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Recovery processes in amorphous polymers

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The release of stored energy and the recovery of dimension and volume of cold compressed polystyrene (PS), polymethyl methacrylate (PMMA) and polycarbonate (PC) were studied. The release of stored energy has two peaks, one broad peak at 70° C (PS), 55° C (PMMA) and 85° (PC) and one sharp peak at 113° C (PS, T_g = 105° C), 123° C (PMMA, T_g = 117° C) and 157° C (PC, T_g = 152° C). The recovery of dimension has only one peak at 114° C (PS), 124° C (PMMA) and 157° C (PC). This peak agrees very well with the second peak in the release of stored energy. The recovery of volume has a broad peak similar to the first peak in stored energy. Thus there are probably two recovery processes in these polymers: one releases energy and recovers volume below T_g and the other releases energy and recovers dimension above T_g. These two processes are consistent with the two-stage formation mechanism of shear bands in amorphous polymers.

1. Introduction

The phenomena of relaxation or recovery processes of amorphous polymers in their quenched states to approach thermodynamic equilibrium have been investigated extensively and reviewed recently [1–5]. These processes, especially near the glass transition temperature, have been studied by volumetric, calorimetric, spectroscopic, dielectric, small-angle X-ray scattering (SAXS), light scattering and other techniques. They were interpreted in terms of models based on both phenomenological results [6–12] and free-volume concepts [13–25] in describing the non-linear, non-exponential and asymmetric characteristics of the relaxation kinetics. However, recovery studies of non-equilibrium states created by mechanical deformation are rather limited.

In 1955, Andrews [26] did isothermal retraction experiments on oriented polystyrene monofilaments. The retraction took place by a rearrangement of molecular chains from an oriented to an unoriented state. He found that the retraction process could be described by a distribution of retardation times. In 1973, Park and Uhlmann [27, 28] studied the isothermal recovery of cold-drawn amorphous polycarbonate (PC), and found that the stored energy release and length retraction were both characterized by an activation energy spectrum implying that many molecular processes were involved in recovery. They further pointed out that the spectrum characterizing stored energy release was similar to that characterizing retraction kinetics, indicating the possibility of identical relaxation processes involved in these two isothermal recovery phenomena. In 1978, Li [29] used second-order kinetics for shear band recovery and also for volume recovery by re-examining the volumetric recovery data of Kovacs [30], and found single activation energies of 160 and 176 kcal mol^{-1} (670 and 737 kJ mol^{-1}), respectively. In 1980, Chang [31] also found second-order kinetics, at least in the later stages of annealing, for the recovery of indentation, compressive strain and enthalpy and found single activation energies of 163, 190 ± 70 and 200 kcal mol^{-1} (682, 795 ± 293 and 837 kJ mol^{-1}), respectively.

In 1973, Matsuoka *et al.* [32] studied the effect of tensile stress on the relaxation time of ABS (a styrene–acrylonitrile and polybutadiene composite system), and concluded that stress might reverse the process of annealing by raising the enthalpy of the annealed glassy polymers. In 1977, Chang [33] reported that pelletized polyvinyl chloride (PVC) had a higher enthalpy than the subsequently annealed PVC. The enthalpy begins to release at about 30 to 40 K below T_g. In 1978, Bershtein *et al.* [34] studied the enthalpy change of polystyrene and styrene–methacrylic acid copolymer due to the effect of thermal and mechanical history, and compared with the intra- and intermolecular changes obtained from infrared spectroscopy. They claimed that the enthalpy changes were associated with the intermolecular changes. In 1980 and 1981, O'Reilly and Mosher [35, 36] and Prest *et al.* [37] studied the recovery of pressure-vitrified PVC glasses by using differential scanning calorimetry (DSC), and observed exotherms associated with the release of frozen-in stresses. Later, Prest and Roberts [38] further reported results on mechanically stressed polymeric glasses, and suggested that the energy introduced by mechanical work might be stored in the form of distorted bond angles or bond lengths and/or in the intermolecular potentials. In 1982, Berens and Hodge [39] studied the effects of annealing and prior history on the enthalpy relaxation in amorphous polymers. A broad exothermic peak was observed by DSC in samples of PVC which were given a variety of thermal, mechanical and vapour treatments. This peak was in addition to the endothermic peak due to enthalpy relaxation.

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Several years ago, Chau and Li [40] reported a two-stage process for the formation of shear bands. The first stage was the formation of thin band packets spreading over a narrow region in preparation for the second-stage process, which was a large-scale shearing of the narrow region to form a shear band. The second-stage process produced all the shear strain in the shear band. It is the purpose of this study to see whether the recovery of stored energy, dimension, and volume is consistent with the two-stage deformation process just described.

2. Experimental details

2.1. Sample preparation

Atactic polystyrene (PS) in the form of 0.25 in. (6 mm) thick sheets were obtained from Westlake Co. Lenni, Pennsylvania. Pieces of 80 mm × 12 mm were cut out and annealed at 115° C for 20 h and furnace-cooled to room temperature. They were then machined in a lathe into rods of 3.0 to 3.5 mm diameter with the axes parallel to the sheet. The rods were then sectioned into 2.0 to 2.2 mm thick discs by using a Buehler Isomet low-speed saw (Lake Bluff, Illinois 60044). These discs were placed in a sample holder and ground over 600 grit emery paper followed by polishing with 1 μm and 0.05 μm alumina slurries. Specimens of polymethyl methacrylate (PMMA) and polycarbonate (PC) obtained from DuPont (Wilmington, Delaware 19898) and Sheffield Plastics (Sheffield Massachusetts), respectively, were prepared in the same way except that PMMA was annealed at 120°C and PC at 165° C.

2.2. Measurement of stored energy

Researchers have pointed out repeatedly the importance of the thermal history of glasses in affecting the enthalpy relaxation by varying the heating and cooling rates [41], and the annealing time and temperatures [42–44]. Thus the thermal history before deformation and after annealing must be identical in order to obtain an accurate value of the stored energy of deformation.

