Latent energy of deformation of amorphous polymers: 1. Deformation calorimetry

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The post-yielding behaviour of some common amorphous polymers was examined in uniaxial tension to determine if these materials were ideally plastic from a thermodynamic viewpoint. Thermodynamic measurements were made during deformation using a novel isothermal deformation calorimeter capable of measuring the work and heat of deformation. A portion of the deformation work was not converted into heat and therefore was stored as a latent energy of deformation. Thermodynamically ideal plasticity was not observed for any of the polymers studied.

(Keywords: latent energy; deformation; calorimetry; thermodynamics; amorphous polymers; plasticity)

INTRODUCTION

An entire family of amorphous polymers based on the bisphenol-A monomer has been synthesized since the discovery of the desirable mechanical properties exhibited by bisphenol-A polycarbonate. Among the thermoplastic resins, polyarylate and polysulphone based on bisphenol-A are currently being critically examined. One important property of most of these materials is the ability to be uniaxially drawn at temperatures far below the glass transition temperature under the proper conditions. The physics of this drawing process are not well understood; in fact it is surprising that these materials are ductile at room temperature despite their relatively high glass transition temperatures. One intuitively expects brittle behaviour at a temperature over 100°C below the glass transition temperature.

One method of examining solid state post-yielding deformations, which has been extensively used for metals, is microcalorimetry. Among the earliest documented studies of this type were those performed on metals by Taylor and Quinney[1,2]. The titles of these two papers, 'The latent energy remaining in a metal after cold working' and 'The emission of the latent energy due to previous cold working when a metal is heated', demonstrate an early recognition of latent deformation energy in addition to latent energy changes accompanying a phase change. Taylor and Quinney's calorimetric studies demonstrated that, for various metals which had been deformed beyond their yield point, a small percentage of the deformation work was stored in the material. Their experimental method was a non-isothermal annealing one in which they compared the energy required to melt a standard *versus* that required to melt the deformed metal. Taylor and Quinney found that typically 10% of the energy of cold work was stored as a latent energy change for some common metals which were cold worked at room temperature. An excellent review of the stored energy of cold work of metals has been prepared by Bever and Holt[3] which gives values of between 2 and 10% for the stored energy of cold work for various common metals measured by a variety of methods.

One characteristic of ideal plasticity, from a thermodynamic point of view, is the ability to convert all of the work of plastic deformation into heat. Most metals approach thermodynamically ideal plasticity very closely, yet there is no reason to expect this behaviour of polymers. An isothermal deformation calorimeter has been developed in our laboratory and previously described in detail[4]. A simultaneous measurement of the work of deformation and heat of deformation, and application of the first law of thermodynamics,

$$dU = dQ + dW$$

(where $dQ > 0$ for heat flow into the sample and $dW > 0$ for work done on the sample), enables one easily to calculate the internal energy changes during deformation. An ideally plastic material is one which exhibits no change in internal energy during plastic deformation.

The deformation calorimetric behaviour of bisphenol-A polysulphone and polyarylate during room temperature uniaxial tensile deformation was studied to determine if these polymers were ideally plastic during post-yielding deformation. The deformation thermodynamic behaviour of poly(methyl methacrylate) (PMMA) deformed in uniaxial tension at a temperature slightly below its glass transition temperature (T_g) was also examined as a comparison. Previous investigations of bisphenol-A polycarbonate[5–7] have demonstrated that the deformation thermodynamic behaviour of this polymer deviated significantly from ideal plasticity, converting approximately 60% of the work of deformation into heat.

EXPERIMENTAL

Sample preparation

The amorphous glassy polymers studied were formed in a variety of ways. Bisphenol-A polycarbonate

