Energy storage during inelastic deformation of glassy polymers

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In this paper, aspects of the microstructural state of glassy polymers that evolve during physical ageing and inelastic deformation were studied. Differential scanning calorimetric (d.s.c.) measurements were performed on specimens of three glassy polymers: polystyrene (PS), polycarbonate (PC) and poly(methyl methacrylate) (PMMA). Materials were subjected to both a quenched and a well annealed heat treatment and subsequently deformed in compression to various levels of strain. Stress–strain curves and companion d.s.c. scans were compared.

The well known enthalpy overshoot at T_g was observed for the annealed samples, showing that ageing is accompanied by enthalpy relaxation. The annealed material was also found to require a higher stress to yield, and the additional work required to strain-soften the annealed polymer to the flow stress level of its quenched companion was found to correlate well with the area of the enthalpy overshoot of the annealed specimen.

Inelastic deformation was found to increase the specific enthalpy of both annealed and quenched specimens. In the annealed material, the enthalpy overshoot at T_g was found to decrease with inelastic strain and was completely erased by about -20% strain. Simultaneously, a pre-T_g exotherm was observed to develop with inelastic strain over a wide range of temperature. The pre-T_g exotherm was found to evolve until essentially reaching a steady-state profile at approximately -25% strain. This evolution coincided with the strain-softening phenomenon observed in the corresponding stress–strain results. A pre-T_g exotherm was also found to evolve with straining of the quenched material. Furthermore, the steady-state exotherms of the quenched and annealed materials were found to be nearly identical, as were their corresponding flow stress values after strain softening.

Finally, a second, post-T_g exotherm was found to develop with further straining beyond strains of -25%. This exotherm was found to increase with inelastic strain and coincided with the occurrence of strain hardening (due to chain orientation) in the materials.

The presence of two distinct and separately evolving exotherms in the inelastically deformed polymers indicates the existence of two separate deformation resistances in glassy polymers, one related to the initial yield and strain-softening behaviour, and the other to the orientation-induced strain hardening of the material. The observation that the pre-T_g exotherm is spread over a wide temperature range reflects the distributed nature of the structural state and may be quantified using a distribution in activation energy for the local rearrangements. The results therefore provide valuable information about the processes that must be accounted for in the development of accurate constitutive models of mechanical behaviour.

(Keywords: glassy polymer; ageing; inelastic deformation)

INTRODUCTION

Glassy polymers are not in a state of thermodynamic equilibrium below their glass transition temperature and undergo local rearrangements to attain a more stable thermodynamic state. This process of structural relaxation is accompanied by a decrease in thermodynamic properties such as enthalpy, volume and entropy. Conversely, inelastic deformation in this class of materials is observed to increase the extent of thermodynamic disorder, as will be shown in this paper. Here, we use the term 'inelastic' to refer to deformation that results in some 'permanent' strain upon unloading in terms of a timeframe of at least weeks at room temperature. To understand better the evolution in material state with thermal history and inelastic deformation, a careful set of experiments were carried out on three glassy polymers, polystyrene (PS), polycarbonate (PC) and poly(methyl methacrylate) (PMMA). The measurements involve the isothermal deformation of each polymer to several different compressive strain levels followed by differential scanning calorimetric (d.s.c.) measurement on each specimen to monitor one aspect of the change in material state with strain. The measurements were conducted on quenched (unaged) and annealed (well aged) specimens deformed to true strains ranging from 0% to values in excess of 100%. Although other workers[1–4] have used d.s.c. to observe changes in thermodynamic properties with deformation, they have not considered the effect of initial material state, and the relation between stored energy and the physical mechanism of inelastic deformation over a sufficiently large range of strain.

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EXPERIMENTAL PROCEDURE

Specimen preparation

All three materials used in this investigation were obtained from commercial vendors. PS and PMMA were obtained as cylindrical bar stock and the PC in plate form. For both PS and PMMA, cylindrical specimens 10 mm in diameter and 8 mm in height were machined; and for PC, cubic specimens with linear dimension of about 11 mm were obtained. To erase any prehistory, the specimens were heated in a VWR vacuum oven to about 15°C above the glass transition temperature and maintained there for about an hour. Thereafter, two widely different initial states for our experiments were obtained either by quickly transferring the specimens into a bath of ice–water and stirring vigorously (giving the 'quenched' material state) or by switching off the oven and allowing the specimens to cool to room temperature over a period of 6–8 h† (giving the 'annealed' material state). After the mechanical testing, specimens typically about 10 mg in mass were micro-machined for the d.s.c. measurements using a Buehler low-speed saw fitted with a SiC tool and operating in an oil-based coolant bath. D.s.c. measurements were also performed on both annealed and quenched samples prior to mechanical testing. By comparing scans on undeformed d.s.c. specimens annealed prior to or after micro-machining, it was concluded that the process zone created by machining has little effect on the calorimetric measurements. The specimen mass was measured with a Perkin–Elmer electronic balance having a resolution and repeatability of 0.001 mg.

Mechanical testing

To isolate the effect of inelastic deformation on material state from other factors, we have performed isothermal, constant true strain rate, uniaxial compression tests on an Instron 1350 machine. Liquid soap films between Teflon sheets were used to minimize end-friction and a globally homogeneous mode of deformation was obtained. Note that this would not be possible in the case of uniaxial tension (post-yield strain localization and necking) or simple shear (gripped end-effects and macro-shear-band localization). All the tests were performed at room temperature at a true strain rate of $-0.001\,\mathrm{s}^{-1}$. A Mikron infra-red thermometer was used to monitor the surface temperature, which was found to remain constant to within 1°C. The Instron was connected to a data acquisition and control system to monitor true stress–true strain response in real time (for further details of the mechanical testing procedure, see Arruda and Boyce[5]).

