Latent energy of deformation of amorphous polymers: 2. Thermomechanical and dynamic mechanical properties

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Thermomechanical and dynamic mechanical measurements were made on some common amorphous polymers which had been deformed in uniaxial tension below their glass transition temperatures (T_g). Stress–temperature experiments showed that a stress increase began just above the draw temperature for constrained samples which had been uniaxially predrawn. Similarly, unconstrained samples heated above the deformation temperature shrank in the draw direction. Dynamic mechanical experiments demonstrated the appearance of a relaxation below T_g which disappeared upon annealing for the drawn samples. This behaviour was attributed to a partial release of energy stored during deformation. A qualitative explanation of the energy storage mechanism is proposed.

(Keywords: latent energy; deformation; thermomechanics; thermal shrinkage; amorphous polymers; plasticity)

INTRODUCTION

The application of stress to amorphous polymers in order to form oriented structures with modified mechanical properties is common practice in many industrial processes. Fibre drawing, blow moulding, extrusion, cold stamping and calendering are typical examples of such processes. The application of sufficient stress to cause flow below the glass transition temperature (T_g) is of particular interest. Sub-T_g post-yielding deformation results in the maximum opportunity for structural changes to occur since applied stresses may be 'frozen in' due to the lack of mobility in a sub-T_g polymer glass. Non-equilibrium polymer glasses may be easily formed by two common methods: rapid quenching through T_g and the application of stress below T_g.

This paper will concentrate on the effects of uniaxially drawing some amorphous polymers below T_g. It is important to note that the behaviour of quenched glasses may be analogous to that of the non-equilibrium glasses obtained by the application of stress. The preceding paper[1] established that a portion of the energy of deformation, for some typical amorphous polymers uniaxially drawn below T_g, was stored as a latent internal energy change. Thermomechanical tests were performed on the drawn polymers to ascertain the effects of this latent energy. The thermomechanical studies include stress *versus* temperature behaviour for uniaxially constrained samples and thermal expansion *versus* temperature for unconstrained samples. Since dynamic mechanical and dielectric relaxations have been previously observed for various non-equilibrium polycarbonate glasses (samples which had been either quenched or deformed below T_g)[2–5], dynamic mechanical measurements were also made on the drawn samples. A simple qualitative model, which proposes one possible mechanism for energy storage during deformation and is consistent with previously reported deformation thermodynamic data[1], is also described.

EXPERIMENTAL

Materials

The details concerning the commercial sources of the polymers studied and the sample preparation are presented in the preceding paper[1].

Density

Density measurements were made using a hydrostatic weighing technique. The polymer samples were first weighed in air. The samples were then weighed under water using a special attachment on an analytical balance (Sartorius 1600). The water was distilled water which was degassed by boiling before hydrostatic weighing. The sample sizes were 5–30 mg weight in air. Small sample sizes were used to facilitate the elimination of air entrapment when placed under water and to reduce the occurrence of voids.

Dynamic mechanical measurements

The dynamic mechanical results were obtained from a mechanical spectrometer (IMASS DynaStat) used in tensile–tensile mode in both displacement control and load control. In tensile–tensile mode, a static load is applied in uniaxial tension upon which a pre-set dynamic load (load control) or pre-set dynamic displacement (displacement control) is superimposed. The tensile specimens were rectangular bars 0.5 mm thick, 2.0 mm wide and 20 mm long. The samples were clamped at each end with split metal thumbscrew clamps which held the samples tightly over a small area. The applied static load was 2 MPa with an amplitude of 1 MPa and a frequency of 1 Hz for the superimposed sine wave. The heating and cooling rates for temperature scans were 3°C min^{-1}. A heating rate of 5°C min^{-1} was preferred (to agree with the thermomechanical measurements) but could not be

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Table 1 Densities of BPAPC, BPAPA and BPAPS before drawing at 25°C, subsequent to drawing and subsequent to annealing at 80°C for $\frac{1}{2}$ h ($\lambda = l/l_0$, draw ratio)

Sample		Density (g cm^{-3})
Isotropic	BPAPC	1.196
	BPAPA	1.202
	BPAPS	1.233
Drawn	BPAPC ($\lambda = 1.9$)	1.216
	BPAPA ($\lambda = 1.6$)	1.222
	BPAPS ($\lambda = 1.8$)	1.2699
Annealed	BPAPC	1.198
	BPAPA	1.225
	BPAPS	1.2705