A disc specimen was heated in the Perkin-Elmer DSC-2 at a rate of 5 K $\min^{-1}$ to 415 K and immediately cooled down to 270 K at a rate of 40 K $\min^{-1}$. Then the specimen was compressed in an Instron tester at room temperature at an initial strain rate of 0.01 $\sec^{-1}$. Teflon tapes were placed between the specimen and the Instron to reduce friction. The deformed specimen was then put in the DSC apparatus and heated up at a rate of 5 K $\min^{-1}$ from 270 to 415 K to obtain a thermogram. As soon as the specimen reached 415 K, it was cooled down at 40 K $\min^{-1}$ to 270 K. A second thermogram was then obtained by heating up the specimen again at 5 K $\min^{-1}$. The two thermograms should match at both the low-temperature and high-temperature ends. The difference was then calculated by using a Bascom-Turner digital recorder (Newton, Massachusetts 02158) with its data-processing capability. The proper matching of the thermograms was due to the same thermal history of the specimen in the annealed and deformed conditions. Hence the heating and cooling cycle before compression was absolutely necessary. Both the heating and cooling rates should be identical before deformation and after annealing.

2.3. Measurement of dimensional recovery

Macroscopic dimensional recovery of a deformed specimen upon heating was monitored by using a thermomechanical analyser (TMA). The TMA used was a Perkin-Elmer TMS-1. A quartz expansion probe was resting on the top of the compressed specimen with a very small but constant force (1.8 g dead weight, most of which was compensated by buoyancy) so that it moved in accordance with the thickness changes of the specimen during heating. The displacement of the quartz expansion probe was recorded by linear variable differential transformer (LVDT).

After a proper thermal history control, a specimen was first compressed at room temperature in an Instron at an initial strain rate of 0.01 $\sec^{-1}$ and then was heated in the TMS-1 at a rate of 5 K $\min^{-1}$ to 420 K (PS, PMMA) or 455 K (PC) and immediately cooled down at a rate of 10 K $\min^{-1}$ to 273 K. A displacement–temperature curve was recorded for the heating process in which the axial displacement represented both the dimensional recovery of the deformed specimen and the thermal expansion of the same. The annealed specimen was again heated and then cooled in the TMS-1 at rates of 5 K $\min^{-1}$ and 10 K $\min^{-1}$, respectively, in the temperature range described above. The second displacement–temperature curve represented an axial displacement due to only the thermal expansion of the specimen. Then the difference between these two displacement–temperature curves was the dimensional recovery of the deformed specimen.

2.4. Measurement of volume recovery

The quartz dilatometer accessory for the TMS-1 was used for the determination of the volumetric changes of the sample during annealing. The experimental arrangement is shown in Fig. 1. The filling fluid used was methyl silicone 30 000, supplied by William F. Nye, Inc. (New Bedford, Massachusetts). The proper selection of an inert filling medium in the desired temperature range was critical in doing a successful experiment. If the viscosity was too low, the capillary action could push the fluid up in between the walls of the quartz plunger and the barrel as the temperature rose. This leak would interfere with the correct measurement of the volume change of the specimen. If the viscosity was too high, it would be difficult to get rid of bubbles in the filling fluid. The volume of bubbles would change with changing temperature. Many filling fluids were tried including mercury, 0.05 μm alumina powder, and silicone fluid supplied by Perkin-Elmer. Methylsilicone 30 000 was found to be the best in the temperature range used for this study.

The deformed specimen was placed in the filling fluid and left in a vacuum for at least 15 min to remove all the bubbles. Then, the plunger was inserted carefully by removing excess fluid and air. The plunger was then rotated so that the groove was 180° away from the hole in the wall of the barrel. Thereafter, the

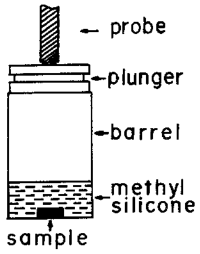


Figure 1 Volume recovery measurement.

system was heated up in the TMS-1 to obtain a displacement–temperature curve at a rate of $5\,\mathrm{K\,min^{-1}}$ to $410\,\mathrm{K}$ (for PS, PMMA) or $450\,\mathrm{K}$ (for PC), and immediately cooled down at a rate of $10\,\mathrm{K\,min^{-1}}$ to $273\,\mathrm{K}$. The plunger displacement caused by the volume changes of the deformed specimen and the thermal expansion of the dilatometric system during heating was monitored by the LVDT of TMS-1. Thus, the volume changes could be obtained by multiplying the plunger displacement by the cross-sectional area of the quartz plunger. Again, the system was heated to obtain a second displacement–temperature curve in which the plunger displacement was only due to the thermal expansion of the dilatometric system. The differences between these two displacement–temperature curves is the volume recovery curve of the deformed specimen. In order to eliminate the effect caused by the thermal history differences, the specimen was heated and then cooled at rates of 5 and $10\,\mathrm{K\,min^{-1}}$, respectively, in the temperature range of 273 to $410\,\mathrm{K}$ (PS, PMMA) or at $450\,\mathrm{K}$ (PC) before it was compressed in an Instron at a strain rate of $0.01\,\mathrm{sec^{-1}}$. As just described, the same heating and cooling rates were used on the deformed specimen in the dilatometer. A temperature calibration was carried out by using two K-type thermocouples, one inside the dilatometer and the other outside. The dilatometer had a specimen in it and was filled with methylsilicone 30 000. A temperature difference of 14 to $15\,\mathrm{K}$ was found at a heating rate of $5\,\mathrm{K\,min^{-1}}$.

3. Results and discussion

3.1. The stored energy release

3.1.1. The two possible release processes

The stored energy measurements after room-temperature compression were carried out on amorphous PS, PMMA and PC by using the DSC-2 as shown in Fig. 2. In Figs 2a, b and c, Curve 1 consists of two DSC scans of the same specimen. The lower curve for the deformed sample was the first scan and the upper curve for the annealed sample was the second scan. The area enclosed by the two curves was the amount of energy stored during compression. Curve 2 in Figs 2a, b and c is the integral of the difference between the two parts of Curve 1, and is the change in the total stored energy. Curve 3 is the difference of the two parts of Curve 1. It is obvious that there are two peaks, one broad peak below T_g and one sharp peak above T_g. It indicates two kinds of stored energy release processes.

To see whether the two release processes are separable the following experiment was performed. A deformed sample of PS was heated in the DSC-2 at a rate of $5\,\mathrm{K\,min^{-1}}$ from 270 to $382\,\mathrm{K}$ ($4\,\mathrm{K}$ above its T_g) and immediately cooled down to $270\,\mathrm{K}$ at $40\,\mathrm{K\,min^{-1}}$. This procedure should release the stored energy below T_g. The partially recovered PS was heated again at $5\,\mathrm{K\,min^{-}}$ to $415\,\mathrm{K}$ to obtain the first thermogram in Curve 2 of Fig. 3. As soon as the specimen reached $415\,\mathrm{K}$ it was cooled down to $270\,\mathrm{K}$ at $40\,\mathrm{K\,min^{-1}}$. The second thermogram in Curve 2 of Fig. 3 was obtained by heating up the specimen again at $5\,\mathrm{K\,min^{-1}}$. Curve 1 of Fig. 3 is the two previously described stored energy release thermograms as obtained in Fig. 2. Comparing Curves 1 and 2 of Fig. 3, it is seen that the two release processes are separable in PS.