Calorimetric measurements

Differential scanning calorimetry is used here to monitor the rate of change of specimen enthalpy when heating at a constant rate. In the literature (e.g. ref. 6) polymer specimens of 10–20 mg have been found to give repeatable results, and this is the typical specimen size used in our experiments. An important testing parameter is the scanning rate; for our experiments, a compromise must be sought between minimizing the ageing of the material during the measurement (especially near T_g) by choosing a high scanning rate, and ensuring uniform heating of the specimen by using a low scanning rate. Heating rates of 5–20 K min^{-1} have typically been used in testing with polymers. For our work, a rate of 10 K min^{-1} was used for all experiments. While the heating rate affects the resulting scan, using a consistent scanning rate for all measurements enables direct comparison of exotherms and endotherms resulting from different amounts of inelastic deformation and/or ageing. A Perkin-Elmer DSC-7 is used for this work and was calibrated to within ±0.5°C.

EXPERIMENTAL RESULTS

The results of the experimental work are shown in *Figures 1–11*. In *Figure 1*, we see the enthalpy scans of annealed (aged) vs. quenched (or unaged) polystyrene. The annealed specimen exhibits the well known endothermic overshoot near T_g (e.g. refs. 1, 2 and 4). This has been interpreted to be the result of the reduction in specific enthalpy due to structural relaxation; hence, on reheating, additional energy is absorbed in equilibrating above the glass transition temperature. Conversely, the quenched specimen does not show any significant overshoot by virtue of having sufficient degree of 'frozen' structural disorder.

To gain insight into the evolution of material state with inelastic straining, annealed and quenched specimens were deformed to different values of inelastic strain accompanied by d.s.c. scans at each stage. The results of these measurements are shown in *Figures 2* and *3*. *Figure 2* depicts the yield and subsequent isothermal strain softening of annealed and quenched polystyrene. It can be seen that the annealed PS has a

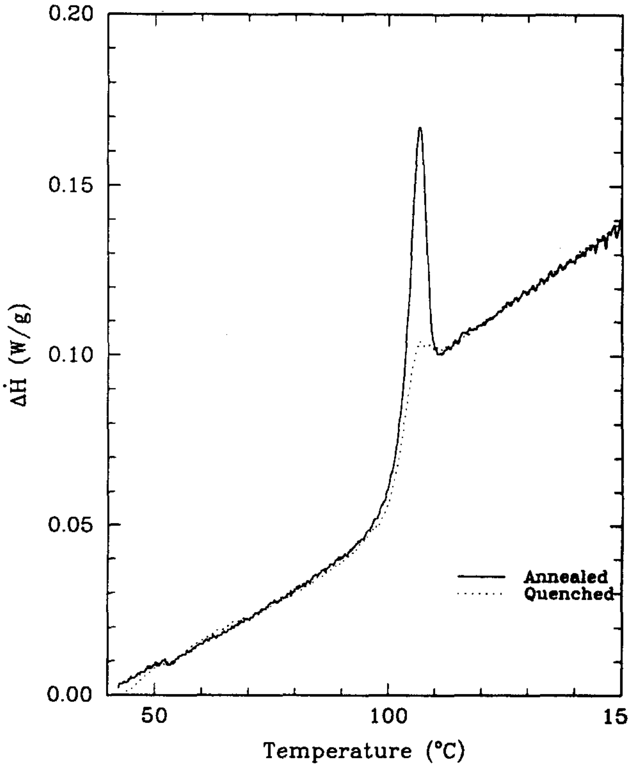

Figure 1 D.s.c. scans for annealed and quenched PS using a heating rate of 10 K min^{-1}

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† The glass transition temperature of PC is about 50°C higher than that of the other two polymers and the cooling time is consequently longer

substantially higher yield stress than the quenched PS (92 MPa as opposed to 72 MPa), yet for both prehistories, the material softens to virtually the same flow stress of approximately 55 MPa. The corresponding d.s.c. scans, shown in *Figures 3a* and *3b*, depict the gradual erasure of the post-T_g endotherm with inelastic strain for the annealed material and the simultaneous evolution of a pre-T_g exotherm as (part of the) external work is stored as internal energy. This exotherm evolves concurrently with strain softening and reaches a steady-state value when strain softening ceases, providing powerful evidence that the material evolves to a preferred or maximum degree of disorder with inelastic strain. Our d.s.c. scans for initially quenched PS (*Figure 3b*) differ from the initially annealed ones primarily in the absence of a post-T_g overshoot, the origin of which has been discussed earlier. Note that the pre-T_g exotherms of the initially annealed and quenched specimens are identical after -25% strain.