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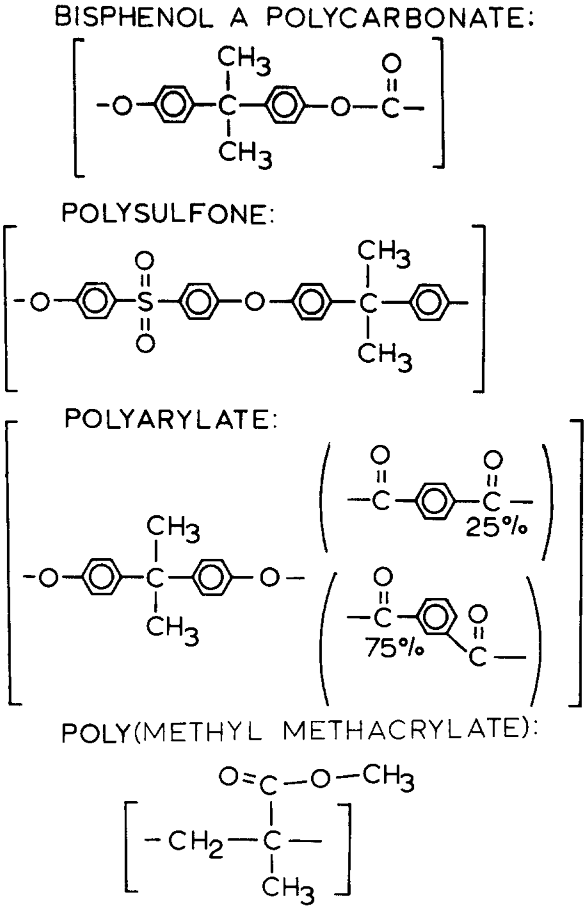

Figure 1 Schematic representation of molecular repeat units for glassy polymers studied

(BPAPC) was Lexan® obtained from the General Electric Corporation in the form of 0.10–0.50 mm thick films. This BPAPC has a T_g of 150°C measured by differential scanning calorimetry (d.s.c.) and $M_w = 3.7 \times 10^4$ determined by light scattering. The poly(methyl methacrylate) (PMMA) and polysulphone (BPAPS) were both purchased from Aldrich Chemical Company. The PMMA had a very high molecular weight and an inherent viscosity of 1.20. The BPAPS had $M_w = 3 \times 10^4$, a reported density of $1.24\,\mathrm{g\,cm^{-3}}$, and $T_g = 190$°C. The aromatic polyester (BPAPA) was a sample of experimental resin Durel® DKX-008 having no additives or stabilizers and was supplied by the Celanese Corporation. The sample was of medium molecular weight with a reported $T_g = 180$°C measured by d.s.c. at $20°\mathrm{C\,min^{-1}}$. A schematic representation of the molecular repeat units of the polymers studied is given in *Figure 1*.

The BPAPA and BPAPS films were melt-pressed from pellets. BPAPC, BPAPA and BPAPS films were all heated above T_g for 1 h and cooled at $10°\mathrm{C\,min^{-1}}$ to obtain films with a well known thermal history. PMMA was solution cast from methylene chloride followed by careful steps to remove residual solvent. No evidence of residual solvent was observed using d.s.c. The tensile specimens used were stamped out of these films with a sharp steel die, at room temperature for BPAPA, BPAPS and BPAPC and at 100°C for PMMA.

Deformation calorimetry

The uniaxial extension experiments in the deformation calorimeter were performed on small dumbbell shaped samples having a width in the narrow region of 3.2 mm and a straight section length of 25 mm according to ASTM test D638. Samples were placed in the calorimeter sample cell at least 1 h before beginning a deformation, to ensure thermal equilibrium and to enhance the stability of the baseline. The isothermal experiments at elevated temperatures were executed by pre-heating the calorimeter fluid bath and allowing the sample cell–transducer assembly containing a sample to equilibrate for at least 5 h before beginning an experiment. The initial sample dimensions, used for calculation of the engineering stress–strain curves, were measured using a hand held micrometer. The initial grip separation was determined with a vernier caliper and was taken as the distance between the centre of the nylon fasteners used to secure the tensile specimens to the stretching mechanism.

The deformation calorimeter operates by relating the difference in pressure between two sealed cells to the heat flow into (or out of) the sample. One cell contains the sample while the other cell is a reference. The heat flow into the sample is calculated directly fom a differential pressure *versus* time curve. The calorimetric experiments were performed using ambient air as the working gas since no variation in the heat calibrations was observed for various ambient (humidity and barometric) variations. Additional experimental details concerning the operation and calibration of the deformation calorimeter appear elsewhere[4,8].

Differential scanning calorimetry

The thermal analysis measurements were made using a Perkin–Elmer DSC-4 differential scanning calorimeter equipped with a thermal analysis data station (TADS) package. The scan rate used for all samples was $20°\mathrm{C\,min^{-1}}$ and sample sizes were in the 10–12 mg range. Calibrations for transition temperature and melting enthalpy were completed using indium and tin. The deformed samples were allowed to shrink freely in conventional aluminium pans during scanning. An attempt was made to constrain drawn BPAPC samples but reproducible results were not obtained for the constrained samples due to premature failure of these samples during the first heating.

