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The effect of molecular orientation on the physical ageing of amorphous polymers — dilatometric and mechanical creep behaviour

M. D. Shelby and G. L. Wilkes*
Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg , VA 24061-0211, USA

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The objective of this study was to determine whether molecular orientation has an effect on the rate of physical ageing in amorphous glassy polymers. To achieve this, samples of atactic polystyrene and bisphenol-A polycarbonate were uniaxially hot-drawn to various stretch ratios and then quenched into the glassy state to freeze in orientation. Physical ageing rates were then measured as a function of orientation with dilatometry and tensile creep measurements. The volume relaxation rate, β, was approximately 50% higher for the stretched samples and did not vary with orientation over the range of stretch ratios tested. This was true despite the fact that the initial free volume was actually decreasing with increasing elongation. In contrast, creep measurements showed a slight decrease in the horizontal shift rate, μ_h, upon stretching (i.e. a decreased ageing rate). Possible explanations for these unusual trends in terms of a stretch-induced activated state are discussed. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: molecular orientation; physical ageing; amorphous glassy polymers)

INTRODUCTION

Physical ageing is a well documented and distinctly important phenomenon which occurs in glassy materials. This is apparent from the number of reviews addressing this topic in the literature[1–5]. In the case of amorphous polymers, quenching the sample from above the glass transition temperature, T_g, into the glassy state introduces a non-equilibrium structure where physical properties change with time. The most common changes include densification and a gradual decrease in ductility.

The fact that most amorphous polymers are processed above T_g and then quenched into the glass makes physical ageing an important concern for any designer utilizing polymeric glasses. Couple this with the fact that many processing methods introduce at least some degree of orientation[6], intentional or not, one of the motivations for this study becomes clear. If orientation is indeed found to alter the ageing behaviour of an amorphous glass, then design criteria may need to be modified accordingly.

Ideally, for this type of study, one would like to isolate the effects of molecular orientation in *purely amorphous* systems. A few studies in the literature have been performed on hot-drawn (i.e. stretched above T_g) polymers; however, interpretation of the results is complicated by the possible formation of strain-induced crystallinity[1,7]. Since strain-induced crystallinity varies with orientation—and crystal regions do not physically age in the classical sense—it becomes very difficult to deconvolute the effects of amorphous orientation from the overall changes in physical ageing behaviour.

Similarly, a number of studies also exist with regard to ageing behaviour in cold-drawn systems (the polymer is stretched below T_g)[8,9]. Here crystallinity is not necessarily a problem; however, the high internal stresses which develop from stretching a glass are. As with the crystallinity, these glassy internal stresses have a significant influence on the ageing behaviour, making interpretation of the data difficult. A more detailed discussion of theses various studies along with the differences between cold and hot drawing is provided in a later section.

For the present study, samples of bisphenol-A polycarbonate (PC) and atactic polystyrene (PS) have been hot-drawn to various stretch ratios, quenched to room temperature to freeze-in the orientation, and then held isothermally at temperatures below T_g while relaxation behaviour was measured. These two specific systems do not undergo measurable strain-induced crystallization, so the problems discussed above are avoided. Volume relaxation was monitored by dilatometry, and mechanical relaxation by using creep measurements. Supplemental tests—including the determination of isothermal linear shrinkage with time and the measurement of density at room temperature—were also performed to help in the characterization of the oriented state. While both dilatometry and mechanical creep are applied routinely to the study of isotropic polymers, they each pose their own special problems when applied to oriented systems. These problems arise primarily from the sub-T_g shrinkage which occurs during annealing, an issue which will be discussed in more detail in the Experimental section.

AGEING RATE DETERMINATION

Dilatometry and creep provide two commonly utilized, but slightly different, methods for measuring the ‘rate’ of

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* To whom correspondence should be addressed

physical ageing. For volumetric measurements, the volume relaxation rate, β, is defined as

$$\beta = \frac{1}{V(t)}\frac{\mathrm{d}V(t)}{\mathrm{d}\log(t)} \tag{1}$$

where $V(t)$ is the volume at time t. The parameter β has a value ranging from 10^{-4} to 10^{-3} for most polymers in the temperature range between T_g and the first secondary transition below T_g. Alternatively, one can measure the rate of linear relaxation, α_l, which is analogous to equation (1) except $V(t)$ is replaced by the length $L(t)$. For isotropic systems β equals $3\alpha_l$, although for anisotropic systems α_l will vary in each material direction. In the special case of uniaxial orientation, β will equal $\alpha_{MD} + 2\alpha_{TD}$ because of symmetry. The subscripts MD and TD refer to the machine (stretch) and transverse directions, respectively.

For creep measurements, the mechanical shift rate is defined as

$$\mu_h = -\frac{\mathrm{d}\log(a_h)}{\mathrm{d}\log(t_e)} \tag{2}$$

where a_h is the horizontal shift factor required to properly superimpose the creep curve at ageing time t_e with the reference curve. The subscript h refers to horizontal shifting although there is also a vertical shifting counterpart which will be discussed in more detail later. The value for μ_h is usually close to unity over the 'normal' ageing temperature range, which is between T_g and the next lowest secondary transition temperature corresponding to chain backbone motions[1]. Outside this temperature range, μ_h approaches (but is not necessarily) zero.

While μ_h and β are defined similarly, they do not generally follow the same trend with changes in ageing temperature. Struik has defined a parameter S, denoted the volume sensitivity, where[1]

$$S = 2.303\frac{\mu_h}{\beta} \tag{3}$$

This can be related to the molecular mobility, M,

$$S = \left[\frac{\partial \ln M}{\partial (ffv)}\right]_T \tag{4}$$

where ffv is defined as the fractional free volume. Struik found that S typically increases with decreasing temperature below T_g for a wide range of polymers, although McKenna and Kovacs[10] found the opposite trend for poly(methyl methacrylate) (PMMA).

