Shrinkage and related relaxation of internal stresses in oriented glassy polymers

M. Trznadel and M. Kryszewski
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Boczna 5, 90-362 Łódź, Poland
(Received 21 April 1987; revised 6 July 1987; accepted 24 August 1987)

Stability of oriented glassy polycarbonate and poly(ethylene terephthalate) subjected to physical ageing has been investigated in terms of shrinkage forces measurements. It was shown that the temperature and time dependent traces of shrinkage forces are very sensitive to the ageing effects and when compared with the results of other experiments concerning instabilities of oriented polymers they may throw some light on the nature of internal stresses relaxation. Observed shrinkage behaviour was qualitatively described on the basis of a multi-state mechanical model.

(Keywords: ageing; oriented polymers; relaxation; shrinkage forces)

INTRODUCTION

Stability of oriented polymers is determined by the molecular mobility of chain elements and is strongly dependent on the temperature and the magnitude of internal stresses. These stresses exist in the sample as a result of entropic forces produced during the deformation by increasing end-to-end distances of macromolecules. Increased mobility leads to conformational changes towards a coiled arrangement of chain elements and to a decrease in molecular orientation.

In amorphous polymers the oriented conformation is stabilized for prolonged times if the macromolecular segments are frozen after or during the deformation, so they will not move owing to entropic forces. The 'stored' internal stresses are of the same order of magnitude as the stress of plastic flow and they must relax more or less slowly, producing dimensional changes of oriented samples.

Considerable dimensional instabilities of oriented glassy polymers can be observed as time and temperature dependent thermally stimulated shrinkage (retraction)[1-3] or time and temperature dependent thermally stimulated shrinkage (retractive) forces generated when samples dimensions are kept constant[4-7].

The investigation of shrinkage forces produced in oriented polymers kept constrained at elevated temperatures has recently attracted a great deal of interest for use as a tool in examining the behaviour of oriented samples. Comprehensive studies performed by Ward and coworkers[8-12] on the origin of shrinkage forces revealed that they can be employed as a useful method to provide information about the state of orientation and the nature of the network in relation to the draw ratio.

Our recent investigations[13] showed that the traces of shrinkage forces are dependent on the magnitude of internal stresses stored after the deformation, giving evidence of the stability of oriented polymers and also their thermal history after the deformation.

In this paper we aim to show that the traces of shrinkage forces (recorded as a function of both temperature and time) are very sensitive to the physical ageing proceeding well below the glass transition temperature and to compare these traces with other measurements related to dimensional instabilities of oriented polymers. Observed shrinkage behaviour is qualitatively described on the basis of a multi-state mechanical model. We will first focus on the physical ageing[14] taking place when the samples are stored at constant temperature for long periods of time.

In oriented polymers the usual ageing processes should be enhanced by the presence of internal stresses. A decrease of these stresses and an increase of intermolecular interactions during physical ageing are reflected both in dimensional instabilities, which are discussed in this paper, and in dynamic mechanical spectra and differential scanning calorimetry traces, which will be described in the next paper.

Polycarbonate was chosen as an example of an amorphous polymer. In some cases, however, results obtained for amorphous poly(ethylene terephthalate) (crystallizing above T_g) are also reported.

EXPERIMENTAL

Two commercial forms of polycarbonate (PC) samples were used: 0.3 mm thick films of Macrolon of $M_w \approx 30\,000$ and 1 mm thick plates of Lexan of $M_w \approx 27\,000$. The mechanical behaviour of both polymers was similar and they were used alternatively according to the various geometrical requirements of different experiments. Some measurements of shrinkage forces were also done on 0.5 mm thick plates of commercial poly(ethylene terephthalate) (PET). Samples were drawn at room temperature with drawing rates of 10 mm min^{-1} (PC) and 2 mm min^{-1} (PET) to the natural draw ratios of 1.9 and 4 for PC and PET, respectively. An Instron Model 6022 tensile testing machine was used. After the deformation the external force was released and the samples were kept with free ends for various periods of time. All the samples were deformed and stored at 21°C, stabilized to an accuracy of 0.5°C.

Time dependent shrinkage forces were measured in two

0032-3861/88/030418-08$03.00

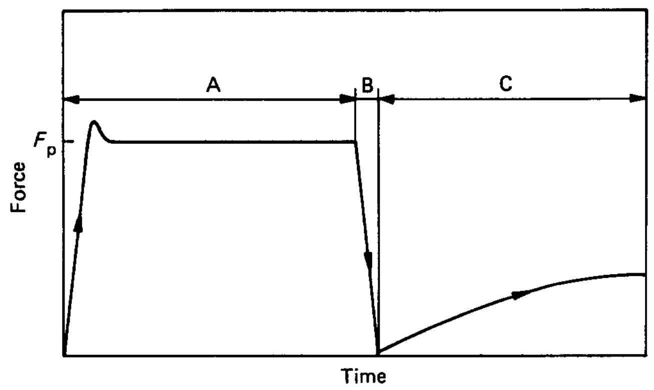

Figure 1 Schematic diagram of mechanical treatment leading to 'immediate' shrinkage force measurements

ways, as the 'immediate' shrinkage forces at room temperature and at elevated temperatures after a temperature jump. A schematic diagram of mechanical treatment leading to 'immediate' shrinkage forces measurements is shown in *Figure 1*. The procedure consist of three steps: A, the sample is drawn with necking to its natural draw ratio; B, the external force is released at a constant rate of 200 mm min^{-1} until the moment when it becomes zero; C, the length of the sample is fixed again and the shrinkage force measurement begins.