The varied stored energy release thermograms in Fig. 2 among PS, PMMA and PC could be rationalized in terms of the varied molecular structures. Polystyrene and polymethyl methacrylate are vinyl polymers; their structural differences are in the pendant side-groups. PS has a relatively big, rigid phenyl group to hinder the rotation and translation of molecular chains relative to each other, while PMMA has a rather small, linear and flexible side-group which makes it easier for the molecular chains to pass over each other. This may be the reason why PS has an apparent for PMMA. In other words, for PS some stored energy can be released only when the temperature is high enough. Polycarbonate is a non-vinyl polymer, but it carries a rigid, rather inflexible molecular backbone. As a result the intramolecular deformation such as bending, stretching and twisting is more difficult than for PS and PMMA. If the recovery of intramolecular deformation is easier than intermolecular deformation so that the former takes place below T_g and the latter takes place above T_g, a smaller amount of stored energy in PC should be released below T_g compared to PS and PMMA. This is seen in Fig. 2c.

3.1.2. The relationship between stored energy and compressive strain

From Fig. 4, the amount of stored energy is seen to increase with compressive strain. The stored energy (ΔH) and the compressive strain (ε) relationships are empirically: $\Delta H = 1.99\varepsilon^{0.31}\,\mathrm{cal\,g^{-1}}$ for PS, $\Delta H = 2.9\varepsilon^{0.45}$ for PMMA and $\Delta H = 1.63\varepsilon^{0.50}$ for PC ($1\,\mathrm{cal} = 4.1868\,\mathrm{J}$). The compressive strain was calculated as the natural logarithm of the thickness ratio. The thicknesses were measured before and after compression. The input energy was the mechanical work done on the specimen during compression. It was calculated from the load–displacement relation.

If the standard linear solid model (Fig. 5) is used to explain the stored energy–strain relationship, the expression for the total stored energy is

$$\Delta H = \frac{\sigma_1^2}{E_1} + \frac{\sigma_2^2}{E_2} = E_1\varepsilon_1^2 + E_2\varepsilon_2^2 \qquad (1)$$

Since $\sigma_1 + \sigma_2 = 0$ upon unloading, $\varepsilon_2 = -(E_1/E_2)\varepsilon_1$. Substituting into Equation 1,

$$\Delta H = E_1\left(1 + \frac{E_1}{E_2}\right)\varepsilon^2 \qquad (2)$$

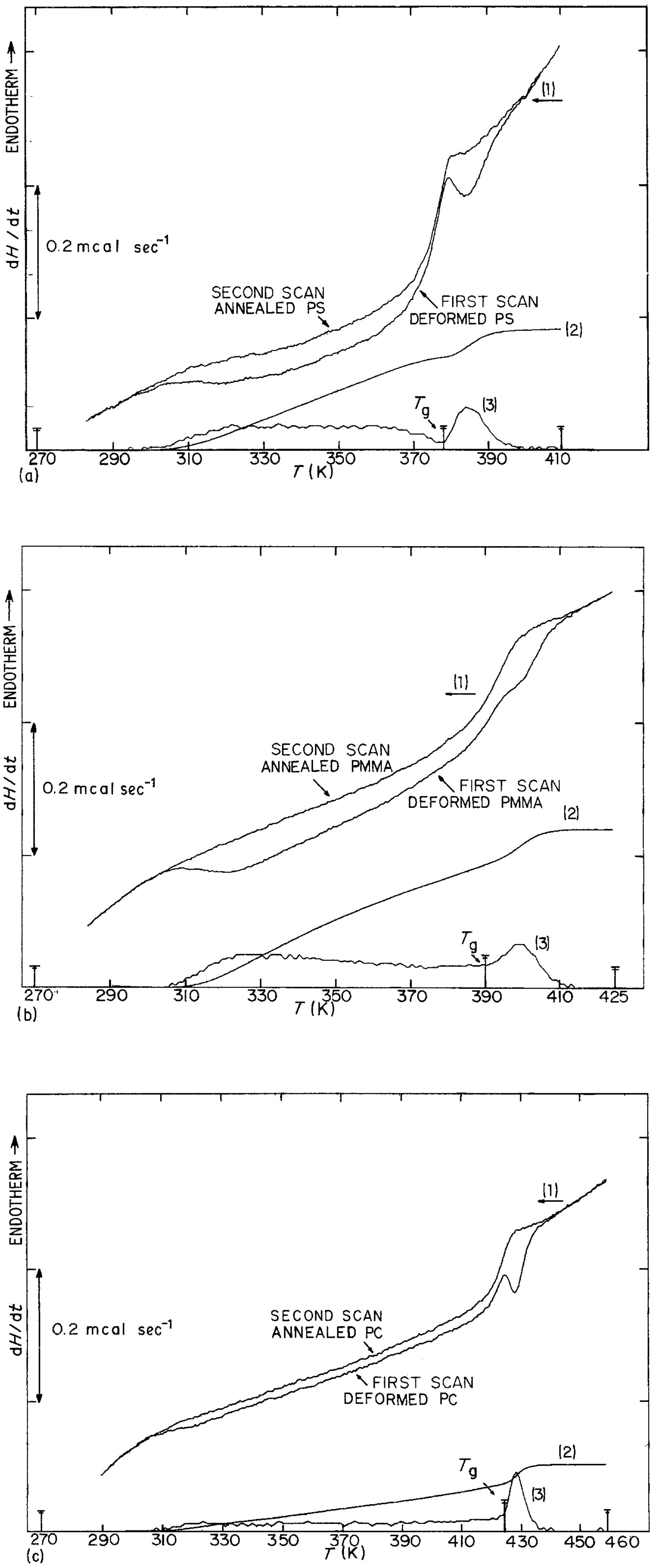


Figure 2 DSC thermograms for deformed and annealed polymers. (a) PS: strain -0.420, 22.39 mg, stored energy $\Delta H = 1.626 \text{ cal g}^{-1}$ (6.808 J g^{-1}), DSC between 270 and 410 K at 5 K min^{-1} (heating) and 40 K min^{-1} (cooling). (b) PMMA: strain -0.450, 27.34 mg, $\Delta H = 2.195 \text{ cal g}^{-1}$ (9.190 J g^{-1}), DSC between 270 and 425 K at 5 K min^{-1} (heating) and 40 K min^{-1} (cooling). (c) PC: strain -0.467, 22.64 mg, $\Delta H = 1.408 \text{ cal g}^{-1}$ (5.895 J g^{-1}) DSC between 270 and 460 K at 5 K min^{-1} (heating) and 40 K min^{-1} (cooling).

