followed by a shallow minimum before rising to the breaking stress. No lubricant was employed in the experiment and so the frictional restraint between the compression platens and the ends of the specimens caused some bulging as seen in the photographs. Since this lateral deformation was only obvious at strains over 12% and was not evident at the yield point, the evaluation of the yield stress can be assumed to be unaffected by the bulging.

Figure 6 illustrates the room temperature stress–strain behaviour of DGEBA/BA at various strain rates. As the material is well into the glassy state at this temperature, the modulus shows little dependence on strain-rate, however the yield stress (and hence yield strain) increases with rising strain rate. According to the Eyring theory[5,11,12] yielding occurs by stress-activated jumps of molecular segments, known as flow units. The shear (τ) and uniaxial

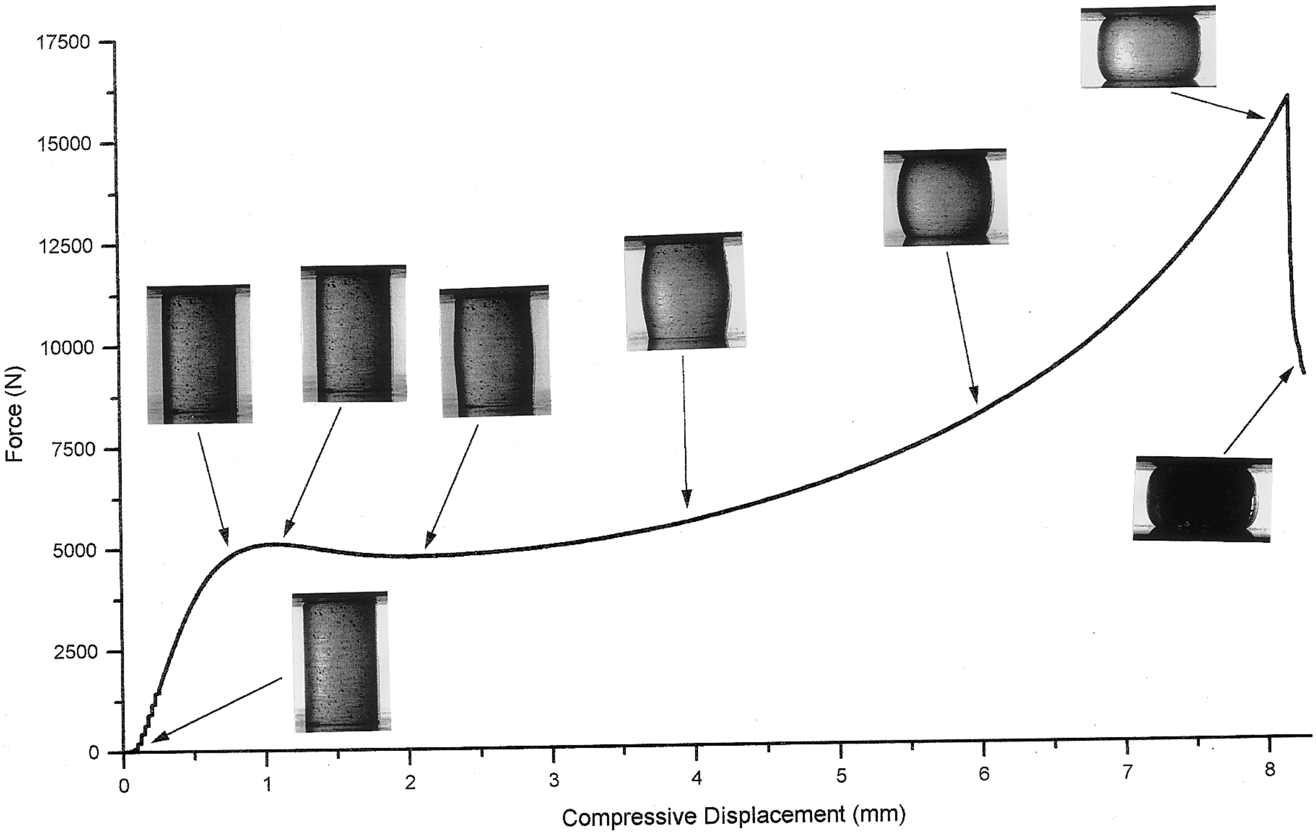

Figure 5 Nominal stress–strain curve obtained during the uniaxial compression yielding experiment of DGEBA/50%BA/50%DAO at a strain rate of 0.0625 min^{-1}. Photographs of the specimen at various indicated stages in the