RESULTS AND DISCUSSION

Deformation calorimetry

The thermodynamic quantities heat, work and internal energy change as well as the stress are plotted *versus* extension ratio for BPAPA in *Figure 2*. These quantities were calculated from differential pressure *versus* time and force *versus* displacement raw data taken from the deformation calorimeter. Similar plots for BPAPS and PMMA are given in *Figures 3* and *4*. The *x*-axis of these figures was determined by dividing the grip separation at any time by the initial grip separation. Once the sample yields, strain is non-uniform since the necked region is highly strained and the sample ends experience a low strain. Thus, the *x*-axis is valid for early values of strain on the sample and does not represent the true strain in the necked region. The *y*-axis values for the thermodynamic quantities in all cases were not normalized by the sample mass. The total mass of the necked or deformed region was 3.6 mg for BPAPA, 7.5 mg for BPAPS and 9.1 mg for PMMA.

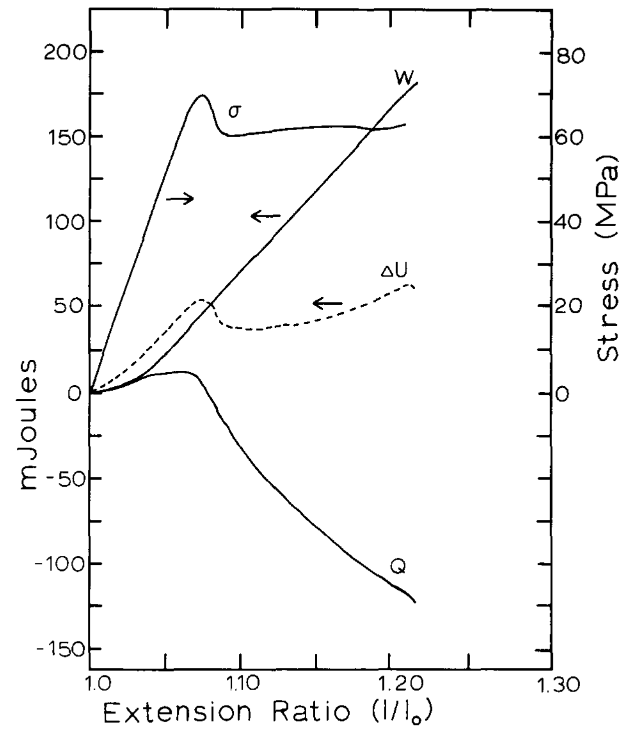

Figure 2 Thermodynamic quantities, heat (Q), work (W) and internal energy change (ΔU), and stress (σ) *versus* extension ratio for BPAPA drawn in the deformation calorimeter at 0.18 min^{-1} and 25°C

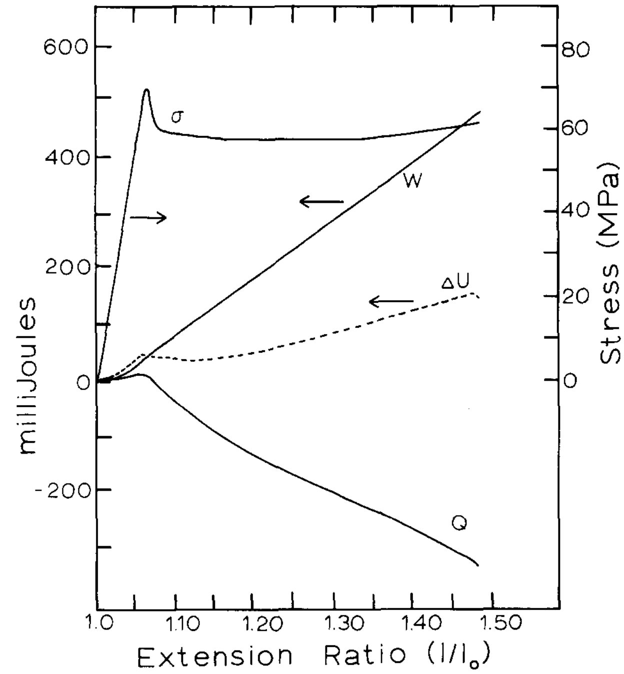

Figure 3 Thermodynamic quantities, heat (Q), work (W) and internal energy change (ΔU), and stress (σ) *versus* extension ratio for BPAPS drawn in the deformation calorimeter at 0.18 min^{-1} and 25°C