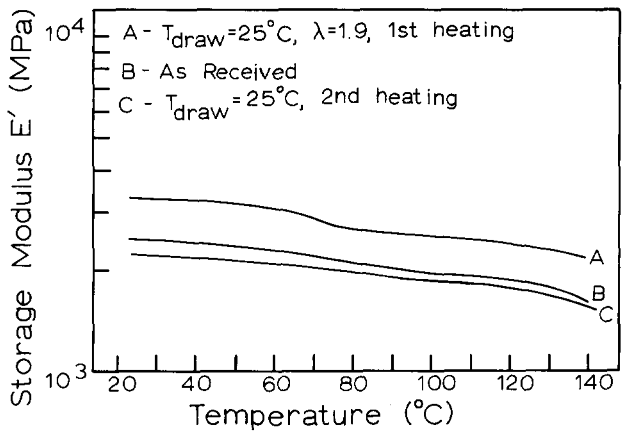

Figure 1 Storage modulus *versus* temperature for various BPAPC samples taken at 1 Hz in tensile–tensile deformation and load control on the Dynastat

achieved due to the large thermal mass of the dynamic mechanical spectrometer oven.

Thermomechanical measurements

Two separate types of thermomechanical measurement were made: change in stress at constant length and change in length under no load. The stress *versus* temperature measurements were performed using an apparatus which has been described elsewhere[6]. The shrinkage measurements were made using a Perkin–Elmer TMS-2 which was computer controlled by a System 4 Microprocessor Control. The shrinkage measurements were executed on 7.5 mm long, 0.10–0.20 mm thick films which had tiny metal crimp-on cylindrical clamps at each end. These clamps rested on the oven at one end and on an extensometer attachment at the other. The thermal expansion measurement was calibrated using lead foil. The heating rate for the temperature scans was 5°C min^{-1}.

RESULTS AND DISCUSSION

Density

Density measurements were made on the following isotropic and drawn amorphous polymers: bisphenol-A polycarbonate (BPAPC), bisphenol-A polyarylate (BPAPA) and bisphenol-A polysulphone (BPAPS). The results of these experiments are shown in *Table 1*. The trends in these data are far more important than the exact numbers since the changes in density were small. In all cases, the glasses densified slightly after drawing. The drawn glasses were then annealed at 80°C. The BPAPC returned to its original undeformed density but the BPAPA and BPAPS were essentially unchanged. The differential scanning calorimeter (d.s.c.) thermograms exhibited a sub-T_g exotherm at 80°C for BPAPC, but this sub-T_g exotherm was not observed for BPAPA or BPAPS until a slightly higher temperature[1]. Thus a density decrease accompanies this sub-T_g exotherm. The sample dimensions did not change appreciably during the annealing experiment. This demonstrates the interrelation of stress and physical ageing since annealing a BPAPC drawn sample results in density changes in the same magnitude though opposite in sign to physical ageing. Densification as a result of deformation has been observed by others for polymer glasses[7–9]. This densification is attributed to closer chain packing which occurs as a result of deformation.

Dynamic mechanical measurements

Dynamic mechanical measurements were made on the drawn BPAPC, BPAPA and BPAPS glasses to determine if any sub-T_g relaxations could be detected. Plots of storage modulus *versus* temperature for BPAPC are shown in *Figures 1–3*. The cross-sectional areas used for all of the modulus determinations for the drawn samples

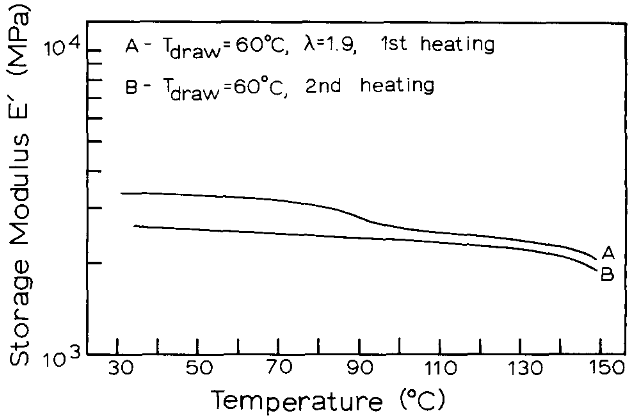

Figure 2 Storage modulus *versus* temperature for a BPAPC sample taken at 1 Hz in tensile–tensile deformation and load control on the Dynastat

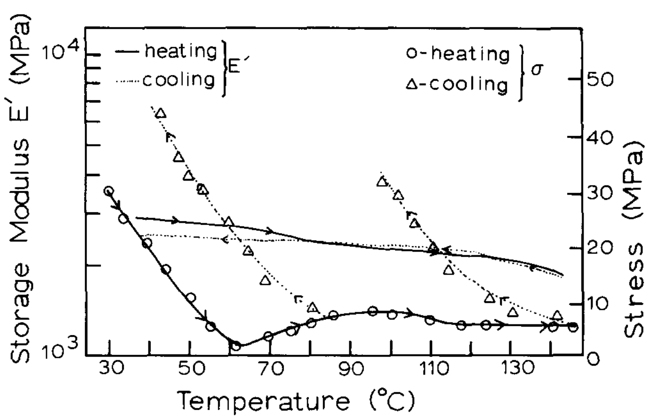

Figure 3 Storage modulus and stress *versus* temperature for a BPAPC (draw ratio, $\lambda = 1.9$) sample taken at 1 Hz in tensile–tensile deformation and displacement control on the Dynastat

