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# Yielding behaviour in model epoxy thermosets — II. Temperature dependence

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The temperature and strain-rate dependence of yielding in compression has been investigated for a series of model thermosets in which crosslink density is varied without compositional change. The yield stress was only indirectly influenced by the crosslink density through its effect on the molecular mobility and the glass transition temperature. The Eyring activation volume was relatively insensitive to changes in crosslink density or composition but increased as the temperature was raised. The Robertson theory of yielding was found to give an approximate prediction for the temperature and strain rate dependence of the yield stress and the adjustable molecular parameter in this theory was close to the theoretical value. Neither the Argon nor the Bowden theories yielded significantly improved fits to the data. The use of these structurally related polymer systems appears to provide a very sensitive test of yielding theories. © 1998 Elsevier Science Ltd. All rights reserved.

**(Keywords: yielding; temperature effects; strain rate)**

## INTRODUCTION

The low toughness of thermosetting polymers is one of their major weaknesses and new methods of improving their fracture resistance are being sought. Yielding is an important mechanism in the toughening of a polymer and an improved understanding of this phenomenon should provide insight into ways in which further toughening of networks may be achieved.

Whilst the role of dislocations in the yielding of the crystalline lattice of semicrystalline polymers is reasonably well understood[1], it is less clear how yielding occurs in amorphous polymers and, in particular, in the molecularly more restricted thermoset polymers. However, at a simple level it is accepted that in amorphous polymers, yielding involves the slipping of molecular segments past one another under the action of stress. The recent use of powerful instrumental techniques is leading to a deeper understanding of the process. For example, polarized FTIR[2] has provided new information on the changes in the molecular orientation during yielding and the technique of deformation calorimetry[3] has indicated how the application of mechanical stress activates new segmental motions into a yielding process. Also, small angle X-ray diffraction[4] has shed more light on the yielding process in rubber-toughened polymers. An alternative approach is used in this paper, by using two series of chemically similar but architecturally different epoxy resins[5] to test theories of yielding behaviour.

## 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, MW = 198 g/mol, supplied by Aldrich) were of standard analytical or laboratory grade and were dried with 4 Å molecular sieves before use. The structures of the monomers are shown in *Figure 1*. The DGEBA epoxy was cured with the amines using stoichiometric ratios of amino-hydrogen and epoxide groups. Ratios of the monofunctional to difunctional amines are expressed as the ratio of active hydrogens on each amine. Thus a 95/5 ratio of An to DDM is a 95:2.5 molar ratio of monofunctional to difunctional amine. However, since the molecular weight of the difunctional amine is approximately twice that of the monofunctional amine, this is approximately equivalent to a 95/5 weight ratio.

Since the DAO (MP = 50°C) and DDM (MP = 85°C) are solids at room temperature, they were melted at 60 and 90°C, respectively, and then combined with the other pre-heated component(s). Mass balances were 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 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, $T_g$) 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 near or above the ultimate $T_g$) for a further 12 h before cooling in the mould to room temperature. The specimens prepared with 100% An were too brittle to test (presumably because slight imbalances in stoichiometry produced a low

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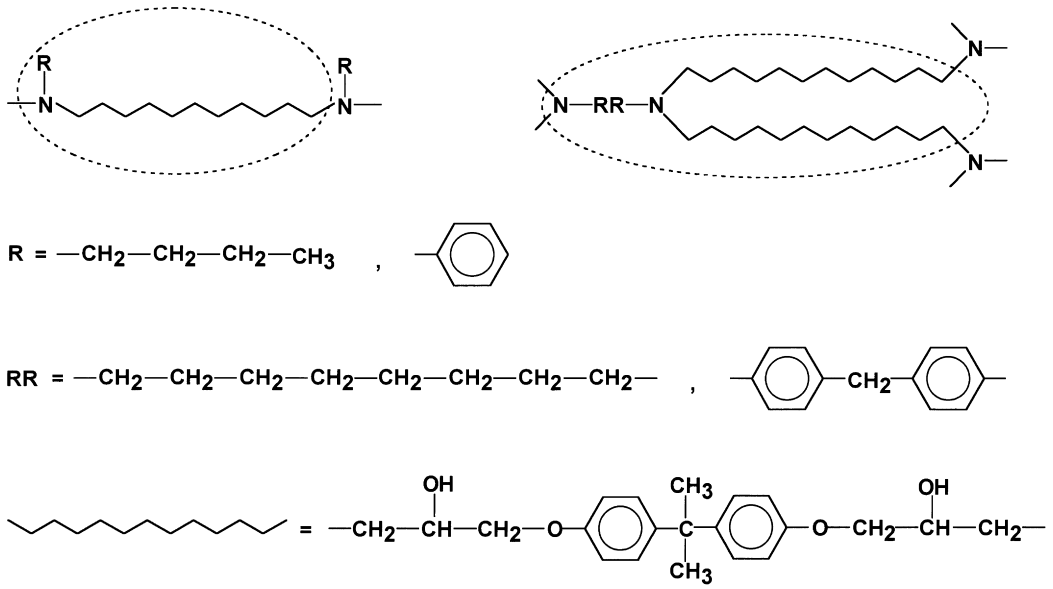

**Figure 1** Schematic of the idealized polymer structures. The dashed loop encloses the repeat units which were used to calculate the volume per pair of non-colinear bonds (equation (3))

