

Ageing and yielding in model epoxy thermosets

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Abstract

The effect of physical ageing on the d.s.c. heat flow and yielding behaviour has been investigated for two series of epoxy resins in which the crosslink density is varied without significant compositional variation. At low degrees of undercooling, the extent of enthalpic ageing approached a thermodynamic limit with increased ageing time, but at larger degrees of undercooling, full densification was not achieved in the time-scale of the experiments due to kinetic control of the ageing process. At constant degree of undercooling, the relaxation enthalpy decreased as the crosslink density was raised, which is attributed to topological restrictions on the process of segmental re-organization leading to densification. However, neither crosslink density nor amine nature appeared to significantly affect the ageing kinetics when measured at the same degree of undercooling. The influence of ageing on the room temperature yield stress was also investigated. Even though the yield stress increased with crosslink density, the influence of ageing on the yield stress was reduced. The time-scales for enthalpic ageing and yield stress enhancement did not appear comparable. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

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 (T_g) which result from the highly crosslinked network structures. Unfortunately (and in common with thermoplastic polymers) when thermosets are continuously exposed to elevated temperatures close to the T_g for prolonged periods, they undergo embrittlement known as physical ageing [1].

The conventional methods of measuring physical ageing in polymers (particular epoxy resins) include volumetric [2–4], free volume [5] and enthalpy techniques [2,3,6–11], but the phenomenon also has been studied by changes in mechanical properties such as viscoelasticity [2–4,8,12–14], yielding [2,3,8,9,15–18] and fracture behaviour [2,8,19]. In general it has been concluded [1] that the ageing phenomenon is caused by molecular segmental rearrangement causing collapse of free volume, densification of the structure and the approach of the material to the equilibrium thermodynamic state. Although it has been commonly believed [1,18,20] that physical ageing can be reversed by

the application of large stresses, McKenna and co-workers [12,21] have produced data which challenge this theory.

The influence of crosslinking of epoxy resins on the ageing phenomenon has been investigated by varying the curing time and temperature [6,10,17], as well as by varying the functionality of the crosslinker [22] or molecular weight between crosslinks [14,15]. However, the properties of crosslinked polymers (such as the glass transition temperature [23] or fracture toughness [24]) depend on the chemical composition as well as the molecular architecture or topology of the network. Because changes in crosslink density invariably result in a change in the chemical composition of the system, it is usually difficult to separate the two effects. Here, a method of systematically varying the crosslink density with minimal compositional change has been used to investigate the factors affecting the enthalpic ageing and yield behaviour of crosslinked epoxy polymers.

2. Experimental

The epoxy resin used in the study, the diglycidyl ether of bisphenol-A (DGEBA), was supplied as GY 2600 by Ciba-Geigy and had a molecular weight of 375 g mol^{-1} (as determined by HBr titration [25], assuming a bifunctional

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monomer) which compares with the suppliers range (372–380 g mol⁻¹) and the theoretical value of 340 g mol⁻¹ for pure DGEBA (see Fig. 1). The aliphatic curing agents, butylamine (BA, MW = 73 g mol⁻¹, supplied by Merck) and its dimeric analogue, diamino-octane (DAO, MW = 144 g mol⁻¹, supplied by Aldrich), and the aromatic curing agents, aniline (An, MW = 93 g mol⁻¹, supplied by Unilab) and the dimeric analogue, diaminodiphenyl methane (DDM, MW = 198 g mol⁻¹, supplied by Aldrich) were of standard laboratory grade and were dried with 4 Å molecular sieves before use. The structures of the curing agents are also shown in Fig. 1, along with a schematic illustration of the development of an amine-cured epoxy.

The DGEBA epoxy was cured with the amine mixtures, BA/DAO or An/DDM using stoichiometric ratios of amino-hydrogen and epoxide groups (based on the titration results). Ratios of the monofunctional (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, the molecular weight of the difunctional amine is approximately twice that of the monofunctional amine, so that a 50/50 ratio 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 pre-heated DGEBA. Mass balances were monitored so that any evaporation by the volatile BA or An amines could be corrected. Following thorough mixing, the epoxies were then poured into PTFE moulds 10 mm diameter by 20 mm high. The DGEBA/An/DDM materials were cured at 70°C/16 h and postcured at 160°C/2 h, while the DGEBA/BA/DAO were cured 50°C/16 h and postcured at 120°C/2 h, and then were cooled slowly in the mould.

Studies of the change in enthalpy on ageing were performed on small samples (5–10 mg) of the cured resins with a Perkin-Elmer DSC7. The samples were heated in the d.s.c. to a de-ageing temperature located at 20–40°C above the T_g , and after 5 min of equilibration the sample was rapidly cooled (using a Perkin-Elmer Intracooler where necessary) to a predetermined ageing temperature (T_a) below T_g for a particular ageing period. The sample was then rapidly cooled (at the maximum cooling rate) to room temperature (or below) and the sample re-scanned back to the de-ageing temperature at 10°C min⁻¹, thus recording the heat capacity trace of the physically aged material. The heat capacity trace for unaged material was obtained by rapidly cooling from above the T_g to a sub-ambient temperature and then immediately scanning at