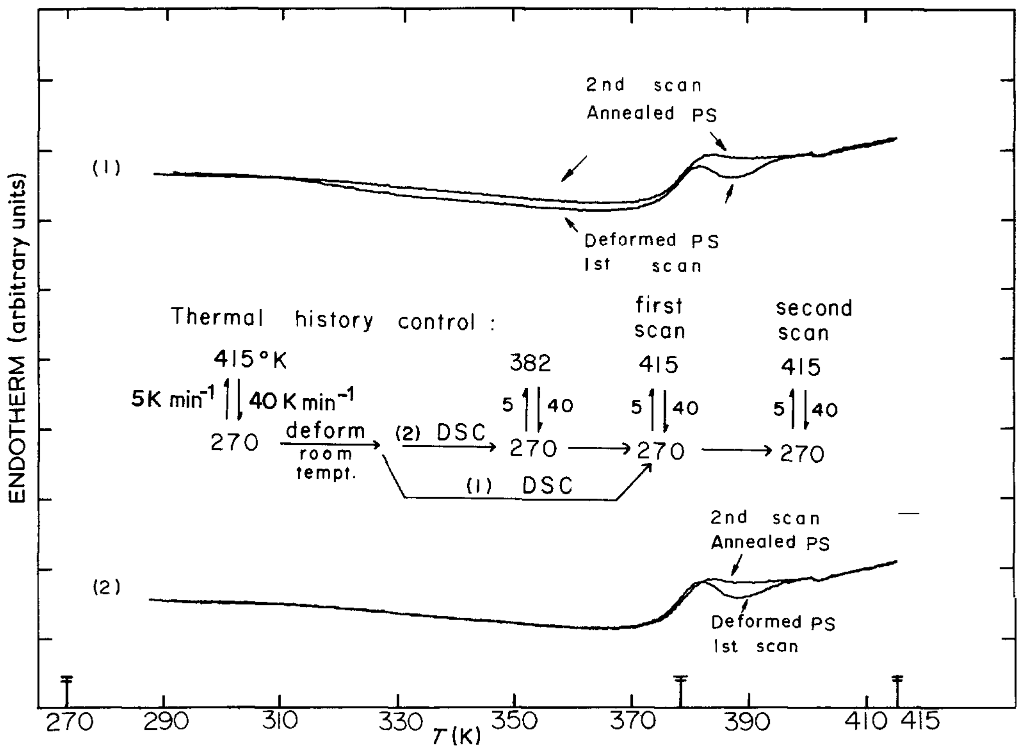


Figure 3 DSC thermograms for deformed and partially and fully annealed PS showing the separability of the two-stage process: strain -0.220, 24.66 mg, 2 mcal sec^{-1} full scale.

where $\varepsilon = \varepsilon_1 = \varepsilon_2 + \varepsilon_3$ with ε_3 being the strain of the dashpot. Equation 2 shows that the stored energy and strain relationship can be expressed as $\Delta H = K\varepsilon^2$. This result is quite different from what is observed experimentally. Obviously the standard linear solid is not a good model for stored energy, not even for small strain, although it works fairly well for creep and stress relaxation.

3.2. The dimensional recovery

3.2.1. *The recovery mechanism*

The uniaxial dimensional recovery of compressed PS, PMMA and PC was measured by using a Perkin-Elmer TMS-1. In Figs 6a, b and c, Curve 1 is the direct recording of dimensional changes of a deformed specimen with increasing temperature and Curve 2 is the thermal expansion of the same specimen after annealing. The net dimensional recovery due to deformation was obtained by subtracting the two as shown in Curve 3. It is apparent that for large strain compression very little dimensional change occurred below T_g. Most of the changes took place above T_g as shown in Table I.

It is known that compression of amorphous polymers generates shear bands in the polymer matrix. These bands are responsible for the major compressive strain of the deformed specimens. The shear bands remain intact below T_g as indicated by the surface profiles of the shear bands in the heating process. It is plausible that conformational changes of molecular chains during recovery at low temperatures do not seem to contribute to dimensional recovery, which takes place only when the temperature reaches T_g and above.

3.2.2. *Deformation processes and recovery processes*

A deformed amorphous polymer can totally return to its original undeformed dimension after heating the polymer over its T_g. This phenomenon is known to most polymer researchers. However, the deformation processes are different from the recovery processes in terms of the stored energy–compressive strain relationship.

In Figs 7a, b and c, the curves for deformation processes were obtained by using the empirical equation from Fig. 4, and the curves for recovery processes were obtained by comparing the stored energy release thermograms and the dimensional recovery curves for the same specimen deformed to a certain strain and heated at the same heating rate. Fig. 7 shows that at any given strain, the specimen has a higher stored energy in deformation than in recovery. It appears that the deformation processes must be

TABLE I Dimensional recovery before and after T_g for all three polymers

PS		PMMA		PC	
Strain	Recovery below T_g (%)	Strain	Recovery below T_g (%)	Strain	Recovery below T_g (%)
-0.220	14.9	-0.170	61.1	-0.217	28.9
-0.587	10.8	-0.386	38.4	-0.441	23.0
-0.595	7.4	-0.562	22.5	-0.620	17.8

