The influence of internal stresses on viscoelastic and thermal properties of oriented and aged glassy polymers

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Viscoelastic loss spectra and differential scanning calorimetry (d.s.c.) traces of oriented and aged glassy polycarbonate and poly(ethylene terephthalate) were recorded and compared with the results of shrinkage and shrinkage force measurements. It was shown that ageing effects such as 'intermediate relaxation' (in damping test) and the development of sub-T_g endotherm (on d.s.c. traces) coincide well with dimensional instabilities of oriented samples. Observed correlations are explained on the basis of internal stress relaxation, which seems to be an important feature of physical ageing of oriented glassy polymers.

(Keywords: ageing; oriented polymers; relaxation of internal stresses; shrinkage; shrinkage forces)

INTRODUCTION

Glasses usually exist in a non-equilibrium state and their relaxation towards equilibrium is called physical ageing. This process is important from a practical point of view because it affects a great number of mechanical, dielectric and thermal properties[1]. The molecular origin of ageing is still not well understood[2,3]. However, it is well documented in the literature that mechanical relaxation spectra[4] and differential scanning calorimetry (d.s.c.) traces of glassy polymers are significantly dependent on the ageing phenomenon.

Illers[5] and Gray and Gilbert[6] recorded endothermic d.s.c. peaks below the glass transition temperature in annealed poly(vinyl chloride) (PVC) samples. Wysgoski[7] observed the development of small broad endotherms in aged acrylonitrile–butadiene–styrene copolymer (ABS) and styrene–acrylonitrile copolymer (SAN). Shultz and Young[8] reported similar behaviour in annealed polystyrene (PS) and poly(methyl methacrylate) (PMMA). Berens and Hodge[9] investigated the influence of various thermal, mechanical and vapour treatments on the evolution of sub-T_g endotherms in PVC, showing that their heights increase and maximum values shift to higher temperatures with increasing ageing time.

All those studies suggest that the development of sub-T_g endotherms in glassy polymers seems to be a general feature of the ageing phenomenon, usually explained on the basis of volume reduction and enthalpy relaxation[10–12]. However, the direct influence of internal stresses frozen in the glassy samples was rarely mentioned. Watts[13] suggested that 'intermediate relaxation' recorded in the dielectric loss of quenched polycarbonate is associated with the presence of non-relaxed stresses induced in the moulding of the specimen. Bauwens-Crowet[14] measured a similar effect in mechanical loss spectra and attributed it, as well as the observed 'exothermal tendency' on d.s.c. curves of quenched polycarbonate, to the stresses frozen into the material during manufacture or quenching.

In the previous paper[15] we concluded that the ageing of oriented glassy samples is associated mainly with the gradual relaxation of internal stresses frozen in the sample after deformation. The purpose of this paper is to show that this relaxation affects the dynamic mechanical spectra and sub-T_g endotherms, playing a substantial role in the ageing processes. The shrinkage behaviour, treated as a measure of internal stresses, is here compared with the results of damping tests and d.s.c. thermograms. Observed correlations extend and further support the conclusions of the previous paper[15].

The majority of experiments were carried out on polycarbonate (PC). However, several results obtained for amorphous poly(ethylene terephthalate) (PET) are also reported.

EXPERIMENTAL

The preparation of the samples as well as the measurements of shrinkage forces are described in detail elsewhere[15].

Films (0.3 mm thick) of Macrolon 2408 polycarbonate (PC) and 0.5 mm thick plates of commercial poly(ethylene terephthalate) (PET) were drawn at room temperature to the natural draw ratios of 1.9 and 4 for PC and PET, respectively. Such a deformation leads to oriented amorphous samples, which was confirmed by X-ray analysis.

After the deformation, the samples were stored with free ends at a temperature of 21±0.5°C.

The method of forced oscillations in torsion was employed to determine the dynamic mechanical spectra.

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A Rheometrics Mechanical Spectrometer model 800 was used with rectangular sample geometry. Spectra were taken in the glassy state of polycarbonate by heating the samples at a heating rate of 3°C min^{-1} in the temperature interval between -150°C and the onset of the glass transition at about 145°C using 10 Hz frequency of torsional vibrations. The results are presented in terms of real shear modulus G' and loss factor $\tan\delta = G''/G'$. During these measurements the sample ends were maintained under a small, constant normal force and the changes of the lengths of the samples were recorded.