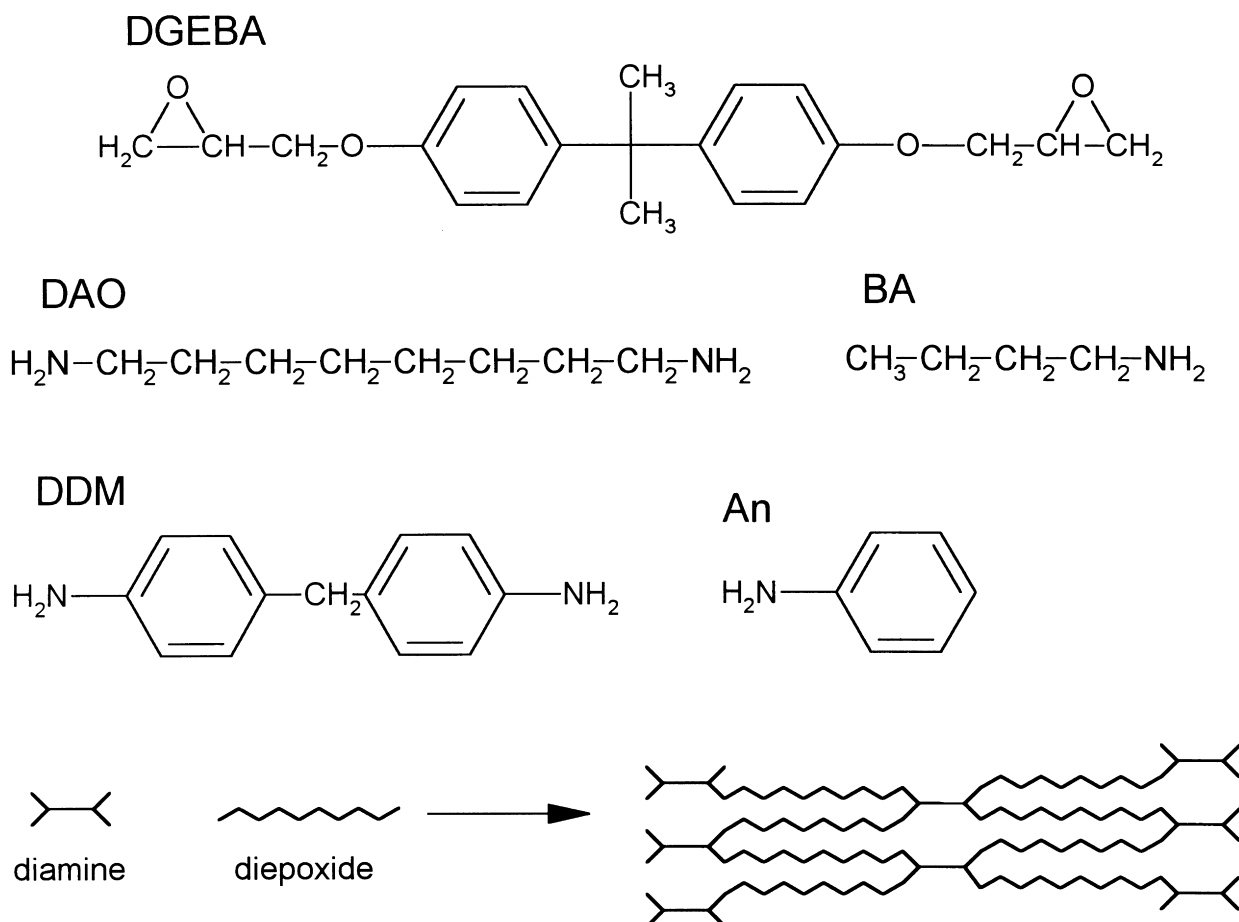


Fig. 1. Structure of the monomers used and a schematic illustration of the development of an amine-cured epoxy.

10°C min⁻¹ through the glass transition region. The effect of ageing on the heat flow curve was determined [7,26] by matching the heat capacity of aged and unaged samples at temperatures well below T_g and well above T_g , and subtracting the heat capacity curves. The relaxation enthalpy was then obtained by integrating the resulting difference curve, using the Perkin-Elmer DSC software.

The effect of ageing on the compressive stress–strain behaviour was also investigated on cylindrical specimens machined to 10 mm diameter and 16 mm high. To reduce oxidation of the cylindrical specimens during ageing, the specimens were enclosed in aluminium foil (which still allowed rapid heat transfer). Each specimen was first de-aged at a temperature 20–40°C above the polymer's T_g for 30 min. Specimens selected for ageing were then rapidly transferred to another oven at a preset ageing temperature and aged for periods of up to 4 weeks. After the ageing period had elapsed, the specimens were rapidly cooled to room temperature by quenching in ice water and then allowed to reach thermal equilibrium before testing. To verify that the polymer was not chemically changed during physical ageing, some of these aged specimens were subsequently de-aged above their T_g and rapidly quenched in ice water prior to compression testing at room temperature.

The stress–strain measurements were performed at $22 \pm 1^\circ\text{C}$ with an Instron 4505 tensile testing machine in compression mode, using a strain rate of 0.0625 min⁻¹ (crosshead of 1 mm min⁻¹). No correction has been made for the compliance of the compression rig and so the strain is overestimated by approximately 30%. The yield stress was

defined at 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 ± 2 MPa. It was found that the specimens of the linear polymer DGEBA/An were extremely brittle (possibly due to low molecular weights caused by slight imbalances in stoichiometry) but suitable specimens could be prepared by the addition of a small amount (5 mol% based on amino hydrogen groups) of the crosslinking amine, DDM, which allowed yield strength measurements to be obtained.

3. Results and discussion

3.1. Enthalpy behaviour

As shown previously by scanning differential calorimetry [27], the polymerization rates of DGEBA/BA and DGEBA/DOA are almost equal. Similarly, DGEBA/DDM polymerizes only slightly faster than DGEBA/An due to the induction effect of the methylene bridge [28] in DDM. Thus these two systems are ideal for separating the influence of crosslink density from compositional changes on the physical ageing process.

The dependence of T_g and the heat capacity step (ΔC_p , the difference in gradients of the glassy and liquid enthalpies) on crosslink density is illustrated in Fig. 2. As discussed elsewhere [23,28], the T_g increases with increased crosslinking due to the restriction on molecular mobility imposed