Time dependent shrinkage forces after a temperature jump were recorded using the apparatus described in the previous paper[15]. The oriented polymer sample was clamped at room temperature and quickly immersed in an oil bath thermostatically controlled at an elevated temperature. From this moment, the force of shrinkage was measured as a function of time. The apparatus was made from two materials (brass and steel) of different thermal expansivities in such a way that the dimension between the jaws was constant (25 mm) over the whole range of temperatures used.

The measurements of temperature dependent shrinkage forces were carried out in the same apparatus for samples heated in air at a constant heating rate of 3 deg min^{-1}.

The coefficient of thermal expansion for polycarbonate was recorded during measurements of dynamic mechanical spectra (which will be reported in the next paper) using a Rheometrics Model 800 mechanical spectrometer. The sample was subjected to torsional vibrations with ends under a small normal force and the changes in length were measured in terms of the thermal expansion coefficient. The birefringence of oriented samples stored at room temperature was measured using an interference microscope with fringed interference field.

RESULTS

The lengths of PC and PET samples were measured during ageing at room temperature assuming that the initial lengths L_0 and time $t=0$ corresponded to the moment when the external stresses were released after the cold drawing process. The dependencies are shown in *Figure 2*.

For both polymers the sample lengths decrease linearly on a logarithmic time-scale having a small slope, so that even after reasonably long ageing times the changes are less than 5% of the initial lengths. Because of the high elastic moduli of the samples at room temperature, these small dimensional changes involve significant shrinkage forces if the samples are kept at constant length. This is shown in *Figure 3* as the immediate shrinkage forces plotted vs. logarithm of time. The maximum values of shrinkage forces are about 1/3 of plastic flow forces for cold drawn samples. The appearance of the maximum points on the curves of shrinkage forces has been predicted by the four-state model proposed in earlier papers[13,15] and results from the time lag between the relaxation of internal entropic forces and the relaxation of external stresses.

Temperature dependencies of shrinkage stresses measured for oriented and aged samples are shown in *Figure 4*. Typical traces of shrinkage forces recorded for

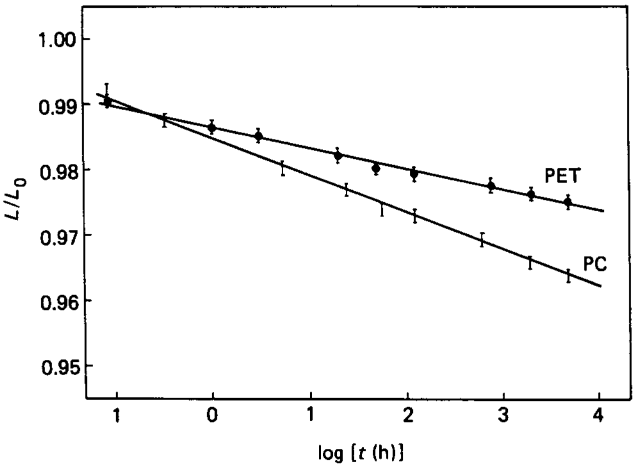

Figure 2 Changes of the relative length L/L_0 as a function of ageing time for oriented PC and PET samples

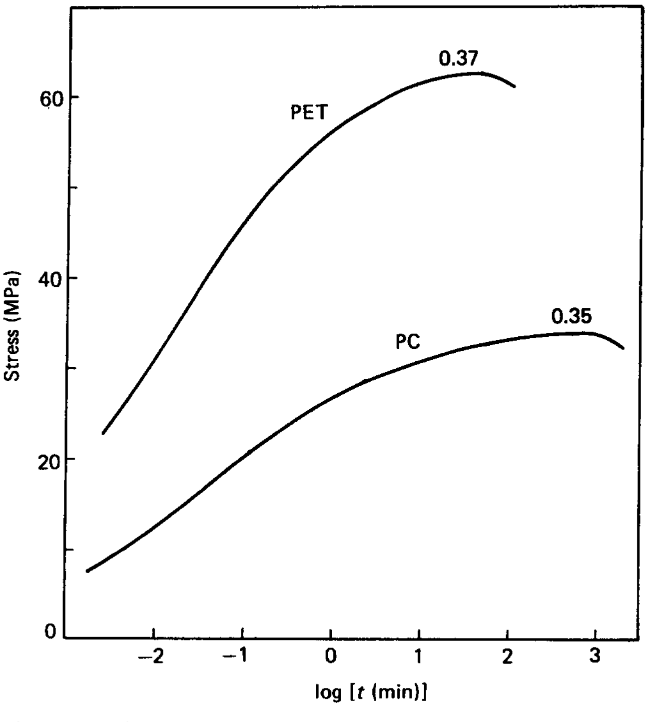

Figure 3 Time dependencies of immediate shrinkage stresses (shrinkage force per cross-section area of deformed sample) generated in oriented PC and PET. Numbers denote the ratios of maximum shrinkage forces to F_p (compare *Figure 1*)