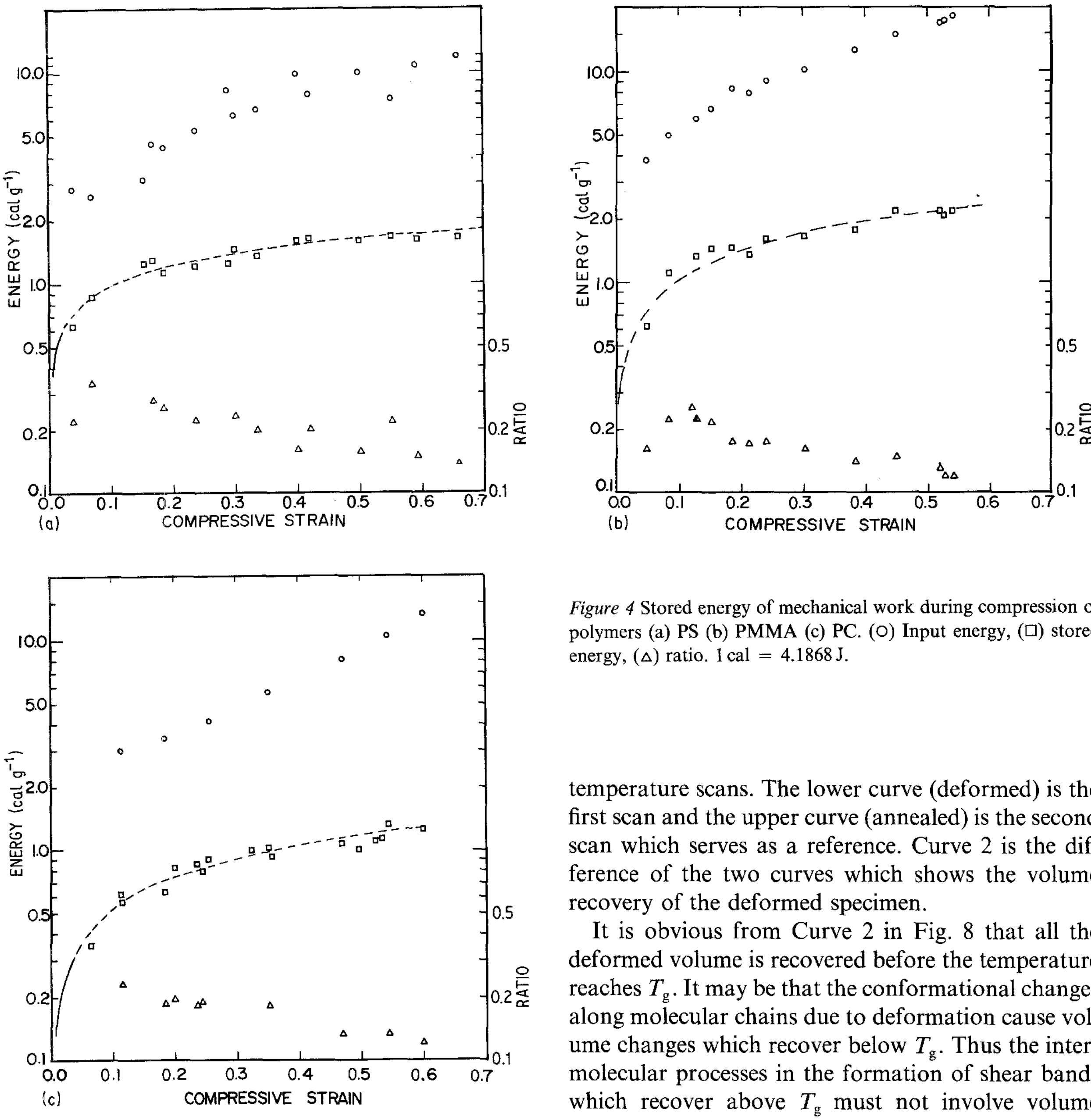


Figure 4 Stored energy of mechanical work during compression of polymers (a) PS (b) PMMA (c) PC. (○) Input energy, (□) stored energy, (△) ratio. 1 cal = 4.1868 J.

different from the recovery processes. Otherwise the two curves should be identical.

3.3. The volume recovery

The recovery of volume of deformed amorphous polymers, such as PS, PMMA and PC, was measured by using the TMS-1 and a quartz dilatometer as shown in Figs 8a, b and c. Curve 1 consists in each case of two temperature scans. The lower curve (deformed) is the first scan and the upper curve (annealed) is the second scan which serves as a reference. Curve 2 is the difference of the two curves which shows the volume recovery of the deformed specimen.

It is obvious from Curve 2 in Fig. 8 that all the deformed volume is recovered before the temperature reaches T_g. It may be that the conformational changes along molecular chains due to deformation cause volume changes which recover below T_g. Thus the intermolecular processes in the formation of shear bands which recover above T_g must not involve volume changes. The volume after compression is smaller compared to the annealed volume for PS, PMMA and PC with a density increase of 0.67% at a strain of -0.706 (PS), 0.50% at -0.664 (PMMA) and 0.42% at -0.513 (PC). Brady and Yeh [45] also reported an overall density increase of about 0.15% upon plastic deformation of PS, PMMA and PC. Uhlmann and Park [27] also reported a density increase of 0.23% due to cold-drawing of PC.

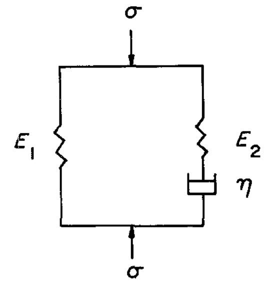


Figure 5 Standard linear solid: σ, applied stress; E, Young's modulus; η, dashpot viscosity.

3.4. The two-stage recovery process in amorphous polymers

Three different quantities have been measured during the annealing of three cold-compressed amorphous polymers. As shown in Table II, there is agreement between the first peak of stored energy and the broad peak of volume recovery (rate of volume change) and also between the second peak of stored energy and the peak of dimensional recovery. These agreements suggest that there are at least two apparent recovery processes, one above and one below T_g. The recovery process below T_g is attributed to the localized conformational changes of molecular chains during compression in preparation for the formation of shear