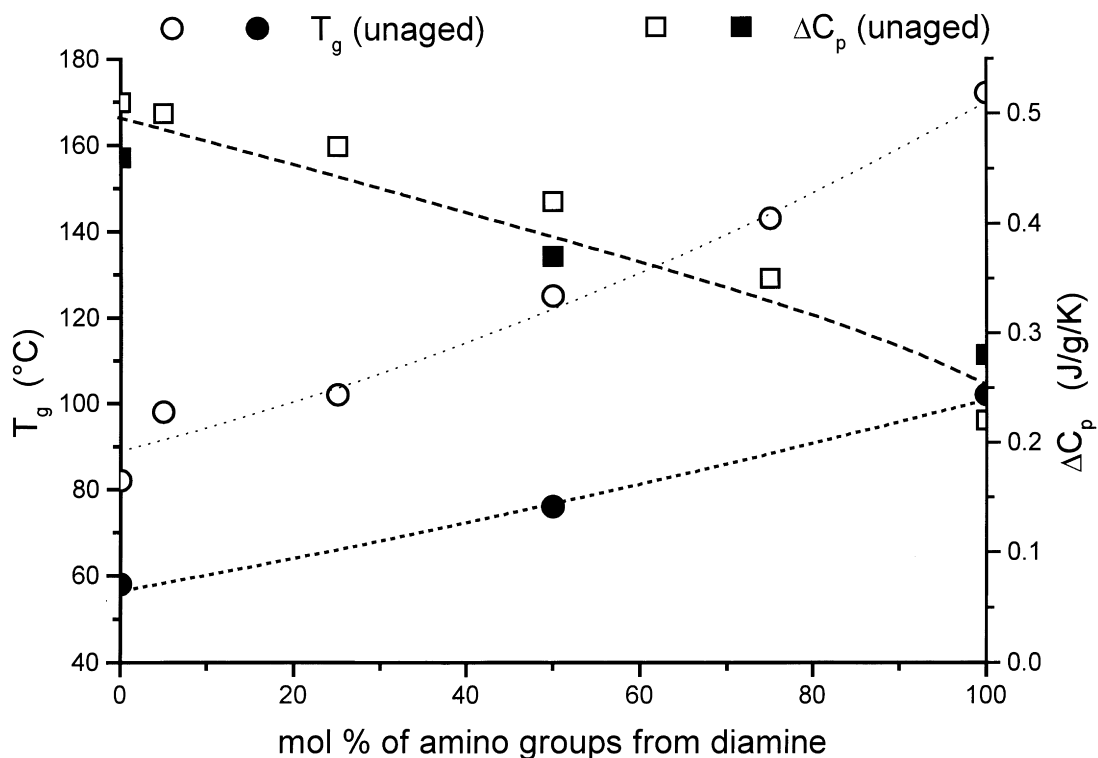


Fig. 2. Effect of composition on the T_g and ΔC_p of unaged DGEBA/An/DDM (open symbols) and DGEBA/BA/DAO (closed symbols) systems.

by the crosslinks. The heat capacity step decreases with increased crosslinking, but shows little dependence on the nature of the amine curative. Montserrat observed a similar dependence of ΔC_p on crosslink density for epoxy resins with varying extents of cure, and attributed it to the reduced configurational entropy of the more crosslinked systems [29]. In contrast, Lee and McKenna [22] found no dependence of ΔC_p on crosslink density, but this apparent discrepancy may be due to the fact that in that study [22], the chemical composition was also varying.

The influence of ageing time on the heat flow is shown for DGEBA/An and DGEBA/DDM in Fig. 3 and for DGEBA/BA and DGEBA/DAO in Fig. 4. For very short ageing times, the heat flow passes through a sigmoidal step due to the glass transition; however, as the ageing time increases, an ageing endotherm is superimposed on the sigmoidal step as observed by others [1–3,6–11]. As schematically illustrated in Fig. 5, this maximum is caused by an enthalpy overshoot (often called the relaxation enthalpy) which increases in size with increased ageing. As the samples are aged, the temperature corresponding to the heat capacity peak tends to rise, as has been found elsewhere for epoxy networks [6–11,16]. At long ageing times and at low degrees of undercooling (as defined by $T_g - T_a$) the magnitude of the enthalpy overshoot tends to approach a

constant value as shown in Fig. 4 for DGEBA/BA aged at 50°C and DGEBA/DAO aged at 90°C for 960 min. Similar behaviour has been observed by other workers [6,7,26] at ageing temperatures close to the T_g , and this suggests that the samples have nearly attained equilibrium at these low degrees of undercooling.

Figs 3 and 4 also reveal that the extent of ageing is reduced for the more highly crosslinked systems (DGEBA/DAO and DGEBA/DDM). This was generally observed for all the epoxy samples when compared at constant degrees of undercooling (constant $T_g - T_a$), suggesting that the number of potential molecular rearrangements which lead to densification (ageing) are reduced as the crosslink density increases, presumably because the crosslinks restrict the range of molecular motions allowed.

The kinetics of the ageing phenomenon are quantified in Figs 6 and 7. As noted above, the extent of the ageing process decreases as the crosslink density rises. However, the rate of the molecular rearrangements does not appear to be so much affected by crosslinking, and so similar dependencies on the logarithm of ageing time are observed. This observation can be rationalized in simple terms by consideration of the WLF equation:

$$\tau = \tau_g \exp\{-2.303c_1(T - T_g)/(T - T_g + c_2)\} \quad (1)$$

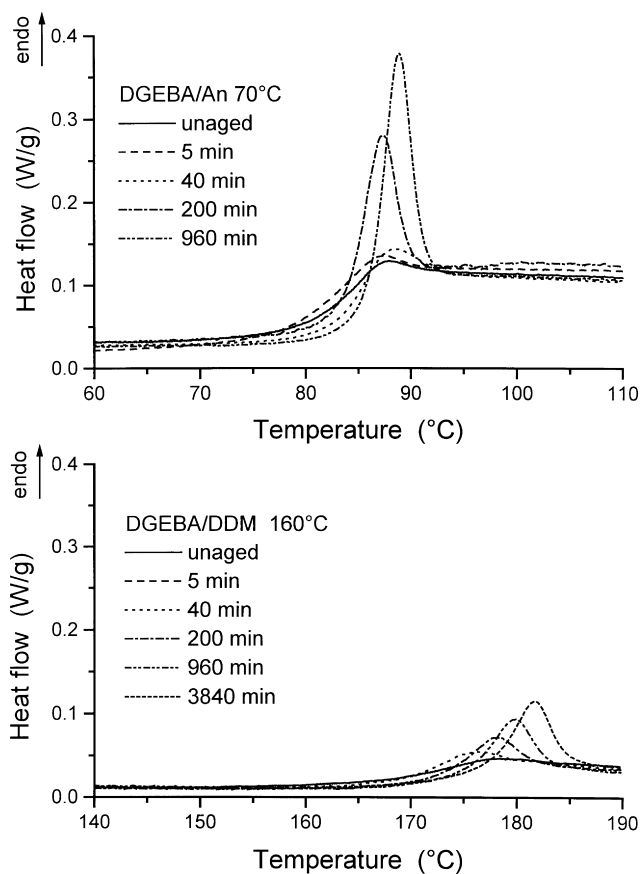


Fig. 3. Temperature dependence of heat flow for DGEBA/An and DGEBA/DDM aged for varying times at 70°C (undercooling 12°C) and 160°C (undercooling 12°C), respectively.

