Rejuvenation of epoxy glasses subjected to uniaxial compression

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Two epoxy networks, differing significantly in their glass transition temperatures (T_gs), were subjected to uniaxial compression tests in the glassy state (20°C). One of the systems was based on the diglycidyl ether of bisphenol-A (DGEBA) cured with ethylenediamine (EDA). The other one was based on an epoxidized novolac (EPN) cured with 4,4′-diaminodiphenyl sulfone (DDS). Both systems were physically aged by specific thermal treatments. The endothermic enthalpy relaxation peak, characteristic of aged glasses, could be erased at temperatures well below T_g by large mechanical deformations, i.e. close to the incipient strain hardening level in uniaxial compression tests. This phenomenon, which was accompanied by an increase in specific volume, constitutes a clear manifestation of rejuvenation produced by large mechanical stimuli. The validity of statements presenting an opposite point of view is also discussed.

(Keywords: epoxy glasses; rejuvenation; physical ageing)

INTRODUCTION

Polymers in the glassy state exhibit non-equilibrium behaviour. Properties such as specific volume, enthalpy and entropy evolve continuously towards the equilibrium value (*Figure 1a*). This process, known as physical ageing, produces a change in the viscoelastic properties of the glass which can be represented by a time–ageing time correspondence. The shift rate is independent of the applied deformation or stress in the small-deformation range, i.e. in the linear viscoelastic regime[1].

When an aged glass is subjected to large deformations or stresses it is found that the shift rate decreases as the applied deformation or stress increases[1,2]. This and other related phenomena have been associated with the removal of ageing or rejunevation of the glass by the application of large stresses or deformations[1,3–6]. However, McKenna and coworkers have disputed this interpretation[7–9]. They argued that the experimental results support the fact that the change in the thermodynamic state that occurs during ageing affects the small-deformation behaviour differently than it does the large-deformation response. However, based on the fact that the length of time required for an epoxy network glass to attain equilibrium was unaffected by the application of large stresses, they concluded that the thermodynamic state of the glass did not change by the application of large mechanical stimuli, i.e. rejuvenation in the thermodynamic sense did not take place[7].

Our aim is to show that aged epoxy glasses subjected to large deformations (i.e. well beyond the yield point) exhibit rejuvenation as revealed by the erasure of the enthalpy relaxation peak.

MATERIALS AND METHODS

Specimen preparation

Two epoxy systems, differing significantly in their glass transition temperatures (T_gs), were selected for the experiments.

One of the systems was based on the diglycidyl ether of bisphenol-A (DGEBA, DER332; Dow), with an equivalent weight of 174.3 g eq^{-1}, as determined by acid titration. The hardener was ethylenediamine (EDA, Carlo Erba), used in stoichiometric proportion. Specimens were prepared by degassing the epoxy resin under vacuum at 90°C over 3–4 h, cooling to 40–50°C and then adding the stoichiometric amount of EDA. The solution was cast into disposable polypropylene cylindrical moulds and allowed to cure for 24 h at room temperature, and then postcured at 120°C for 2 h. This procedure carried the epoxy–amine reaction to completion[10,11], giving a network with a T_g close to 120°C (defined at the mid-point of the transition). This system will be called DGEBA–EDA in the following.

The other system was based on an epoxidized novolac (EPN 1138, Ciba Geigy), using a batch with an epoxy equivalent weight of 176.5 g eq^{-1}, as determined by acid titration. The hardener was 4,4′-diaminodiphenyl sulfone (DDS, HT 976; Ciba Geigy), used in stoichiometric proportion. The DDS hardener was dissolved in the epoxidized novolac at 135°C and the solution cast into glass tubes which had been pretreated with a demoulding agent. The cure cycle used was 3 h at 160°C, 2 h at 220°C and 1 h at 235°C, leading to a network cured to the maximum possible conversion as imposed by topological restrictions (conversion close to 0.80)[12,13]. This material exhibited a broad glass transition temperature range (from ~170 to 260°C), with a mid-point value close to 215°C. This system will be referred to as EPN–DDS in the following.