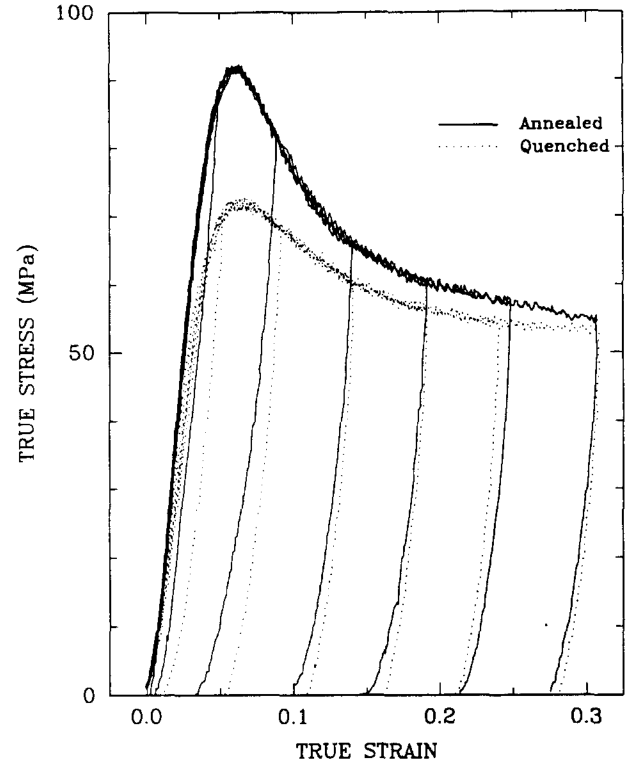

Figure 2 Annealed and quenched PS loaded to different strains at temperature 296 K and strain rate $-0.001\ \mathrm{s^{-1}}$

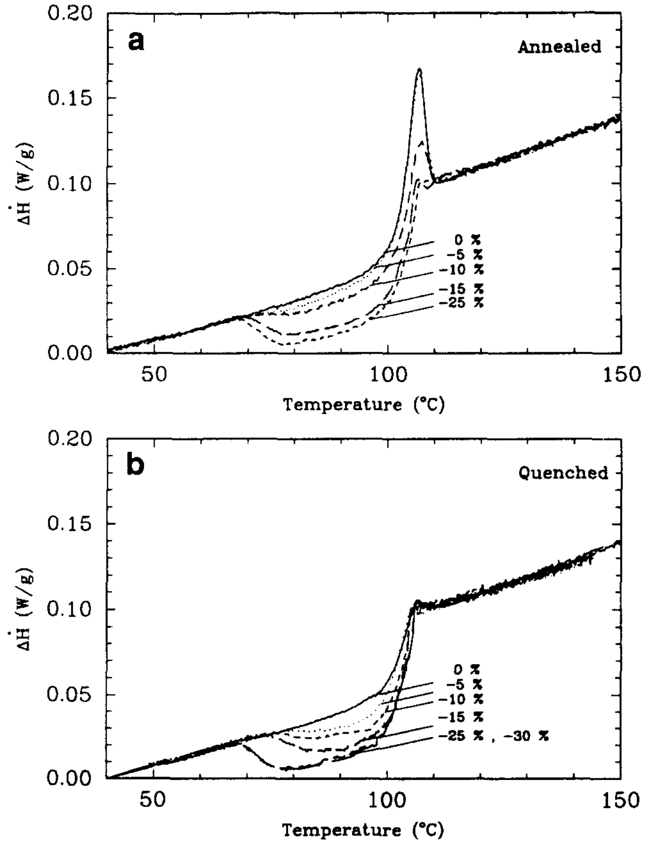

Figure 3 D.s.c. scans for (a) annealed and (b) quenched PS specimens deformed to different (%) applied strains (scan rate $10\ \mathrm{K\ min^{-1}}$)

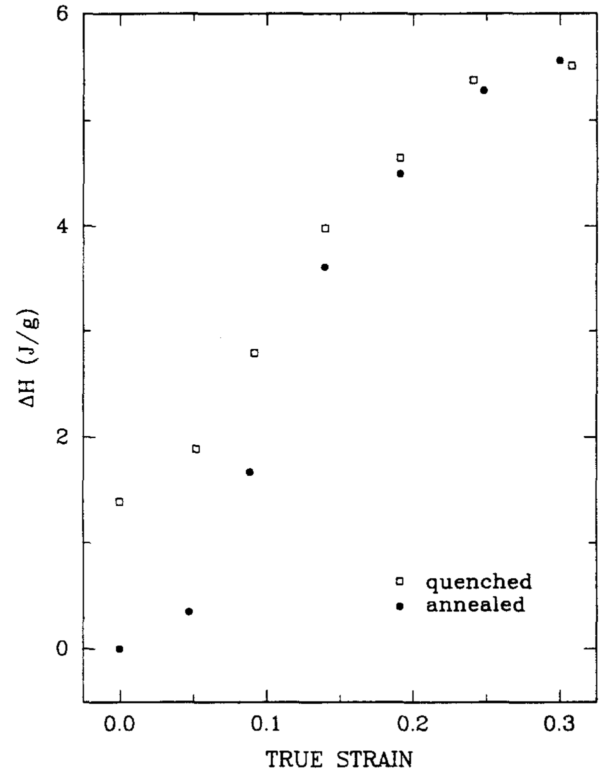

Figure 4 Change in enthalpy of annealed and quenched PS with increasing strain ($\rho = 1.06\ \mathrm{g\ cm^{-3}}$)

The evolution is net enthalpy change (sum of the exotherm and endotherm areas) with total strain has been plotted for both thermal histories in *Figure 4*. It can be seen that this quantity has a higher initial value for the quenched material, which is consistent with the greater degree of structural disorder preserved by quenching[*]. Moreover, after strain softening, both initially annealed and quenched specimens attain virtually the same steady-state value of net enthalpy. The additional work done during the strain softening of the annealed polymer compared to the quenched polymer (such that they both have the same final state) is about $2.0\ \mathrm{J\ g^{-1}}$[†] in a room-temperature test. This compares well with the $1.35\ \mathrm{J\ g^{-1}}$ difference in the specific-enthalpy content for the undeformed case (see *Figure 4*) observed in the enthalpy overshoot at T_g. These results, in conjunction with the similar values of steady-state flow stress for the

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[*] Note that we have arbitrarily taken our annealed specimen to be the initial zero reference state

[†] The density of polystyrene obtained from our measurements is $1.06\ \mathrm{g\ cm^{-3}}$

two cases, amply demonstrate that the material de-ages to a preferred state during strain softening, independent of initial thermomechanical state. The de-ageing effect of strain softening to a preferred steady-state structure has also been shown by Hasan *et al.*[7] using compression testing and positron annihilation lifetime spectroscopy on PMMA. There the free volume was found to increase with inelastic strain until reaching a steady-state value at the end of strain softening.