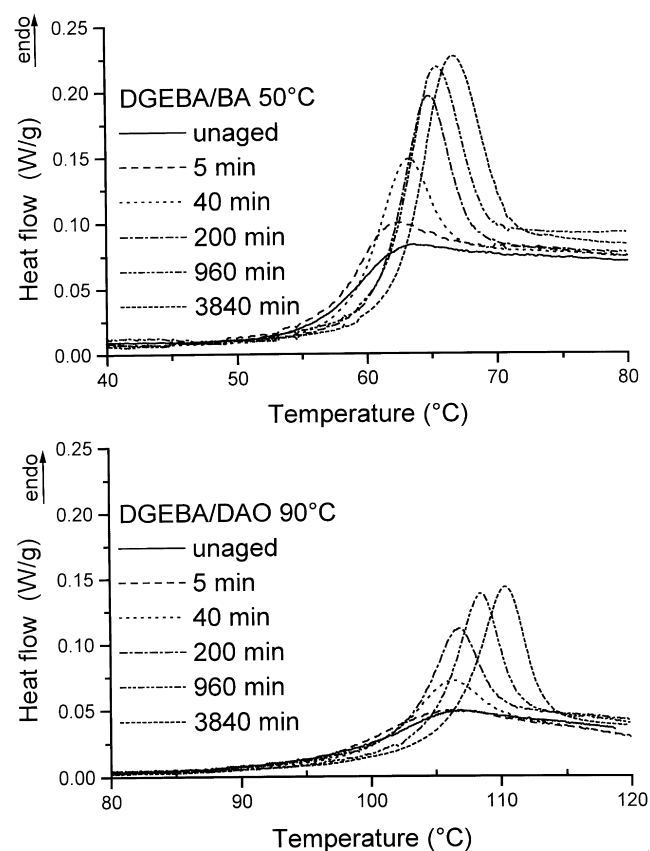


Fig. 4. Temperature dependence of heat flow for DGEBA/BA and DGEBA/DAO aged for varying times at 50°C (undercooling 8°C) and 90°C (undercooling 12°C), respectively.

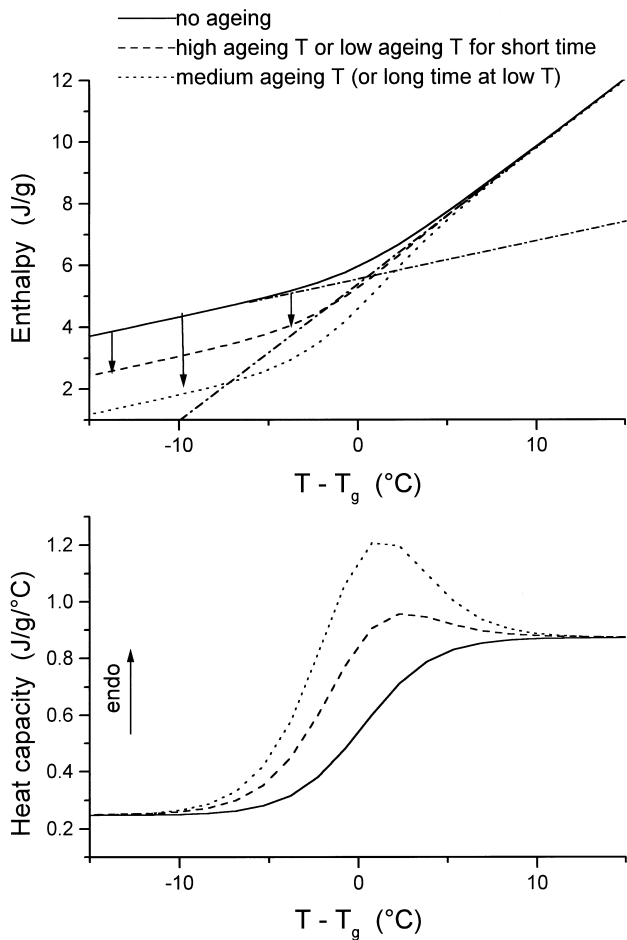


Fig. 5. Schematic of temperature dependence of enthalpy and heat capacity for systems aged at low, intermediate and large degrees of undercooling.

where τ and τ_g are the relaxation times at temperatures T and T_g and c_1 and c_2 are the 'universal' constants. Eq. (1) predicts that, at a certain degree of undercooling, the relaxation time and hence the rate of molecular mobility, should be constant. Since ageing relies on molecular mobility, this suggests that the rate of physical ageing should also be constant. Bauwens-Crowet and Bauwens [30] have derived an expression for ageing based on free volume and activation concepts which is consistent with the simple concepts expressed above. Furthermore, these workers have suggested [26] that, as a first approximation, the relaxation enthalpy (ΔH) is logarithmically related to the ageing time (t_a) by the relationship:

$$d\Delta H/d\log(t_a) = 3 \cdot \Delta C_p \quad (2)$$

This equation is plotted in Figs 6 and 7 using an arbitrary ordinate shift to bracket the experimental data. As found for other epoxy resins by Montserrat [7], it appears that Eq. (2) is in reasonable agreement with the experimental data.

Fig. 8 illustrates the influence of ageing temperature (at constant ageing time) on the heat flow curves of DGEBA/An near T_g . As seen in Fig. 3, the ageing peak appears as a maximum superimposed on the heat capacity step. Although

the related data for DGEBA/DDM in Fig. 8 are analogous at the higher ageing temperatures, more complex behaviour is observed at lower ageing temperatures where two sigmoidal steps or in some cases double maxima are observed. Similar behaviour was observed for the DGEBA/DAO system as a function of the degree of undercooling (see Fig. 9). Other workers have also reported this phenomenon [1,3,6,8,11,31] and have interpreted it [31] as being due to a broad distribution of relaxation times which causes a low temperature enthalpy peak below the glass transition sigmoidal step. On ageing for short times, the more mobile segments (with shorter relaxation times) are able to relax to a greater extent than less mobile regions. As the polymer is re-heated, these more mobile segments are able to re-adjust their enthalpy at a temperature below the less mobile material and so a relaxation enthalpy peak is observed prior to the main glass transition region. It is interesting to note that a sub- T_g ageing peak was only observed for the more highly crosslinked materials (DGEBA/DDM and DGEBA/DAO in Figs 8 and 9). This may be explained by the presence of a wider distribution of relaxation times associated with a range of molecular environments caused by the crosslinking process [32].

As shown in Figs 8 and 9 (and also observed for the other systems), when the ageing temperature is much less than T_g , the magnitude of the enthalpy overshoot increases as the ageing temperature is raised but as the ageing temperature approaches T_g the magnitude of the enthalpy overshoot declines. As discussed by Montserrat [6], and explained in Fig. 5, these observations are caused by the differing roles of kinetics and thermodynamics on the ageing phenomenon. At large degrees of undercooling, the reduction in molecular mobility decreases the rate of densification and so, within the time-scale of the ageing experiment, only a small loss of enthalpy occurs. When the ageing temperature is raised, the molecular mobility is enhanced, enabling more densification to occur. Thus the ageing process is under kinetic control and an increase in temperature results in an enhanced ageing peak. However, at even higher ageing temperatures (close to the T_g), the enthalpy of the glass is not very different from that of the equilibrium state and so the sample can only densify to a small extent. Thus the ageing process is now under thermodynamic control and so the magnitude of the enthalpy overshoot decreases as the ageing temperature is raised.