D.s.c. traces of oriented samples were recorded at a heating rate of 20°C min^{-1} using a Perkin–Elmer 7 calorimeter. Thermograms were obtained for both unconstrained and constrained specimens—for the latter a special sample holder was used to keep their dimensions constant (within the accuracy of thermal expansion of the holder). Two holders were employed, measuring and reference, each consisting of two brass plates with an inlet for the sample. The polymer specimens were fixed at constant length by clamping between these plates with a set of screws. Before the experiments care was taken to control the mass of the sample holders, the baseline of the d.s.c. apparatus and the additional temperature lag introduced by the presence of modified d.s.c. pans.

RESULTS

The results of two tests among several experiments related to dimensional instabilities of oriented glassy polymers[15] are reported here for comparison with the dynamic mechanical spectra and d.s.c. traces. These are the changes of length and thermally stimulated shrinkage forces, both recorded as a function of temperature for oriented and aged polycarbonate.

Figure 1 shows the dependence of the length of various PC samples, expressed in terms of the coefficient α defined by $\mathrm{d}L/L\,\mathrm{d}T$, where L is the current length of the specimen. This coefficient describes the resultant length changes of the material and consists of two components: reversible thermal expansion and irreversible entropic contraction. The latter, observed at higher temperatures, leads to the rapid fall of α to about $-10^{-3}\,\text{K}^{-1}$. At these temperatures the effect related to the reversible component (about $10^{-5}\,\text{K}^{-1}$) may be neglected.

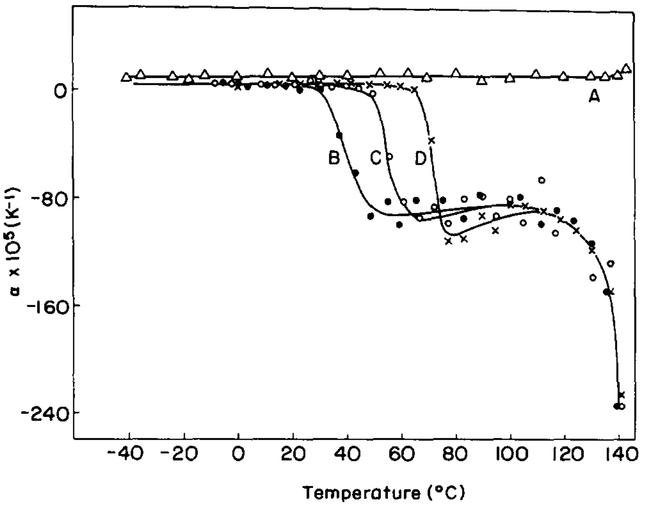

Figure 1 Temperature dependence of expansion coefficient of various PC samples: A, non-oriented; B, oriented, aged 8 min; C, oriented, aged 21 h; D, oriented, aged 180 days

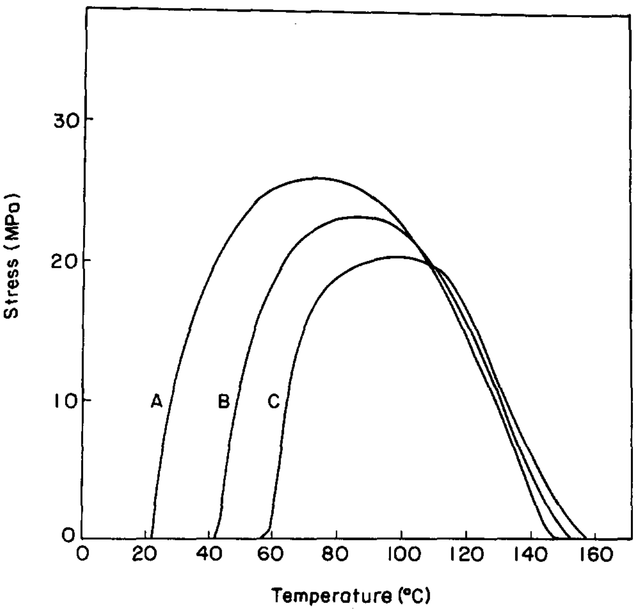

Figure 2 Temperature dependence of shrinkage stresses in oriented and aged polycarbonate. Ageing times: A, 8 min; B, 3 days; C, 95 days

Thermally stimulated shrinkage forces are shown in *Figure 2*. The stress begins at a certain temperature, reaches its maximum value, then decreases and falls to zero in the glass transition region. The curves are shifted to higher temperatures and their maximum values decrease with increasing ageing time. Such a shift is in good agreement with the data presented in *Figure 1*.