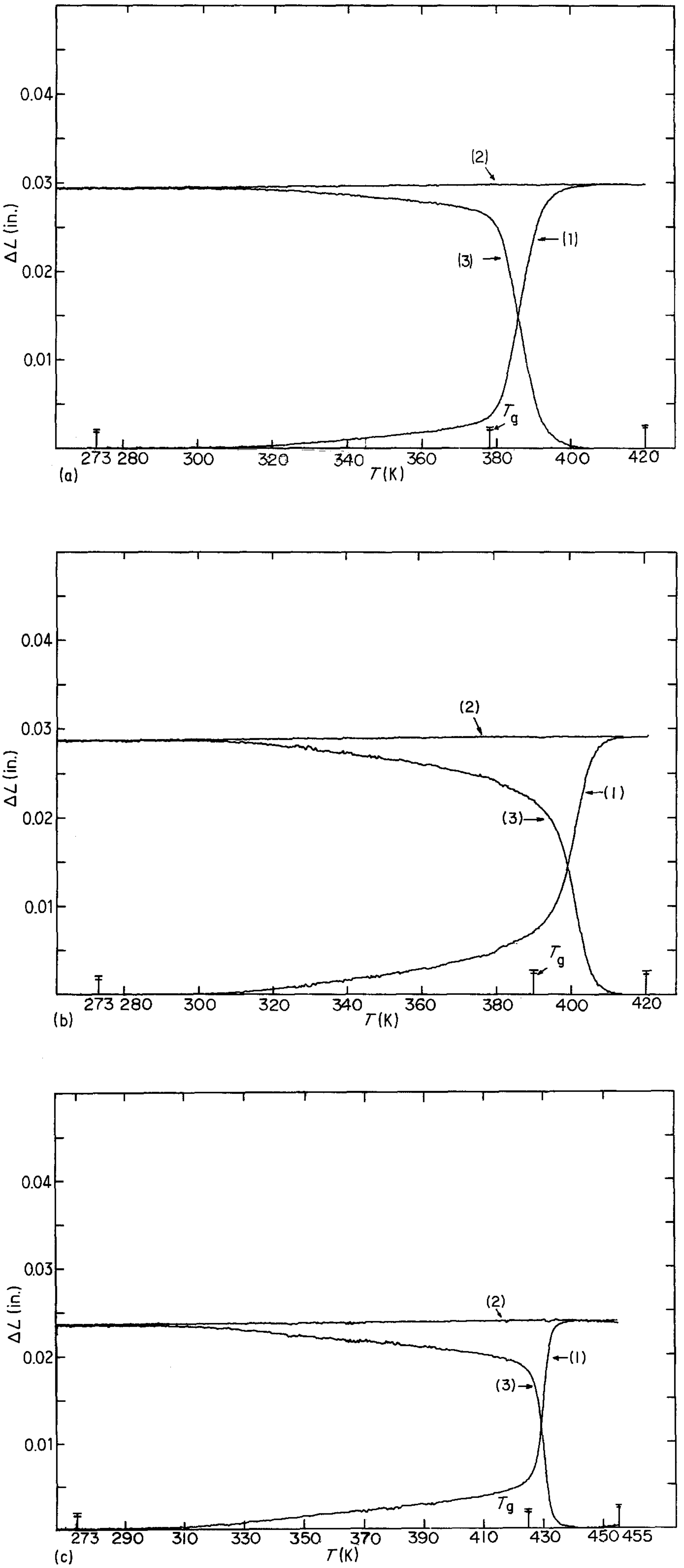
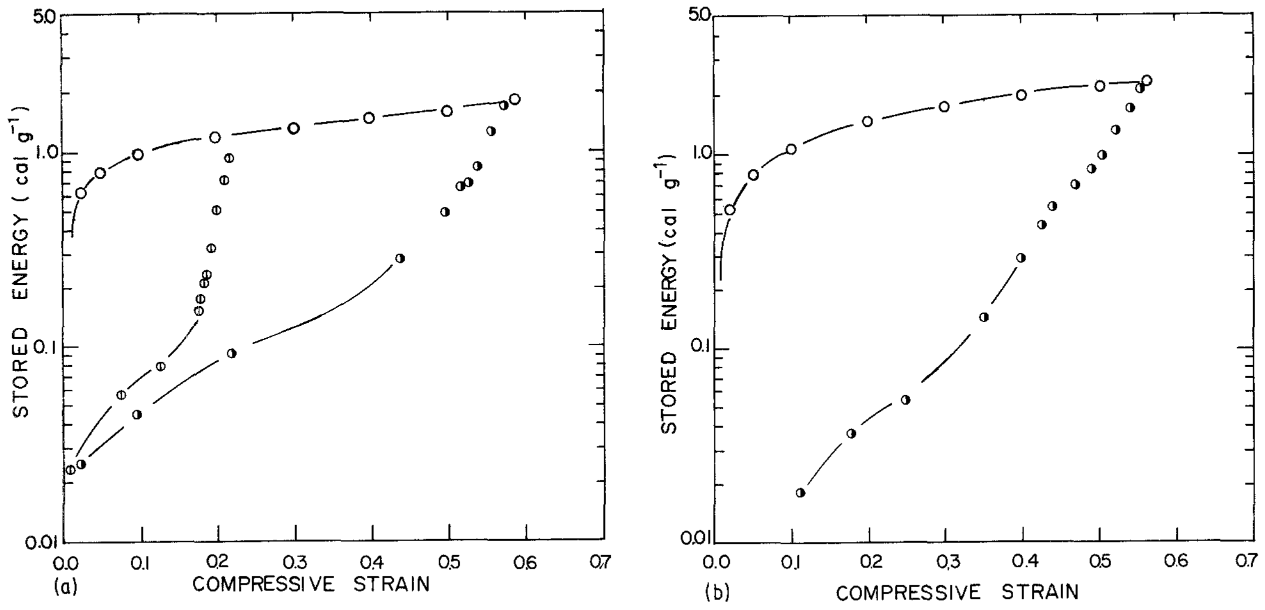


Figure 6 TMA traces of dimensional recovery of deformed polymers: (a) PS (strain −0.587), (b) PMMA (strain −0.562), (c) PC (strain −0.441). Curve 1, dimensional recovery of deformed polymer; Curve 2, pure thermal expansion of annealed polymer; Curve 3, difference. 0.05 in. full-scale sensitivity (1 in. = 25.4 mm). Heating rate 5 K min^{-1}, cooling rate 10 K min^{-1} between 273 K and (a, b) 420 K or (c) 455 K.



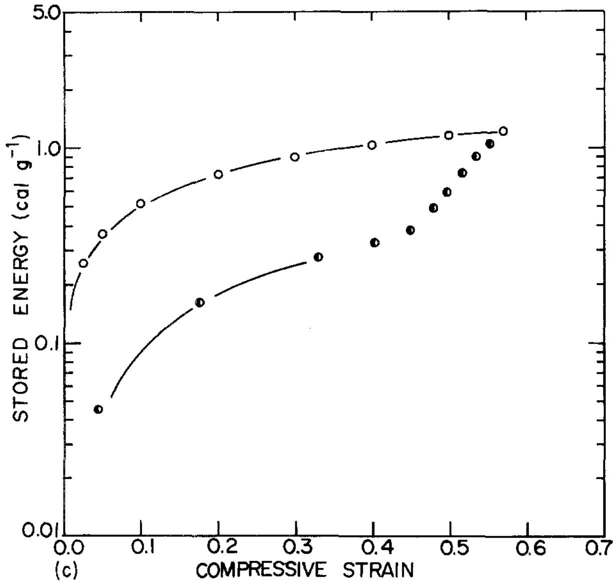


Figure 7 The relation between stored energy and compressive strain during deformation and subsequent annealing: (a) PS, (b) PMMA, (c) PC. (○) Deformation; (◍, ◑, ◐) annealing. 1 cal = 4.1868 J.

bands. This is a process which stores energy and changes volume but produces very little strain. The recovery process above T_g is associated with the large-scale shearing step during compression in the production of shear bands, a process which produces strain and stores energy but does not change volume. This two-stage scheme is consistent with direct observations of the formation of shear bands [46]. A detailed study of the recovery of thick shear bands has been reported [47].