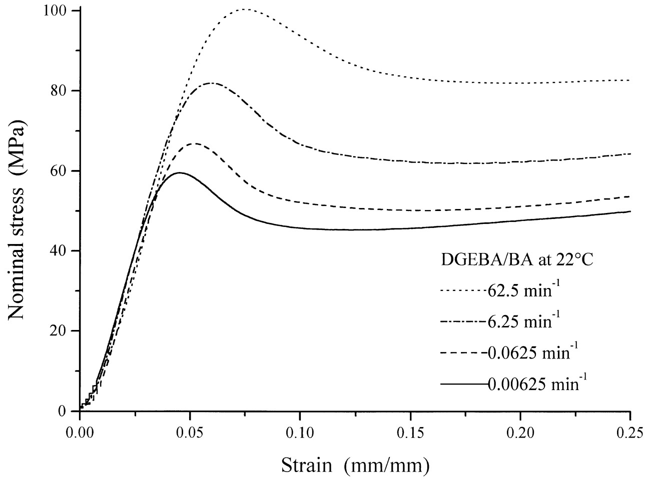

Figure 6 Nominal stress–strain curves for DGEBA/BA at 22 ± 1°C and various strain rates

(σ) yield stress are predicted* to depend logarithmically on the shear strain rate $\dot{\gamma}$[12]:

$$\tau = \frac{\sigma}{2} = \frac{\Delta H}{v_{\text{flow}}} - \frac{RT}{v_{\text{flow}}} \ln\left(\frac{\dot{\gamma}_o}{\dot{\gamma}}\right) \qquad (1)$$

where v_{flow} is the activation volume (or volume of the flow unit), ΔH is the activation energy, R is the gas constant, T is the absolute temperature and $\dot{\gamma}_o$ is a constant ($\dot{\gamma}_o \gg \dot{\gamma}$). As shown in *Figure 7*, where the uniaxial yield stress (assumed to be twice the shear yield stress as in equation (1)) is plotted *versus* the logarithm of strain rate, good agreement is found with the Eyring Equation. Similar results were obtained for all of the systems studied. *Table 1* tabulates the activation volumes calculated from equation (1). The average activation volume was 2.2 ± 0.1 nm^3 which corresponds approximately to the volume occupied (1.5 nm^3) by two DGEBA molecules linked to two amino units (two mono-amines or a diamine). The value also compares well with 3.0 nm^3 found by Tcharkhtchi *et al.*[13] for DGEBA/norbornene

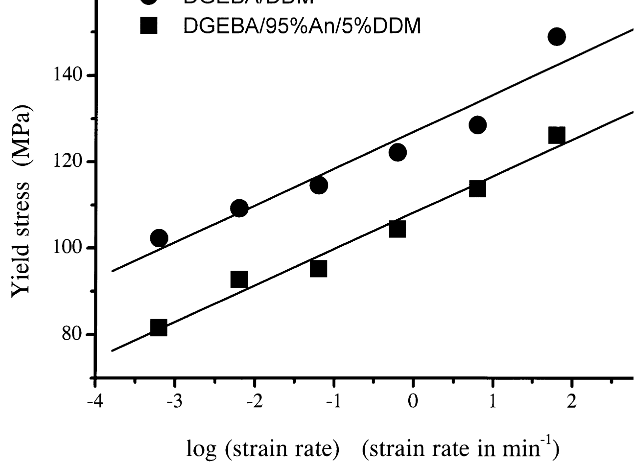

Figure 7 Yield stress (at 22°C) *versus* logarithm of strain rate fitted to the Eyring equation (equation (1))

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* Note that the Eyring equation has been written in three forms [5,11,12] which differ from each other by a factor of 2 in the value of v_{flow} in equation (1). In this paper, the literature data has been recalculated to be consistent with the form given in equation (1).