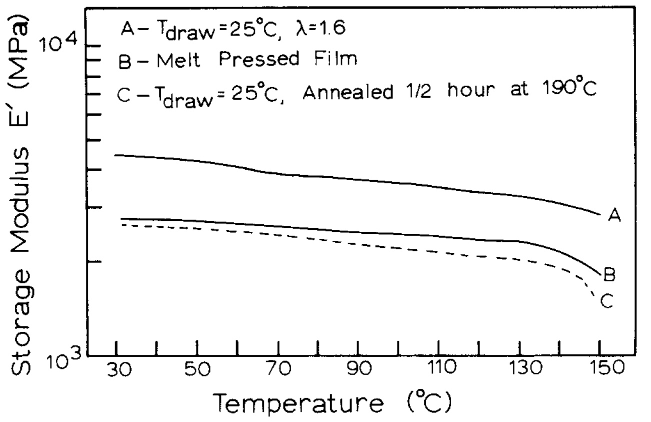

Figure 4 Storage modulus *versus* temperature for BPAPA samples taken at 1 Hz in tensile-tensile deformation and load control on the Dynastat

were based on the dimensions of the drawn samples, not the original isotropic sample dimensions. The data in *Figures 1* and *2* were taken on the mechanical spectrometer in load control and tensile–tensile mode. The tensile stress on the sample was 2.5±1.0 MPa. The data in *Figure 3* were taken on the mechanical spectrometer in tensile–tensile mode and displacement control for a BPAPC sample pre-drawn at 25°C. The stress on this sample increased with temperature due to a negative thermal expansion coefficient above 60°C. The maximum stress was 40±2.5 MPa. *Figures 1–3* clearly demonstrate the appearance of a relaxation in the drawn samples. The relaxation became visible at 70°C for samples drawn at room temperature and 90°C for samples drawn at 60°C. The relaxation was not detected on either the as received samples or on second scans of annealed, drawn samples. The relaxation was not strongly affected by the high stresses which developed for the sample measured in displacement control, though these stresses did decrease the modulus and temperature of the onset of T_g. The observed relaxation at 70–90°C has been termed the β relaxation and has been previously observed for both stressed and quenched samples of BPAPC[2–5].

Since relaxation behaviour below T_g was observed for various drawn samples of BPAPC, dynamic mechanical temperature scans were also taken for BPAPA and BPAPS. These polymers had very similar deformation calorimetric behaviour to BPAPC[1,10]. If the relaxation behaviour were related to the thermodynamic state, dynamic mechanical relaxations should be observed in the BPAPA and BPAPS samples also. The results for dynamic mechanical experiments taken on the mechanical spectrometer in tensile–tensile mode and load control for various BPAPA samples are shown in *Figure 4*. The drawn sample exhibited relaxation behaviour at 65°C but the annealed samples did not. Similar experiments for BPAPS showed evidence for an extremely small change in E' at 90°C, though it was not as clear as either BPAPC or BPAPA. It should also be noted that the BPAPA had a slightly higher initial storage modulus than BPAPC so that the changes due to relaxation behaviour appear less when plotted on a logarithmic scale. This was also true for BPAPS, which had the greatest initial value of storage modulus. The tangent δ values are not shown because the loss modulus was very small and extremely difficult to measure accurately using the mechanical spectrometer. The storage modulus values were very reproducible, varying by not more than ±5%.

Thermomechanical measurements

The stress–temperature behaviour for the room temperature drawn and isotropic melt pressed BPAPA and BPAPS samples is shown in *Figure 5*. These samples failed when heated above 140°C during heating. The BPAPA sample shown in curve B failed during cooling, probably due to cracks or crazes which occurred at the maximum temperature. These drawn samples exhibited nearly identical stress–temperature behaviour to BPAPC drawn samples[10]. The stress build-up occurred at a slightly higher temperature for these two samples than for BPAPC. This higher temperature is consistent with the higher relaxation temperatures observed in dynamic mechanical and d.s.c. measurements for these two polymers[1,10]. The difference in slope of the curves is not significant. This is an artefact of the sample dimensions used. Only very short (<15 mm) BPAPA and BPAPS drawn samples could be prepared before failure during uniaxial drawing. The BPAPC drawn samples were ≈100 mm long. Though a much shorter oven was used for the BPAPS and BPAPA experiments, these short samples were much more sensitive to compliance resulting from expansion of the clamps and support rods. The difference between final and initial stresses is nearly the same for these two samples as for BPAPC. The thermal cycling behaviour, which is not shown, exhibited the same characteristics as that observed for BPAPC[10].