HERMANS' ORIENTATION FUNCTION

To characterize the orientation state of the uniaxial system, one can utilize Hermans' orientation function, f, which can be determined from birefringence measurements[11]

$$f = \frac{\Delta}{\Delta^\circ} = \frac{3\langle\cos^2\theta\rangle - 1}{2} \tag{5}$$

Here Δ is the birefringence ($\Delta = n_{MD} - n_{TD}$ where n is the refractive index and the subscripts MD and TD refer to the machine and transverse direction, respectively), Δ° is the intrinsic birefringence (i.e. the birefringence for a perfectly oriented chain), and θ is the angle between the stretch direction (MD) and the chain axis. The angle brackets denote an average over all of the chains. The orientation function will assume the value of zero for an unoriented system, unity for perfect orientation along the stretch direction, and $-1/2$ for perfect orientation along the TD. These cases correspond to average values for θ of 54.7°, 0° and 90°, respectively. It is emphasized that this equation only applies to single-phase systems. For multiphase systems (e.g. crystalline polymers, blends, etc.), a separate orientation function has to be defined for each phase. Fortunately, neither polycarbonate nor atactic polystyrene exhibits any significant strain-induced crystallization upon hot drawing and so a single value of f is sufficient.

For polycarbonate, the intrinsic birefringence was determined to be 0.16 based on sonic modulus measurements[12]. This resulted in a maximum value for f of *ca.* 0.19 at a stretch ratio of 2.5 ×. Likewise, for PS, a maximum orientation function of 0.11 at a stretch ratio of 4 × was obtained by assuming an intrinsic birefringence of -0.16[13]. These values for f in PC and PS, while low relative to the upper value of unity, are typical of amorphous polymers in general and represent the difficulty in aligning entangled polymer chains. It is not that relaxation during stretching is necessarily the cause for the low values of f, since the samples, which were immersed in an oil bath at 160°C (120°C for PS) for 1 min, typically exhibited shrinkage recovery of 99% or greater. In fact, the maximum theoretical stretch ratio, λ_{max} (defined as the ratio of the extended chain length to the unperturbed chain root-mean-square end-to-end distance—the latter obtainable from the polymer characteristic ratio, C_∞), was calculated previously for both polymers and found to be approximately 6 to 7 for PC and 15 for PS assuming the current molecular weights[14]. This is considerably larger than the maximum experimental stretch ratios of 2.5 × and 4 × for each polymer, respectively.

COMMENTS ON PREVIOUS STUDIES OF AGEING IN ORIENTED SYSTEMS

Cold versus hot drawing

As stated earlier, there have been a limited number of studies on the physical ageing behaviour of oriented systems, most related to cold drawing. Both cold and hot drawing introduce entropic stresses due to alignment of the polymer chains. However, cold drawing is expected to produce a greater volume dilatation owing to the greater compressibility (i.e. lower Poisson's ratio). The Poisson's ratio of a glass is typically 1/3 as compared to *ca.* 1/2 (the incompressible limit) for rubbers. Also, cold-drawn samples are at a much higher internal stress state as a consequence of the addition of 'glassy' stresses caused by distortion of the 'van der Waals' bonds (i.e. internal-energy-derived stresses). These distortional stresses are responsible for a number of behavioural changes in the polymer. For example, cold-drawn samples generally show considerable shrinkage ($>$ 10% recovery) at temperatures well below T_g. Hot-drawn samples, on the other hand, do not show significant shrinkage except at temperatures near (and above) T_g. Struik[15] discusses the shrinkage behaviour of amorphous polymers and provides a simple model for the differences in shrinkage between cold- and hot-drawn polymers. The interested reader should refer to this source for more information.

Ageing studies on hot-drawn samples

One of the only hot-drawn studies was performed by Struik[1] wherein tensile creep measurements were performed on melt-oriented (rigid) poly(vinyl chloride) (PVC) drawn at 82°C. The T_g was not specified but the stretch temperature was listed as being above T_g (a typical T_g for rigid PVC is *ca*. 80°C). Samples were drawn up to a maximum stretch ratio of 2.2 × and then quenched to 20°C, at which point ageing commenced. Analysis of the shift rates from the creep tests at 20°C showed little change with increased stretching although there was considerable scatter in the data. Struik suggested that, because the level of molecular orientation is actually very small in most oriented amorphous polymers (i.e. very low f), the ageing behaviour should not be affected significantly. No data on the orientation functions or possible formation of strain-induced crystallinity in the stretched samples were presented.

Mukherjee and Jabarin[7] measured enthalpy relaxation and mechanical properties as a function of orientation in biaxially and constrained uniaxially stretched poly(ethylene terephthalate) (PET) ($T_g = 80°C$, stretch temperature $= 100°C$). They found a correlation between the ductile–brittle transition and the enthalpy of relaxation although the results must be interpreted with caution since significant levels of strain-induced crystallization occurred. This crystallinity effectively reduces the amount of amorphous region undergoing physical ageing as was also shown by Tant and Wilkes[16].

Ageing studies on cold-drawn polymers

It has been shown by a number of researchers that, between room temperature and 100°C, the rate of volume relaxation in cold-drawn polycarbonate is roughly twice that of isotropic PC[8,9]. Above 100°C, however, the volume relaxation rate does not vary much with the level of cold drawing. As will be discussed later, this transition is probably correlated with the α'-relaxation known to exist in PC around 90°C.

Another important finding made by Pixa and co-workers was that polycarbonate actually densified upon stretching[8]. This has also been observed for polycarbonate by others for cold drawing[18–21] and by Ito and co-workers for hot drawing[22]. The densification is less in the cold-drawn samples due to the Poisson expansion. Nonetheless, even with the initial densification, the cold-drawn samples still showed faster rates of volume relaxation!

By using the absolute small-angle X-ray intensity in the small-angle regime, Bartos *et al*. found that the density fluctuations increase as a consequence of drawing, even though the overall density is higher in the stretched sample[9]. These larger fluctuations correlate with the volume relaxation data, dissappearing above 100°C, and are indicative of a broader free volume distribution in the cold-drawn samples.