Shrinkage stress curves were recorded at a heating rate of 3°C min^{-1}, i.e. the same as was employed for dynamic mechanical tests. To compare the shrinkage stress relaxations with d.s.c. thermograms, retraction forces were also recorded at a heating rate of ~20°C min^{-1}. The shape of the curves obtained remained unchanged and the traces were shifted only by ~5°C to lower temperature.

The results of isochronal measurements of dynamic mechanical spectra for various samples of polycarbonate are shown in *Figure 3*. In *Figure 3a* the curve of the 'fresh oriented' sample is compared with the spectra of two undrawn PC specimens: the first annealed for 20 h at 120°C and the second non-treated. In all spectra the broad loss peak at low temperatures reflects the β relaxation process. The sharp increment of $\tan\delta$ at higher temperatures is the onset of α relaxation. The intermediate loss process merging with the α relaxation, observed in various samples with various intensities, is most intense for drawn polymer whereas it disappears completely for the annealed sample.

The effect of ageing of drawn PC on the dynamic mechanical spectra is presented in *Figure 3b*. The main changes are reflected in the intermediate loss process. The onset of this relaxation shifts considerably to higher temperatures with increasing ageing time, and this shift is well correlated to those observed in shrinkage and shrinkage force experiments (compare *Figures 1* and *2*).

The d.s.c. traces obtained for oriented and aged PC samples kept unconstrained during the measurements are shown in *Figure 4*. For unoriented polycarbonate the d.s.c. curve is flat until the region of the glass transition temperature, while for oriented and aged samples the broad endothermal peak appears at temperatures of

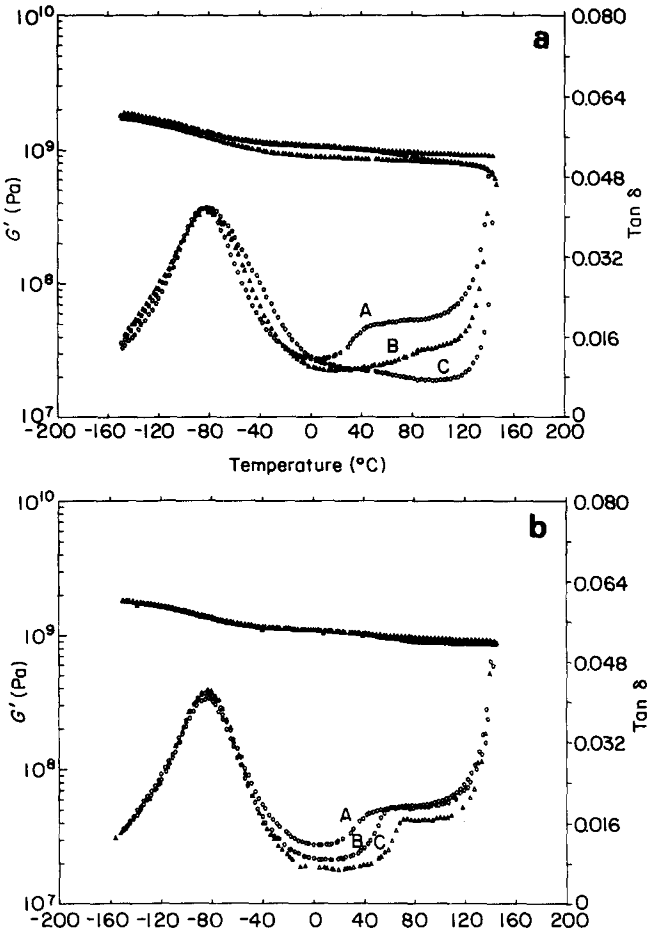

Figure 3 Real part of shear modulus (G') and tan δ vs. temperature. (a) Various PC samples: A, oriented; B, unoriented, non-treated; C, unoriented, annealed 20 h at 120°C. (b) Oriented and aged PC: A, ageing time $t_a = 8$ min; B, $t_a = 21$ h; C, $t_a = 180$ days