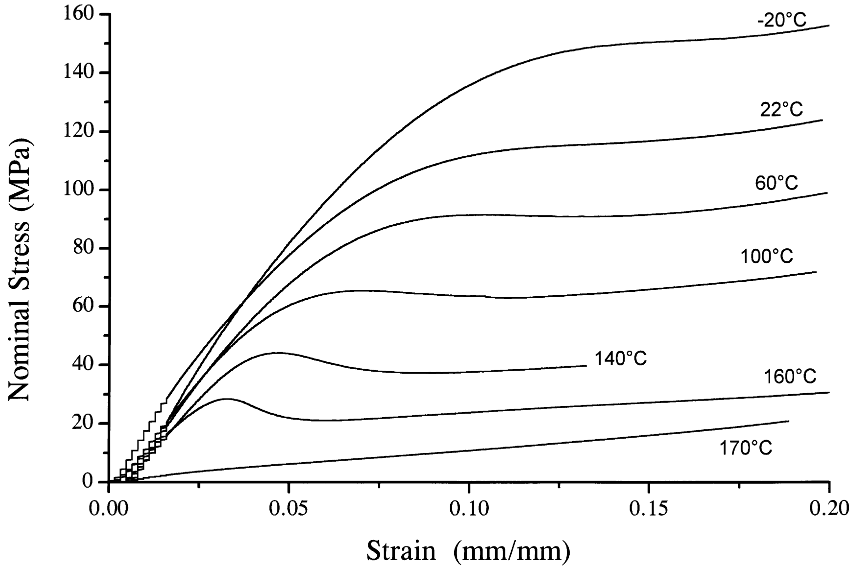

**Figure 2** Nominal stress–strain curves for the yielding of DGEBA/DDM at 0.0625 min$^{-1}$ and at various temperatures

molecular weight polymer) and so the low crosslink density analogue of DGEBA/DDM was prepared from a 95/5 ratio of An to DDM.

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 for brittle failure before it exhibits macroscopic yielding. Accordingly, uniaxial compression testing was used to determine the yield characteristics. 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. No lubricant was used between the surfaces. Testing was performed in duplicate or triplicate at temperatures ranging from −20 to 170°C and at nominal strain rates varying from $6.25 \times 10^{-4}$ to 62.5 min$^{-1}$ (crosshead speeds of between 0.01 and 1000 mm/min). The yield stress was defined as the point where the stress passed through a maximum or at the obvious 'knee' in the stress–strain curve (when a maximum in stress was not observed), with a maximum error of ± 3 MPa. The stress–strain data presented is uncorrected for changes in cross-sectional area or compliance in the testing rig.

The compressive modulus was determined from the stress–strain curves after correction for the compliance of the tensile testing machine and testing rig. Since the deflections are additive in the compression setup, the total stiffness ($K_T$) measured is given by the formula: $1/K_T = 1/K_{sample} + 1/K_{rig}$, where $K_{rig}$ is the stiffness of the machine and rig, and $K_{sample}$ is the true stiffness of the specimen. The stiffness of the rig was measured in compression using a steel specimen of the same dimensions as the polymeric specimens. Since steel has a modulus which is approximately 100 times that of the polymers studied in this paper, the relative deflection of the steel specimen can be

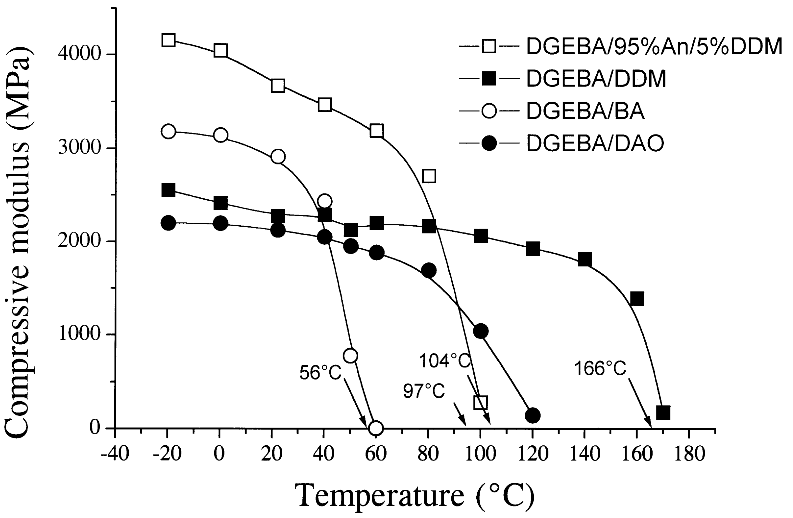

**Figure 3** Compressive modulus as a function of temperature at 0.0625 min$^{-1}$ for the systems DGEBA/BA, DGEBA/DAO, DGEBA/95%An/5%DDM, DGEBA/DDM. The $T_g$ values, determined by DSC (at 5°C/min)[5], are indicated

considered to be negligible (with an error of less than 1%) compared with the epoxy specimens at the same stress. From these measurements, the machine stiffness was determined to be $4.1 \times 10^4$ N/mm. This is much greater than the typical compressive stiffnesses of our specimens (for example, DGEBA/DDM is $9.93 \times 10^3$ N/mm at 22°C).

## RESULTS AND DISCUSSION

*Figure 2* shows the stress–strain behaviour of DGEBA/DDM as a function of temperature. As expected, the modulus (given by the initial gradient of the stress–strain curve) is relatively insensitive to temperature until close to the $T_g$ (166°C). The yield stress and the yield strain, however, decrease as the temperature is raised until, near the $T_g$, no yielding is observed in the sample.

The dependence of compressive modulus on temperature for pure resin systems is shown in *Figure 3*. The glass transition temperature measured by DSC corresponds well with the region where the modulus rapidly decreases. The figure also shows that the $T_g$ is increased by the rigidity of the aromatic structures and by the presence of crosslinks as expected[6]. It is interesting to note that in the glassy region, the moduli of the uncrosslinked systems are higher than those of the corresponding network, as has been found by others[7,8]. This suggests that the crosslinks separate the chains, thus lowering the intermolecular bonding and reducing the molecular rigidity, but the 22°C density was found to vary by only 1–2% and showed no systematic variation. However, it should be noted that other thermoset systems[9] have exhibited an increase in modulus with crosslinking. This inconsistency may be a result of the concomitant variation in composition as the crosslink density was varied.