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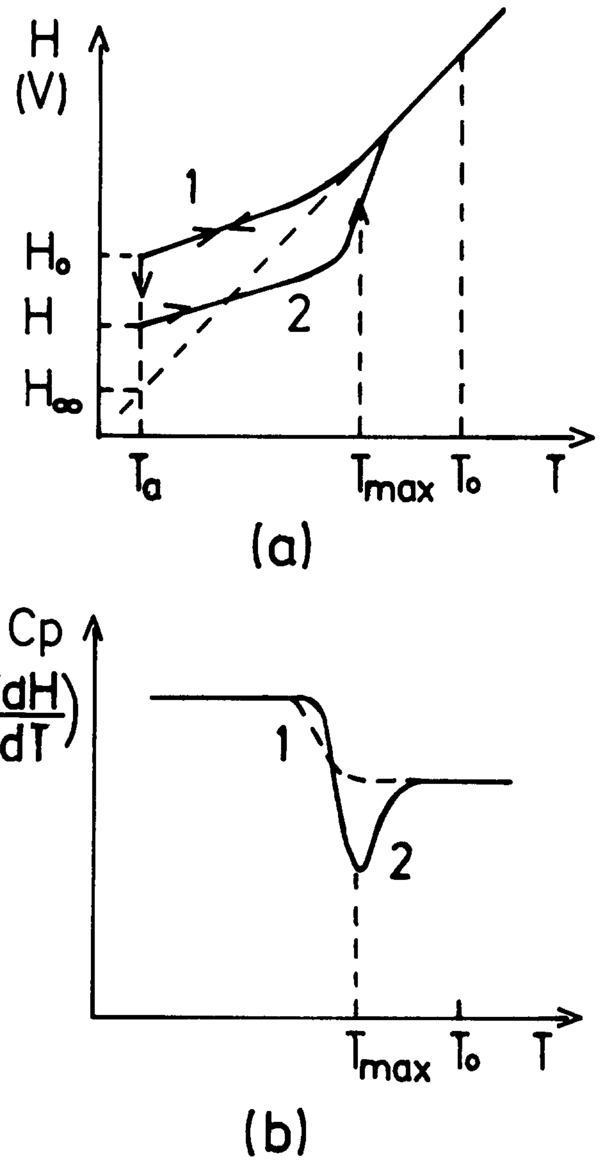

Figure 1 Schematic diagrams of (a) enthalpy vs. temperature and (b) C_p (or $\mathrm{d}H/\mathrm{d}T$) vs. temperature illustrating the fact that physical ageing at T_a leads to a decrease in the specific enthalpy (volume) and the appearance of an endothermic enthalpy relaxation peak in the differential scanning calorimetry thermogram: (1) unaged sample; (2) aged sample; T_{max} = temperature where the maximum endothermic effect is observed; T_0 = temperature in the rubbery region

Minicylindrical specimens were machined out of the cured products ($l = 9$ mm, $d = 6$ mm for DGEBA–EDA, and $l = 6.5$ mm, $d = 4$ mm for EPN–DDS). Care was taken to obtain smooth and parallel end surfaces. No bubbles or internal flaws were revealed by visual inspection.

Thermal treatments

In order to generate (or increase the magnitude of) the enthalpy relaxation peak associated with physical ageing, specimens were subjected to specific thermal treatments. Rejuvenation in the thermodynamic sense will be judged from the disappearance of the enthalpy relaxation peak by a large mechanical deformation.

After a normalization treatment above T_g, DGEBA–EDA specimens were aged at 75°C over 12 days and then stored at −20°C for a further 12 days before testing at 20°C. Most of the ageing took place in the first stage (at 75°C). Unaged specimens were obtained by deleting this first stage and by minimizing the storage period at −20°C.

In the case of the EPN–DDS specimens, the endothermic enthalpy relaxation peak appeared in the last stage of the cure cycle (the cure temperature was contained in the broad glass transition temperature range). A second ageing stage was carried out by treatment at 170°C over 20 h. After cooling to 20°C, specimens were then mechanically tested.

Compression tests

Uniaxial compression tests (at 20°C), were performed on a Shimadzu Autograph SC-500 machine, between lubricated plates, at 0.5 mm min^{-1}. The compressive stress, σ, was estimated from the following:

$$\sigma = P(1-e)/A_0 \tag{1}$$

where P is the load, A_0 is the initial cross-sectional area, and e is the strain determined from the cross-head displacement, corrected for the machine softness.

Characterization

Samples for thermal and specific volume characterization were taken from the bulk of the minicylindrical specimens used in the mechanical tests. Differential scanning calorimetry (d.s.c.) thermograms (10°C min^{-1}, N_2 flow) were obtained using a Du Pont 990 Thermal Analyzer provided with a 910 d.s.c. cell. Densities were determined by using toluene–carbon tetrachloride solutions of different compositions, according to the ASTM D 1505-85 standard.

The dimensional recovery after uniaxial compression was analysed by applying a certain deformation level, releasing the load and then following the height evolution at 20°C as a function of time, for periods up to 48 days.