Finally, in order to consider the large-strain evolution of material state, we extended the above experimental procedure, for the case of annealed PS, to applied true strains of about −150%. The resulting stress–strain curves and d.s.c. scans are shown in *Figures 5* and *6*. The strain-hardening response can be seen quite clearly in *Figure 5*. The corresponding scans show that the pre-T_g exotherm virtually stops evolving by the end of strain softening (around −25% strain); however, at about −60% strain, there appears a post-T_g exotherm, which evolves with strain and which we attribute to the energy stored in the material during strain hardening (caused by extensive molecular chain orientation). Note that the post-T_g exotherm evolves very slowly beyond about 120% applied strain. This may be due to the fact that part of the stored energy is used to drive strain recovery upon unloading and therefore cannot be detected by the d.s.c. measurements, which were performed on the fully recovered specimens. For example, a polystyrene specimen deformed to 140% strain was measured to undergo 20% strain recovery (at room temperature) in the unloaded configuration within two days, giving a residual strain of 120%; thereafter, the strain recovery was extremely slow.

The 'transformation' and the total net enthalpy change vs. residual strain have been plotted in *Figure 7*. Here we use the term 'transformation' to indicate the energy associated with the pre-T_g exotherm as opposed to that associated with the anisotropic molecular chain orientation, which is picked up by the post-T_g exotherm. It is encouraging to note that, unlike deformation calorimetry (for example, see Adams and Farris[8]), d.s.c. enables us to differentiate between the contributions

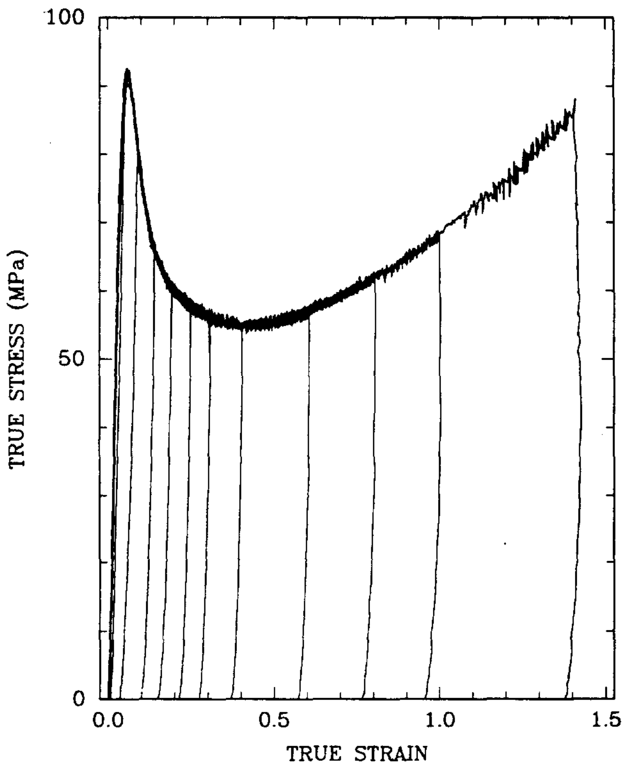

Figure 5 Annealed PS loaded to different strains at temperature 296 K and rate −0.001 s^{-1}

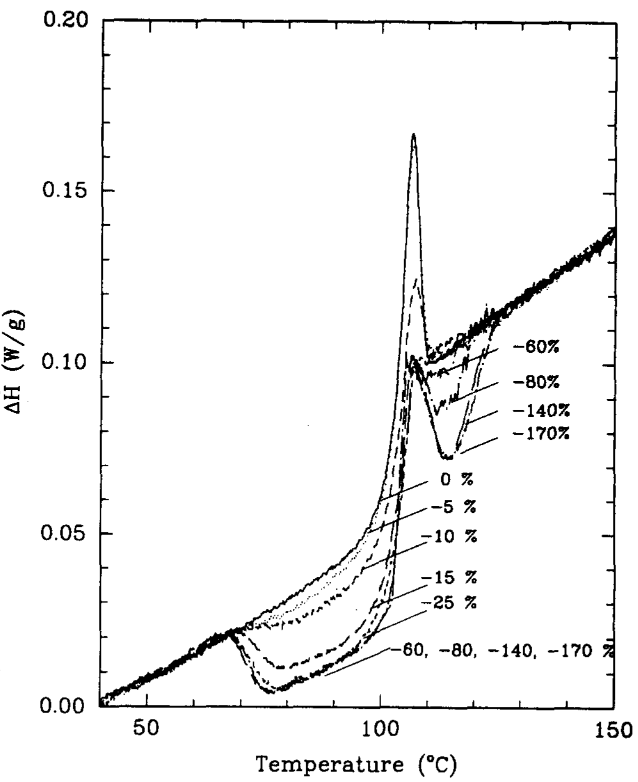

Figure 6 D.s.c. scans for annealed PS specimens deformed to different (%) applied strains (scan rate 10 K min^{-1})