### *Eyring equation*

According to the Eyring theory[1,10,11], yielding occurs by stress-activated jumps of molecular segments, known as flow units. The application of the stress effectively lowers the activation barrier to the jumping of these molecular units causing the flow units to move in a coordinated motion which is equated with yielding. In the Eyring theory, the shear ($\tau$) and uniaxial ($\sigma$) yield stress are predicted* to be logarithmically related to the shear strain rate $\dot{\gamma}$ [10]:

$$\tau = \frac{\sigma}{2} = \frac{\Delta H}{v_{\mathrm{flow}}} - \frac{\mathrm{k}T}{v_{\mathrm{flow}}} \ln\left(\frac{\dot{\gamma}_o}{\dot{\gamma}}\right) \tag{1}$$

where $v_{\mathrm{flow}}$ is the activation volume (or volume of the flow unit), $\Delta H$ is the activation energy, k is the Boltzmann constant, $T$ is the temperature and $\dot{\gamma}_o$ is a constant. Since $\dot{\gamma}_o \gg \dot{\gamma}$, this equation predicts a decrease in the yield stress with increased temperature, provided $\Delta H$ and $v_{\mathrm{flow}}$ are approximately constant. However, as illustrated in *Figure 4*, the yield stress–temperature relationship is not linear, in contrast to the prediction of the Eyring equation (equation (1)), with deviations from linearity being most obvious near the glass transition where the yield stress tends to zero. Similar results were obtained for 50/50 mixtures of the mono- and diamines.

When plotted *versus* $T_g - T$ (*Figure 5*), the yield stress data (in MPa) approximately obey a useful engineering rule:

$$\sigma = 0.70(T_g - T) + 30 \tag{2}$$

Such a relationship was suggested by the studies of Kambour[12] and is similar to that found by Tcharkhtchi *et al.*[13] for anhydride-cure epoxies, where the proportionality constant was 1.1 MPa/K. Fischer[14] has also noted a correlation between the yield stress and the glass transition temperature with a proportionality constant of 1.5 MPa/K for a series of bisphenol-A-cured DGEBA oligomers while for amine cured resins, Lesser and Kody[9] found the constant to be 0.5 MPa/K for DEGEBA cured with ethylene diamine derivatives.

The yield stress increases with crosslink density for each system and at all test temperatures which is consistent with previously reported yielding studies at 22°C[5]. Interestingly, the yield stresses of the aromatic amine-cured epoxies are not necessarily higher than the aliphatic systems since the $T_g$ of the DGEBA/95%An/5%DDM system (97°C) is lower than that for DGEBA/DAO (104°C). This observation illustrates that the molecular mobility is the most important

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* Note that the Eyring equation is often written in one of three forms[1,10,11] which differ from each other by a factor of 2 in the value of $v_{\mathrm{flow}}$ in equation (1)

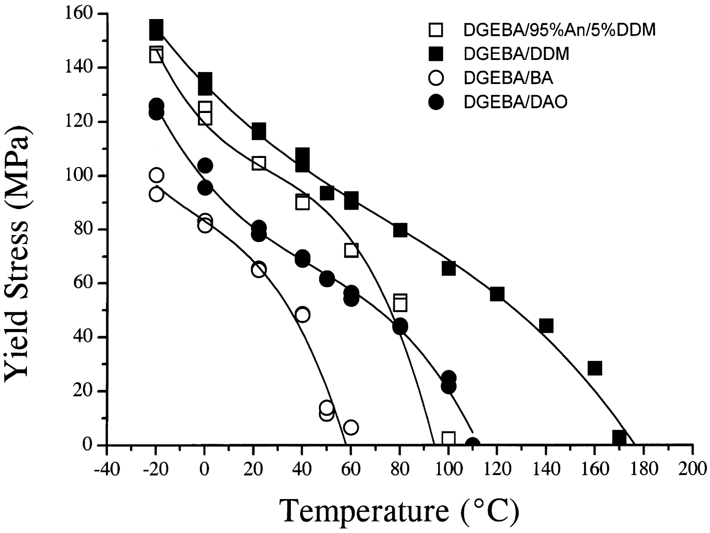

**Figure 4** Yield stress *versus* temperature at a strain rate of 0.0625 $\mathrm{min}^{-1}$ for the systems DGEBA/BA, DGEBA/DAO, DGEBA/95%An/5%DDM and DGEBA/DDM

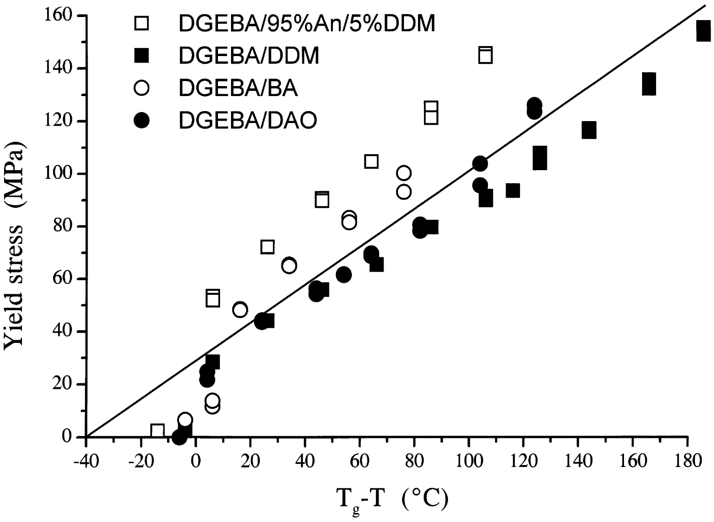

**Figure 5** Yield stress *versus* $T_g - T$

factor in determining the yield stress and that the main role of crosslink density on yielding is in its effect on molecular mobility and hence on the $T_g$, as suggested by Lesser and Kody[9]. It is interesting that the data in *Figure 5* can be grouped into two classes which represent the uncrosslinked and crosslinked polymers. This suggests that when compared in terms of the separation from $T_g$, the uncrosslinked materials have higher yield stresses than the crosslinked polymers. A similar trend appears to be evident in the data of Lesser and Kody[9] for DGEBA cured with substituted ethylene diamine monomers. The justification for using a plot of yield stress *versus* $T_g - T$ in *Figure 5* is the WLF equation[15] which effectively states that relative molecular mobility is only dependent on $T_g - T$. However, when the concept of corresponding states[16] is used and the yield stress plotted *versus* $T/T_g$, a similar trend is observed with the more highly crosslinked materials having lower yield stresses.