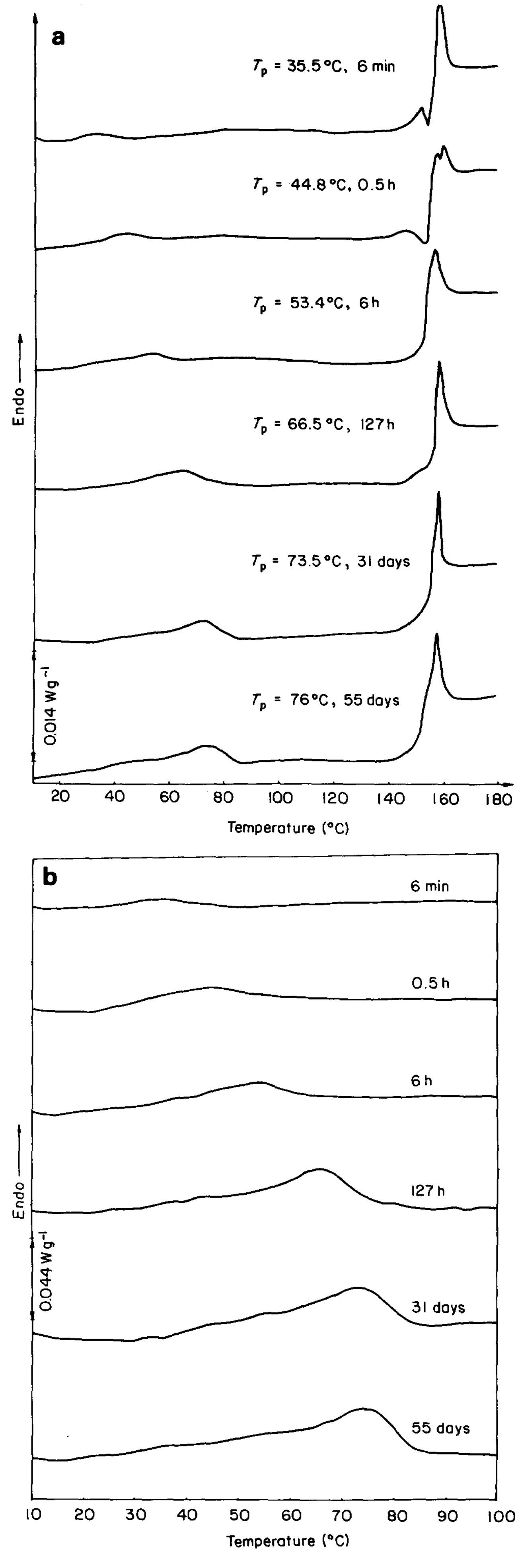

Figure 4 D.s.c. thermograms of oriented and aged PC: (a) temperature scale from 10 to 180°C; (b) extended temperature interval 10–100°C. Peak temperature T_p of broad endotherm and ageing time for each trace are given on the figure

about 30–80°C, depending on the ageing time. The height of this peak increases and the maximum value shifts to higher temperatures for the samples measured after longer ageing times.

From the comparison of d.s.c. traces with shrinkage force curves, it is seen that the onset temperature of the broad endotherm corresponds well with the temperature of stress appearance, while the temperature of its maximum is in good coincidence with the temperature of maximum rate of stress increase (for fixed ageing time).

Figure 4b presents the extended temperature interval 10–100°C to make the evolution of the peak with ageing time more legible. D.s.c. traces recorded for oriented and aged PC kept at constant length during the measurements, shown in *Figure 5*, reveal two important features, which cause them to differ from the traces obtained for unconstrained samples. The first is the lower height of the broad endotherm for constrained polymer measured after a longer ageing time, and the second concerns the appearance of the exothermal step at temperatures ~ 100°C. This step decreases and shifts to higher temperatures with increasing ageing time and its commencement (on the temperature scale) corresponds

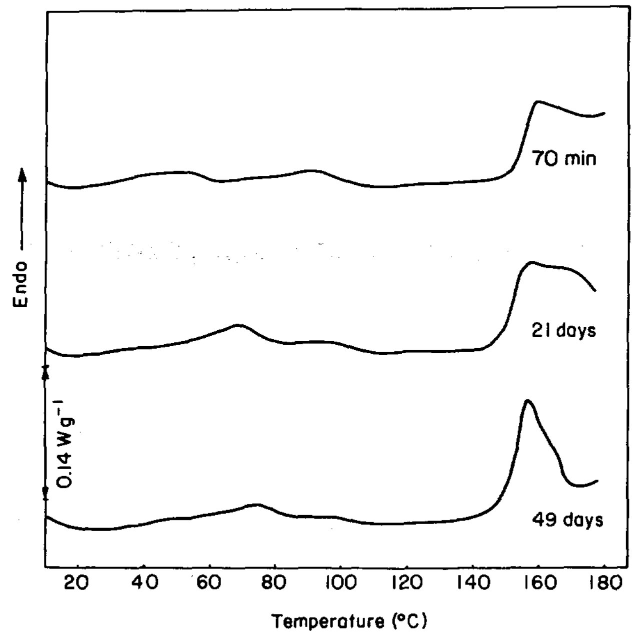

Figure 5 D.s.c. traces of oriented and aged PC samples kept constrained during the measurement. Ageing times are shown on the figure

well with the temperature of the maximum value of shrinkage stresses.