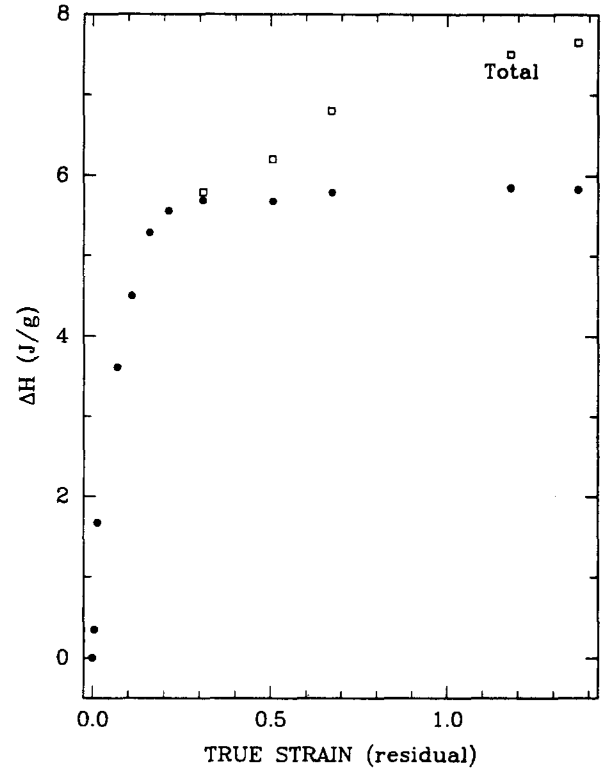

Figure 7 Change in enthalpy of annealed PS with residual strain ($\rho = 1.06$ g cm^{-3})

of transformation and orientation (strain-hardening) deformation modes to the material state because d.s.c. can independently monitor the evolution of these energy storage events.

The experiments described above for PS were also repeated for two other glassy polymers, PC and PMMA. For both cases, the same trends as those obtained for annealed and quenched PS were observed. *Figure 8a* shows the stress–strain curves for annealed PC deformed to different strains and *Figure 8b* shows the corresponding enthalpy scans. It can be seen again that, during the initial stages of deformation, the endothermic peak due to annealing is 'erased' by inelastic straining; thereafter, there is a broad exotherm below the glass transition temperature indicative of disordering of the material. This exotherm evolves very slowly after strain softening is complete, indicating that the glass has evolved to some preferred maximum degree of disorder during this part of the deformation. The energy stored in the glassy polymer during the orientation hardening stage is released at or slightly above the glass transition temperature as for the case of PS. *Figure 9* shows the evolution of stored energy with residual strain. For PC, the contribution of 'transformation' and 'orientation' deformation to stored energy becomes less distinct at large strains as the two peaks merge into one. The corresponding results for the case of annealed PMMA are shown in *Figures 10* and *11*. Finally, *Figure 12* shows the work of deformation for the three polymers as a function of applied true strain. A comparison with the increase in enthalpy (as a function of residual strain) indicates that, during the initial stages of deformation, a substantial portion of the mechanical work (30–60%) is stored within the material. This coincides with the de-ageing observed via the strain softening and is indicative of a structural disordering process that occurs during strain softening. Thereafter, the stored 'transformation' energy with increasing strain remains constant. However, additional work is done to align the polymer chains in the principal tensile stress direction(s). The fraction of work stored within the material is now somewhat smaller (10–20%). Note that the stored work or change in enthalpy is measured in the fully unloaded state and therefore does not reflect energy storage