For each temperature, as shown in *Figure 6* for DGEBA/DDM, the yield stress rises with increasing strain rate and, as found previously[5], the stress is approximately linearly related to the logarithm of the strain rate over more than five decades, in accordance with equation (1). Similar results were obtained for resins prepared from DGEBA with the three other amines. From the slope of these lines, the Eyring activation volume can be calculated. In *Figure 7*, the activation volume is seen to increase as the temperature is raised. This behaviour can be rationalized on the basis that since the flow unit is the molecular segment involved in the cooperative process which results in yielding, and because increased temperature enhances the molecular mobility of the structure, the activation volume should increase as temperature is raised. Although not observed in the data, it might also be presumed that the activation volume should tend to infinity as the temperature approaches $T_g$, because at that temperature the whole structure is undergoing cooperative rearrangements. In fact, Melot *et al.*[17] have found that for unsaturated polyester resins, $v_{\mathrm{flow}}$ increases at an accelerating rate as the material approaches the glass transition region. In support of previous findings[5] at 22°C, the data in *Figure 7* do not show any systematic dependence of $v_{\mathrm{flow}}$ on crosslink density. It can be shown that this result is in accordance with the results of Galy *et al.*[18] for an epoxy system where

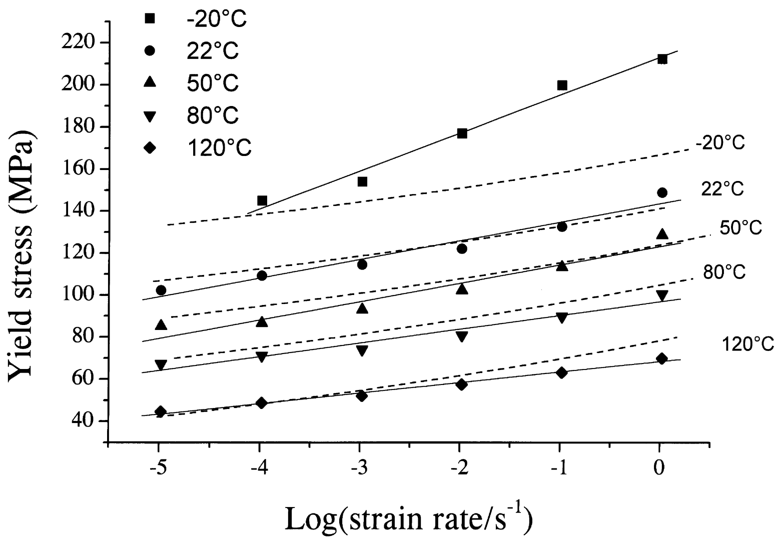

**Figure 6** Compressive yield stress *versus* the logarithm of compressive strain rate for DGEBA/DDM at various temperatures. The solid lines are fits of the Eyring equation[10] (equation (1)). The dashed lines are fits of the Robertson equation[19,20] (equation (3)) using the fitted parameters obtained from *Figure 8*

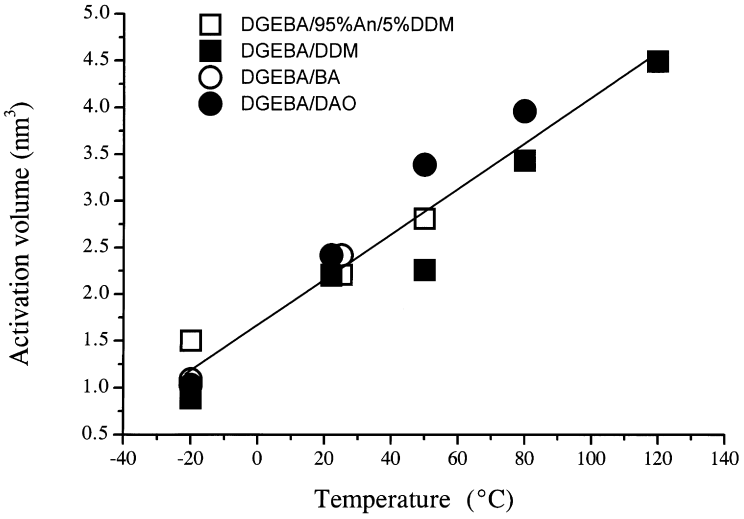

**Figure 7** Eyring's activation volume[10] *versus* temperature

the crosslink density was also varied without significant alteration in chemical composition.