D.s.c. thermograms of oriented and aged PET samples measured with free ends are shown in *Figure 6*. Their interpretation is more complicated because the crystallization taking place at elevated temperatures screens the shrinkage effects. However, considerable changes resulting from the ageing processes are also observed. These changes are more precisely exhibited in *Figure 6b*, which presents extended traces between 10 and 220°C.

DISCUSSION

Viscoelastic properties

Figure 3a shows that the differences between oriented and isotropic polycarbonate observed in dynamic mechanical spectra depend on the temperature interval. At low temperatures, near the β relaxation, the differences are slight both in the real part of the shear modulus and in $\tan\delta$. Above about 20°C the intermediate loss process appears with magnitude and shape strongly dependent on the treatment of the sample—it is most pronounced for the oriented polymer, less for the unoriented non-treated sample and disappears completely for the unoriented, annealed sample. A similar intermediate peak was found in dielectric and mechanical relaxations and reported by several authors[13,14], who pointed out that it is small in magnitude and disappears on annealing, consistent with our results.

Watts and Perry[13] suggested that 'intermediate temperature relaxation' is some kind of precursor to the α process, probably originating from the unrelaxed stresses induced during manufacture or quenching. To confirm this, we show the direct comparison of damping effects for oriented and aged polycarbonate (see *Figure 3b*). The intermediate process is broad and shifts to higher temperatures as internal stresses relax during the physical ageing.

The connection of damping effects with internal stress relaxation becomes more evident if the loss curves are

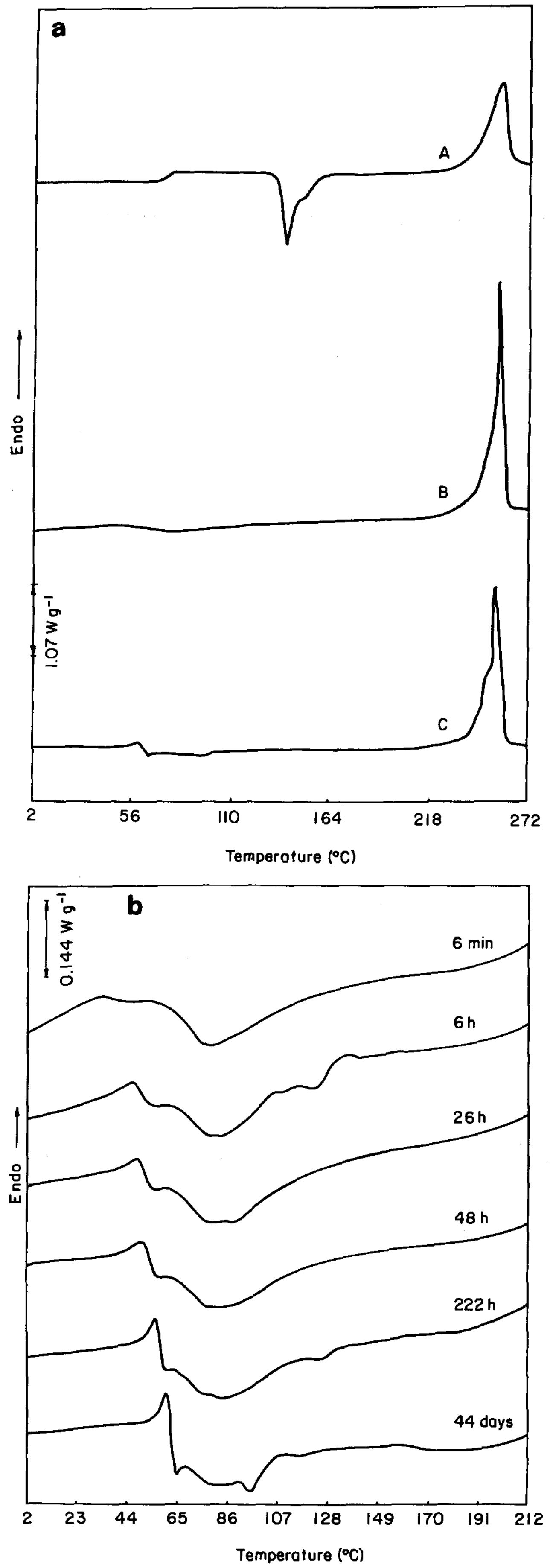

Figure 6 D.s.c. thermograms of various PET samples: (a) unoriented (A) and oriented aged 6 min (B) and 44 days (C); (b) extended temperature interval for oriented and aged samples (ageing times shown near the traces)