There are a number of important similarities and differences among *Figures 2–4*. The two polymers deformed at room temperature yielded at approximately the same values of stress while PMMA deformed at 65°C yielded at a considerably lower stress. Yield strain for all the polymers was 5–7%. The samples all exhibited an initial endotherm before yielding and in all cases demonstrated an increase in the internal energy as the deformation progressed. The internal energy increase per gram was comparable for the two polymers deformed at room temperature; it was slightly less for PMMA. There was an abrupt decrease in the internal energy change after yielding for BPAPA; a much more gradual decrease was observed for BPAPS and PMMA. This decrease in internal energy does not appear to be related to the post-yield stress drop since all the polymers studied had an appreciable post-yield stress drop. The post-yield decrease in internal energy is unrelated to the ductility of the polymer since BPAPS was the most easily drawn polymer under the experimental conditions.

The deformation calorimetric data from the glassy polymers examined are tabulated in *Tables 1–3*. The thermodynamic data in *Tables 1* and *2* for the BPAPA and BPAPS, respectively, were not significantly different from that previously obtained for BPAPC using this deformation calorimeter[7]. The internal energy change at 0.18 min^{-1} deformation rate for all three polymers was approximately 20 J g^{-1} even though the work of deformation was considerably greater for BPAPS. The thermodynamic data for PMMA in *Table 3* demonstrate that the change in internal energy decreased with temperature. The value for work was less at 45°C due to

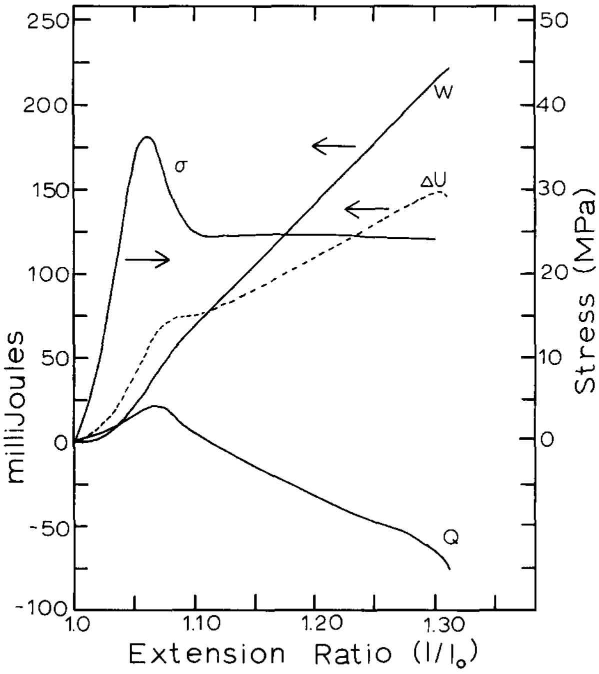

Figure 4 Thermodynamic quantities, heat (Q), work (W) and internal energy change (ΔU), and stress (σ) *versus* extension ratio for PMMA drawn in the deformation calorimeter at 0.45 min^{-1} and 60°C

Table 1 Thermodynamic data for BPAPA drawn to its natural draw ratio ($NDR = 1.65$) in the deformation calorimeter at 25°C

Strain rate (min^{-1})	Q (J g^{-1})	W(J g^{-1})	ΔU (J g^{-1})	Q/W (%)
0.18	32	55	23	58
0.18	35	53	18	65
0.18	44	63	19	70
0.18	38	55	17	70
Av. 0.18	37	56	19	66
0.45	34	51	17	67
0.45	34	49	15	70
0.45	36	56	20	65
Av. 0.45	35	52	17	67

Table 2 Thermodynamic data for BPAPS drawn to its natural draw ratio ($NDR = 1.8$) in the deformation calorimeter at 25°C

Strain rate (min^{-1})	Q ($\mathrm{J\,g}^{-1}$)	W ($\mathrm{J\,g}^{-1}$)	ΔU ($\mathrm{J\,g}^{-1}$)	Q/W (%)
0.18	43	67	24	64
0.18	43	75	32	58
0.18	39	71	32	55
0.18	40	70	30	58
Av. 0.18	42	71	29	59
0.45	42	63	21	66
0.45	47	63	16	75
0.45	48	66	18	72
0.45	43	64	21	68
Av. 0.45	45	64	19	70