*Robertson's theory*

The theory of yielding by Robertson[19,20] has many similarities to the simpler Eyring approach. The main concept in the Robertson theory[19,20] is that the application of a stress makes the material more liquid-like by increasing the ratio of gauche to trans bond conformations in the polymer towards that found at the glass transition temperature. The conditions for yielding are given by the following expressions which are implicit in stress and temperature and explicit in terms of strain rate:

$$\Theta = \Delta E\left\{ \mathrm{k}\ln\left(\frac{2\tau v}{\mathrm{k}T}\left[\ln\frac{1+\exp(-\Delta E+\tau v)/\mathrm{k}T}{1+\exp(-\Delta E/\mathrm{k}T_{\mathrm{g}})} + \left(\frac{\tau v}{\mathrm{k}T}+\frac{\Delta E}{\mathrm{k}T}-\frac{\Delta E}{\mathrm{k}T_{\mathrm{g}}}\right)\frac{\exp(-\Delta E/\mathrm{k}T_g)}{1+\exp(-\Delta E/\mathrm{k}T_g)}\right]^{-1} - 1\right)\right\}$$

$$\dot{\gamma}_{\max} = \tau\eta_{\mathrm{g}}^{-1}\exp\left[\frac{(-2.303c_1c_2\Theta)}{T(\Theta-T_{\mathrm{g}}+c_2)}+2.303c_1\right] \qquad (3)$$

Here $\Theta$ is the equivalent temperature of the glass when it is under the shear stress $\tau$, $v$ is the average volume of the chain segment containing two non-colinear bonds, $\eta_{\mathrm{g}}$ is the viscosity at $T_{\mathrm{g}}$ and is set at $10^{13.6}$ Pa s, $\Delta E$ is the flex energy between gauche and trans states and is given as $16T_{\mathrm{g}}$ J/K/mol (i.e. $2.65 \times 10^{-22}T_{\mathrm{g}}$ J/K/unit in equation (3)) and $c_1$ and $c_2$ are the WLF parameters with values of 17.44 and 51.6 K, respectively. For a polymer with a particular $T_{\mathrm{g}}$, equation (3) predicts the dependence of the yield stress on strain rate and temperature with only one independent variable, the chain segment volume ($v$), which can be theoretically calculated. However, because of the implicit nature of the equation, the volume parameter, $v$, was set at a particular value and an estimated value for stress was used to calculate an approximation for the strain rate. Based on the difference between the calculated and experimental strain rate, an improved estimate for the stress was made and re-substituted in the equation. This

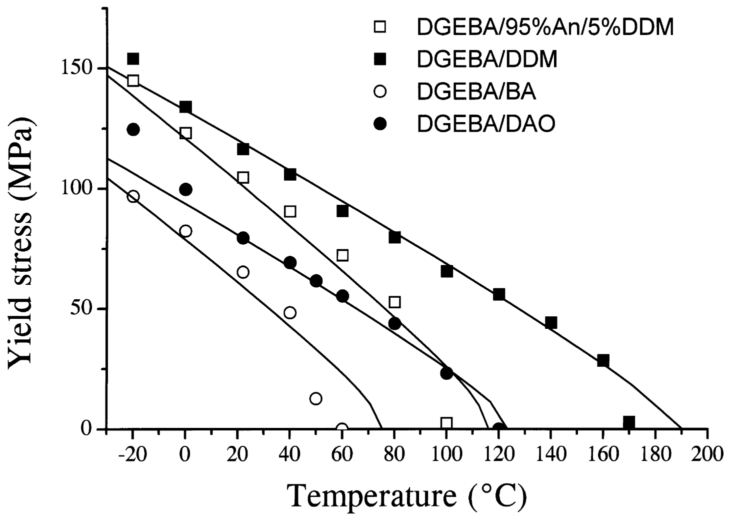

**Figure 8** Yield stress *versus* temperature at a strain rate of 0.0625 $\mathrm{min}^{-1}$ for the systems DGEBA/BA, DGEBA/DAO, DGEBA/95%An/5%DDM and DGEBA/DDM compared with the predictions (solid lines) of the Robertson equation[19,20] (equation (3)) with the listed values of the parameter $v$

**Table 1** Parameters obtained from yielding theories

| Polymer | $T_g$ (°C) | $v^a$ ($\mathrm{nm}^3$) theoretical | $v^a$ ($\mathrm{nm}^3$) experimental | $A^b$ | $B^b$ (MPa/K) | $a^b$ (nm) | $b^c$ (nm) |
|---|---|---|---|---|---|---|---|
| DGEBA/BA | 56 | 0.100 | 0.125 | 0.11 ± 0.01 | 0.16 ± 0.05 | 0.46 ± 0.07 | 0.34 ± 0.04 |
| DGEBA/DAO | 104 | 0.072 | 0.150 | 0.19 ± 0.02 | 0.23 ± 0.05 | 0.49 ± 0.05 | 0.49 ± 0.06 |
| DGEBA/95%An/5%DDM | 97 | 0.100 | 0.110 | 0.11 ± 0.01 | 0.17 ± 0.02 | 0.45 ± 0.03 | 0.33 ± 0.13 |
| DGEBA/DDM | 166 | 0.088 | 0.146 | 0.20 ± 0.01 | 0.22 ± 0.01 | 0.50 ± 0.01 | 0.55 ± 0.10 |

[a] Robertson's theory. [b] Argon's theory. [c] Bowden's theory

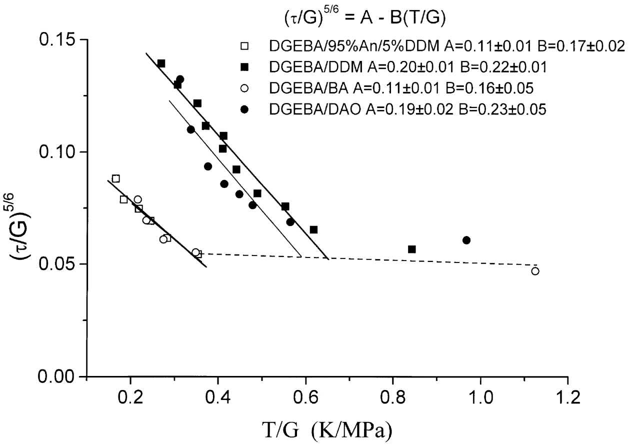

**Figure 9** Analysis of the yield stress data according to the Argon model[21,22] (equation (4))

process was iterated until the calculated and experimental strain rates agreed. This process was repeated at a range of temperatures to give the predicted thermal dependence of yield stress. This curve was compared with the experimental data and the magnitude of the volume parameter, $v$, was varied until optimal agreement in the calculated and experimental yield stresses was obtained.