compared with the temperature dependences of length and shrinkage forces in *Figures 1* and *2*, respectively. It is seen that the temperature intervals of intermediate relaxations are in good agreement with changes of lengths and the observed shift to higher temperatures corresponds well with the beginning of shrinkage forces recorded for oriented and aged samples.

These experimental results and the fact that the intermediate relaxation is not observed in unoriented annealed PC indicate that this effect should be attributed to the internal stresses frozen in the material.

The influence of internal stresses on the viscoelastic behaviour of oriented samples becomes more clear if stress relaxation is considered on the basis of the simple mechanical model presented in *Figure 7*. This model was previously employed for the description of shrinkage and shrinkage forces in oriented and aged polymers[15]. The properties of the glassy sample are modelled by a parallel connection of elementary units, each consisting of two springs: S_1, related to the chain elasticity, and S_2, representing an elastic junction of the subunit with the matrix. In the oriented state, springs S_1 are extended, and the sites of lower numbers are assumed to be on the barrier element connected in parallel to S_1. Considering a parallel connection of model units, each element acts independently, and when the system is kept unconstrained the spring S_2 and the second barrier element are not involved. The spring S_1 can decrease its extension by thermally activated jumps over the Helmholtz free energy barriers modified by local stress.

The viscoelastic loss behaviour recorded in oriented PC below the glass transition may be explained as the influence of local internal stresses on the relaxation times of the model elements in sites i. The relaxation time τ of the single unit that occupies site i (on the first barrier element) is related to the transition rate $K(i)$ from site i to $i+1$ (ref. 16):

$$\tau \sim K(i)^{-1} = A \exp\left(\frac{\Delta F_1 - \sigma(i)V_1}{kT}\right)$$

where A is a constant, ΔF_1 is the height of the Helmholtz free energy barrier, $\sigma(i)$ is the stress exerted by the spring S_1 in site i (representing internal stresses frozen in oriented polymer), and V_1 denotes the activation volume of the first barrier element (see also the appendix in ref. 15).

After the deformation, as a result of ageing, the model units change their states from $i=1$ towards lower internal stresses. Let us assume that for a certain time after the orientation all the units occupy the same state i. This implies the lack of an internal stress distribution, which generally is not valid, but such an assumption enables a better understanding of the model considerations. After cooling, the system is heated at constant rate and subjected to the oscillating force field. At a temperature at which the relaxation time estimated from the above equation becomes close to the period of the oscillating force, the loss process occurs. At this moment each model unit overcomes the free energy barrier and enters state $i+1$ as a result of cooperative action of three contributions: the temperature, the applied oscillating force (which is in resonance with the system) and the extra heat produced by dissipated mechanical energy. State $i+1$ is characterized by higher relaxation time and the next damping effect will proceed if the system reaches the relevant temperature. This process will last until the internal stresses are relaxed and three-dimensional segmental motions begin, close to the region of the glass transition.

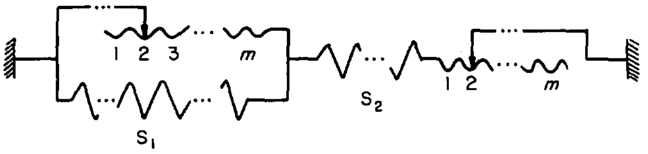

Figure 7 Basic scheme of multi-state mechanical model

It is easy to see that for longer ageing time the initial state i occupied by the system is higher, so the intermediate relaxation must start at higher temperatures. The strength of the process is relatively small because it involves preferably one-dimensional molecular motions.

The proposed explanation is very simplified, and it should be extended to an internal stress distribution and relaxations taking place on the second barrier element. However, even on such a simple level it describes qualitatively the intermediate relaxation observed in oriented polycarbonate.