From a comparison of the data in Figs 3 and 4, it appears that for equal degrees of undercooling (at constant $T_g - T_a$), the relaxation enthalpy was reduced with increased crosslinking apparently due to restriction of the molecular re-adjustment required for densification and ageing. The same conclusion can be drawn from the data in Figs 8 and 9. This is illustrated more clearly by the data in Fig. 10, where the relaxation enthalpy is plotted versus the degree of undercooling for an ageing time of 960 min. For geometrical reasons, and as a first approximation [7,30,33], the extent of physical ageing is limited thermodynamically

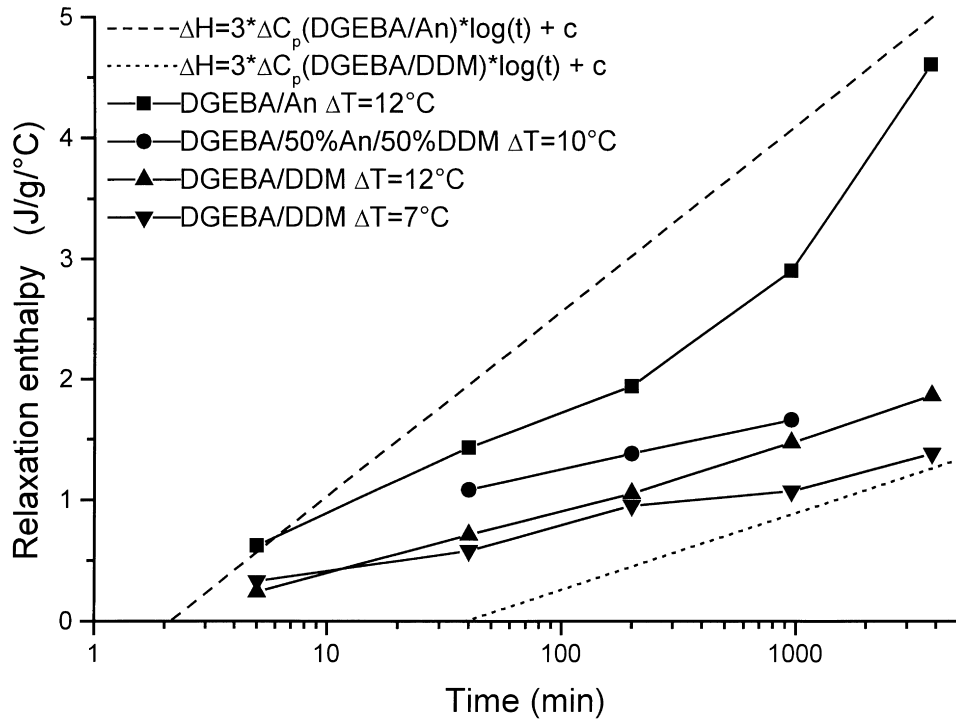


Fig. 6. Relaxation enthalpy versus time for DGEBA/An/DDM systems at various degrees of undercooling. The dashed and dotted lines correspond to the relationship observed by Bauwens-Crowet and Bauwens [26] (see Eq. (2)).

by the following relation:

$$\Delta H_{\infty} = \Delta T \Delta C_p \quad (3)$$

where ΔH_{∞} is the maximum change in enthalpy and ΔT is

the degree of undercooling. It is interesting to note that since ΔC_p has been found to decrease with crosslink density (see Fig. 2). Eq. (3) also suggests that the extent of ageing should also be reduced for the more highly crosslinked systems, as

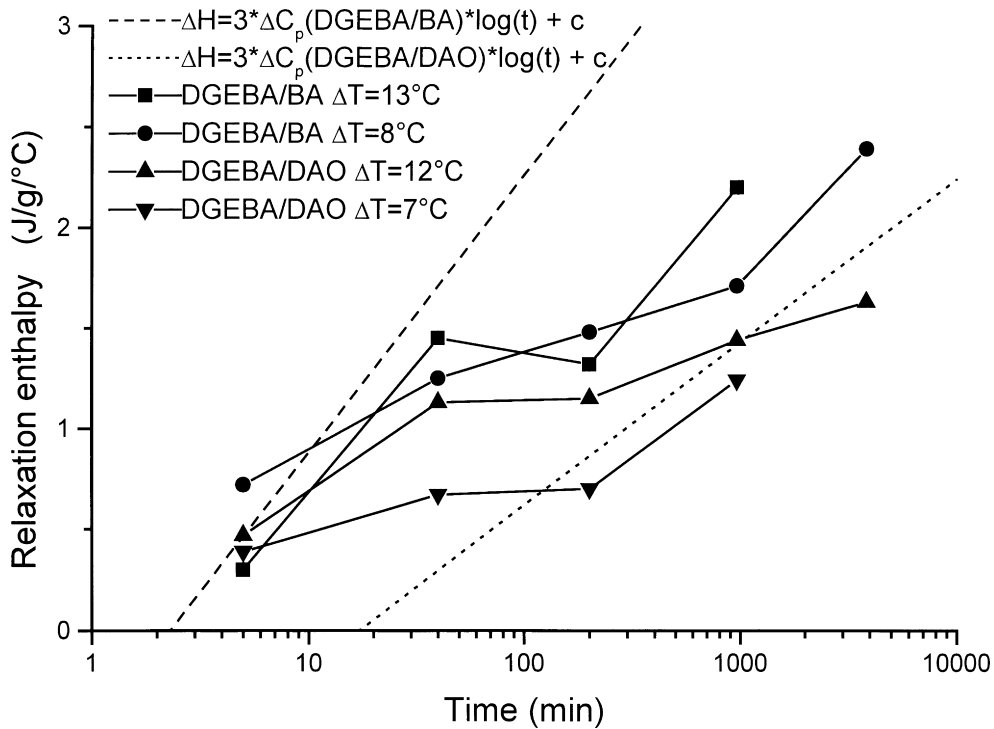


Fig. 7. Relaxation enthalpy versus time for DGEBA/BA/DAO systems at various degrees of undercooling. The dashed and dotted lines correspond to the relationship observed by Bauwens-Crowet and Bauwens [26] (see Eq. (2)).