The fit of this model to the yield stress data is shown in *Figure 8*. In this calculation, the shear stress was equated[19,20] to half of the compressive stress and the shear strain rate was equated to $\sqrt{2}$ times the uniaxial strain rate. Unlike the Eyring model, the Robertson theory[19,20] specifically predicts a nonlinear dependence of yield stress on temperature and the fits in *Figure 8* are produced with only one adjustable parameter, the volume $v$, given in *Table 1*. In most cases the theory predicts that the yield stress extrapolates to zero at a higher temperature than exhibited by the experimental data. This may be due to the use of a fixed 'universal' value for $c_2$ which is known to vary with differing polymer systems[15]. Equation (3) also allows the prediction of the strain rate dependence of the yield stress illustrated in *Figure 6*. Although the data are not well fitted at low temperatures, the fit is adequate in the higher temperature region with no other adjustable parameter.

Although the Robertson theory is reasonably successful in fitting the yield stress data and the volume parameter, $v$, is of the correct magnitude, it does not show the correct variation with crosslink density. Assuming ideal structures for the monomers and resins and using the densities determined at 22°C (which vary between 1.136 and 1.192 $\mathrm{g/cm^3}$), $v$ is calculated to be 0.100, 0.072, 0.100 and 0.088 $\mathrm{nm}^3$ for DGEBA/BA, DGEBA/DAO, DGEBA/An and DGEBA/DDM, respectively (see *Figure 1*). For simplicity, the slight difference between DGEBA/An and DGEBA/95%An/5%DDM is neglected here. These calculated values for the volume per two non-colinear bonds show the opposite trend to that displayed by the values giving the best fit to the data (*Table 1*). There are two possible reasons for the disagreement between theory and experiment. Firstly, in the theory, side chains are not considered to be involved in the gauche to trans bond flexing process although they will bear some of the external stress. However, inclusion of these bonds in the calculation would only decrease the theoretical values for the uncrosslinked polymers. A more likely cause is that the analysis assumes an equality of the various types of

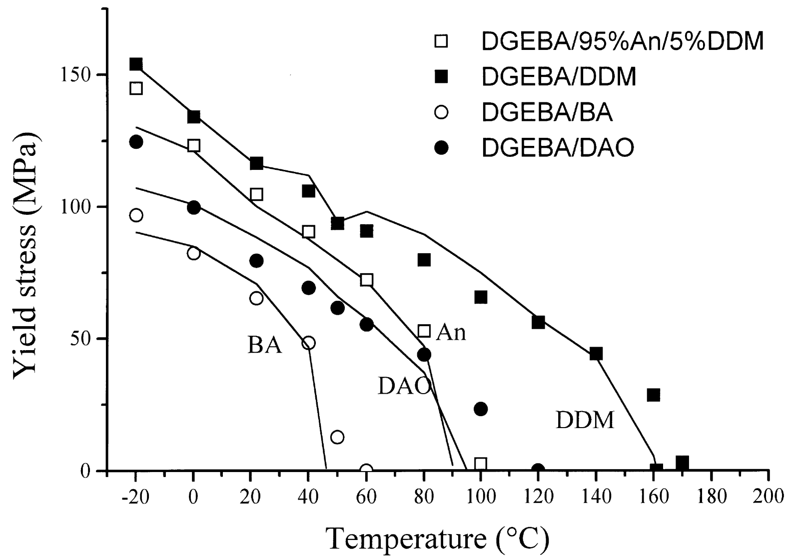

**Figure 10** Fit of the Argon theory[21,22] to the yield stress *versus* temperature data. The points are experimental values and the solid lines are the fit using the parameters $A$ and $B$ and the experimental compressive modulus data

chain bonds and of the network strand types in the yielding process. In particular, since the crosslinking process restricts the number of chain configurations available, the actual number of flexing bonds should be reduced and the calculated volume per two non-colinear bonds of the crosslinked polymers should be larger than that calculated in *Table 1*, thus bringing the values into better agreement.

### *Argon's theory*

Argon[21,22] has suggested that yielding can be considered to arise by the formation of pairs of molecular kinks (such as in the formation of a crankshaft defect) and that the work done by the stress applied to the polymer is opposed by the intermolecular resistance to chain flexing. This results in the relationship:

$$\left[\frac{\tau}{G}\right]^{5/6} = A - B\left[\frac{T}{G}\right] \tag{4}$$

where $A$ is related to the ratio of $\tau$ to the shear modulus $G$ at 0 K, and $B$ is another constant in providing the temperature dependence of $\tau$. The constants $A$ and $B$ are given by:

$$A = \left(\frac{0.077}{1-\nu}\right)^{5/6} \tag{5}$$

$$B = A\frac{16(1-\nu)k}{3\pi\omega^2 a^3}\ln\left(\frac{\dot{\gamma}_o}{\dot{\gamma}}\right)$$

where $\nu$ is Poisson's ratio, $\omega$ is the angular rotation (in radians) between the initial and activated position, and $a$ is the average radius of one chain. If $\nu$ is taken to be 0.35, the parameter $A$ should be 0.169.