The draw ratios of BPAPC, BPAPA and BPAPS could not be varied for freely drawn samples strained below T_g since all of these materials form a neck. PMMA was also studied so that the influence of draw ratio on the stress–temperature behaviour could be examined. PMMA uniaxially freely drawn at 60°C deforms uniformly and the draw ratio could be varied from 1.0 to 2.4 before the samples failed. The undrawn sample exhibited the usual positive thermal expansion behaviour, with the applied stress steadily decreasing with increasing temperature. The stress–temperature behaviour for PMMA samples deformed to the indicated draw ratios at 60°C is shown in *Figure 6*. Stress build-up occurs in these samples at or

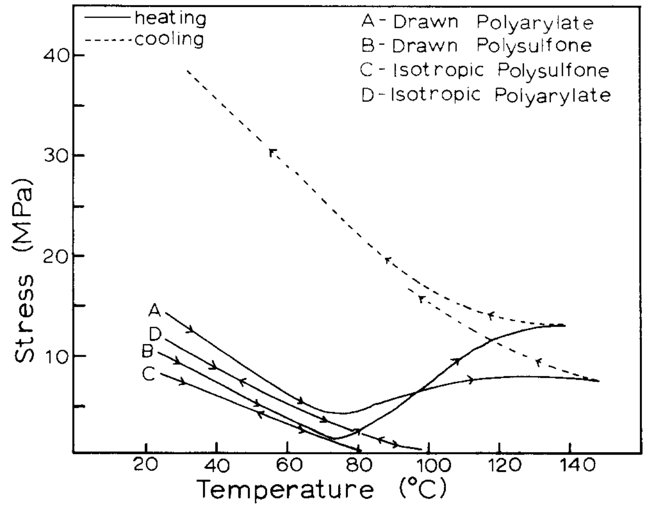

Figure 5 Stress *versus* temperature for constrained BPAPA (λ=1.6) and BPAPS (λ=1.8) samples predrawn at 25°C to their natural draw ratios

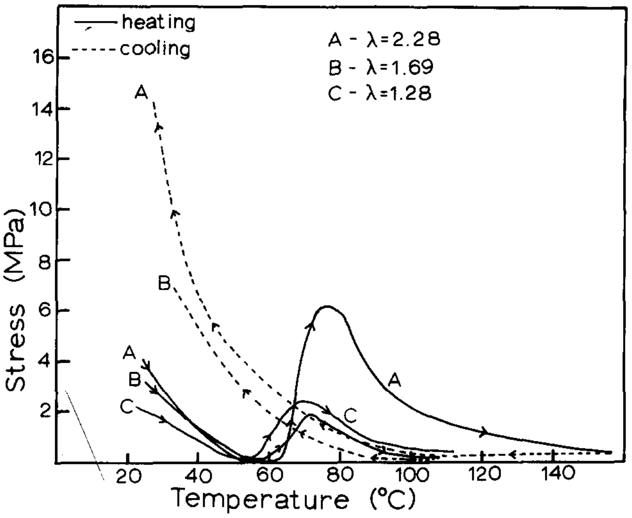

Figure 6 Stress *versus* temperature for constrained PMMA samples predrawn to the indicated draw ratios at 65°C

slightly below the draw temperature, with the maximum value of stress obtained at 80°C during heating. The maximum stress increased with increasing draw ratio. The highly drawn sample A was heated to 150°C, 35°C higher than the T_g. This sample exhibited negative thermal expansion coefficient behaviour during cooling above T_g similar to the stress–temperature behaviour observed for crosslinked rubbers strained beyond the thermoelastic inversion point. This sample was acting much like a strained crosslinked rubber since the molecular weight was high. The entanglements were acting as crosslinks, lending mechanical integrity to the sample even above T_g. The stress build-up which occurred for sample A was comparable to that obtained for the other glasses which were drawn to similar draw ratios. The final stress obtained for this sample would have been even greater if cooling began at 80°C, the temperature of the maximum stress value.

Temperature-dependent shrinkage forces have been measured in drawn amorphous poly(ethylene terephthalate) and BPAPC by Pakula and Trznadel[11]. They observed that these shrinkage stresses depended on the thermal history of the samples after drawing and that the isothermal stress behaviour was time dependent[12]. Trznadel[13] also noted that the isothermal stress build-up required an induction time. These experimental observations led them to propose a four-state mechanical model to describe the thermally induced stress build-up. Their four-state mechanical model contained one spring in parallel with a two-state element attached to a spring in series with a two-state element. This model was intended to represent a molecular sub-unit and its interactions. They calculated the kinetics of the transitions between various states, which allowed a prediction of the population of each state. They also were able to calculate the probabilities of transition between the states using an Arrhenius type expression.