RESULTS AND DISCUSSION

When an aged glass is heated beyond the glass transition temperature, an endothermic enthalpy relaxation appears in the d.s.c. thermograms (see *Figure 1b*, curve 2). The area of the relaxation peak is a measure of the enthalpy recovery[14,15]. In a second cooling from T_0 to T_a and a subsequent reheating to T_0 (*Figure 1a*) no endothermic relaxation is observed (see *Figure 1b*, curve 1). Thus, the heating of the aged glass to a temperature $T > T_g$ has erased the previous physical ageing, i.e. rejuvenation of the glass has taken place.

Therefore, rejuvenation is defined as an increase in the specific enthalpy and a corresponding increase in the specific volume of the glass, i.e. going up in the H vs. T diagram shown in *Figure 1a*. Whether this process leads to the unaged state of the original glass is very difficult to assess. Instead, it may be stated that physical ageing is erased as revealed from the disappearance of the enthalpy relaxation peak and the increase in the specific volume of the glassy polymer. Our aim is to analyse if large mechanical deformations in the glassy state are also capable of erasing the endothermic enthalpy relaxation appearing in the d.s.c. thermograms. This should be regarded as a proof of the change in the thermodynamic state of the glass when subjected to large mechanical deformations.

Figure 2 shows stress–strain curves corresponding to the aged and unaged states of DGEBA–EDA networks.

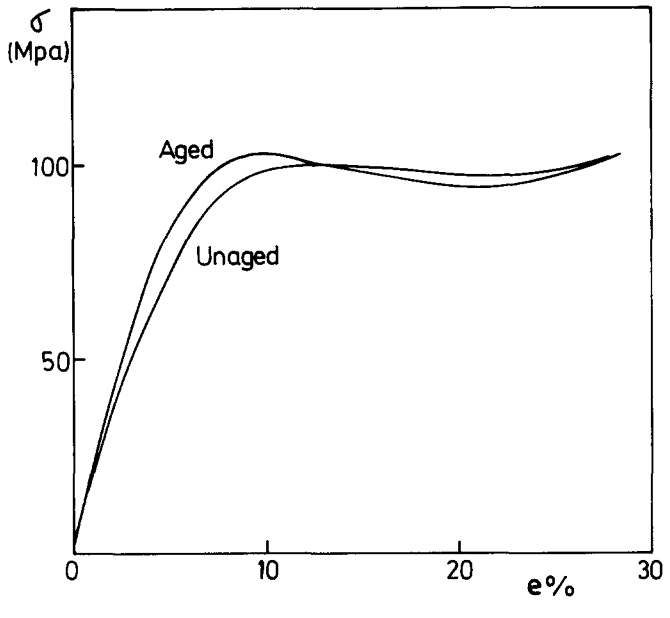

Figure 2 Stress–strain curves of DGEBA–EDA networks in uniaxial compression, showing the effect of physical ageing

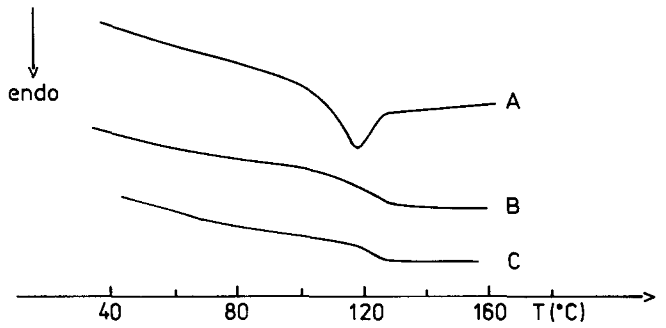

Figure 3 D.s.c. thermograms of DGEBA–EDA networks: (A) aged specimen showing an endothermic enthalpy relaxation peak; (B) a second scan (following A) showing that heating above T_g has erased the endothermic peak; (C) aged specimen subjected to 28% strain in uniaxial compression at 20°C, showing the erasure of the endothermic peak

Physical ageing leads to a slight increase in the yield stress but practically no change in the plateau value (lower yield stress). This agrees with the trends reported by G'Sell and McKenna[16] for model DGEBA/poly(propylene oxide) epoxy glasses.

Figure 3 shows d.s.c. thermograms of the DGEBA–EDA networks. Curve A, which corresponds to an aged specimen, shows an endothermic enthalpy relaxation peak. Curve B is a second scan (following A) of the same specimen showing that heating above T_g has erased the endothermic peak. Curve C represents an aged specimen that had been subjected to 28% strain in uniaxial compression at 20°C. The large mechanical deformation in the glassy state has undoubtedly rejuvenated the glass.