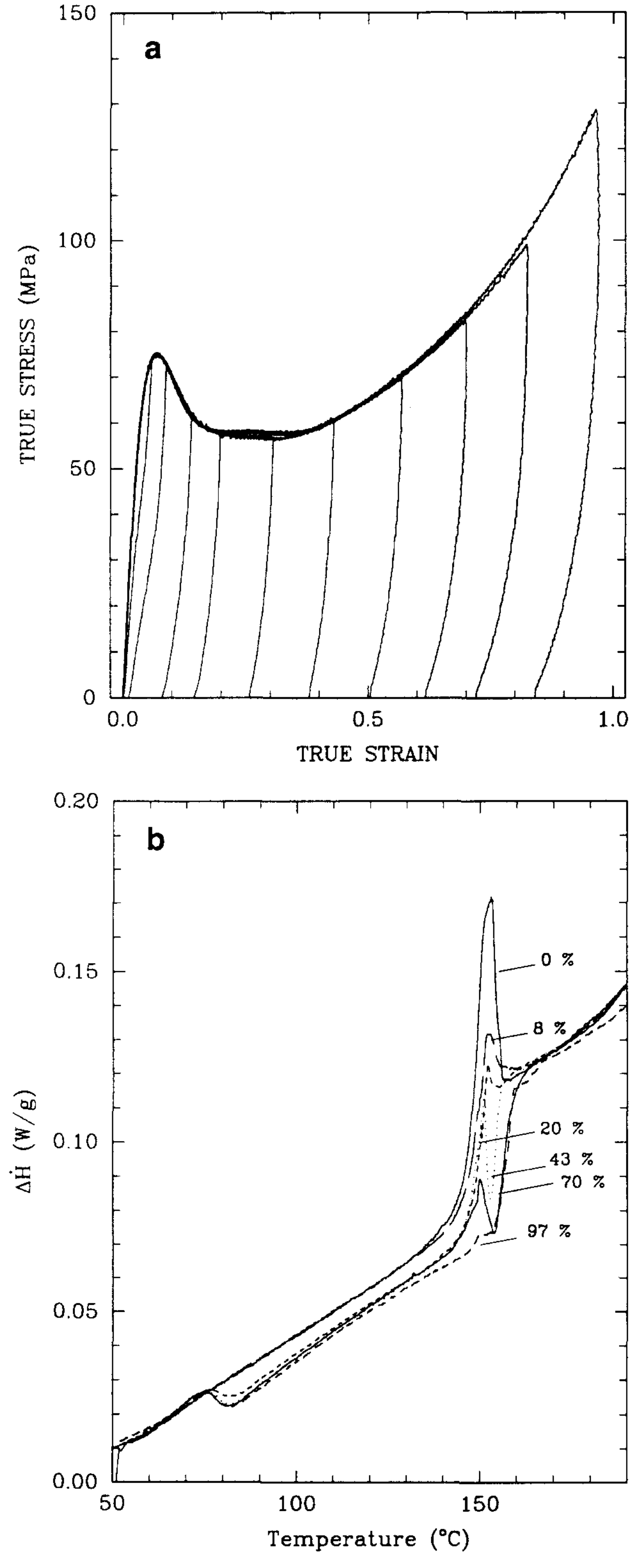

Figure 8 (a) Annealed PC loaded to different strains at temperature 296 K and rate $-0.001\,\mathrm{s}^{-1}$. (b) D.s.c. scans for annealed PC specimens deformed to different (%) strains (scan rate $10\,\mathrm{K\,min}^{-1}$)

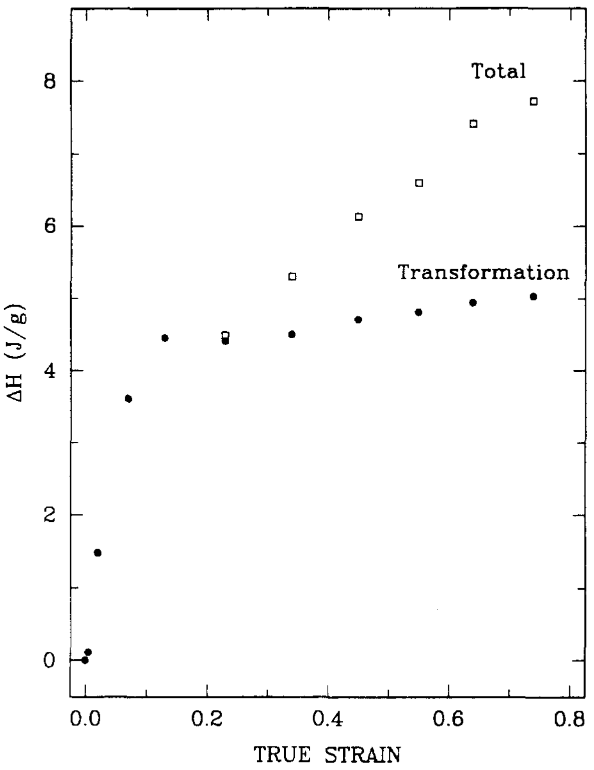

Figure 9 Change in enthalpy of annealed PC with residual strain ($\rho = 1.19\,\mathrm{g\,cm}^{-3}$)

that leads to the observed non-linear recovery upon unloading‡.

DISCUSSION AND CONCLUSIONS

In the constitutive modelling work of Haward and Thackray[9], Argon[10], Boyce *et al.*[11] and Arruda and Boyce[12], the inelastic deformation of glassy polymers has been postulated to consist of two distinct barriers to deformation: one being an isotropic, viscoplastic barrier to chain segment rotation, or in the same sense, local shear transformations[1]; the second being an anisotropic barrier to chain alignment. Each barrier was considered to evolve separately and differently with strain. The d.s.c. measurements presented in this paper confirm the presence of these two distinct barriers and also act to describe quantitatively the important features of their evolution with both physical ageing and inelastic strain§. Chang and Li[2] similarly considered the two exotherms in highly deformed polymers to be indicative of a population of two distinct classes of 'defects' in their d.s.c. measurements.

The microstructural rearrangements that occur in glassy polymers during ageing and deformation are thermally activated (i.e. rate-, stress- and temperature-dependent) and, as shown here, are accompanied by changes in specific enthalpy. As such, d.s.c., which can monitor the rate of change in enthalpy, provides valuable insight into the nature of these rearrangements. Our results indicate that any microstructural changes that have occurred during ageing and/or deformation are *reversed* by heating at a constant rate and that by simultaneously monitoring the material's enthalpy release we can obtain information on the internal energy storage due to microstructural rearrangements. The experimental results for annealed vs. quenched polymer indicate that the topological rearrangements associated with physical ageing can occur at meaningful rates only in the vicinity of T_g in the absence of externally applied stress. This is evident from the fact that, for the relatively fast scanning rates used here (see earlier footnote), these processes are reversed by heat only upon going through the glass transition temperature, and, moreover, are confined to a small range of temperature. Moreover, since inelastic rearrangements are thermally activated, the position of the endothermic peak indicates that the activation energy for these rearrangements is large and the width shows that this distribution is narrow. The high activation energy associated with the endotherm at T_g is consistent with the large increase in stress required to initiate plastic flow in the annealed material. Physically, this suggests that highly cooperative and long-range rearrangements occur during physical ageing.