The results of thermal shrinkage measurements for BPAPC, BPAPA and BPAPS are summarized in *Figure 7*. All the samples except for BPAPC deformed at 65°C exhibited positive thermal expansion behaviour between 20 and 60°C. The BPAPC deformed at 65°C began shrinking slightly at ≈40°C. The maximum rate of shrinkage below T_g, as evidenced by derivative curves A′ and B′, for both BPAPC samples occurred at 75–80°C. The thermal shrinkage behaviour of BPAPA and BPAPS was essentially the same below 140°C, with the sub-T_g maximum rate of shrinkage taking place at 80–90°C. The maximum shrinkage obtained below T_g was <10% in all cases. Thermal shrinkage data is reported in *Figure 8* for a BPAPC sample which was cycled (curves A and B) and a BPAPC sample measured perpendicularly to the draw direction (curve C). Once shrinkage had taken place, the samples behaved in the same way as the as-received isotropic materials until the previous maximum temperature was exceeded. No shrinkage was observed for the time scale of this experiment below 65°C. The sample expanded perpendicular to the draw direction since the volume change during this shrinkage is extremely small. The perpendicular expansion was approximately the same absolute value as the shrinkage between 80 and 100°C. Above 100°C, the transverse

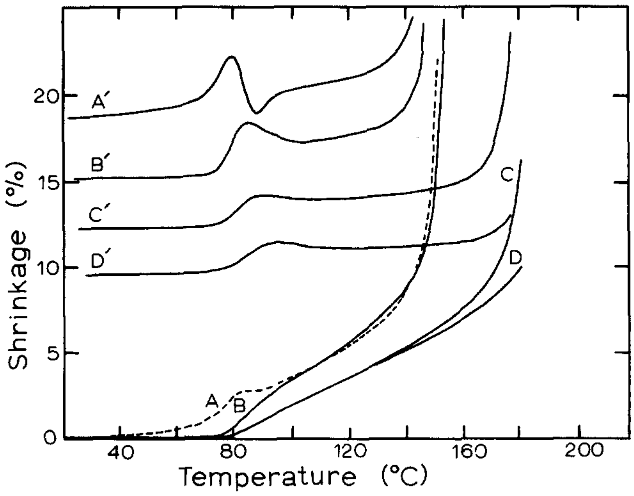

Figure 7 Thermal shrinkage *versus* temperature for: A, BPAPC drawn at 65°C; B, BPAPC drawn at 25°C; C, BPAPA drawn at 25°C; D, BPAPS drawn at 25°C. Curves A′, B′, C′, D′ are the derivatives of curves A–D

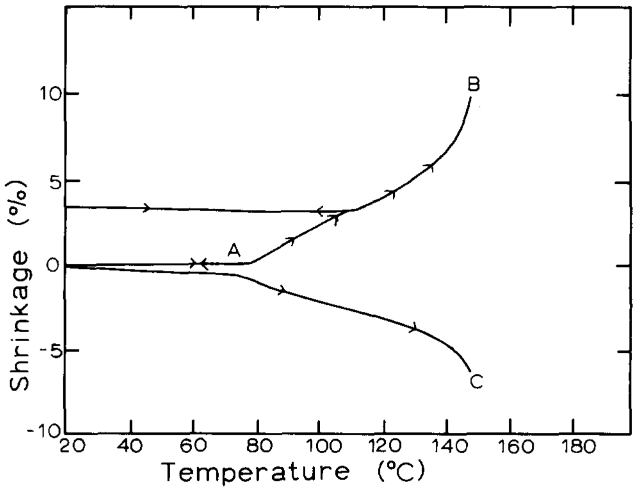

Figure 8 Thermal shrinkage *versus* temperature for two BPAPC samples drawn to the natural draw ratio ($\lambda = 1.9$) at 25°C and thermally cycled. A, uniaxial sample (draw direction) heated to 65°C, cooled to 25°C, reheated to 110°C. B, uniaxial sample (draw direction) cooled to 25°C, heated to 150°C. C, sample perpendicular to uniaxial draw direction heated to 150°C