The densities of different specimens were determined at 23°C. The values obtained for an unaged specimen (ρ_U), an aged sample (ρ_a) and a sample which had been subjected to 28% strain at 20°C (ρ_c) were 1.1920, 1.1936 and 1.1925 g cm^{-3}, respectively. The partial recovery of the specific volume gives extra evidence of the rejuvenation produced by the large mechanical deformation.

In order to exclude interpretations which might be related to localized temperature increases at high mechanical deformations, the response of the high-T_g EPN–DDS system was also investigated. *Figure 4* shows d.s.c. thermograms of the aged specimen (A), with the enthalpy relaxation peak at ~250°C, a second scan of the same specimen (B), showing the rejuvenation produced by heating beyond the relaxation peak, and the aged specimen after being subjected to about 28% strain in uniaxial compression at 20°C (C). Rejuvenation due to the large mechanical deformation is again evidenced by the disappearance of the enthalpy relaxation peak. The density of the 28% deformed specimen (ρ_c) was 1.283 g cm^{-3}, compared to an initial value (ρ_a) of 1.312 g cm^{-3}. The relatively large increase in specific volume resulting from the large mechanical deformation gives another sign of the occurrence of the rejuvenation process.

Figure 5 shows the stress–strain response of the aged EPN–DDS networks. The residual strains measured after 1 h and 1152 h of releasing the load are shown (every point represents a different specimen). As expected, up to the yield point there is a rapid recovery of the initial dimensions. At the onset of generalized plastic flow (the stress plateau)[16], a residual deformation is observed even after prolonged times (although recovery is still taking place). For example, the rejuvenated specimen subjected to 28% strain exhibits 10% residual deformation 1 h after the mechanical test.

A set of different specimens was subjected to uniaxial compression up to a particular deformation level, indicated by the numbers 0 (initial specimen) to 4 in *Figure 5*. The resulting materials were characterized by d.s.c. in order to observe the possible erasure of the enthalpy relaxation peak (*Figure 6*). Although the location of this peak showed small variations among different specimens, it could only be erased at deformation levels

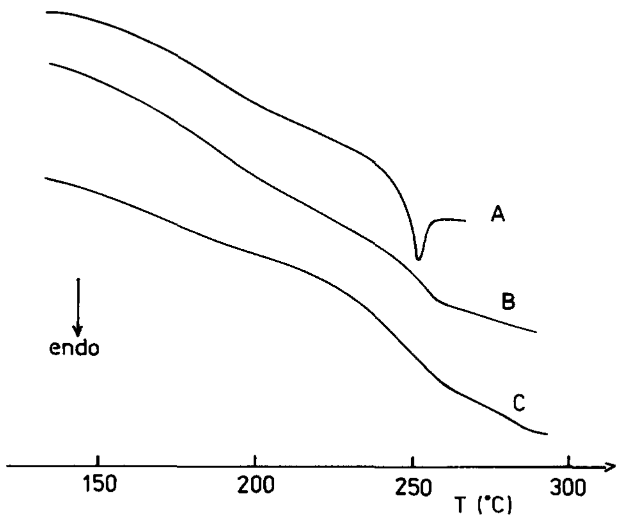

Figure 4 D.s.c. thermograms of EPN–DDS networks: (A) aged specimen showing an endothermic enthalpy relaxation peak; (B) a second scan (following A) showing that heating above T_g has erased the endothermic peak; (C) aged specimen subjected to 28% strain in uniaxial compression at 20°C, showing the erasure of the endothermic peak

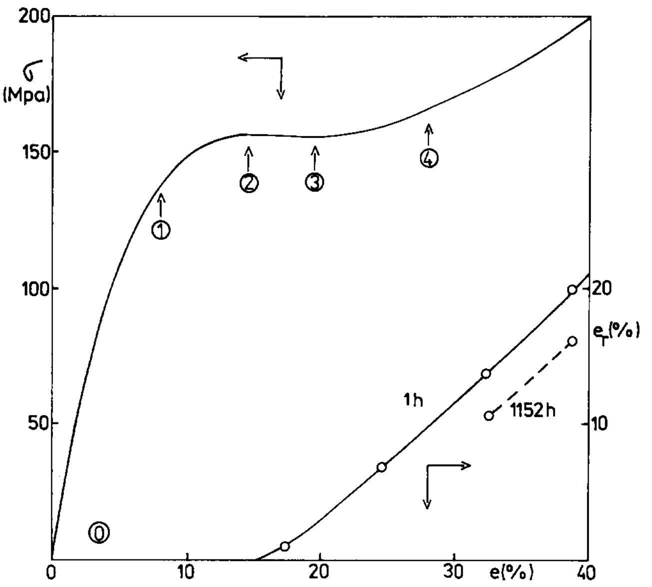

Figure 5 Stress–strain curve in uniaxial compression of an EPN–DDS network sample and the residual strain, after 1 h and 1152 h, of specimens subjected to particular deformation levels before releasing the load; the numbers 0 (initial specimen) to 4 represent particular strain levels where specimens were unloaded and characterized by d.s.c. (every point corresponds to a different specimen)

which were close to that at which incipient strain hardening occurs (as revealed from *Figure 5*).