On the other hand, if we consider the enthalpy release associated with the inelastically deformed polymers, the corresponding exotherm is distributed over a much wider temperature range. Strain recovery is observed at relatively low temperatures and can occur only if the activation energy is low. This suggests that the rearrangements associated with inelastic deformation act to store energy locally, thus biasing and reducing the activation energy barrier. The fact that the exotherm

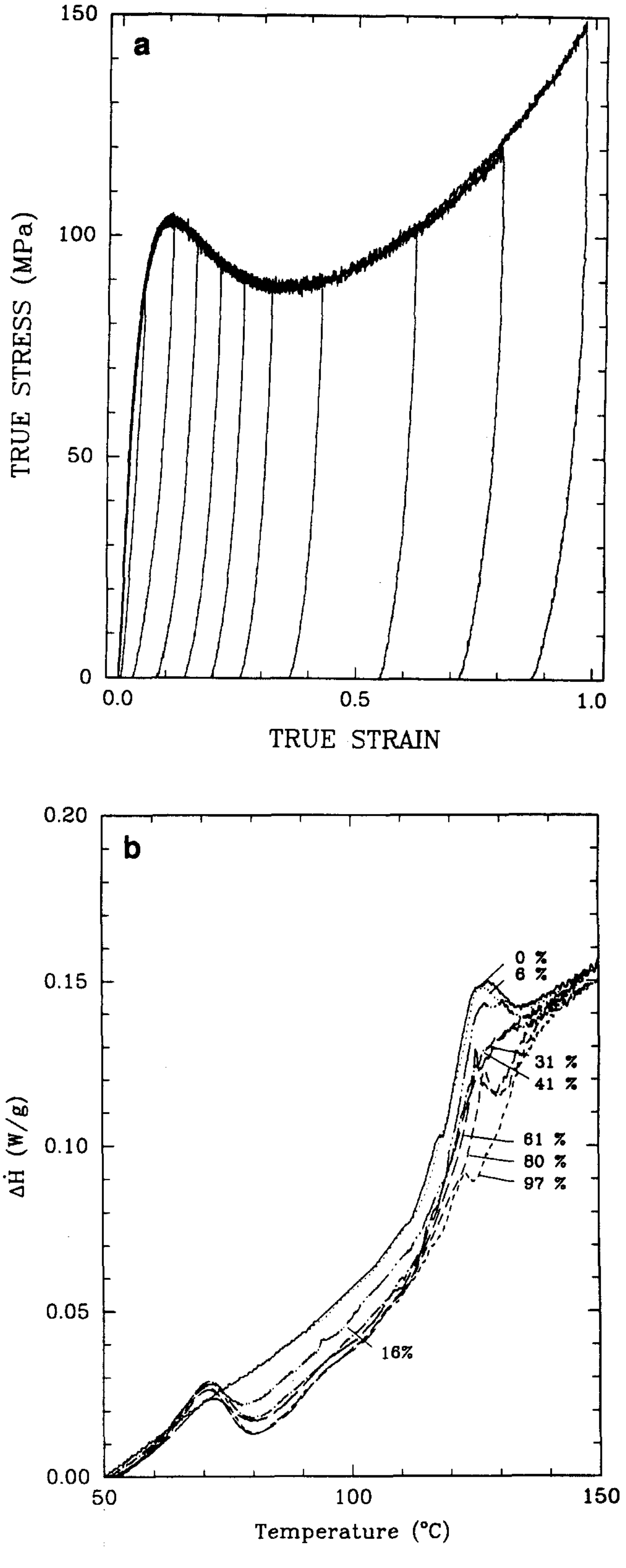

Figure 10 (a) Annealed PMMA loaded to different strains at temperature 299 K and rate $-0.001\,\mathrm{s}^{-1}$. (b) D.s.c. scans for annealed PMMA specimens deformed to different (%) strains (scan rate $10\,\mathrm{K\,min}^{-1}$)

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‡ This illustrates an advantage of deformation calorimetry, which measures energy storage during deformation, i.e. in the loaded state

§ We note that the thermodynamic and mechanical aspects of polymer deformation are highly rate- and temperature-dependent and expect the d.s.c. scanning rate to influence the exotherms. A faster scanning rate should shift the exotherms to a higher temperature and a sufficiently slower scanning rate may broaden the endotherm and may produce significant overlap of the two exotherms as well as some physical ageing, thus obscuring the presence and significance of two separate exotherms

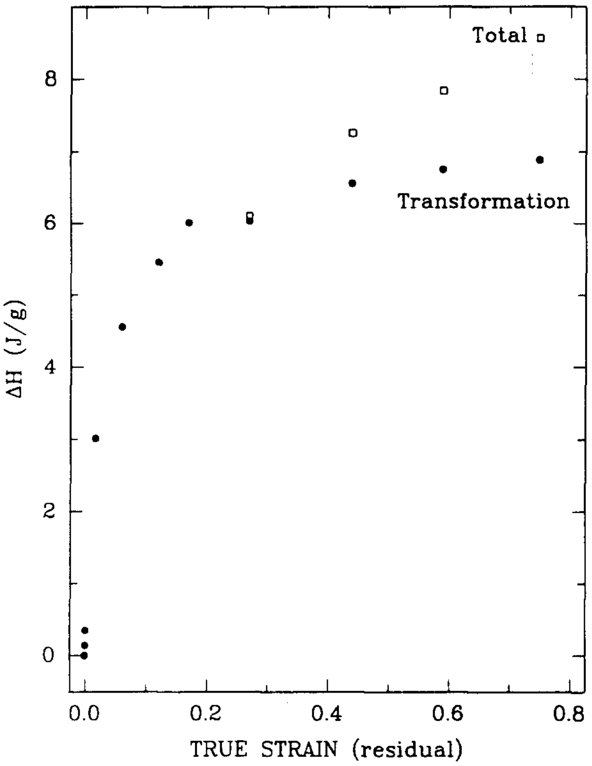

Figure 11 Change in enthalpy of annealed PMMA with residual strain ($\rho = 1.18\ \mathrm{g\,cm^{-3}}$)