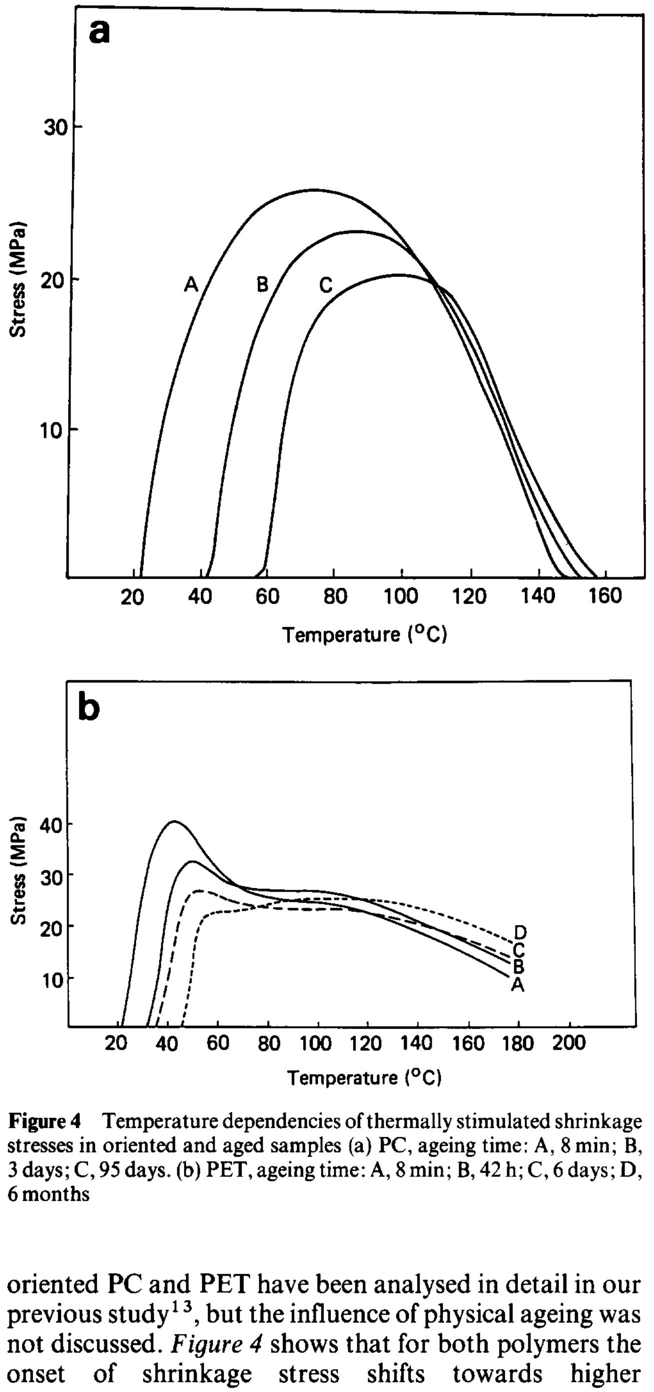

Figure 4 Temperature dependencies of thermally stimulated shrinkage stresses in oriented and aged samples (a) PC, ageing time: A, 8 min; B, 3 days; C, 95 days. (b) PET, ageing time: A, 8 min; B, 42 h; C, 6 days; D, 6 months

oriented PC and PET have been analysed in detail in our previous study[13], but the influence of physical ageing was not discussed. *Figure 4* shows that for both polymers the onset of shrinkage stress shifts towards higher temperatures and the maximum stress decreases with increasing ageing time. The traces recorded for PET are more complicated because of crystallization taking place close to the glass transition temperature. The shrinkage stresses then reach maximum values; however, in contrast to PC samples, they do not fall to zero but stabilize at a certain plateau level which results from the crosslinking effects of growing crystallites.

Figure 5 shows the temperature dependence of lengths expressed in terms of the α-coefficient, defined analogously to thermal expansion ($\alpha = \mathrm{d}L/L\mathrm{d}T$, where L is the current length of the specimen) and recorded for various PC samples heated at a rate of 3 deg min^{-1}.

The α-coefficient, considered in this way, describes the resultant length changes of oriented samples and consists of reversible and irreversible components. The first, related to the thermal vibrations of molecules around their equilibrium positions, is observed not only for isotropic samples but also for oriented samples at lower temperatures, where relaxations of extended segments are not involved. At higher temperatures, irreversible entropic contraction makes the α-coefficient assume negative values, falling rapidly to about $-1 \times 10^{-3}\,\mathrm{K}^{-1}$. In this region the effects related to the reversible component (of magnitude about $10^{-5}\,\mathrm{K}^{-1}$) may be neglected.

A significant effect of ageing time was observed in time dependent shrinkage stresses measured after a temperature jump. *Figure 6* shows the results obtained for oriented polycarbonate after a temperature jump from room temperature to 60°C. An induction time at which the non-zero stress appears is observed for aged samples. For samples measured directly after the deformation this induction time disappears. After the induction period the stress increases quickly, slowing down after longer times. Time dependencies of shrinkage forces are very sensitive to ageing effects. A large increase in induction time, by several orders of magnitude, and a lower rate of increase of shrinkage stress were found for samples after longer ageing times.

DISCUSSION

Oriented polymers which are kept unconstrained shrink as a result of entropic forces which tend to reduce the

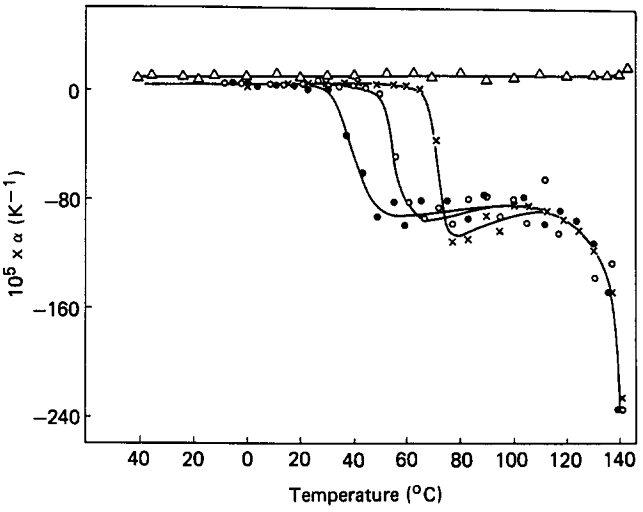

Figure 5 Temperature dependence of α-coefficient of various PC samples: △, non-oriented; ●, oriented, aged 8 min; ○, oriented, aged 21 h; ×, oriented, aged 180 days