Lunn and Yannas performed a comprehensive study of the orientation of polycarbonate (hot and cold drawing) by means of infrared spectroscopy[23]. They found that the dimensional stability of the drawn polycarbonate increased with increasing stretch temperature. Samples hot-drawn at $T_g + 5°C$ did not reach this threshold until about 120°C. Their work also showed the presence of cooperative motions between chain segments and no change in interchain bonding with orientation. They did find, however, that bond strength perpendicular to the stretch direction increased with orientation (based on frequency shifting of the absorption peaks) which may be a result of shorter interchain distances.

Even with all of the findings discussed in the previous studies, it is still uncertain how molecular orientation affects physical ageing. It is clear that large internal glassy stresses induced by cold drawing significantly enhance the ageing process; however, the focus of our specific study is segmental/chain orientation. Thus, the only way to isolate molecular orientation sufficiently as the variable of interest is to hot draw polymers that do not crystallize. This is why atactic PS and PC were chosen for this study. The details of this hot stretching will now be discussed.

EXPERIMENTAL

Film stretching

Samples of Makrolon 2608 bisphenol-A polycarbonate were stretched uniaxially at 160°C on a T. M. Long film stretcher. The film samples, prior to stretching, had a nominal T_g of 150°C as determined from differential scanning calorimetry (d.s.c.) measurements at a heating rate of 20°C min^{-1}. The number-average molecular weight, M_n, was 16 500 g mol^{-1} as obtained from solution viscosity measurements (in tetrahydrofuran (THF) at 23°C). M_n was determined from the viscosity-average molecular weight, M_v, by assuming a polydispersity of 2 and applying correction factors[24]. The PC samples, with initial gauge lengths of 10 cm, were stretched with a crosshead speed of 12.7 cm s^{-1} to elongation ratios of 1.25 × , 1.5 × , 2 × and 2.5 × .

Samples of Dow 685D atactic polystyrene having a T_g of 103°C (from d.s.c. at 20°C min^{-1}) were stretched at 120°C. These samples had an M_n of 174 000 g mol^{-1} and a weight-average molecular weight, M_w, of 297 000 g mol^{-1} as determined from gel permeation chromatography (g.p.c.). The polystyrene was stretched at a rate of 17.8 cm s^{-1} to a final stretch ratio of 2 × and 4 × . The upper limit of 4 × for PS was due to stretch limitations of the T. M. Long apparatus and not any material limitations.

After stretching, samples were quenched below T_g with a blast of cold air in order to freeze-in orientation. Because of fluctuations in the stretching environment, the orientation function for a given stretch ratio will vary slightly from sample to sample. Orientation was therefore determined for each sample by way of birefringence measurements with an Abbe refractometer (Na *D*-line, 589.3 nm). For a given sample, the point-to-point variability in orientation function was ± 0.01. Variability in the average value of f for different samples of a given stretch ratio was ± 0.03 at the highest stretch ratios.

Density measurement

Density data were obtained with a gradient column made with salt solutions of either potassium bromide or sodium bromide and water. The column was maintained at 23 ± 0.1°C. A minimum of 12 h was allowed for the samples to reach equlbrium after insertion in the column.

Shrinkage measurement

One of the motivations for performing isothermal shrinkage measurements was to determine the temperature range over which creep measurements could be performed. Excessive shrinkage makes it very difficult to obtain accurate creep curves since the shrinkage component of strain has to be removed. Another motivation is that shrinkage is a good indicator of the molecular mobility in oriented systems. Shrinkage measurements were performed on 2.5 × samples of PC ($f = 0.16$) and 4 × samples of PS ($f = 0.11$) by using a Seiko TMA 100 in the tensile mode. Samples of the film approximately 4 mm wide, 0.2 mm thick and 25 mm long were mounted in the test fixture after it was preheated to the annealing temperature. After mounting the sample, it took approximately 2 to 3 min to reach thermal equilibrium. Measurements were started when the temperature was within 1°C of the annealing temperature. A small preload of 7 g was applied to maintain sample alignment in the test fixture. After accounting for the weight of the mounting clamps (~3 g), the resulting tensile stress exerted on the sample was nominally 50 kPa or less, which produces a negligible strain in the glassy state. All tests were run isothermally out to 10 h. Shrinkage temperatures ranged from 70°C to 132°C for PC and 50°C to 90°C for PS. Emphasis was placed on this temperature regime since lower temperatures resulted in almost immeasureable shrinkage rates. Higher annealing temperatures resulted in an α-transition (T_g) dominated shrinkage which exceeded the accurate measurement limits of the TMA instrument. Simultaneous measurement of birefringence with annealing was also performed but the loss in orientation was almost negligible except at the highest annealing temperatures. Because the changes in Δ did not exceed the scatter range of the measurement, the results are not reported.

Dilatometry

Our dilatometer was constructed on the basis of recommendations provided by Drs Greg McKenna and Carl Schultheisz of the National Institute of Standards and Technology (NIST). Unlike more conventional volume dilatometers, this system combines a linear variable differential transformer (LVDT), commonly used in linear dilatometry, with a larger-bore capillary section which results in high accuracy and ease of sample preparation (see Duran and McKenna[25]). A more detailed description of the construction and error analysis is provided elsewhere[14]. For now, only a brief summary is presented, primarily to illustrate some of the difficulties associated with dilatometric testing of oriented samples.

Combining the errors resulting from equipment variability and thermal fluctuations, an uncertainty in volume change measurement of approximately 0.0001 cm^3 at the 99% confidence limit (3σ) was obtained[14]. This error is also equivalent to the limit of detection (LOD, where $LOD = 3\sigma$) whereas the limit of quantitization (LOQ, where $LOQ = 10\sigma$) is 0.00033 cm^3. For a 3 g sample, this corresponds to an error in density measurement of 5×10^{-5} g cm^{-3} at the 99% confidence limit.