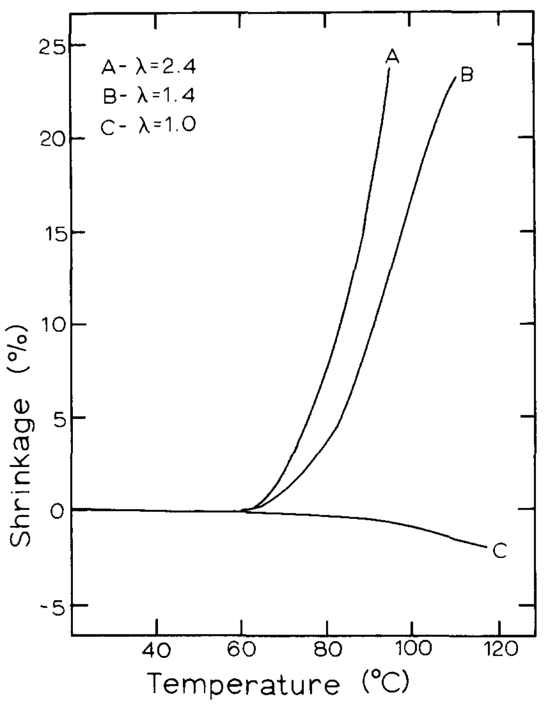

Figure 9 Thermal shrinkage *versus* temperature for various PMMA samples drawn at 60°C to the indicated draw ratios

expansion was about one half the uniaxial shrinkage, which is the approximate value required to maintain constant volume.

Thermal shrinkage measurements were also made on two PMMA samples drawn to different draw ratios and one undeformed sample. These results are presented in *Figure 9*. At temperatures <60°C, the PMMA samples expanded slightly. The two drawn samples shrank at the same rate from 60–65°C. Above this temperature, the highly drawn sample shrank at a much more rapid rate. Nearly 100% of the deformation was recovered by 110°C for the sample drawn to a draw ratio of 1.4. These samples exhibited much greater shrinkages than the other glassy samples, presumably due to the proximity of the shrinkage temperatures to the T_g of the polymer.

The data in *Figure 7* were replotted to determine if the observed differences in shrinkage behaviour between BPAPC, BPAPA and BPAPS deformed at 25°C were related to the T_g of the polymers. *Figure 10* is a plot of shrinkage for these three polymers *versus* normalized temperature ($T-T_g)/T_g$. The glass transition temperatures used to normalize the data were 423 K for BPAPC, 453 K for BPAPA and 463 K for BPAPS. The temperatures were expressed in kelvin so that the temperature axis from absolute zero to T_g would range from -1 to 0 for each polymer. Plotting shrinkage *versus* $T-T_g$ yields similar behaviour. The polymer which began shrinking at the lowest temperature, BPAPC, shrinks at the highest normalized temperature in relation to its T_g. However, all the data, when presented in this manner, fall on nearly the same curve. This similarity in sub-T_g relaxation behaviour may arise from the analogous molecular structures of the three polymers.

Thermal shrinkage below T_g has been observed previously for BPAPC. Kato and Kambe[14] measured the thermal shrinkage of cold drawn BPAPC and observed a sub-T_g maximum rate of shrinkage occurring at 60–70°C. They found that annealing at 140°C erased the shrinkage behaviour. They also observed that the maximum shrinkage obtained below 100°C was 10%. Studies of the dependence of shrinkage behaviour on heating rate demonstrated that the shrinkage was rate dependent, the shrinkage at a given temperature decreasing with increasing heating rate. An Arrhenius plot of inverse maximum temperature *versus* logarithmic heating rate yielded an activation energy of 140 kJ mol^{-1} mol^{-1} for the molecular motion causing the shrinkage. Evidence for polymer chain backbone motion was also observed by Yannas and Lunn[15] using spectroscopy.

The results of these thermomechanical measurements indicate that macroscopic sample motion takes place for a variety of drawn polymer glasses at temperatures as much as 100°C below T_g. Macroscopic shrinkages of 10% and stress buildups of 20–30 MPa certainly could not take place without molecular backbone motion. This motion appears to be somewhat restricted since only a portion of the deformation is recovered below T_g. Once the backbone motion has taken place, no additional large scale motions occur until the previous maximum temperature is exceeded.

RATIONALIZATION FOR EXPERIMENTAL OBSERVATIONS

A number of models have been proposed to explain the deformation behaviour of glassy polymers. One of the earliest and most general treatments of necking behaviour is given by Vincent[16]. Vincent's explanation states that necking or yielding occurs due to a non-uniformity of the tensile specimen resulting in a stress concentration. Another less phenomenological explanation is that applied stress reduces the T_g until at the yield point the T_g and deformation temperature are coincident[17,18]. The increase in free volume brought about by the dilational hydrostatic component of the stress tensor is responsible for the decrease in T_g according to these authors. Another theory for the flow or yield behaviour for polymers is proposed by Eyring[19]. This theory assumes that yielding is an activated rate process with a potential energy barrier of some height, dE. The energy barrier may be surmounted due to random thermal fluctuations. The effect of applied stress is to reduce the average height of the barriers in the forward direction but increase the