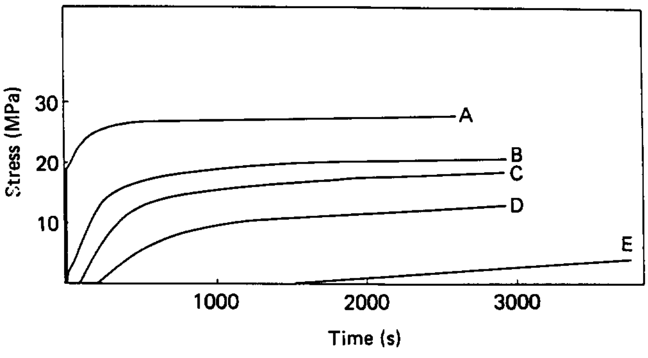

Figure 6 Time dependencies of shrinkage stresses of oriented and aged PC measured at $T = 60$°C. Ageing times: A, 6 min; B, 24 h; C, 3 days; D, 14 days; E, 48 days

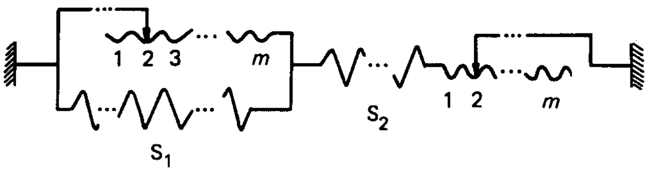

Figure 7 Basic scheme of multi-state mechanical model

molecular orientation. Changes in length are linear on a logarithmic time-scale (see *Figure 2*), which indicates that the rate of contraction is high immediately after the deformation and then slows down at longer ageing times. This effect is even more evident from an analysis of measurements of immediate shrinkage forces, as shown in *Figure 3*. Externally recorded stress increases from zero to the moment until it balances the relaxing internal stresses transduced at the sample ends along the macromolecular elements. Then the shrinkage force decreases, probably as a result of intermolecular slipping among stressed macromolecular segments.

The gradual contraction that takes place during ageing (see *Figure 2*) is associated with the relaxation of internal stresses. Differing magnitudes of residual stress are reflected in the different shrinkage behaviours of oriented and aged samples, as shown in *Figures 4–6*.

A reasonable qualitative explanation of this behaviour is to attribute the observed effects as the resultant action of local relaxations of internal stresses 'unfrozen' by thermally activated processes. Various local components give rise to the externally detected effect by means of the physical network existing in oriented sample. According to this description, the local volume in an oriented glassy polymer consisting of aligned macromolecular segments may reach the unoriented state by thermally activated jumps through a series of intermediate states characterized by different local orientation.

For the mathematical calculations the properties of such local volume were approached by the behaviour of a mechanical model.

The model

The basic scheme of the proposed multi-state model is shown in *Figure 7*. It consists of two springs, S_1 connected in parallel to the element of consecutive energy barrier and S_2 connected in series to another barrier element. Molecular interpretation assumes that S_1 is related to the chain elasticity and when extended it represents an oriented chain conformation. The barrier element attached in parallel to the spring S_1 depicts the hindrances applied to the chain elements frozen in the glassy state and is defined by the Helmholtz free energy difference related to the excitation of the local frozen-in molecular conformations. Spring S_2 represents an elastic junction of the subunit with the matrix and its eventual extension can be relaxed by overcoming the Helmholtz free energy contour of another consecutive energy barrier connected in series to S_2. In oriented polymers such relaxation is realized by intermolecular slipping, which does not necessarily lead to the decreased chain orientation.

In the real system the barriers of both elements are influenced by the configuration of the surrounding submolecular units and the local stresses which are related to the extension of springs S_1 and S_2.

Each barrier element consists of $m-1$ barriers which separate m available positions at the bottoms of consecutive energy contour. If m is confined to 2 the multi-state model becomes identical with previously introduced four-state unit, which was successfully used to explain the mechanism of shrinkage in oriented glassy polymers[13,15,16]. The four-state model was much simplified, for it allowed the elementary volume to assume either a fully oriented or completely relaxed conformation, hence it must be extended to a more realistic multi-state system if the subtle effects of internal stresses relaxation are to be considered.

The properties of the whole glassy sample may be characterized in the simplest way by the assembly of the model elements connected in parallel. Generally, a single unit shown in *Figure 7* can assume m^2 states which differ from one another in the internal stresses and external response. In parallel connection each model unit acts independently and its state may be specified by two numbers i,j denoting the positions on the barrier elements associated to springs S_1 and S_2 respectively.

Model description of shrinkage

In order to relate the behaviour of the model to the shrinkage effects we can consider the state 1,1 of each unit as representing the local situation in an oriented glassy polymer immediately after deformation. Springs S_1 are highly extended and the assembly is internally stressed. From this moment on, thermally activated jumps take place over the Helmholtz free energy barrier modified by local stresses dependent on the interactions between the elements and the external conditions. These motions lead to the gradual relaxation of spring S_1, and this is macroscopically reflected as time and temperature dependent shrinkage (when the assembly is unconstrained) or time and temperature dependent shrinkage forces generated when the assembly is kept at constant length.

Shrinkage behaviour was calculated according to the equations derived in the Appendix for the following values of parameters which characterize transition rates over the energy barriers: Helmholtz free energy differences $\Delta F_1/k=\Delta F_2/k=16\,000$ K (k is the Boltzmann constant), the frequency factor $A=1\times10^{13}\,\mathrm{s}^{-1}$, and the activation volumes $V_1=V_2=1000$ Å^3. Computations made following assumptions:

(a) each barrier element consists of 20 barriers ($m=21$);

(b) the length a between the neighbouring barriers is constant for all the elements;

(c) the expression $\Delta\sigma_1=bT$ (see equation (6) in the Appendix) for $T=294$ K is equal to $\Delta\sigma_2$ (see equation (11)), which means that the stresses related to the extension of springs S_1 and S_2 by the length a are equal at room temperature.