The sample—consisting of approximately 3 to 5 g of the polymer film cut into rectangular strips (~1 cm wide by 4 cm long)—was inserted into the bottom along with a glass plug prior to the sealing of the glass. The dilatometers were then placed under vacuum at room temperature for 12 to 24 h after sealing in order to remove any trapped moisture or gases. Next, the evacuated dilatometer was filled with mercury via a three-way stopcock mounted on the top of the capillary. After filling, the system was maintained under vacuum at room temperature for approximately 2 days in order to remove trapped air.

Many of the procedures described in the literature for degassing *isotropic* samples could not be used in this study. For example, isotropic samples are often degassed at elevated temperatures or by alternately heating and cooling the dilatometer. Any physical ageing that results can be erased prior to measurement simply by heating the sample/dilatometer above T_g. Unfortunately, this same procedure applied to an oriented sample would cause the sample to shrink excessively which is not acceptable. Care had to be taken not to allow the oriented samples to reach elevated temperatures since there is no way to ‘pre-erase’ the ageing prior to dilatometric measurement. In essence, each dilatometer constructed for an oriented sample was good for only one measurement! In order to maintain consistency throughout the tests, the isotropic controls were also subjected to the same thermal and pressure history as the oriented samples.

After completion of the degassing procedure, the sample was maintained at atmospheric pressure for 24 h prior to testing. It was found by accident that the mercury/gas bubbles in the dilatometer exhibited a slight but measurable volume relaxation after removal of the vacuum which subsided after about 5 to 10 h. This mercury ‘relaxation’ was large enough to alter significantly the measured relaxation rates of the polymer systems. It is uncertain why this occurs but it is believed that trapped air, which has coalesced under vacuum, diffuses back into the mercury after the vacuum is removed, thereby causing the overall volume to decrease.

Dilatometric tests

Samples of PC with varying orientation functions were aged isothermally at 90°C and 120°C for approximately 5 days. Samples of PS were aged at 60°C. The temperatures of 60°C for PS and 90°C for PC were selected based on the shrinkage data. They were a compromise between faster volume relaxation rates and minimal shrinkage. One does not want the added effect of shrinkage convoluted into the volume relaxation data. Nonetheless, the measurements at 120°C for PC were performed *specifically* to see just how the added effect of shrinkage might affect the volume relaxation data.

Each dilatometer was good for only one measurement so it is important to maximize the useful data gained from it. For that reason, some of the PC samples, after being aged at 90°C, were then heated to 120°C where they were allowed to relax further. If sufficient ageing time is allowed after this ‘T-jump’, the relaxation rate obtained should eventually be the same as if the polymer had been aged solely at 120°C. This provides an additional data point at 120°C and a useful check on the reproducibilty of the data. It can also provide an indication as to whether shrinkage is affecting the volume relaxation process.

Time zero is defined when the dilatometer was first inserted into the oil bath. Approximately 5 to 10 min was required for the sample, mercury and glassware to attain thermal equilibrium. All data were normalized to the volume at 16 min (~1000 s) at which time thermal equilibrium was guaranteed. Note that only relative volume changes were measured.

Linear dilatometric tests

Because of the anisotropy in the uniaxially oriented samples, it is expected that there will be a directional dependence to the volume relaxation rate. Unfortunately, volume dilatometry only gives the total change in volume and says nothing about directional dependence. To circumvent this problem, a 50 mm sample of 1.5 × PC was annealed at 90°C for 6 days in a manner similar to the shrinkage measurements described earlier. This intermediate orientation was chosen since it would result in less shrinkage. The longer times were required in order for shrinkage to subside and true, ageing-related length/volume changes to predominate. Linear relaxation rates were determined for samples tested in both the MD and TD directions. From this, the relative relaxation rates (α_{MD} and α_{TD}) in the different material directions could be compared to gain an understanding of the anisotropy of the relaxation process. In addition, a value for β could also be obtained from this technique ($\beta = \alpha_{\mathrm{MD}} + 2\alpha_{\mathrm{TD}}$) although the error is larger than with volume dilatometry.

Tensile creep measurements

Tensile creep measurements were performed by using a Seiko TMA 100 outfitted with a tensile testing fixture. This fixture was modified from the original to allow for longer sample lengths. Rectangular tensile coupons were cut from the stretched film samples having a nominal width of 2 mm and a length of 50 mm. The long direction of the tensile samples was parallel to the MD. Sample thickness varied with stretch ratio but was typically around 0.2 mm. Creep loading schedules followed the standard procedure outlined by Struik[1]. Loads were applied at 1 h, 2 h, 4 h, 8 h and 16 h. The loading time for each test was one-tenth of the ageing time in order to keep the measurement time short compared with the changing ageing condition. Creep strains were generally 0.1 to 0.2% or less. The loading rate for the TMA was 150 g min^{-1} (0.025 N s^{-1}). This resulted in a loading time of approximately 20 to 30 s—considerably longer than dead-load testers. Consequently, the first minute of creep data was discarded.

Both horizontal and vertical shifting were employed to form a master curve at a reference time of 4 h. In addition to the horizontal shift rate μ_{h} defined in equation (2), a vertical shift rate can be defined

$$\mu_{\mathrm{v}} = -\frac{\mathrm{d}\log(a_{\mathrm{v}})}{\mathrm{d}\log(t_{\mathrm{e}})} \tag{6}$$

where a_{v} is the vertical shift factor. Vertical shifting is assumed to account for the decrease in the instantaneous compliance, D_0, brought about by the ageing process although, as indicated by Chai and McCrum, its proper usage requires that the relaxation strength, ΔD, does not change with ageing[26]. It is assumed for this study that ΔD remains constant with ageing although it is certainly expected to vary with *f*.

Creep ageing studies were performed at 60°C for PS and 90°C for PC since shrinkage was reasonably small at these temperatures. Corrections for this shrinkage were still required, however, and the procedure is depicted in *Figure 1*. The baseline, which is decreasing with time due to shrinkage, was linearly extrapolated into the creep region. The creep data were then corrected by subtracting the extrapolated baseline. This, in effect, rotates the baseline to the horizontal. The fact that shrinkage is highest at short annealing times is the main reason why ageing times less than 1 h were not utilized.