D.s.c. measurements

It is a common feature of several amorphous polymers to develop peculiar thermal effects connected with physical ageing[5-9]. They are revealed on d.s.c. thermograms as T_g overshoot and sub-T_g endotherms recorded for polymers subjected to various thermal or mechanical treatments.

In isotropic polycarbonate, the T_g overshoot is observed as the effect of ageing. However, the sub-T_g endotherm is not developed but confined only to a slight bend of the d.s.c. trace[14] and disappears on annealing. On the other hand, in oriented PC the broad endotherm appears and develops considerably during ageing, as is shown in *Figure 4*, which indicates that in oriented glassy PC the ageing processes usually existing are enhanced by the presence of internal stresses. The stress origin of this effect is confirmed by the fact that the onset temperature of the peak and its maximum value correspond well with the beginning of shrinkage stress and with the maximum rate of shrinkage stress increase, respectively (compare *Figure 2*).

We propose to explain the broad endotherm as a combination of entropy and energy effects associated with the shrinkage of the oriented sample.

Qualitative plots of both components and the resultant trace are shown in *Figure 8*. The entropy contribution (proportional to $T\Delta S/\Delta T$, where ΔS is the total entropy change) increases at a certain temperature as a result of decreasing intermolecular interactions and assuming more coiled conformations. The energy contribution originates from energy dissipation and heat generation during extensive molecular motions in a medium of high viscosity. It is plausible to assume that the energy effect per unit volume is proportional to the rate of relative dimensional changes ($d\varepsilon = dL/L$):

$$dE/dt \sim d\varepsilon/dt \sim d\varepsilon/dT \sim \alpha$$

Hence at constant heating rate it is proportional to the length changes expressed in terms of the coefficient α (compare *Figure 1*).

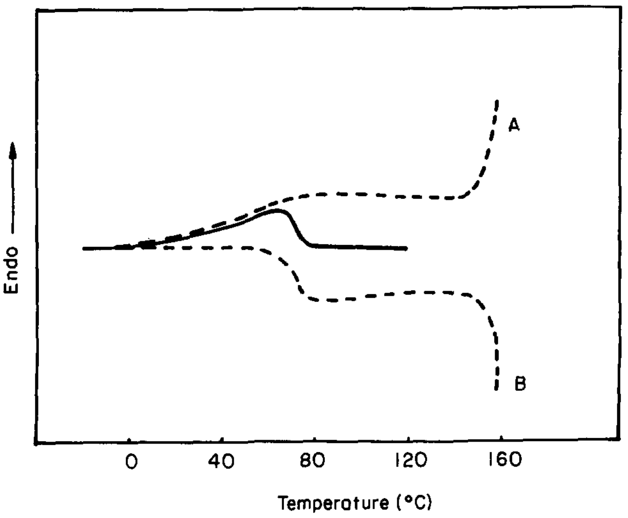

Figure 8 Proposed explanation of sub-T_g effect; the entropy contribution (A) and energy contribution (B) are shown

The temperature lag between these two components originates, we suggest, from the fact that at lower temperatures, before detectable contraction occurs, the overall entropy may increase as a result of minor local relaxations. This temperature lag increases for the aged samples, which is consistent with the phenomenon of induction time observed in isothermal shrinkage[15].

The broad endotherms developed on the d.s.c. traces of oriented PC kept constrained during the measurement and shown in *Figure 5* are similar to those obtained for unconstrained samples. The entropy and energy components must also be superimposed. However, both are not so enhanced considering the molecular mobility hindered by external constraints.

The exothermal step following the broad endotherm has an energy origin and may be attributed to the relaxation of external stresses as shown in *Figure 2*. As the temperature increases, the sample with fixed ends remains under a tensile force caused by the constrained shrinkage. At sufficiently high temperature, the generated stress relaxes, most likely as a result of intermolecular slips. Such slips, proceeding in a medium of high viscosity, are associated with heat generation and are reflected on d.s.c. thermograms as an exothermal step commencing at the temperature at which the shrinkage stress attains the maximum value. This exotherm decreases and shifts to higher temperature for samples with longer ageing time. This is consistent with the changes of maximum shrinkage stress, which is connected with the magnitude of internal stresses frozen in the sample and relaxed as a result of ageing.