Table 3 Thermodynamic data for PMMA drawn in the deformation calorimeter at the indicated temperatures and a strain rate of 0.45 min^{-1}

Temp. (°C)	Sample no.	Q ($\mathrm{J\,g}^{-1}$)	W ($\mathrm{J\,g}^{-1}$)	ΔU ($\mathrm{J\,g}^{-1}$)	Q/W (%)
45	1	8	18	10	45
45	2	7	18	11	44
Draw ratio = 1.15					
62	1	13	31	18	41
62	2	10	27	17	36
62	3	9	24	15	40
Draw ratio = 1.30					

the lower extension ratios obtained for the PMMA samples drawn at 45°C. PMMA was not ductile below 45°C. The internal energy stored for PMMA was considerably less than the values obtained for the other three polymers, though the ratio of internal energy stored to applied work was much greater. The PMMA therefore exhibited the greatest deviation from ideal plasticity. The PMMA was much closer to its T_g than the other three polymers were to theirs, which might lead one to expect the material to exhibit deformation thermodynamic behaviour more similar to a typical rubber. The PMMA was also a much higher molecular weight sample than the other polymers. Deformation calorimetric results for various polyethylenes[9] demonstrated that for the polyethylene deformation, molecular weight was an extremely important parameter in determining deformation thermodynamic behaviour. The internal energy stored was a much greater percentage of the work for the ultra high molecular weight polyethylene. It is possible that any other differences in deformation thermodynamic behaviour between PMMA and the other three glasses were not apparent due to this large difference in molecular weight.

Differential scanning calorimetry

The results of the d.s.c. experiments on the deformed glasses are summarized in *Figure 5*. The samples were allowed to shrink freely in conventional d.s.c. aluminium pans. Recovery was not measured in this experiment, but shrinkage *versus* temperature data for some of these samples are presented in the following paper[10]. A number of features are common to all the thermograms. The exothermic heat capacity changes during the first heating of BPAPC, BPAPA and BPAPS appeared near the deformation temperature. The temperature of these heat capacity changes was 75–90°C but did not appear to depend on the T_g of the polymer. The temperatures for these heat capacity changes were very similar for all the polymers, even though the glass transition temperatures were separated by more than 40°C. These three polymers also exhibited an exotherm at T_g during the first heating. Heating above T_g erased this behaviour completely; the second heating thermograms for the drawn samples were indistinguishable from the thermograms for the original undeformed polymers. The PMMA exhibited slightly different behaviour from the other three polymers. A sub-T_g endothermic heat capacity change appeared at the deformation temperature. The apparent T_g for this deformed sample occurred at approximately 15°C less than the T_g for the undeformed polymer.

A series of d.s.c. thermograms for BPAPC deformed at three different temperatures is shown in *Figure 6*. BPAPC deformed at various temperatures between 25°C and 65°C exhibited a sub-T_g exotherm and other main features of the d.s.c. curves which were essentially

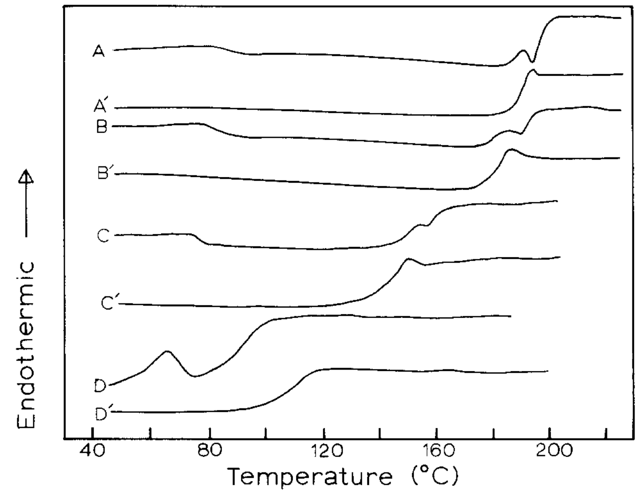

Figure 5 D.s.c. thermograms for various glasses drawn to their natural draw ratios (*NDR*) at 25°C (BPAPC, $NDR = 1.9$, BPAPA, $NDR = 1.65$, BPAPS, $NDR = 1.8$) and at 65°C (PMMA, draw ratio = 2.0). A, A′, BPAPS; B, B′, BPAPA; C, C′, BPAPC; D, D′, PMMA. A, B, C, D, first heating; A′, B′, C′, D′, second heating