Creep error analysis

The TMA is a relatively ‘soft’ instrument from a compliance standpoint. Therefore, compliance corrections were applied electronically by the TMA after first performing a ‘calibration’ run with a 5 mm steel sample (this steel sample approximates a nearly infinite stiffness spring so that the measured deformation is due almost solely to the instrument). Even with this correction, however, the error in absolute compliance is still expected to be significant. Fortunately, for creep ageing studies, what is of more importance is the relative changes in compliance with creep and ageing time (which the instrument can provide accurately). Therefore it is emphasized that the ‘absolute’ compliance values shown are only approximate.

Another source of compliance error results from variations in sample geometry. Point-to-point sample thickness varied by approximately 5% which correspondingly altered the cross-sectional area. In addition, some of the samples

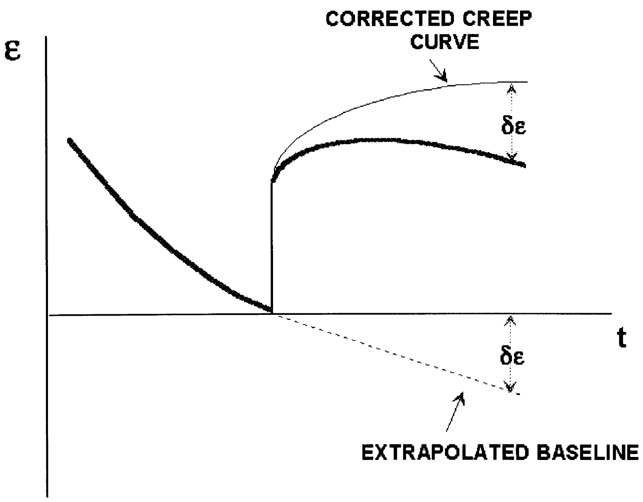
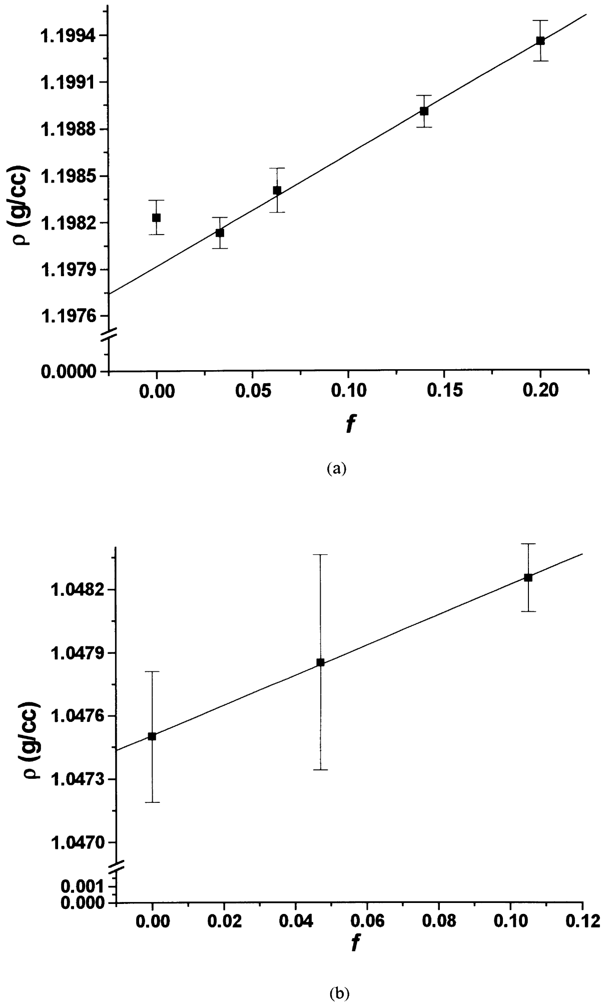


Figure 1 Methodology for shrinkage correction of creep curves



(a)

(b)

Figure 2 Room-temperature density for (a) PC and (b) PS *versus f*. The line fit through high-*f* PC data is solely to illustrate the linearly increasing trend. The high degree of scatter in the PS data can be attributed to brittle microcracking which occurred during sample preparation exhibited slight curvature which arose from warping during the quenching process. This curvature produces artificially high values for the compliance since any sample bend acts as a 'soft' spring. Remember that any attempt to straighten the sample by annealing at high temperature will alter the ageing/orientation state of the sample! This curvature also varied with stretch ratio due to differences in thickness which, in turn, altered the degree of warping during quenching. Curvature was much higher in the PC samples than in PS samples.

Tests were also performed on samples cut parallel to the TD direction in an attempt to measure directional differences in retardation behaviour. The PS samples showed excessive microcracking during the creep testing so the tests were discontinued. The PC samples did not crack but were instead plagued with a high degree of sample curvature due to 'bowing' of the stretched film. This curvature was so high as to affect the horizontal shifting behaviour, resulting in artifically high values for μ_h. A few samples having minimal curvature were tested and these data have been utilized to compare with the MD data.