Our experimental results may be used to analyse controversial arguments concerning the possibility of rejuvenating aged glasses (in the thermodynamic sense) by mechanical means. For example, McKenna and coworkers[7–9] found that the length of time required for an epoxy network glass to attain equilibrium was unaffected by the application of large stresses (no rejuvenation was observed). However, creep compliance tests were stopped when yielding occurred[7,8], with the torsional tests being conducted at deformation levels lying between 0.0025 and 0.05[9]. In fact, the applied deformations were large enough to promote a non-linear viscoelastic response, but still comparatively small in terms of producing any erasure of physical ageing.

On the other hand, Bauwens-Crowet and Bauwens did find rejuventation in thin-walled tubular specimens of polycarbonate from torsional tests carried out well beyond the yield point[17]. Rejuvenation was proved by the decrease in yield stress after retesting. However, no direct proof of any change in the thermodynamic state of the glass was provided.

The experimental evidence presented in this paper enables one to conclude that aged glasses may be rejuvenated in the thermodynamic sense by applying a deformation which is well beyond the yield point.

CONCLUSIONS

The endothermic enthalpy relaxation peak which is characteristic of aged glasses may be erased at temperatures well below T_g by applying large mechanical deformations, i.e. close to the incipient strain hardening level in uniaxial compression. This constitutes clear evidence of the possibility of rejuvenating aged glasses in the thermodynamic sense (i.e. increases in the specific enthalpy and the specific volume).

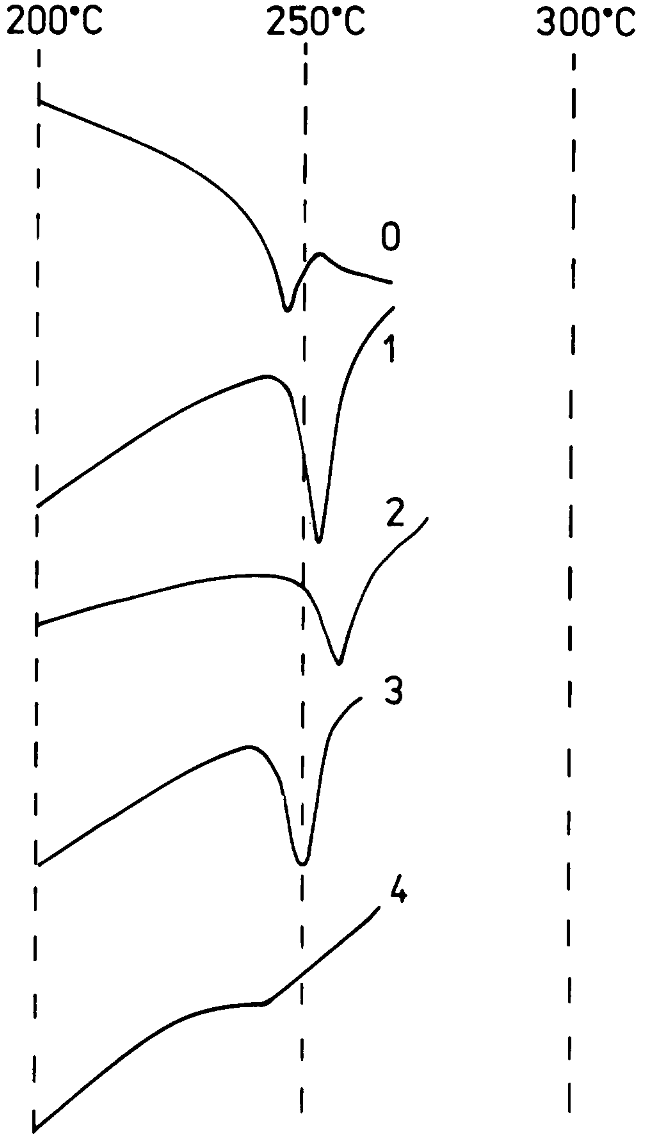

Figure 6 D.s.c. thermograms of EPN–DDS specimens subjected to different deformation levels in uniaxial compression: numbers correspond to the particular strain levels shown in *Figure 5*

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