Based on this two-stage concept, there should be a relation between the dimensional changes and the second part of the stored energy (above T_g) and another relation between the volume changes and the first part of the stored energy (below T_g). Since for PS the two parts of stored energy are clearly separable, it is used for these comparisons.

Fig. 9 shows the two storage processes against compressive strain. It is seen that for the uniformly compressed PS, the first storage mechanism (stored energy below T_g) saturates very early at about 15% compressive strain. The second storage mechanism (stored energy above T_g) continues to increase with compressive strain even though at a decreasing rate with increasing strain. The first part is larger than the second part by at least a factor of two. During annealing, the relation between the second part of the stored energy and the strain (as measured by TMA) as shown also in Fig. 9 turns out to be the same as the relation between the second part of the stored energy and the compressive strain of deformation. Such an agreement explains the discrepancy in Fig. 7 and supports the two-stage postulate.

While the one-to-one relation between the stored energy (second part) and strain for both deformation and recovery is consistent with the model of a standard linear solid, the theoretical relation (Equation 2) does not agree with the experimental results (Fig. 9).

The relation between stored energy and strain is similar to that of metals, namely, the energy stored per unit strain of deformation decreases with increasing strain. The phenomenon is attributed to dynamic recovery in metals–annihilation of dislocations and disappearance of point defects during deformation. Something similar to dynamic recovery may take place also in polymers.

At the risk of speculating too much on the basis of metal behaviour, the first part of the stored energy could be due to the generation of dislocations, the

TABLE II Peak temperatures (° C) for stored energy release, dimensional recovery and volume recovery for all three polymers

Polymers	Stored energy recovery		Dimensional recovery	Volume recovery	T_g
	1st peak	2nd peak			
PS	70 ± 15	113.0	114.0	75 ± 20	105.0
PMMA	55 ± 15	123.0	124.0	65 ± 20	117.0
PC	85 ± 30	157.0	157.0	95 ± 40	152.0

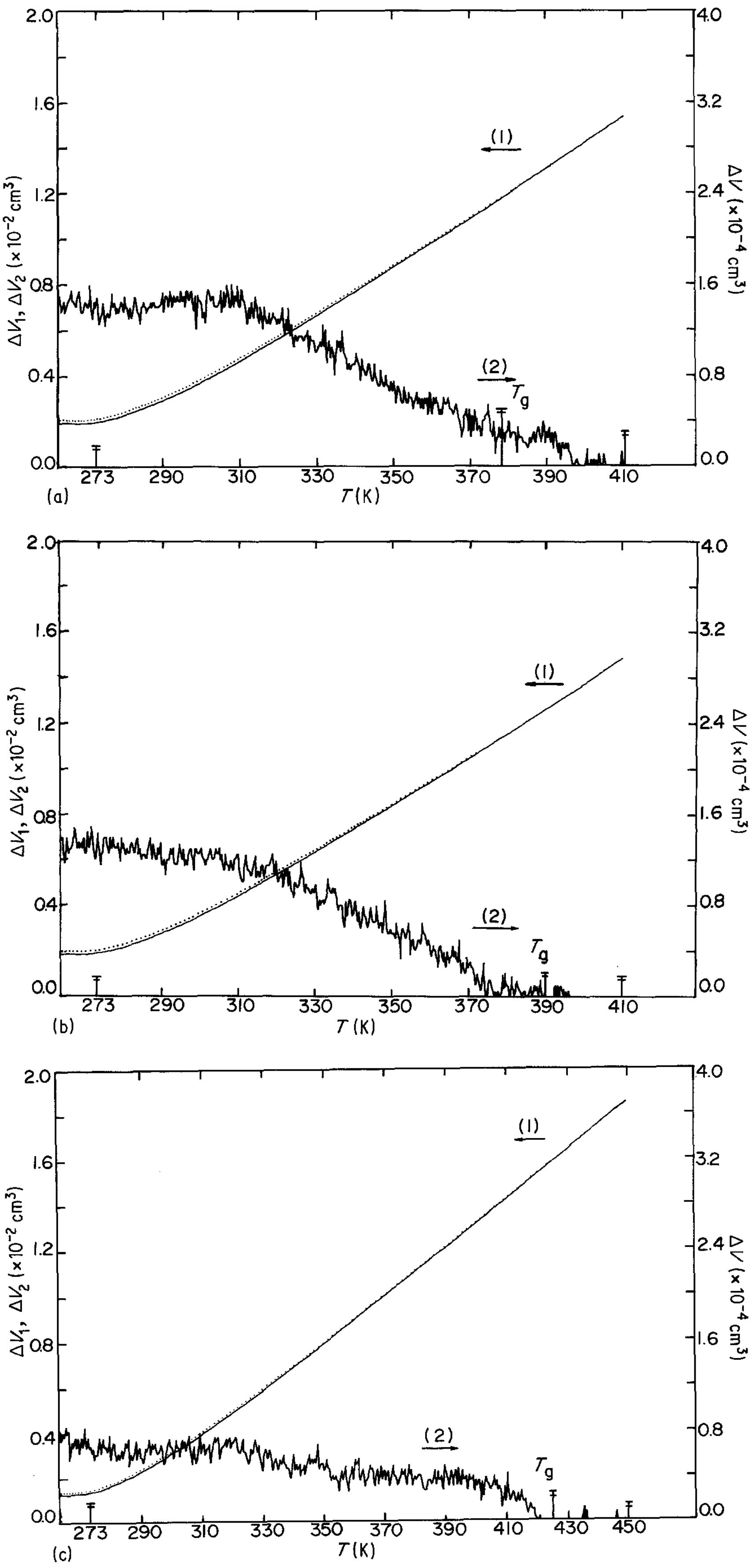


Figure 8 TMA trace of volume recovery of deformed polymers: (a) PS (strain -0.706, 22.82 mg); (b) PMMA (strain -0.664, 27.54 mg); (c) PC (strain -0.513, 24.20 mg). Curve 1 (——) deformed polymer (ΔV_1), (· · ·) annealed polymer (ΔV_2); Curve 2 $\Delta V = \Delta V_2 - \Delta V_1$. Heating rate 5 K min^{-1}, cooling rate 10 K min^{-1} between 273 K and (a, b) 410 K or (c) 450 K.

formation of mobile units, or the creation of configurations to facilitate the shear process. These processes would store energy, change volume, but produce little strain. The second part of the stored energy could be due to the motion of dislocations, the shearing of the mobile units, or the slippage between molecular chains. These processes would produce strain, store some more energy but probably change no volume.