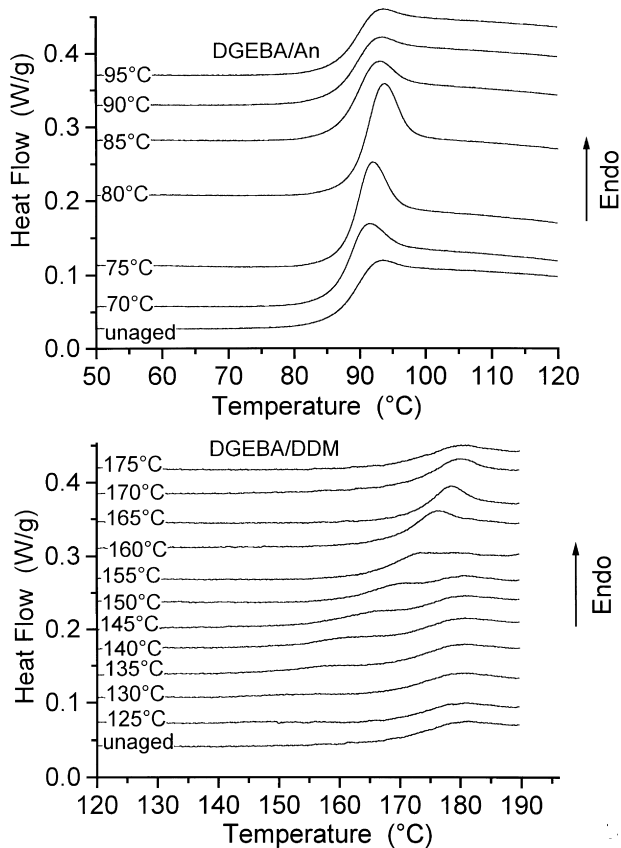


Fig. 8. Temperature dependence of heat flow for DGEBA/An and DGEBA/DDM aged for 40 min at varying temperatures.

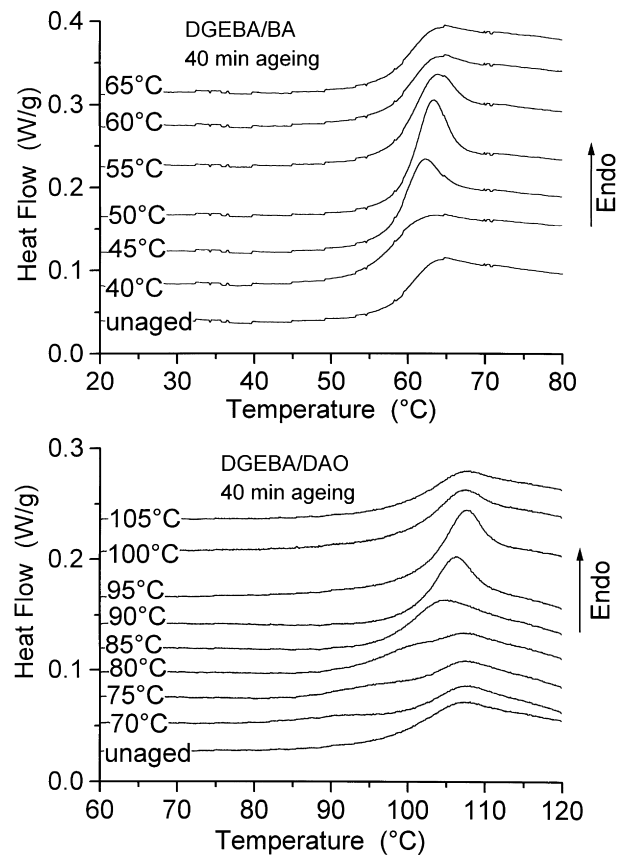


Fig. 9. Temperature dependence of heat flow for DGEBA/BA and DGEBA/DAO aged for 40 min at varying temperatures.

observed in Figs 3, 4, and 9. Eq. (3) is compared in Fig. 10 with the experimental data for DGEBA/An/DDM-based systems. The thermodynamic limit to the magnitude of the relaxation enthalpy predicted by Eq. (3) appears to be in reasonable accord with the data for long ageing times (Fig. 10). However, Eq. (3) was found to overestimate the maximum relaxation enthalpy for short ageing times and low degrees of undercooling, as found elsewhere [26], perhaps due to the assumption [7] in the derivation of Eq. (3) that C_p is independent of temperature.

3.2. Yielding behaviour

Figs 11 and 12 show the stress–strain curves for DGEBA/BA and DGEBA/DAO, measured at 22°C, as a function of ageing time at undercoolings of 8 and 12°C. As reported previously [27], the room temperature yield stress for the uncrosslinked material is lower than the crosslinked analogue, primarily due to the latter's higher T_g and therefore depressed molecular mobility. The lower yield stress following the yield maximum is associated with generalized plastic flow and does not vary with ageing to the same extent as the upper yield stress (the yield stress maximum). This is in agreement with the observations of several other researchers [15,16,34], and it has been argued that this

results from de-ageing (or rejuvenation) of the material after the yield point by the application of the stress [34,35]. As a result, the maximum in the stress–strain curve is accentuated with increased ageing time. Similar behaviour was observed with the DGEBA/95% An/5% DDM and DGEBA/DDM systems at undercoolings of 18 and 12°C. The stress–strain curve for a specimen which had been aged for 4 weeks and then de-aged is shown in Fig. 11 to be virtually identical with that of the original unaged specimen. This observation demonstrates that the variation of yield stress is not associated with a chemical change in the polymer. A similar result was observed for DGEBA/DDM (see Fig. 13).

Fig. 13 shows that the yield stress increases with prolonged ageing time, and appears to approach a plateau at long ageing times. This behaviour is consistent with the observations of other workers [15,16,30]. In agreement with the enthalpy results, the more highly crosslinked systems appear to show less variation in yield stress with ageing time when aged under similar levels of undercooling (compare DGEBA/BA with DGEBA/DAO in Fig. 13). As discussed above, this implies that the more crosslinked polymers are less able to densify, perhaps due to the steric topological restrictions imposed by the crosslinks, as discussed earlier. In relation to this, it is interesting to note that the more highly crosslinked polymers have been found [27]