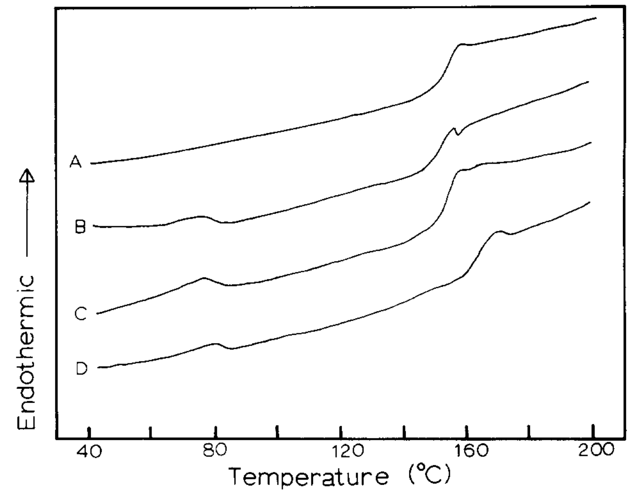

Figure 6 D.s.c. thermograms for BPAPC drawn at various temperatures to its natural draw ratio. A, as received, undrawn sample; B, drawn at 25°C; C, drawn at 40°C; D, drawn at 65°C

identical to the d.s.c. results obtained for BPAPC deformed at 25°C. Heating these deformed samples above T_g eliminated the sub-T_g exotherm. The thermograms for the second heating of the deformed samples were identical to the thermogram obtained for the as-received sample. No evidence of crystalline melting peaks was detected by d.s.c. for any of the four amorphous polymers in either the isotropic or the deformed state.

Heat capacity measurements on deformed or stressed glasses have been made by a number of research groups. Prest and Roberts[11] observed sub-T_g exotherms which were independent of T_g for a wide variety of stressed glassy polymers. These stress-induced thermal events were found to be time dependent, i.e. ageing took place in the stressed glasses. Haward *et al.*[12] demonstrated that the excess enthalpy of physical ageing for BPAPC observed using d.s.c. could be erased by compressively stressing the aged sample before the d.s.c. scan. A similar observation was made by Bershtein *et al.*[13].

The observations made using d.s.c. on the stressed glasses are closely related to the deformation calorimetric results. The results from the deformation calorimetric experiments demonstrated that the stressed glasses were at a higher energy state than the isotropic samples. This state is apparently a quasi-stable state which may be thermally perturbed to return to the original more stable state. The relaxation of the higher energy state towards the original undeformed state is the reason for the exotherm occurring so far below T_g and the reason it is independent of T_g. This return to the original lower energy state took place for the three polymers examined which were based on bisphenol-A: BPAPC, BPAPA and BPAPS. This similarity in molecular structure may have contributed to the observed sub-T_g relaxation taking place at nearly the same temperature. The apparent lowering of T_g for the deformed PMMA probably occurred for a similar reason. The cooperative molecular motion with which T_g is associated must have initiated at a lower temperature for the deformed sample due to the increased internal energy. As the T_g was approached, sufficient thermal energy was available to cause the macromolecular chains to undergo large scale motion to return to the more stable undeformed state. These ideas will be discussed further in the following paper[10].

CONCLUSIONS

Thermodynamic measurements during uniaxial deformation of various amorphous glasses indicated that an appreciable amount of energy was stored during deformation. This deviation from ideal plasticity occurred even though the polymers were amorphous and did not crystallize during deformation, indicating that a crystal structure is not necessary for polymers to exhibit non-ideal plasticity. The internal energy changes during deformation or latent deformation energy resulted in measurable but limited relaxation below T_g which could be detected by d.s.c. The thermodynamic state of these deformed samples was thought to be similar to that of a non-equilibrium quenched glass. It is proposed that physical ageing in glasses is due to the sub-T_g relaxation of the glass to a lower energy thermodynamic state since deformation as well as temperature can erase physical ageing effects. The d.s.c. experiments demonstrated that this relaxation was thermo-reversible; the original glass behaviour could be restored completely by annealing the deformed glass above T_g. Therefore, the changes which took place during deformation were entirely physical in nature. There was no evidence of stress-induced chain rupture or chemical reaction.

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