The results of numerical calculations of internal stresses changing with time during ageing at room temperature are shown in *Figure 8*. It is seen that the model predicts a linear decrease of internal stresses on a logarithmic time scale, observed after a certain time which is dependent on the magnitude of the initial internal stress. This also implies a linear decrease in the length of the oriented sample because the scale $\Delta L/a$ is proportional to $\Delta L/L_0$. Such a model description is in good agreement with the experimental data shown in

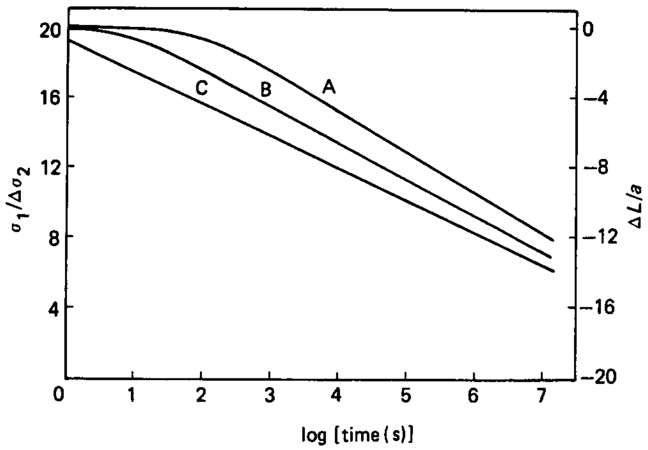

Figure 8 Time dependencies of internal stresses σ_1 calculated for various values of parameter $\Delta\sigma_1$: A, 4 MPa; B, 4.5 MPa; C, 5 MPa

Figure 2, where a linear fall of L/L_0 with the logarithm of time is observed.

Different magnitudes of residual internal stresses must be reflected in different shrinkage behaviours of oriented and aged samples. The calculations were performed for the assembly of model units connected in parallel at constant heating rate.

The influence of the magnitude of initial internal stresses on the dimensional changes (expressed in terms of the α-coefficient) of the system is shown in *Figure 9a*. The curves were computed for various internal stresses created as a result of ageing and corresponding to the different ageing times at $T = 294$ K as shown in *Figure 8*. The coefficient was derived from equation (7) of the Appendix:

$$\alpha = \frac{1}{L_a}\frac{dL_a}{dT}$$

and the value $L_u = (m-1)a$ was taken to the computations to give an initial draw ratio of 2.

The α-coefficient calculated in this way describes irreversible entropic contraction and does not concern the reversible process of thermal expansion. As shown in the figure, α changes rapidly at a certain temperature, reaches an extreme value, then stabilizes and reaches zero when internal stresses are fully relaxed. In the glassy state, sufficiently below the glass transition temperature, the calculated curves are in good qualitative agreement with experimental data shown in *Figure 5*. Discrepancies occur close to the glass transition, where thermally activated and stress induced three-dimensional segmental motions relax the remaining molecular orientation much faster than predicted by the model description. This relaxation starts at the temperature where the viscoelastic α-process begins and its calculation is out of the scope of our model.

Temperature dependencies of shrinkage stresses calculated for the assembly of the model elements kept at constant length and heated at constant rate are shown in *Figure 9b*. The traces were computed for different values of initial internal stress originating as a result of ageing and related to the ageing time by the dependencies shown in *Figure 8*.

Analysis of the curves reveals three basic features. First, the initial and maximum values of shrinkage stress shift to higher temperatures with increasing ageing time. Second, the maximum value of shrinkage stress decreases with ageing time. Third, the temperature of the total relaxation of internal stresses is virtually independent on the ageing effects. Similar relations are observed in amorphous polycarbonate, as shown in *Figure 4a*.

The results and the model interpretation confirm the suggestion that ageing of oriented samples is associated in the first instance with the gradual relaxation of internal stresses. The general description of physical ageing is more complex but the influence of ageing on such model parameters as Helmholtz free-energy difference and the activation volume is not considered here to show that the differences in shrinkage behaviour exhibited by oriented and aged samples may be attributed to the relaxation of internal stresses frozen after the deformation.

Other effects

As already shown, the ageing effects reflected in thermal shrinkage may be satisfactorily explained on the basis of the relaxation of internal stresses. More precise analysis of time dependent shrinkage stresses (see *Figure 6*) indicates, however, that the mechanism of this relaxation is more complex and does not lie only in the simple reduction of end-to-end distances of oriented macromolecules.

The great change of induction time observed for aged samples seems to be the most peculiar feature of these dependencies. As previously reported[16], the induction