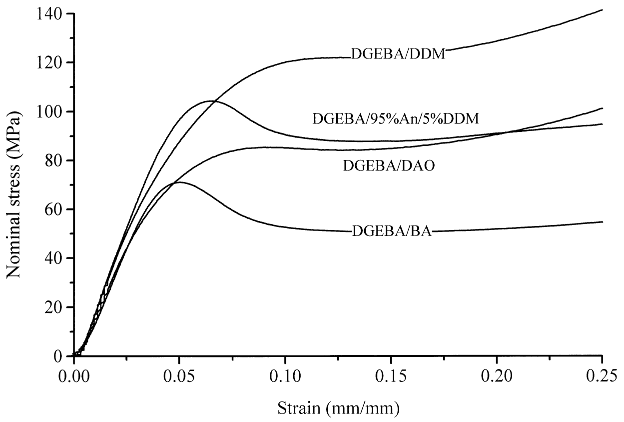

Figure 8 Nominal stress–strain curves (uniaxial compression at 0.0625 min^{-1}) for the epoxy resins with varying crosslink density and structure

Table 1 Activation volumes calculated from equation (1)

Composition	Activation volume (nm^3)
Aliphatic amines BA = chain extender DAO = crosslinker	
100%BA	2.3 ± 0.8
75%BA/25%DAO	2.2 ± 0.5
50%BA/50%DAO	2.3 ± 0.6
25%BA/75%DAO	2.2 ± 0.7
100%DAO	2.4 ± 0.8
Composition	Activation volume (nm^3)
Aromatic amines AN = chain extender DDM = crosslinker	
95%An/5%DDM	2.2 ± 0.7
75%An/25%DDM	2.2 ± 0.3
50%An/50%DDM	1.9 ± 0.5
25%An/75%DDM	2.1 ± 0.9
100%DDM	2.2 ± 0.8

anhydride networks and 2 nm^3 found by Fischer[14] for a series of bisphenol-A-cured DGEBA resins. The activation volume was found (see *Table 1*) to be virtually independent of crosslink density or diamine structure. This result is in accordance with that calculated from the data of Galy *et al.*[15] for a related epoxy system where crosslink density changes were accomplished with little change in composition. These conclusions differ from that of Urbaczewski-Espuche *et al.*[16] in studies of the yield behaviour of diamine-cured mixtures of DGEBA and the diglycidyl ether of butane diol—in that case, the activation volume increased from 2 to 3.3 nm^3 as the fraction of aliphatic epoxy increased.

Figure 8 illustrates typical stress–strain behaviour for the uncrosslinked and crosslinked epoxy resins. For the systems with low crosslink density (e.g. DGEBA/BA, DGEBA/95%An/5%DDM in *Figure 8*), the stress–strain curve revealed a well-defined yield stress maximum, however as the crosslink density was raised (e.g. DGEBA/DAO, DGEBA/DDM in *Figure 8*), this maximum was less well defined. For both amine systems, the yield stress and yield strain increased when the level of crosslinking was raised. As shown in *Figure 9*, the compressive yield stress determined by uniaxial compression testing was generally lower than that obtained from the plane strain rail test at the same strain rate. This is not surprising and is probably due to a combination of two factors. Firstly, the stress state in the plane strain test has a higher compressive hydrostatic component than the uniaxial stress test which could decrease free volume and so increase the yield stress of the material[5,11,17]. Secondly, the equivalent shear stress in plane strain is a smaller fraction of the applied stress than for uniaxial compression[11] and so a higher applied stress would be needed to cause yielding, even if the yield stress was not pressure dependent.

For each strain rate, the aromatic-amine based networks (DGEBA/An/DDM) exhibited a higher yield stress than the epoxies cured with aliphatic amines (DGEBA/BA/DAO). This is illustrated in *Figure 9*, where the yield stress is plotted *versus* the percentage of diamine (corresponding to increased crosslinking). This behaviour can be explained in terms of the structure of the units involved in the yielding process for each system. The networks cured with the aromatic amines have a much stiffer and/or bulkier backbone due to the benzene rings inhibiting molecular movement and thus requiring higher stresses for the molecular segments to slide past each other during the