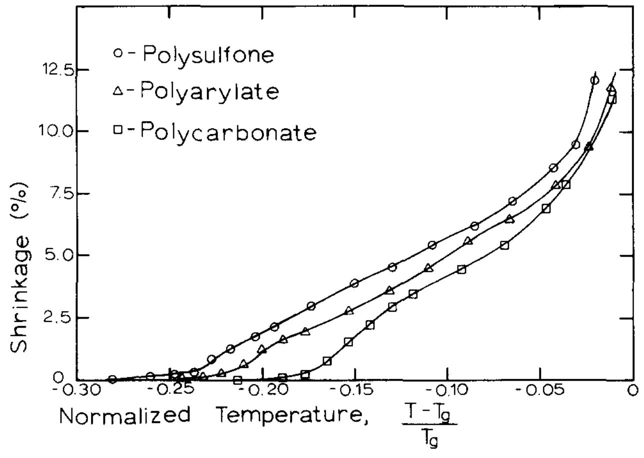

Figure 10 Thermal shrinkage for BPAPC ($\lambda=1.9$), BPAPA ($\lambda=1.6$) and BPAPS ($\lambda=1.8$) samples drawn at 25°C plotted as a function of temperature normalized to the T_g of the polymer

average height in the reverse direction. Thus, once a molecule or molecular segment, or cluster of chains or chain segments have gone over the barrier, they are in a quasi-stable energy well and are unable to return to the ground state. This theory has been refined by Kambour and Robertson[20] to include specific molecular ideas of deformation. Kambour and Robertson propose a very simple model of a polymer with backbone bonds of equal length, bond angles of 90° and two rotational states per bond, *cis* and *trans*. Yielding below T_g occurs when a sufficient number of *trans* bonds are converted to the *cis* conformation by stress. The energy required for this is the dE in the Eyring model.

The theories previously described for the deformation of amorphous polymers below T_g are primarily phenomenological and do not address the fundamental question of why some polymers are ductile below T_g while others are not. If one considers a single isolated polymer chain, a fundamental question one can ask is: Does this chain have a T_g? There is no apparent reason why it should, and we anticipate that if it were possible to grasp the chain ends, the chain would behave in an entropically elastic manner over any temperature range up to the degradation temperature of the macromolecule. The effect of decreasing molecular weight and plasticizers on T_g has been known for a long time. One explanation for the depression of T_g with decreasing molecular weight is that the individual macromolecules have more freedom to move in a cooperative manner. Thus, T_g is a result of interchain interactions.

A simple model is proposed which explains the deformation calorimetric data previously described[1,10] and is consistent with other experimental observations for sub-T_g, amorphous thermoplastics. This model can be best developed by considering the primary forces which act on a glassy macromolecule. These are the forces which are keeping it 'frozen'. The primary forces are the intermolecular interactions. These can be various types of force such as hydrogen bonding, dipole interactions, steric hindrance and Van der Waal's forces. Other forces which are also acting on the chain are intramolecular and intermolecular entanglement and, when a macromolecule's nearest neighbour is another segment of itself, all of the previously mentioned interactions may be intramolecular. The flexibility of the macromolecule is important only in that it determines how tight any loops or entanglements may be. The primary feature of this model is the intermolecular and intramolecular forces which hinder the cooperative motion of each individual macromolecule.

Yielding or ductile behaviour in polymers below T_g is explained as follows using this model. Yielding occurs when a macromolecular segment is entropically deformed sufficiently to break the relatively weak elastic intermolecular and intramolecular interactions. The segments of macromolecules deformed are those between entanglements. As the deformation progresses, eventually these entanglements are strained into tighter loops in much the same way as a tangled ball of string which is being stretched. During this final portion of the deformation, the stiffness of the molecule is increasingly important since the stiffness determines the radius of curvature for the loops. A very rigid molecule has a large radius of curvature for the loops, limiting the deformation which takes place once the macromolecular segments between entanglements become highly strained. In terms of this model, the main differences between brittle and ductile materials are the strength, flexibility, and ease of breaking and re-forming the intermolecular and intramolecular forces.