Following the approach of others[7,23], equations (4) and (5) were fitted to the compressive yield stress and compressive modulus ($E$) data and typical fits to the data are shown in *Figure 9*. The shear modulus was calculated using $G = E/2(1 + \nu)$ and the effective shear stress was taken to be $\tau = \sigma/\sqrt{3}$ in accordance with other workers who have applied Argon's theory[7,23]. This is effectively assuming that yield is caused by a critical value of the deviatoric stress (a von Mises criterion[11]) rather than the critical resolved shear stress (Tresca) criterion[11] assumed in the Eyring and Robinson formulations (which used $\tau = \sigma/2$). As noted by other workers[7,23], the fit is reasonable at low temperatures but the data deviate significantly from the fitted line at high temperatures (high values of $T/G$). The values of the parameters $A$ and $B$ are listed in *Table 1* and are similar to the values found by other studies on epoxy resins[7] and bismaleimide/unsaturated polyester blends[23]. The parameter $A$ is close to the theoretical value of 0.169 (for $\nu = 0.35$), but varies with crosslink density as found by Yamini and Young[7]. The parameter $B$ also shows a dependency on crosslinking. Also shown in *Table 1* is the molecular radius of the chain calculated from the fitted values of parameters $A$ and $B$ and assuming[7] $\omega = 2$ radians and $\dot{\gamma}_o = 10^{13}\,\mathrm{s}^{-1}$. Within experimental error, this parameter is constant at 0.5 nm which is similar to that found by other workers[7,22,23]. Although this value is of the correct magnitude for the diameter of a chain, it is not clear how an accurate theoretical value can be calculated for comparison with the fitted value. *Figure 10* shows the fit to the data using the Argon theory. The fitted lines are stepped due to the discontinuous nature of the modulus data. As observed by other workers[7,23], the prediction is quite good in the low temperature region but is poor in the high temperature region, where the yield stress is underestimated.

### *Bowden's theory*

In this theory[24], it is assumed that yielding starts by the nucleation of a thermally activated disc-shaped sheared region which grows in size as the stress is increased. Strictly for mathematical convenience, the analysis is expressed in terms of dislocation theory. The energy of the dislocation loop is expressed in terms of its radius which grows under the combined action of thermal energy and an increasing shear stress. The critical energy of the dislocation $U_c$ is given by[7,23,24]:

$$U_c = \left[\frac{Gb^2R_c}{4}\right]\left[\ln\left(\frac{2eR_c}{b\sqrt{3}}\right) - 1\right] \tag{6}$$

where $b$ is the Burgers vector of the shear displacement, $G$ is

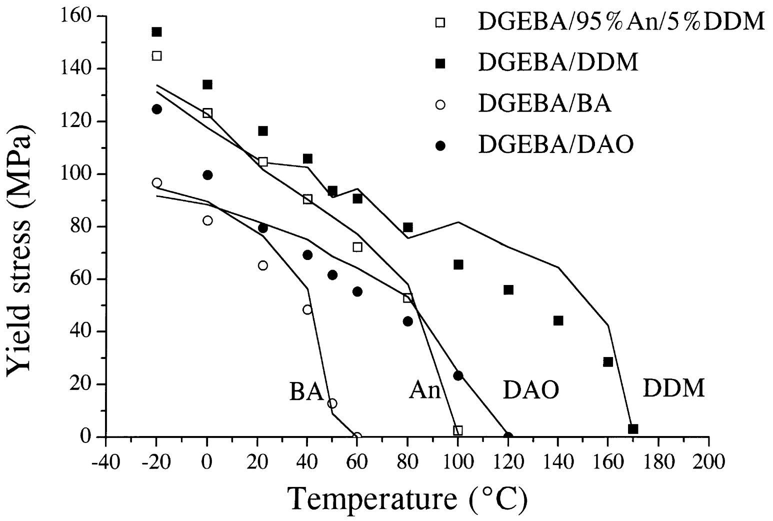

**Figure 11** Fit of Bowden's theory[24] to the yield stress *versus* temperature data

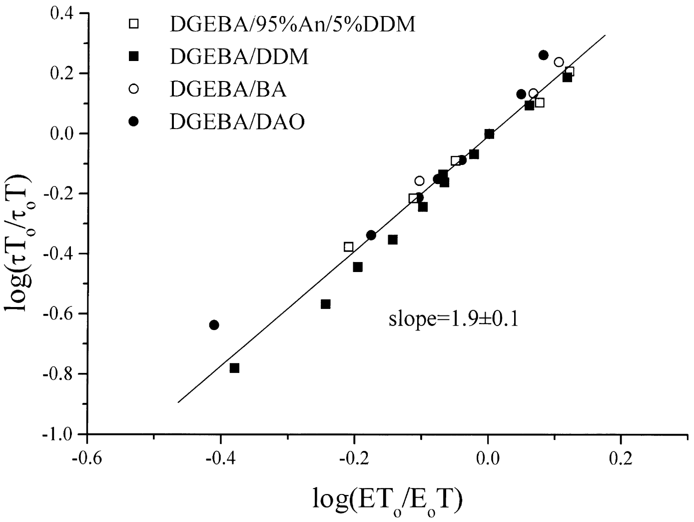

**Figure 12** Plot of the modulus and yield stress data according to the Kitagawa equation[25] where $T_o$ was taken to be 22°C

the shear modulus, $e$ is Euler's constant and $R_c$ is the critical radius of the dislocation loop, given by:

$$R_c = \frac{Gb}{4\pi\tau}\left[\ln\left(\frac{2eR_c}{b\sqrt{3}}\right)+1\right] \qquad (7)$$

Bowden[24] assumes that yielding occurs when $U_c$ reaches an energy of 50 kT. By using this value for $U_c$ at each temperature, equations (6) and (7) can be solved for $\tau$ using the numerical values of $G$ and an appropriately chosen value for $b$. As with the Argon analysis, $G$ and $\tau$ were calculated from the compressive modulus and yield stress. The fitting of the data to equations (6) and (7) was achieved using the elegant algorithm given by Abbate *et al.*[23]. The fitted values for the parameter $b$, listed in *Table 1*, increase with crosslink density as has been observed previously[7] but the explanation for this behaviour in unknown. The fitted lines (which are stepped due to the noncontinuous nature of modulus data) are given in *Figure 11*. As found by other workers[7,23], the theory approximately fits the experimental results over all of the temperature range.