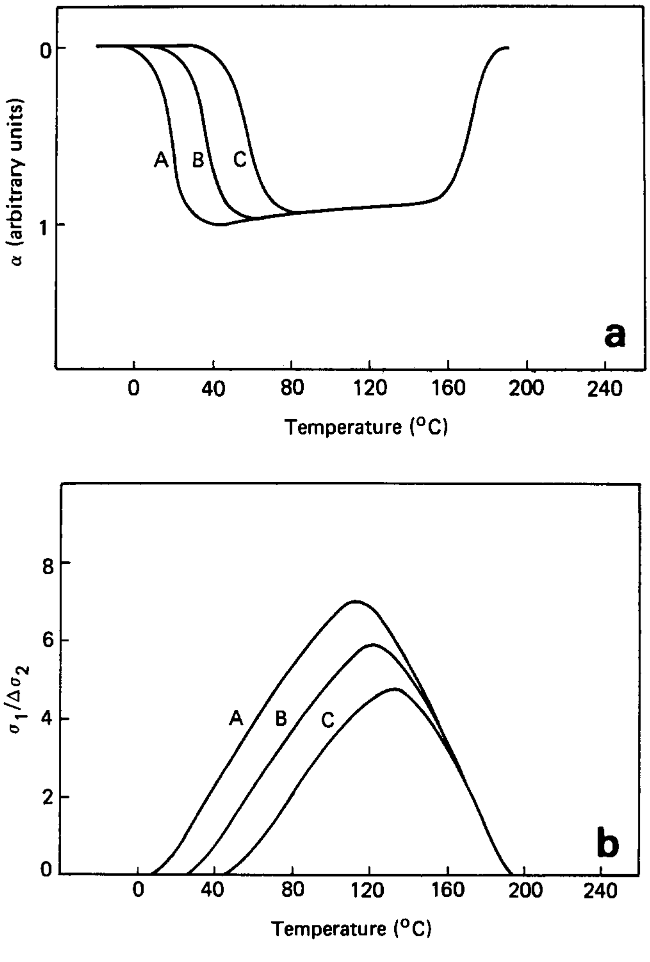

Figure 9 Temperature dependencies of (a) α-coefficient and (b) shrinkage stresses calculated for various values of internal stress $\sigma_1/\Delta\sigma_2$ which correspond to the ageing time according to curve B of *Figure 8* $\sigma_1/\Delta\sigma_2$ = A, 18; B, 15; C, 12

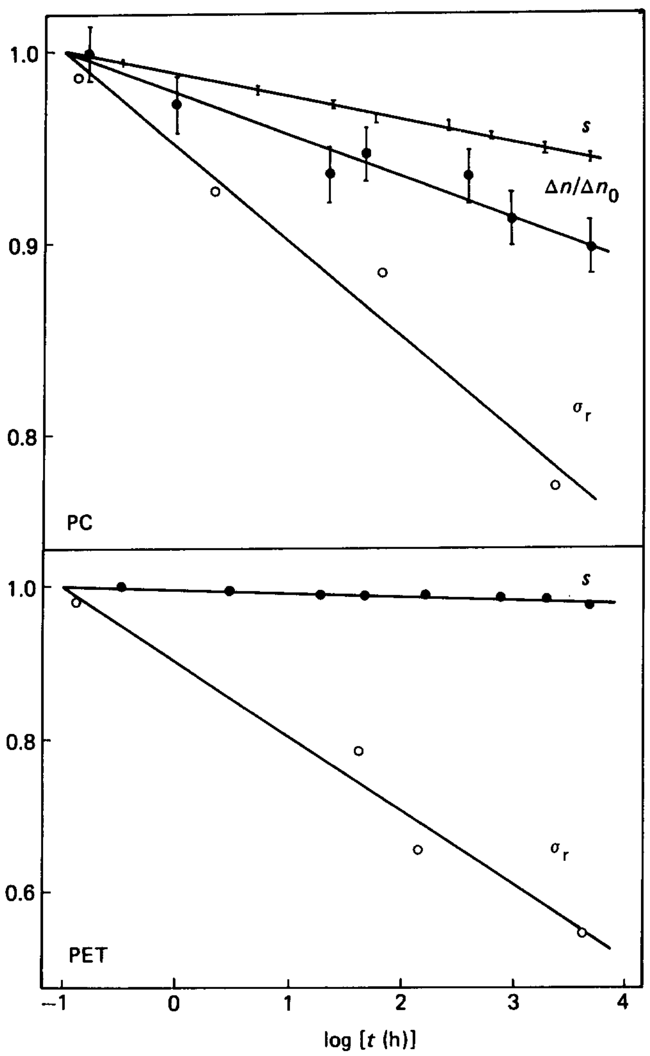

Figure 10 Dimensional relaxation s, relative birefringence $\Delta n/\Delta n_0$ and relative value σ_r of maximum shrinkage stress plotted vs. logarithm of ageing time for oriented PC and PET samples

period which was proposed to originate from the interactions between neighbouring shrinking regions in an oriented polymer is influenced by two components, the magnitude of internal stresses and interactions between the chain elements. The change of induction time by several orders of magnitude during ageing indicates that the ageing process causes not only the gradual relaxation of internal stresses but also the enhancement of intermolecular interactions, changing both components towards an increase in the induction period.

In oriented polymers the enhanced interactions between chain elements can be achieved in the regions of local regularities in which macromolecular segments are aligned in the same direction. Macromolecular orientation and increased molecular mobility allow the easier aggregation in such regions of more stable constitution than the rest of material.

The stabilizing action of such aggregates may lead, in certain conditions, to the gradual relaxation of internal stresses and a decrease of the average orientation without externally observed dimensional changes. When a macromolecular segment tends to reduce its end-to-end distance owing to thermal vibrations its influence on the surroundings results in compressive stresses in the vicinity of the shrinking element, while the element remains still under a tensile stress. This compression makes the shrinkage of the neighbouring region easier and, if thermal activation is high enough, the shrinkage of surrounding segments occurs and the effect can be externally observed as a shrinkage preceded by an induction period[16].

On the other hand, if thermal activation is not sufficient to bring about the shrinkage of the surroundings quickly enough, the shrinking chain element will relax as a result of intermolecular slipping. Such relaxation will not cause dimensional changes but only the decrease of internal stresses and molecular orientation inside the volume involved.