RESULTS

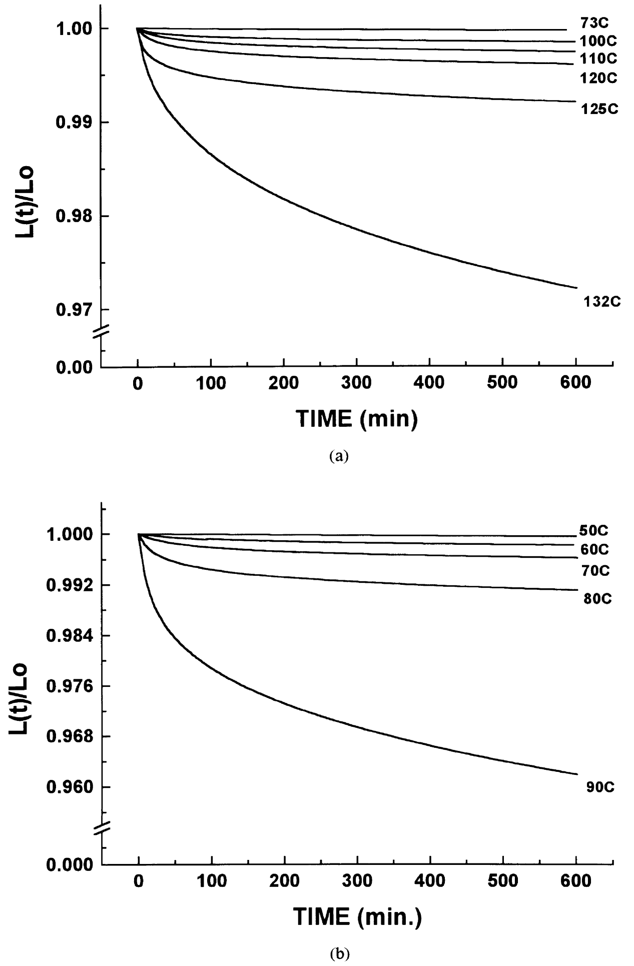
Density measurements

Room-temperature density data for the stretched polycarbonate samples are shown in *Figure 2a*. The density, ρ, is found to increase in approximately a linear manner with increasing f except at the lowest orientation functions where it decreases slightly. As discussed earlier, this density increase with orientation for polycarbonate has also been reported in the literature[22,27,28]. While ideally, stretching a rubbery system is considered to be an incompressable process (i.e. no volume change), it is clear that this belief breaks down for PC and PS at larger strains. The initial down-turn in PC density is believed to be the result of the expected Poisson-type dilatation as predicted from continuum mechanics. However, the increase in density at high f is *not* predicted by continuum mechanics and is possibly the result of better chain packing and the squeezing out of free volume with increased orientation. On the basis of conventional free volume theories, this increase in density with stretching should imply a reduction in molecular mobility; however, later data will show that effective mobility can actually be enhanced. This represents a serious breakdown of the free volume theory.

Density data for the polystyrene (*Figure 2b*) show the same decrease in free volume with f. The large error bars are believed to be due to brittle microcracking which occurred when the samples were punched out of the stretched film stock (this microcracking did not occur in the more ductile PC). While no measurements were made on low-f PS samples, it is suspected that it too would show the initial down-turn in density.

Shrinkage results

The shrinkage data as a function of annealing temperature are shown in *Figure 3* for both PC and PS. The data are plotted as $L(t)/L_0$ where L_0 is the initial stretched sample length. Shrinkage is a measure of molecular mobility in the oriented sample. Interestingly, the shrinkage is quite significant well below the T_g of the material. *Keep in mind, however, that the total shrinkage recovery is only of the order of 1%.* The onset of measureable shrinkage begins in the vicinity of 50°C for PS and 70 to 80°C for PC. These temperatures also correspond to secondary transition regions for both polymers. Above 70°C for PS and 100°C for PC, the shrinkage becomes so large as to make creep measurements nearly impossible. The shrinkage occuring during annealing will overwhelm the measurement of any creep strain occurring in the sample. It is likely that the main-chain motion of the glass transition is becoming more significant in this higher range of temperatures.



(a)

(b)

Figure 3 Isothermal shrinkage curves for (a) 2.5 × PC ($f = 0.16$) and (b) 4 × PS ($f = 0.10$)

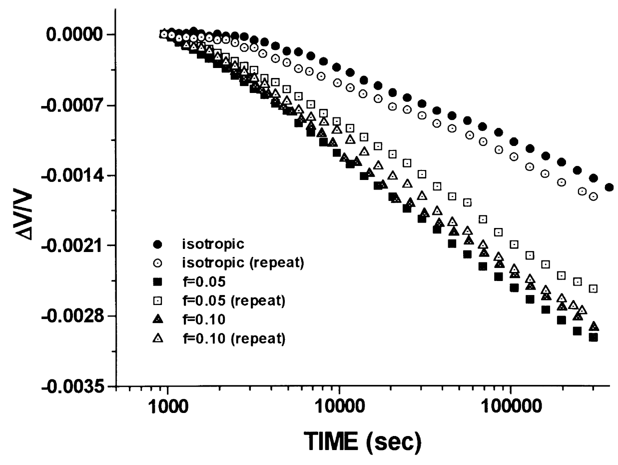


Figure 4 Isothermal volume relaxation data for PS at 60°C. Repeat runs are also shown to illustrate degree of variability in the measurements

Dilatometric results

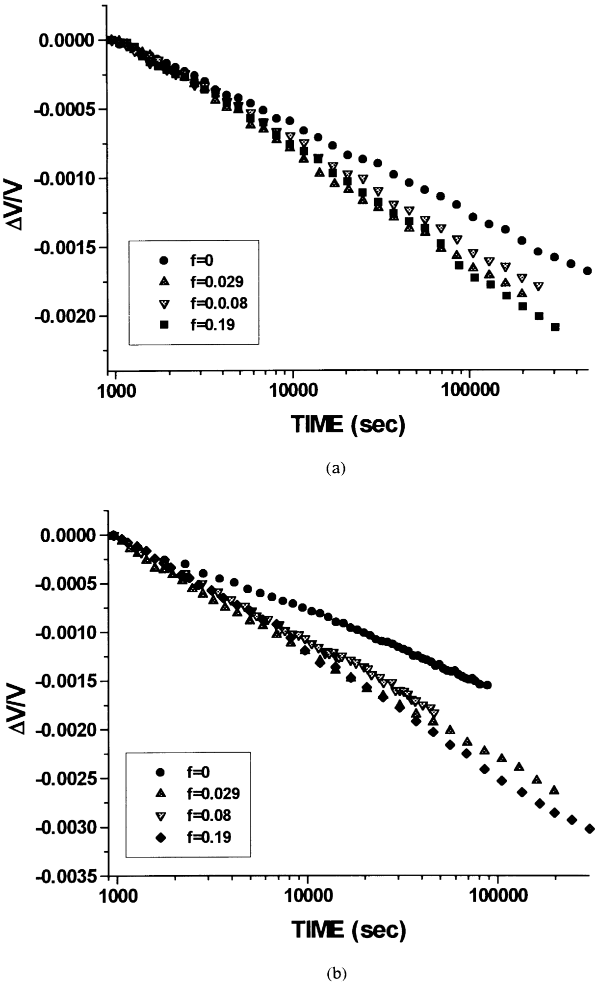
Sample volume relaxation curves for PS at 60°C are illustrated in *Figure 4*. Each curve represents a different value of orientation function *f*. Similar curves for PC at 90°C and 120°C are shown in *Figure 5a* and *Figure 5b*, respectively. Typical curves for the PC *T*-jump experiments, where the sample was first annealed for 300 000 s (5 days) at 90°C and then heated to 120°C for further ageing, are depicted in *Figure 6*. Time zero for this *T*-jump experiment was taken when the bath first reached 120°C (heat-up time was approximately 5 min). The data in *Figure 6* only illustrate the 120°C annealing portion of the experiment.