Bowden's theory[24] has been extended by Kitagawa[25] who predicts that a power-law relation should exist between the yield stress and the modulus†:

$$\frac{\sigma T_o}{\sigma_o T} = \left[\frac{ET_o}{E_o T}\right]^n \qquad (8)$$

Here $n$ is an exponent while $\sigma_o$ and $E_o$ are the uniaxial yield stress and modulus at the reference temperature, $T_o$, which is usually chosen to be room temperature. In *Figure 12*, the data are plotted according to equation (8). The data are reasonably well fitted by the line at low temperatures but deviate from the line at high temperatures (these data lie beyond the region of the plot shown in *Figure 12*). For the low temperature data the exponent in equation (8) is 1.9 ± 0.1. This compares with previously found values of 0.9 for semicrystalline polymers[25] and 1.6 for many amorphous materials and thermosets[23–25].

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† Note that this expression is usually written in terms of shear stress and shear modulus [25].

## CONCLUSIONS

The yielding behaviour of a series of model epoxy networks was investigated so as to separate the effect of crosslinking from that caused by compositional variations. In all cases, the yield strain and yield stress decreased with increased temperature, until at the $T_g$ no yielding was observed. At each temperature and for both amine series, the yield stress increased with raised crosslink density. At low temperatures, the epoxies cured with aromatic amines exhibited a higher yield stress than those with the aliphatic amine systems. However, this trend was not followed at temperatures approaching the $T_g$, suggesting that the molecular mobility, indicated by proximity to $T_g$, is the controlling factor on yielding and that crosslinking only has an indirect role. Thus when plotted *versus* $T_g - T$, the yield stress data approximately fell onto a common line with a slope of 0.70 MPa/K.

When analysed in terms of the Eyring equation[10], the activation volume was relatively insensitive to crosslink density or amine structure but increased as temperature was raised. The Eyring equation was inadequate at quantitatively describing yielding because it did not predict the nonlinear dependence of yield stress on temperature and because it failed to provide any molecular prediction of the magnitude of the activation volume. The Robertson theory[19,20] provided an approximate prediction of the dependence of yield stress on temperature and strain rate with only one adjustable but molecularly based parameter. However, this parameter did not vary with crosslinking as expected from the theory, possibly due to the assumption that all chain bonds make an equal contribution in the yielding process. The Bowden[24] theory appears to predict the yield stress from the modulus over a wider temperature range than the Argon theory[21,22] but both involve parameters which, while molecularly based, are not independently calculable.

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## REFERENCES

1. Crist, B., *Materials Science and Technology*, Vol. 12, ed. R. W. Cahn, P. Hansen and E. J. Kramer. VCH, New York, 1993, Chapter 10.
2. Scherzer, T., *Polymer*, 1996, **26**, 5807.
3. Oleynik, E. F., in *High Performance Polymers: Structure, Properties, Composites, Fibres*, ed. E. Baer and A. Moet. Hanser, Munich, 1991, p. 79.
4. Lovell, P. A., *TRIP*, 1996, **4**, 264.
5. Mayr, A. E., Cook, W. D. and Edward, G. H., accepted for publication in *Polymer* (1997).
6. Charlesworth, J. M., *J. Macromol. Sci. Phys.*, 1987, **B26**, 105–133.
7. Yamini, S. and Young, R. J., *J. Mater. Sci.*, 1980, **15**, 1814.
8. Vallo, C. I., Frontini, P. M. and Williams, R. J. J., *Polym. Gels Networks*, 1993, **1**, 257.
9. Lesser, A. J. and Kody, R. S., *J. Polym. Sci. B, Polym. Phys. Edn.*, 1997, **35**, 1611.
10. McCrum, N. G., Buckley C. P. and Bucknall, C. B., *Principles of Polymer Engineering*. Oxford Science Publishers, New York, 1992, p. 174.
11. Ward, I. M., *J. Mater. Sci.*, 1971, **6**, 1397.
12. Kambour, R. P., *Polym. Commun.*, 1983, **24**, 292.
13. Tcharkhtchi, A., Faivre, S., Roy, L. E., Trotignon, J. P. and Verdu, J., *J. Mater. Sci.*, 1996, **31**, 2687.
14. Fischer, M., *Adv. Polym. Sci.*, 1992, **100**, 313.
15. Ferry, J. D., *Viscoelastic Properties of Polymers*, 2nd edition. Wiley, New York, 1970, p. 316.
16. Hirschfelder, J. O., Curtiss C. F. and Bird, R. B., *Molecular Theory of Gases and Liquids*. John Wiley and Sons, New York, 1967, Chapter 4.
17. Melot, D., Escaig, B., Lefebvre, J. M., Eustache, R. P. and Laupretre, F., *J. Polym. Sci., Polym. Phys.*, 1994, **32**, 1805.
18. Galy, J., Gerard, J. F., Sautereau, H., Frassine, R. and Pavan, A., *Polym. Networks Blends*, 1994, **4**, 105.
19. Robertson, R. E., *J. Chem. Phys.*, 1966, **44**, 3950.
20. Robertson, R. E., *Appl. Polym. Symp.*, 1968, **7**, 201.
21. Argon, A. S., *Phil. Mag.*, 1973, **28**, 839.
22. Argon, A. S. and Bessonov, M. I., *Polym. Eng. Sci.*, 1977, **17**, 174; *Phil. Mag.*, 1977, **35**, 917.
23. Abbate, M., Martuscelli, E., Musto, P. and Ragosta, G., *Die Ang. Makromol. Chemie*, 1996, **241**, 11.
24. Bowden, P. B. and Raha, S., *Phil. Mag.*, 1974, **29**, 149.
25. Kitagawa, M., *J. Polym. Sci., Polym. Phys Ed.*, 1977, **15**, 1601.