In order to throw some light on the possibility of such relaxations the direct comparison of relative residual strain, s, the relative birefringence $\Delta n/\Delta n_0$ and the relative value σ_r of maximum shrinkage stress plotted vs. logarithm of ageing time are shown in *Figure 10*. Relative residual strain is expressed in terms of function s given by the equation:

$$s=\frac{L-L_u}{L_0-L_u}=\frac{\lambda-1}{\lambda_m-1}$$

where L is the current length of oriented sample, L_u and L_0 (connected by the relation $L_0=\lambda_m L_u$) are the lengths of unoriented and 'fresh-oriented' sample, respectively. The relative birefringence measured during ageing is shown in the form of $\Delta n/\Delta n_0$, where Δn_0 corresponds to time $t_0=6$ min after the deformation.

The maximum values of shrinkage stresses were determined from the curves of shrinkage stresses recorded as a function of temperature (see *Figure 4*). All the dependencies shown in *Figure 10* are normalized to their values determined for time $t_0=6$ min after the deformation, so they are equal to 1 for ageing time $t=t_0$ and 0 for the sample without molecular orientation.

The results indicate that not all orientational changes taking place during ageing of oriented PC contribute to the dimensional changes because the decrease of relative birefringence is greater than s for the same period of time.

The maximum shrinkage stress is closely related to the magnitude of internal stresses frozen in the oriented sample, so its relative value σ_r is a reasonable measure of relative value of internal stresses relaxing during ageing at constant external conditions. The lower fall in birefringence than in internal stresses observed during ageing suggests an increase in regions of local order as a result of ageing processes taking place in oriented samples.

It is interesting to note that discrepancies between the relative residual strain and the relative magnitude of internal stresses are more pronounced for oriented PET than PC; however the dimensional stability of oriented PET is higher than PC (compare *Figure 2*). This fact suggests that as a result of ageing the macromolecules of oriented PET tend to form some kind of aggregates which enable the remaining fraction to relax inside such assemblies. The comparison of shrinkage forces recorded as a function of temperature for oriented and aged amorphous PET with similar results for crystalline PET[13] together with the fact that oriented PET crystallizes a little below its T_g (confirmed by differential scanning calorimetry thermograms and wide-angle X-ray scattering analysis) seem to confirm the above suggestion.

CONCLUSIONS

The experimental results presented in this paper show that the measurements of dimensional instabilities of oriented glassy polymers provide information about the molecular mobility and the actual state of sample orientation. The appearance of shrinkage forces as well as their magnitude are significantly affected by the ageing phenomena, indicating that the ageing process in oriented polymers is associated in the first instance with the gradual relaxation of internal stresses frozen after the deformation.

The measurements of shrinkage forces generated in oriented polymers at elevated temperatures make it possible to estimate the degree of internal stress relaxation, while a comparison with birefringence or dimensional relaxations may throw some light on the changes of intermolecular interactions.

The multi-state mechanical model qualitatively explains well the shrinkage behaviour and internal stress relaxation in glassy polymers. The present analysis of the model is simplified and the neglection of interactions between the model units precludes the description of induction time. However, this model can provide a tool for more refined investigations.

ACKNOWLEDGEMENT

The authors thank Professor E. W. Fischer and Dr T. Pakuła, Max Planck Institute, Mainz, FRG, for help with the measurements performed in their laboratories.

This work is partially sponsored by CPBP 01.14.

REFERENCES

1 Andrews, R. D. *J. Appl. Phys.* 1955, **26**, 1061
2 Allison, S. W., Pinnock, P. R. and Ward, I. M. *Polymer* 1966, **7**, 66
3 Tanabe, Y. and Kanetsuna, H. *Polymer* 1979, **20**, 1121
4 Tobias, J. W. and Taylor, L. J. *J. Appl. Polym. Sci.* 1975, **19**, 1317
5 Arridge, R. G. C., Barham, P. J. and Keller, A. *J. Polym. Sci.* 1977, **15**, 389
6 Ram, A., Tadmor, Z. and Schwartz, M. *Int. J. Polym. Mater.* 1977, **6**, 55
7 Decandia, F., Russo, R., Vittoria, V. and Peterlin, A. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 1175
8 Pinnock, P. R. and Ward, I. M. *Trans. Faraday Soc.* 1966, **62**, 1308
9 Kahar, N., Duckett, A. R. and Ward, I. M. *Polymer* 1978, **19**, 136
10 Nobbs, J. H., Bower, D. J. and Ward, I. M. *Polymer* 1976, **17**, 25
11 Rietsch, F., Duckett, R. A. and Ward, I. M. *Polymer* 1979, **20**, 1133
12 Capaccio, G. and Ward, I. M. *Colloid Polym. Sci.* 1982, **260**, 46
13 Pakuła, T. and Trznadel, M. *Polymer* 1985, **26**, 1011
14 Struik, L. C. E. 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
15 Trznadel, M., Pakuła, T. and Kryszewski, M. *Polymer* 1985, **26**, 1019
16 Trznadel, M. *Polymer* 1986, **27**, 871
17 Argon, A. S. and Bessonov, M. I. *Polym. Eng. Sci.* 1977, **17**, 174
18 Haward, R. N. and Thackray, G. *Proc. R. Soc. London (A)* 1968, **302**, 453
19 Ward, I. M. 'Mechanical Properties of Solid Polymers', Wiley, London, 1971

APPENDIX

Mathematical calculations of the model

Let us consider a great number of model elements connected in parallel and assume that immediately after deformation all the units occupy state 1,1.

It is useful to analyse two situations separately, when the assembly is unconstrained and when the system is kept at constant length. The first case corresponds to shrinkage, which is a time and temperature dependent phenomenon. In a model description springs S_2 are relaxed, hence the state assumed by each unit is unequivocally specified by one number i denoting the position on the first barrier element.