Stress has two effects on the macromolecules in terms of the previously described model applied to the sub-T_g deformation calorimetric data[1,10]. One effect is to deform the regions of macromolecules between entanglements in an entropically elastic manner. The other simultaneous effect is the energetically elastic deformation of the secondary interactions. Deformation of these secondary interactions results in a cooling effect in much the same manner as deformation of an energetically elastic material such as steel causes the material to cool. Therefore, the work of entropy elasticity is entirely converted into heat, while the energetically elastic work is manifest as a superimposed endotherm. Eventually the secondary bonds break entirely, recoiling and re-forming. Recoil does not result in a flow of heat since this process is analogous to the free expansion of an ideal gas, i.e. no work is done during recoil of these secondary forces. The secondary forces are re-formed, liberating heat equal to the absorbed heat requred to destroy the secondary bonds. The net result of the energetically elastic deformation of secondary interactions (cooling effect), the destruction and re-formation of secondary bonds (no net heat flow) and the entropically elastic chain deformation (heat liberated) is that only a portion of the applied work is converted into heat. The newly formed intermolecular and intramolecular forces are what holds the macromolecular segments in a non-equilibrium, thermodynamically less stable state. The application of thermal energy to a system in this drawn state does two things. It increases the entropically elastic restoring forces of the macromolecular segments between entanglements, and it provides sufficient activation energy to destroy some of the intermolecular and intramolecular forces which are preventing the macromolecular chain segments from returning to their original, undrawn, preferred dimensions. Thus, heating a constrained sample which has been drawn results in a restoring force, while heating a similar unconstrained sample results in shrinkage. Therefore, the model is consistent with many experimental observations on drawn glasses.

This model does not require that any viscous flow takes place during post-yielding deformation of sub-T_g thermoplastics. It also explains the recovery behaviour and does not restrict macroscopic motion to temperatures above T_g. Relaxations may take place at any temperature which results in sufficient entropically retractive forces to destroy the intermolecular and intramolecular forces, which themselves are weakened by thermal energy. Thus, recovery or relaxation phenomena may be independent of T_g according to this model. Since no viscous flow is involved in this model, it also provides a convenient explanation for the astounding shape recovery of cold formed, amorphous thermoplastics. Amorphous thermoplastics deformed below T_g generally recover their original, undeformed shape almost exactly when heated sufficiently. This model also explains the strong relationship between the heat to work ratio and the molecular weight[6]. Molecular weight primarily affects the number of and molecular weight between entanglements. Both of these parameters strongly influence the ease and extent of deformation in terms of this model. The reason for the partial observed shrinkage below T_g is primarily a time effect. Once a portion of the deformation has been recovered, more extensive thermal energy is required to either induce sufficient entropic recovery forces or activate a sufficient number of unstable intermolecular and intramolecular secondary bonds. Thus, additional macroscopic motion takes place very slowly after the initial shrinkage since the thermodynamic driving force for shrinkage is small. Perhaps on the time scale of years, additional macroscopic motion would be observed below T_g. Heating to near T_g allows large scale cooperative motion to occur, which severely weakens the intermolecular and intramolecular bonds. These bonds hold the macromolecular chain segments between entanglements in the strained configuration. This bond weakening coupled with the entropic restoring force increasing with higher temperatures results in rapid macroscopic motion with nearly 100% recovery of the applied strain. A requirement of 'plastic' deformation then is to destroy the intermolecular bonds before the molecular backbone is broken.

CONCLUSIONS

The thermomechanical measurements were extremely sensitive to the sub-T_g relaxation behaviour for the amorphous samples which had been previously drawn below T_g. These experiments demonstrated striking dimensional mobility of the deformed glasses below T_g, with a shrinkage of approximately 10% observed at more than 50°C below the T_g for BPAPC, BPAPA and BPAPS. Stress–temperature experiments for pre-drawn samples demonstrated that uniaxially constrained samples exposed to thermal cycles far below T_g could develop astounding stresses reaching more than 50% of the yield strength. The sub-T_g relaxation behaviour was not related to T_g for BPAPC, BPAPA or BPAPS. It is probable that the main effect T_g has on the relaxation behaviour is to change the time or kinetics of the relaxation. The molecular motion due to this sub-T_g relaxation appeared to be slightly hindered since 100% recovery of the strain was not obtained below T_g, though this may merely be a time effect. Experiments performed over a sufficient time, perhaps even years, might result in additional dimensional recovery.

The yield behaviour observed with deformation calorimetry and the sub-T_g dimensional recovery are qualitatively consistent with an Eyring model of deformation. In the case of sub-T_g yielding deformation, the shape of the potential energy curve is modified due to stress, facilitating the motion of the macromolecular backbone into a more unstable and hence higher internal energy state. Heating this unstable polymer glass supplies sufficient thermal energy for at least a portion of the macromolecules to return towards their original unperturbed dimensions.

A qualitative explanation is proposed to explain the experimental observations. This model is applicable to the sub-T_g deformation of amorphous polymers. Sub-T_g deformation is explained in terms of the destruction and re-formation of secondary molecular interactions. The secondary bonds re-form while the macromolecules are perturbed from their equilibrium dimensions, resulting in a quasi-stable energy state for the deformed material. The application of thermal energy to the deformed material results in increasing entropic restoring forces coupled with a weakening of the secondary interactions, causing the sample to return towards its undeformed dimensions independently of T_g.

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