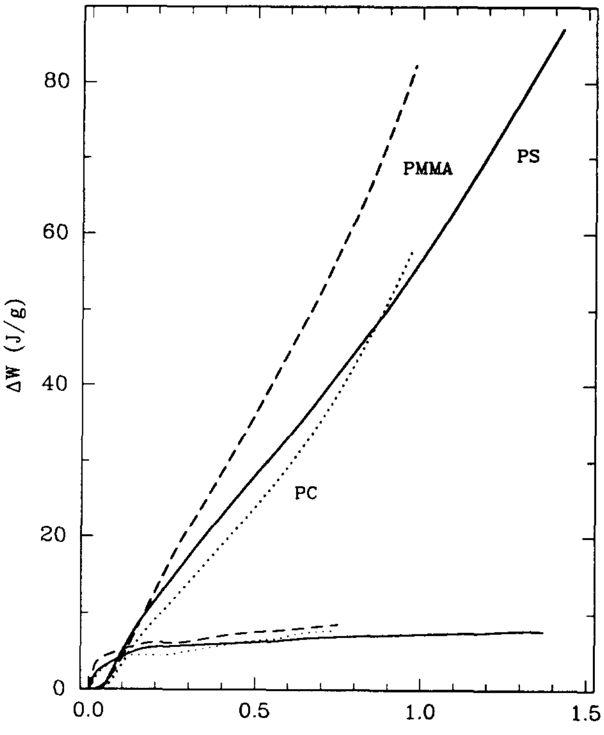

Figure 12 Mechanical work (upper, bold curves) and change in enthalpy (lower, light curves) of annealed PS ($\rho = 1.06\ \mathrm{g\,cm^{-3}}$), PC ($\rho = 1.19\ \mathrm{g\,cm^{-3}}$) and PMMA ($\rho = 1.18\ \mathrm{g\,cm^{-3}}$) with true strain. Note that the former is plotted vs. applied strain less the yield strain and the latter vs. residual strain

occurs over a wide temperature range indicates that inelastic deformation produces a much *broader* distribution of activation energy and a smaller mean value compared to that related to physical ageing. This is consistent with our observation that, although inelastic strain recovery can occur far below T_g, physical ageing effectively ceases below about $(T_g - 30)$ K for timescales of a few days.

The enthalpy release evolves with inelastic strain to a steady-state value. One explanation is to consider inelastic deformation to be the result of highly localized shear transformations (with a low intrinsic activation barrier)[1,10,13]. For small amounts of strain (prior to yield), the occurrence of local transformations is evident from the non-linear mechanical behaviour; however, their small number provides isolation and results in rapid strain recovery upon unloading, even at room temperature. With increasing strain beyond yield, however, the sites become more numerous and interact to produce relaxed configurations of a more long-range nature. The increase in the degree of structural disorder is reflected in the increase in specific enthalpy. Reversing these rearrangements to achieve complete strain recovery means overcoming a locally larger activation barrier; as this is possible (in meaningful timespans) only at somewhat elevated temperatures, enthalpy release occurs over a wide range of temperatures on heating. During inelastic deformation, there will be some regions that have undergone shear transformations just prior to unloading and so have not sufficiently stabilized. These sites result in the non-linear recovery that occurs at the deformation temperature. With increasing time after unloading, strain recovery, which would occur instantaneously at slightly higher temperatures, will also be accessible. This is consistent with the observation that enthalpy release associated with strain recovery in the d.s.c. scan never begins at room temperature for the polymers examined here, but at somewhat higher temperatures. These features of local structural-level rearrangements with deformation are also supported by molecular-dynamics simulations of deformation in atomic glasses[14] and Monte Carlo simulations on glassy structures[15].

An additional feature of the experimental results is the concurrent evolution of enthalpy release rate with material strain softening to a steady or preferred state. This may be interpreted to represent an upper limit to the concentration of sites that can remain 'isolated' in the material and thus store energy; above this concentration, the long-range interactions discussed above will take place.

Finally, we observe that, for material deformed into the strain-hardening regime, enthalpy release continues even beyond the glass transition temperature. The post-T_g exotherm monotonically increases with strain during strain hardening. This may be considered to arise due to energy stored during polymer chain alignment because sufficient energy for orientation recovery in the unloaded configuration will only be possible very near to or in the rubbery state.

The concurrent mechanical testing of and d.s.c. measurements on the three glassy polymers provide valuable insight into the nature of the evolution in material state and mechanical behaviour with deformation. The behaviour can be explained qualitatively by considering inherently short-range (low activation energy, broad exotherm at 'low' temperature) and inherently long-range (high activation energy, narrow exotherm at high temperature) rearrangements. The nature of the observed exotherms suggests that a distribution of activation energies may be a useful approach for characterizing inelastic rearrangements in glassy polymers. The presence of two distinct exotherms suggests the need to model two separate deformation mechanisms, one related to initial yield and strain softening and the other to orientation-induced strain hardening. Implementation of this approach with the aim of modelling non-linear deformation and relaxation phenomena in glassy polymers is the subject of a future communication.

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