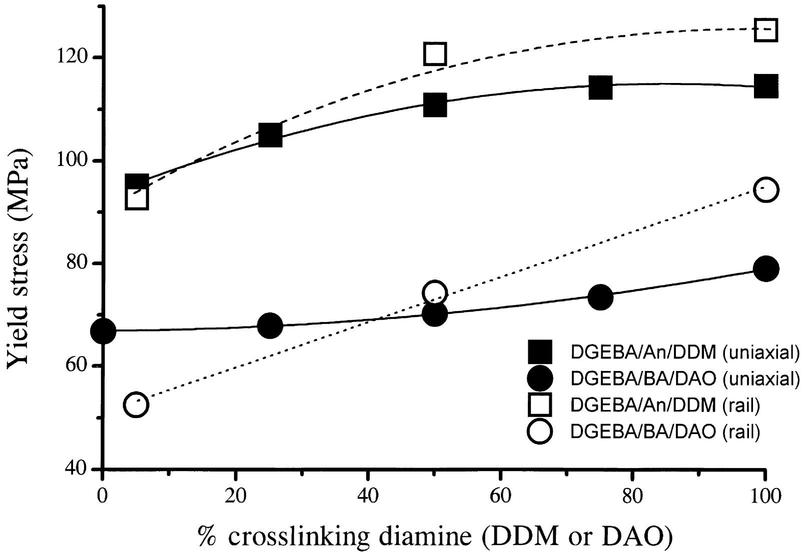

Figure 9 Uniaxial (compression) and plane strain (rail test) yield stress *versus* composition for the systems DGEBA/DDM/An and DGEBA/DAO/BA at 22°C and a strain rate of 0.0625 min^{-1}

yielding process. In contrast, the flexible nature of the aliphatic amines produces a more flexible network and hence a lower yield stress. Urbacaczewski *et al.*[16] used a similar argument to explain the variation of the yield stress caused by substitution of an aliphatic di-epoxy (butane diol diglycidyl ether) by the aromatic based DGEBA.

Previous studies of the dependence of yield stress on crosslinking have produced contradictory results. For example, Oleinik[18] found for a series of amine-cured epoxy resins with varying stoichiometry that the yield stress was virtually independent of crosslinking, except for large positive or negative deviations from the stoichiometric ratio where the yield stress decreased. In a similar study by Fernandoz-Nograro *et al.*[19], the yield stress passed through a maximum close to the aminohydrogen-epoxy stoichiometric ratio. However, Vallo *et al.*[20] and Yamini and Young[21] found the yield stress to monotonically decrease as the amine/epoxy ratio was raised. In contrast to these results, Fischer[14] found the yield stress was raised with increasing crosslinking for a series of bisphenol-A-cured DGEBA oligomers. Supporting this finding, Lesser and Kody[17] studied DGEBA cured with substituted diethylene diamine monomers and found that increased crosslinking raised the yield stress. In networks formed from diallyl adducts of polypropylene terephthalate oligomers however, Cho *et al.*[22] found that the yield stress decreased with increased crosslinking. Finally in contrast to the above, Truong *et al.*[23] found that for a series of partly reacted piperidine-cured DGEBA, the yield stress passed through a minimum with increasing crosslinking. These contradictory results may be reconciled by the observation that in all these cases, significant changes in the chemical composition accompanied crosslinking. *Figure 9* shows that when the chemical composition is unchanged, an increase in crosslink density (i.e. diamine content) raises the yield stress. This observation has also been confirmed[15] for another system (DGEBA cured with mixtures of the monoamine methylcyclohexylamine and the dimeric analogue 4,4′-diamino-3,3′-dimethylcyclohexylmethane) in which the crosslink density was also varied without compositional change. One explanation of this behaviour is that more crosslinks are involved in the yielding process for the systems with higher crosslink density (because v_{flow} is constant) and thus the stress required to slide the molecular unit over other segments will be greater. That is, the increase in crosslink density leads to a larger activation energy for the yield process.

CONCLUSIONS

From studies of the dependence of strain rate on yield stress, the activation volume of the flow unit involved in the yielding process was calculated to be 2.2 nm^3, independent of the crosslink density or amine structure. Epoxies cured with aromatic amines exhibited a higher yield stress at 22°C than the aliphatic amine systems. For both amine series, the yield stress was raised with increasing crosslink density due to the restriction of molecular motion imposed by the crosslinks.

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