Transitions from state 1 to m can be described as a reaction of the type:

$$i \underset{K'(i+1)}{\overset{K(i)}{\rightleftharpoons}} i+1 \qquad i=1,\ldots m-1$$

the kinetics of which are given by a set of differential equations:

$$\frac{\mathrm{d}n_i}{\mathrm{d}t}=n_{i-1}K(i-1)-n_i[K(i)+K'(i)]+n_{i+1}K'(i+1) \quad (1)$$

where the numbers of elements n_i in states i are normalized

$$\sum_{i=1}^{m} n_i=1 \quad (2)$$

Constants $K(i)$ and $K'(i)$ are temperature dependent transition rates from state i towards lower and higher internal stresses, respectively. They are related to the height of the Helmholtz free energy barrier ΔF_1 for the local rearrangement modified by internal stress $\sigma(i)$ on the spring S_1 in state i and can be defined as follows[17]:

$$\begin{aligned} K(i)&=A\exp\left(-\frac{\Delta F_1-\sigma(i)V_1}{kT}\right)\\ K'(i)&=A\exp\left(-\frac{\Delta F_1+\sigma(i)V_1}{kT}\right)\end{aligned} \quad (3)$$

where A is a constant and V_1 is the activation volume of the first barrier element. These simplified relations are valid on the assumption that the Helmholtz free energy contour ΔF_1 is described by the non-zero strain resistance in such a way that only sites i located precisely at the bottoms of ΔF_1 contour can be assumed.

Molecular interpretation of the model assumes that the tension of spring S_1 is related to the chain elasticity, so it may be expressed, generally, in terms of rubber-like stresses, similarly to the Haward–Thackray model[18]. In this case, however, for draw ratio <2 it is sufficient to apply the Gaussian single-chain approximation, according to which stress is proportional to extension and absolute temperature[19]:

$$\sigma(i)=bT(m-1) \quad (4)$$

where b is a constant.

Equations (1), (3) and (4) enable the numerical calculation of populations n_i as a function of time or temperature at constant heating rate $\beta=\mathrm{d}T/\mathrm{d}t$. It is then possible to calculate the average position i_a on the first barrier element:

$$i_a=\sum_{i=1}^{m} \mathrm{i}n_i \quad (5)$$

the average internal stress

$$\sigma_a = bT(m-i_a) = \Delta\sigma_1(m-i_a) \tag{6}$$

and the average length

$$L_a = \sum_{i=1}^{m} [a(m-i)+L_u]n_i \tag{7}$$

Parameter a depicts the distance between the subsequent barriers and L_u is associated with the length of the unoriented assembly. It is useful to note that, when the system is internally stressed, the transition rates going towards higher stresses are much less than the rates going towards lower internal stresses, so the latter can be omitted in equation (1).

When the whole assembly is kept at constant length, springs S_2 transduce internal stresses at the ends of the system and they are generally not relaxed. In this case, the state of each unit is specified by two numbers, i, as defined previously, and j, denoting the position on the second barrier element. It is assumed in the following considerations that the stresses on the springs are sufficiently high, so the transition rates K' may be neglected in comparison with the respective values of K rates. As a result of this simplification only states i,j are available which satisfy the condition $i \geqslant j$.

Transition rates from the initial state to the final state m,m can be considered as a reaction of the type

$$\begin{tikzcd} & i,j \arrow[dl, "K_1(i,j)"'] \arrow[dr, "K_2(i,j)"] & \\ i+1,j & & i,j+1 \end{tikzcd} \qquad \begin{array}{l} i=1,\ldots m-1 \\ j=1,\ldots i \end{array}$$

the kinetics of which are described by a set of differential equations:

$$\frac{dn_{i,j}}{dt} = n_{i-1,j}K_1(i-1,j) + n_{i,j-1}K_2(i,j-1) - n_{ij}[K_1(i,j)+K_2(i,j)] \tag{8}$$

and

$$\sum_{i=1}^{m}\sum_{j=1}^{m} n_{i,j} = 1 \tag{9}$$

where constants K_1 and K_2 are transition rates of type K (i.e. towards decreasing the local stresses) on the first and the second barrier element respectively.

The external stress produced by a single unit which occupies state i,j is related to the extension of spring S_2 and is

$$\sigma(i,j) = (i-j)\Delta\sigma_2 \tag{10}$$

where $\Delta\sigma_2$ is the stress change associated with the extension of S_2 from site j to $j-1$. The resultant internal stress σ_{int} (on the spring S_1) in such element is given by subtraction of stress exerted by the extension of S_1 (equation (4)) and the external stress:

$$\sigma_{int}(i,j) = bT(m-i) - (i-j)\Delta\sigma_2 \tag{11}$$

The transition rates K_1 and K_2 are related to the heights of the Helmholtz free energy barriers ΔF_1 and ΔF_2 modified by the stresses $\sigma_{int}(i,j)$ and $\sigma(i,j)$:

$$\begin{aligned} K_1(i,j) &= A\exp\left(-\frac{\Delta F_1 - [bT(m-i)-(i-j)\Delta\sigma_2]V_1}{kT}\right) \\ K_2(i,j) &= A\exp\left(-\frac{\Delta F_2 - (i-j)\Delta\sigma_2 V_2}{kT}\right) \end{aligned} \tag{12}$$

where V_1 and V_2 are the activation volumes of the first and the second barrier element.

According to equations (8) and (12) it is possible to calculate the populations $n_{i,j}$ as a function of time or temperature (if $\beta = dT/dt$) and the total external stress σ exerted by the whole assembly:

$$\sigma = \Delta\sigma_2 \sum_{i=1}^{m}\sum_{j=1}^{i} (i-j)n_{i,j} \tag{13}$$