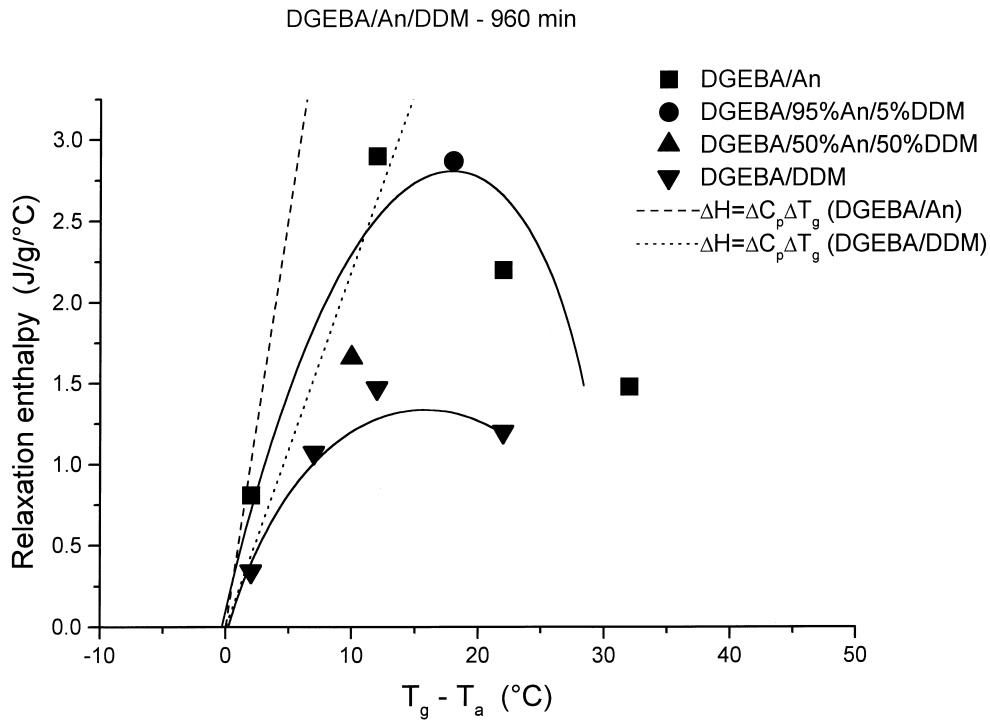


Fig. 10. Relaxation enthalpy versus degree of undercooling for DGEBA/An/DDM systems after 960 min ageing.

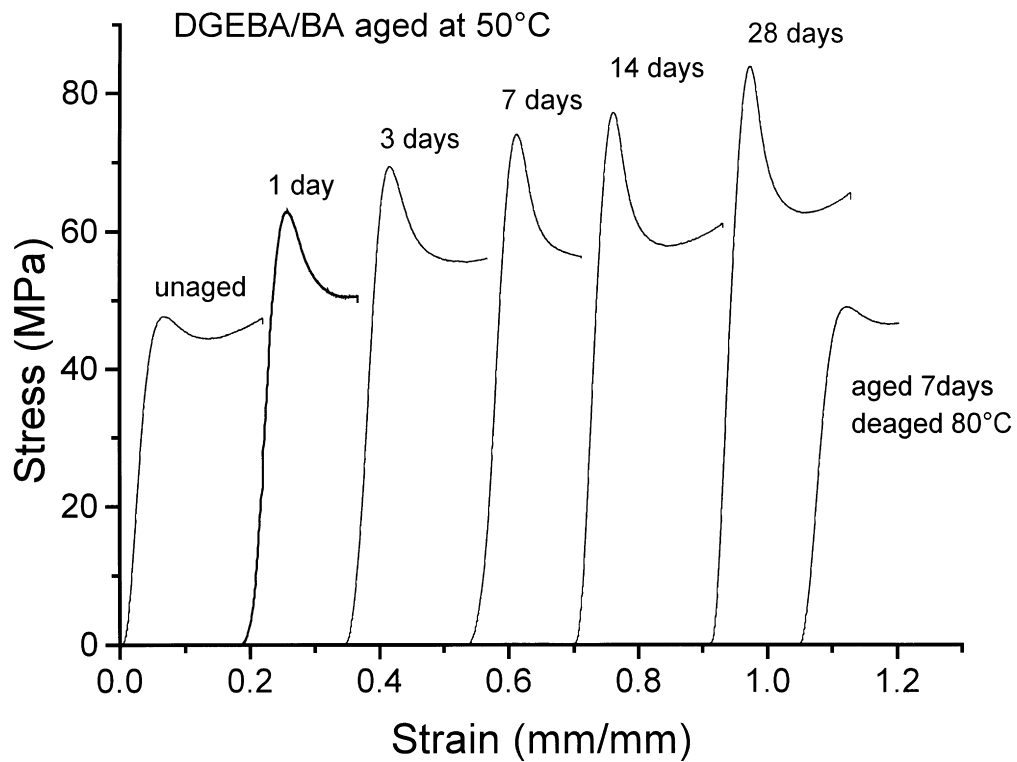


Fig. 11. Stress-strain curves for DGEBA/BA after ageing for various times at 50°C ($\Delta T = 8^\circ\text{C}$). The data for a sample which had been aged for 7 days at 80°C and then de-aged is also shown.