The data in the above figures are plotted as $\Delta V/V_0$ where V_0 is the initial volume at the start of the experiment and ΔV is simply $V(t) - V_0$. When plotted in this form on a log time scale, the slope of the curve becomes equal to the volume relaxation rate β defined as

$$\beta = \frac{1}{V(t)}\frac{\mathrm{d}V(t)}{\mathrm{d}\log(t_\mathrm{e})} \cong \frac{1}{V_0}\frac{\mathrm{d}V(t)}{\mathrm{d}\log(t_\mathrm{e})} = -\frac{\mathrm{d}(\Delta V/V_0)}{\mathrm{d}\log(t_\mathrm{e})} \quad (7)$$

The approximation results from the fact that $V(t) \gg \mathrm{d}V(t)$. The steeper the slope of the volume relaxation curves, the higher is the rate of volume relaxation. Inspection of *Figures 4–6* shows that the relaxation rate is approximately constant for long annealing times. Only for the PS samples at very short annealing times, and for the *T*-jump experiment in *Figure 6*, does one see time-dependent changes in β. Therefore the volume relaxation rates were obtained from the data at t_e of approximately 10^5 s. These values for β, plotted as a function of *f*, are shown in *Figure 7a* for PS and *Figure 7b* for PC. *Of obvious significance is the fact that the oriented samples as a whole relax at a faster rate than the unoriented samples.*

An additional biaxially oriented sample of polycarbonate stretched 1.5 × by 1.5 × (simultaneous stretch using same conditions as for the uniaxial samples) was dilatometrically tested at 120°C. The motivation was to see if there was a



(a)

(b)

Figure 5 Isothermal volume relaxation data for PC at (a) 90°C and (b) 120°C. Data scatter similiar to PS data in *Figure 4*

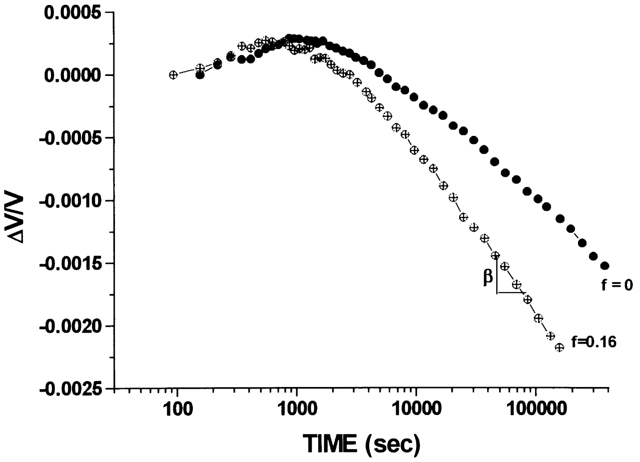
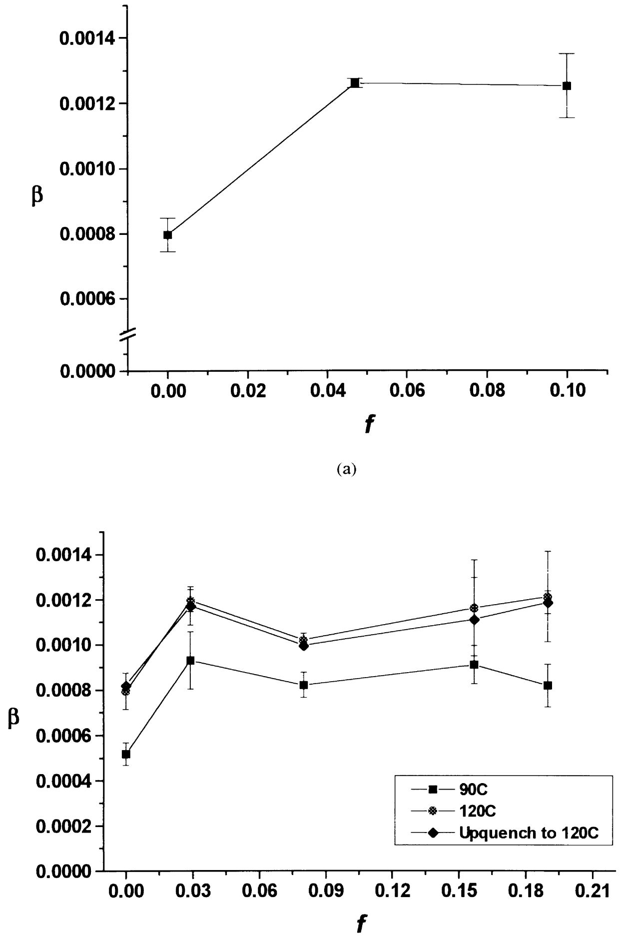