To confirm the observations discussed above, an independent experiment was carried out using styrene–butadiene–styrene (SBS) copolymer, which is a well known and well investigated elastomer[17,18]. A sample of SBS copolymer was extended about three times and clamped into the sample holder to fix its length during the d.s.c. measurement. The thermograms shown in *Figure 9* were recorded for unextended and extended specimens. It is seen that for the stressed sample the significant exothermal effect occurs slightly below the transition temperature of polystyrene, i.e. in the temperature region where the applied stresses relax.

The thermal behaviour of oriented PET shown in *Figure 6* is quite different from that observed in the case of PC. The d.s.c. thermograms of isotropic PET presented in *Figure 6a* consist of three characteristic regions: the glass transition, exothermal crystallization and the melting peak of the crystalline phase. The d.s.c. curves of oriented PET depict different behaviour. A sharp melting endotherm is present, while the lack of a precisely defined crystallization peak indicates that the oriented amorphous sample crystallizes over a broad temperature interval.

The melting endotherm of oriented PET exhibits a second, lower-temperature peak better developed for samples after a longer ageing time. Two peaks of fusion curves were observed and described for both unoriented[19] and oriented[20] PET, and were supposed to originate from the melting and eventual recrystallization of crystallites of lower perfection. The development of a lower-temperature melting peak in oriented and aged samples indicates that physical ageing implies changes in the amorphous phase, leading to different crystallization kinetics at elevated temperatures.

At lower temperatures, in the region where shrinkage begins, the entropy and energy effects contributing to the d.s.c. trace should also be superimposed. However, they are not so effective as in PC and are screened by the crystallization process, which in oriented PET proceeds much faster than in isotropic PET[21]. When the crystallization does take place, the oriented sample does not shrink owing to the stabilizing action of the crystalline structure[15,21], so the typical d.s.c. effects attributed to shrinkage and developed in oriented PC are not observed.

CONCLUSIONS

The results presented show that viscoelastic loss spectra and d.s.c. traces of oriented glassy samples are sensitive to ageing effects. In drawn PC, enhanced relaxation at intermediate temperature is observed. The good

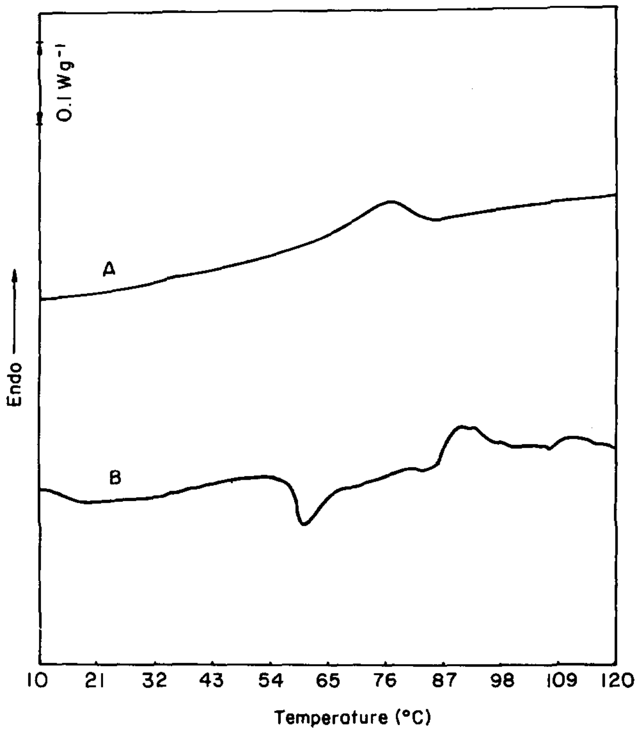

Figure 9 D.s.c. thermograms of SBS copolymer: unextended (A) and extended (B) during the measurement

coincidence of this loss process with the results of measurements on dimensional instabilities enables us to attribute the process to the relaxation of internal stresses frozen in the oriented material. The explanation of the intermediate damping effect on the basis of a multi-state mechanical model describing the shrinkage process is qualitatively successful.

D.s.c. experiments performed on oriented and aged PC revealed the appearance and development of sub-T_g endotherms not recorded in isotropic samples. Direct comparison of the positions and the heights of these endotherms with the results of shrinkage measurements enables us to suggest that d.s.c. peaks are the resultant traces of entropy and energy effects associated with the shrinkage of oriented samples. The development of d.s.c. endotherms during ageing may be explained on the basis of internal stress relaxation.

D.s.c. thermograms of oriented PET show considerable changes with ageing time, indicating that physical ageing implies the reorganization of the amorphous phase. However, for this polymer, more precise conclusions require further studies.

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