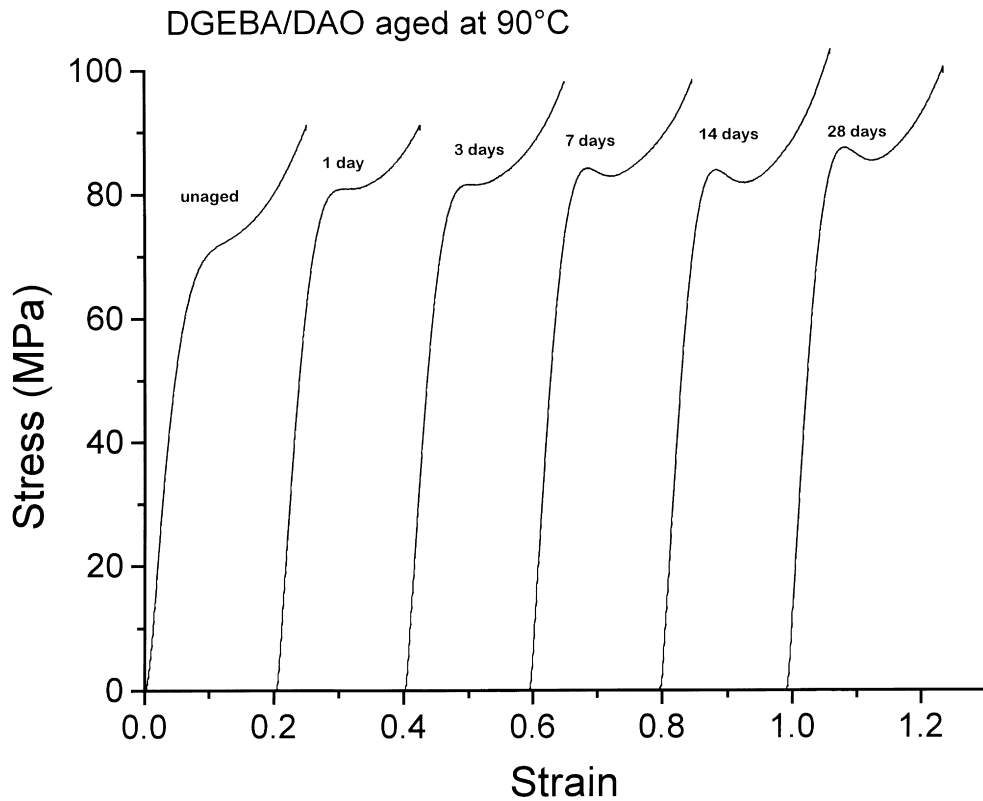


Fig. 12. Stress–strain curves for DGEBA/DAO after ageing for various times at 90°C ($\Delta T = 12^\circ\text{C}$).

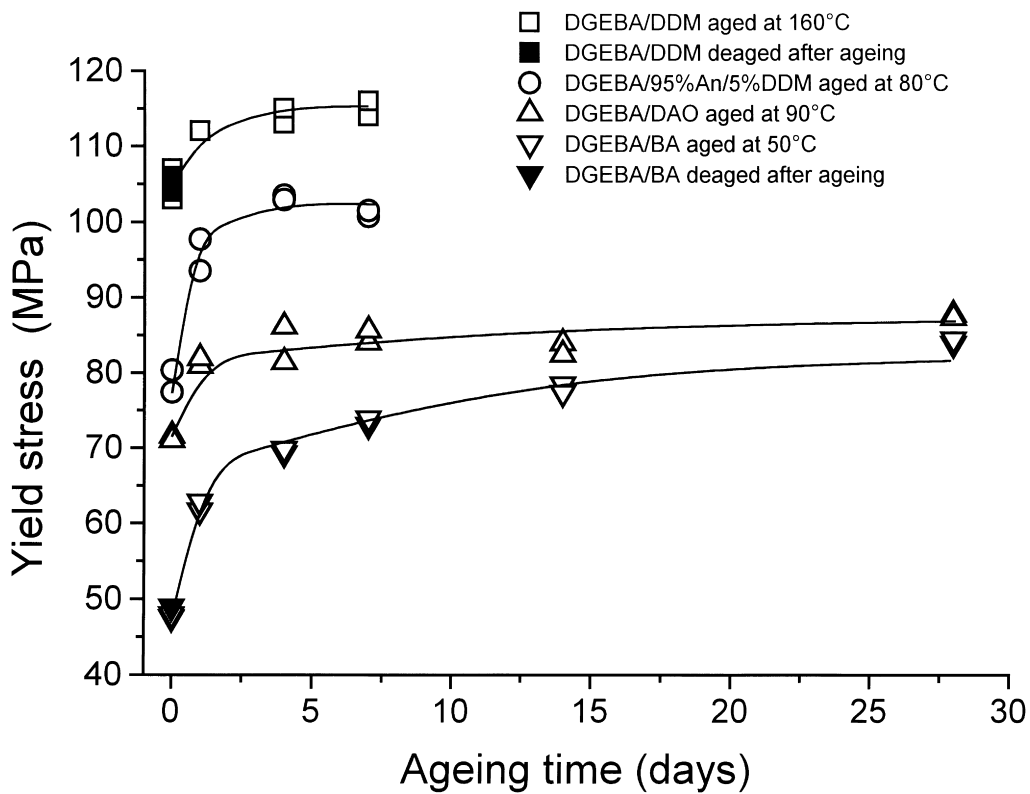


Fig. 13. Yield stress versus ageing time for DGEBA/DDM, DGEBA/95%An/5%DDM, DGEBA/DAO and DGEBA/BA after ageing at 160 ($\Delta T = 12^\circ\text{C}$), 80 ($\Delta T = 18^\circ\text{C}$), 90 ($\Delta T = 12^\circ\text{C}$) and 50°C ($\Delta T = 8^\circ\text{C}$), respectively. Filled symbols identify the yield stress of specimens which were aged for 4 weeks and then de-aged.

to have a lower modulus (at room temperature) which also suggests that the crosslinked chains do not pack as well as the uncrosslinked chains, as suggested by Vallo et al. [34]. However, in the present systems no systematic variations in density have been observed [27].

It is of interest to compare the relative rates of ageing observed by d.s.c. and by yield stress. Bauwens-Crowet and Bauwens [26] have concluded that the kinetics of yield and enthalpy relaxation are the same. Similarly, Truong and Ennis [17] found an approximate correlation between the change in yield stress and the relaxation enthalpy of epoxy networks which had been aged for varying periods. However, a comparison of the d.s.c. and the yield data in the present work suggests that the ageing rate constants are not the same. For example, DGEBA/BA appears to have reached enthalpy equilibrium (see Fig. 4) after ca. 200–960 min when aged at 50°C ($\Delta T = 8^\circ\text{C}$) yet the yield stress (Fig. 13) is still increasing after 20 000 min at 50°C. This observation needs to be further investigated.

4. Conclusions

The effect of physical ageing on the glass transition and yielding behaviour has been investigated for a series of homologous epoxy resins with varying crosslink density. The heat capacity step at T_g decreased and the glass transition temperature increased as the crosslink density rose due to the restrictions on molecular motion by the crosslinks.

The extent of enthalpy relaxation approached a thermodynamic limit when the degree of undercooling was low; however, at greater degrees of undercooling the process was still under kinetic control within the time-scale of the ageing experiments. After subjecting the more highly crosslinked materials to a combination of short ageing times and low ageing temperatures, the enthalpy peak appeared at temperatures below the T_g , suggesting that the more highly crosslinked materials had a wider range of molecular environments than the uncrosslinked analogues.

The relaxation enthalpy was found to be smaller for the more highly crosslinked epoxies, possibly because they have less potential to undergo the molecular rearrangements which occur during physical ageing, and therefore require less energy to re-activate the liquid-like molecular motion on reheating through the T_g . Although the presence of the crosslinks restricts the total extent of ageing, neither crosslink density nor the amine nature appear to significantly affect the kinetics when measured at similar degrees of undercooling.

Physical ageing increased the room temperature yield stress, but the effect could be reversed by de-ageing the

sample above the T_g . The increase in yield stress upon ageing appeared to be greater for the uncrosslinked materials which is analogous to the effect of crosslinking on the relaxation enthalpy.

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