Fig. 10 shows the volume increase during recovery and the first part of the stored energy (below T_g) indicating a monotonically increasing relationship. In view of Fig. 9, the volume change during the deformation process also saturates early, before about 15%

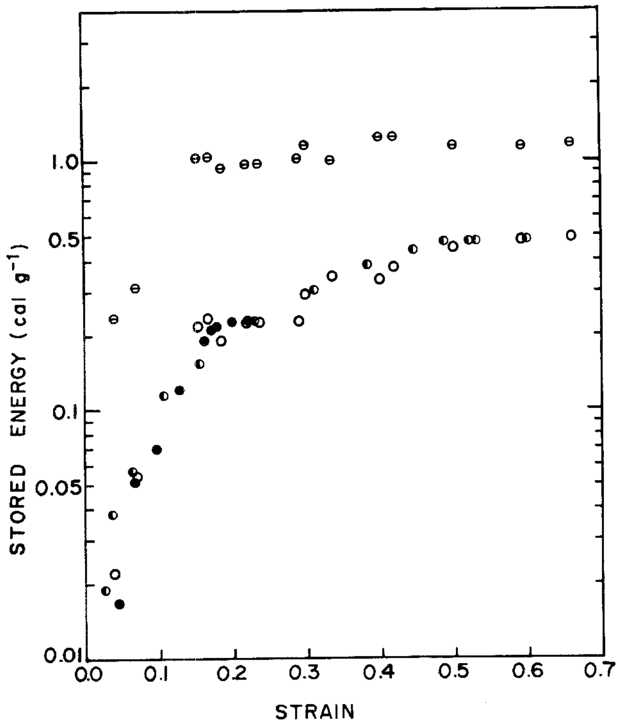


Figure 9 Stored energy (⊖) below T_g as a function of compressive strain and stored energy (○) above T_g as a function of compressive strain and (◐, ●) strain during annealing. 1 cal = 4.1868 J.

strain. Subsequent straining up to 65% produces no further volume increase. Such behaviour is consistent with the idea of the nucleation and motion of dislocations or mobile units as the two-stage process in both deformation and recovery.

The two-stage recovery process has been further confirmed by annealing a deformed polymer under dimensional constraint [48]. When the compressive strain was not allowed to recover, the second part of the stored energy (above T_g) was not released either, while the first part of the stored energy (below T_g) was released as usual.

4. Summary and conclusions

1. The release of stored energy of deformed amorphous polymers has two stages, one below T_g and the other above T_g. The first stage releases some stored energy and recovers volume and the second stage releases the rest of the stored energy and recovers dimension. For PS the two stages are clearly separable. For PMMA and PC the two stages overlap somewhat.

2. The separability of the two stages in PS is shown by heating in DSC a deformed sample to 382 K (4 K above T_g) first and then cooling down. This scan released the first part of the stored energy. A repeated scan showed no more energy released before T_g. The rest of the stored energy was released only after T_g (see Fig. 3).

3. Dimensional recovery of deformed samples takes place after T_g. The peak temperature (fastest rate of recovery) agrees with the second peak of stored energy release in all three polymers. For PS the relationship between strain and the second part of stored energy (above T_g) during annealing is the same as that in deformation (see Fig. 9). This one-to-one relation is not valid if the total stored energy (both parts, above and below T_g) is used instead of the second part (see Fig. 7).

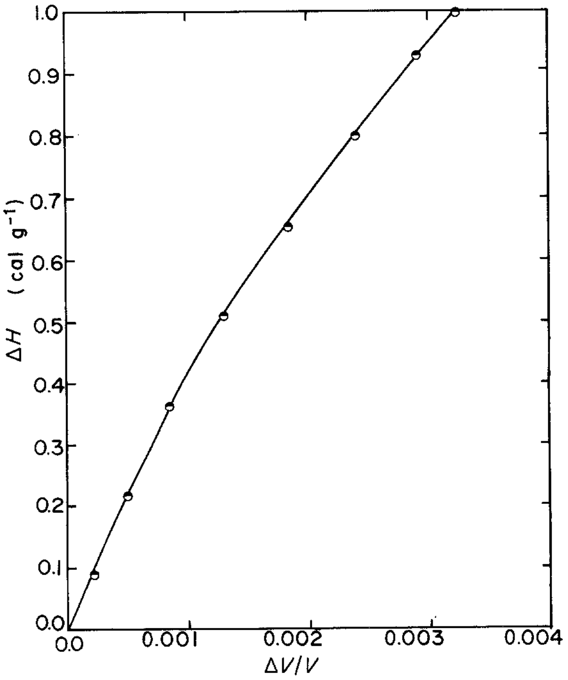


Figure 10 Stored energy below T_g as a function of volume during annealing. 1 cal = 4.1868 J.

4. The relation between stored energy (second part) and compressive strain for PS is not consistent with the model of a standard linear solid. The behaviour is more like that of metals with dynamic recovery. Similar to metals, the first part of the stored energy could be due to the nucleation of dislocations and the second part could be due to their motion.

5. Volume recovery takes place before or below T_g. The compressed samples have a smaller volume (or larger density) than annealed samples. The maximum observed density increase is 0.67% ($\varepsilon = -0.706$), 0.50% ($\varepsilon = -0.664$) and 0.42% ($\varepsilon = -0.513$) for PS, PMMA and PC, respectively. The broad peak of volume recovery is similar to the first part of the stored energy release (before T_g) for all three polymers. In fact there is a monotonically increasing relation between energy release and volume increase during annealing (see Fig. 10).

6. The two-stage process of recovery is consistent with the two-stage mechanism of deformation. In deformation, the first stage produces conformational changes in molecular chains (creating dislocations) to facilitate the chain slippage process which takes place in the second stage. Hence the first-stage process stores energy, changes volume but produces very little strain. In the second stage a large-scale shearing process takes place in which the molecular chains slip relative to each other (such as by the motion of dislocations). This second-stage process produces strain, stores some more energy but apparently changes no volume.

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