Figure 6 Temperature-jump data for PC annealed at 120°C after 5 days of conditioning at 90°C



(a)

(b)

Figure 7 Isothermal volume relaxation rates for (a) PS at 60°C and (b) PC at 90°C and 120°C as a function of Hermans' orientation function *f*

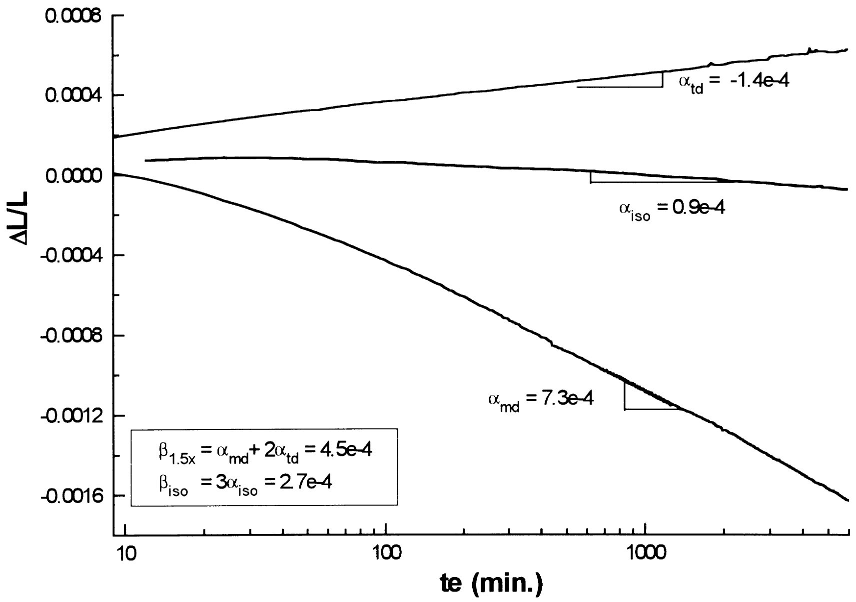


Figure 8 Linear relaxation rates for a 1.5 × PC sample tested separately at 90°C in the MD and TD directions. Isotropic control also tested for comparison. Calculated volume relaxation rates are shown in the inset and follow the same relative trend as the volume dilatometric data

significant difference between uniaxial and biaxial stretching. The resulting value for β was found to be 13.5×10^{-4} which is slightly higher than that of the uniaxial samples, although the difference is not statistically significant.

Linear dilatometry

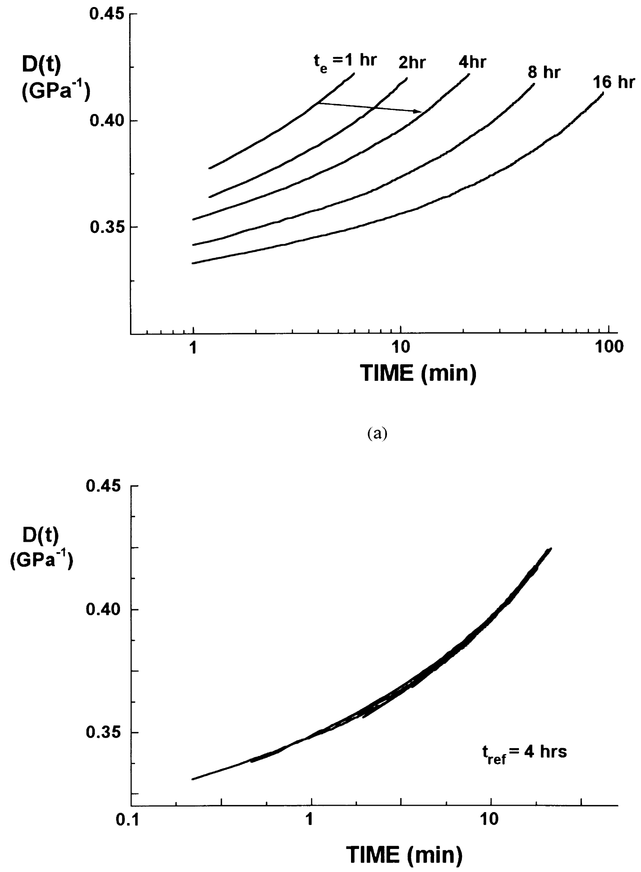
The linear relaxation curves for the 1.5 × PC sample aged at 90°C are shown in *Figure 8* along with an isotropic control. Values for α were obtained at times greater than 1000 min since thermal shrinkage was greatly reduced at this point, resulting in less curvature. What is of great importance is the fact that the volume relaxation occurs almost solely along the MD or stretch direction. In fact, the transverse direction actually expands slightly. This indicates that thermal shrinkage may play a role in the enhanced volume relaxation rates of the oriented samples. It is almost as if the oriented chains are being 'reeled in' during annealing while simultaneously being packed into an ever tighter structure. However, since changes in f and sample length were small, it is likely that this reorientation is only occurring on a very localized scale and is not due to long-range reptation[29].

It is also noted that the calculated values for β were slightly lower than those obtained from volume dilatometry. This is believed to be due to a combination of poorer temperature control and sample creep arising from the tensile stress. This creep would counteract some of the volume relaxation occurring during ageing, resulting in an artificially low value for β. *Nonetheless, the relative change in β between the isotropic and oriented samples is approximately the same for both the linear and volume dilatometric measurements.*

Results from tensile creep testing

For illustrative purposes, the entire time–ageing time superposition process will be shown for a single oriented PS sample. Following this, the horizontal shift factor curves for each polymer at varying values of f will be displayed. In order to compare the effects of orientation on the shape of the creep compliance curve, only the isochronal data at the 4 h reference time will be plotted together and the retardation behaviour compared.

Formation of a master curve. A sample set of creep curves for an oriented polystyrene sample (f = 0.105) is shown in *Figure 9a*. Both horizontal and vertical shifting were employed to obtain the master curve in *Figure 9b*. The



(a)

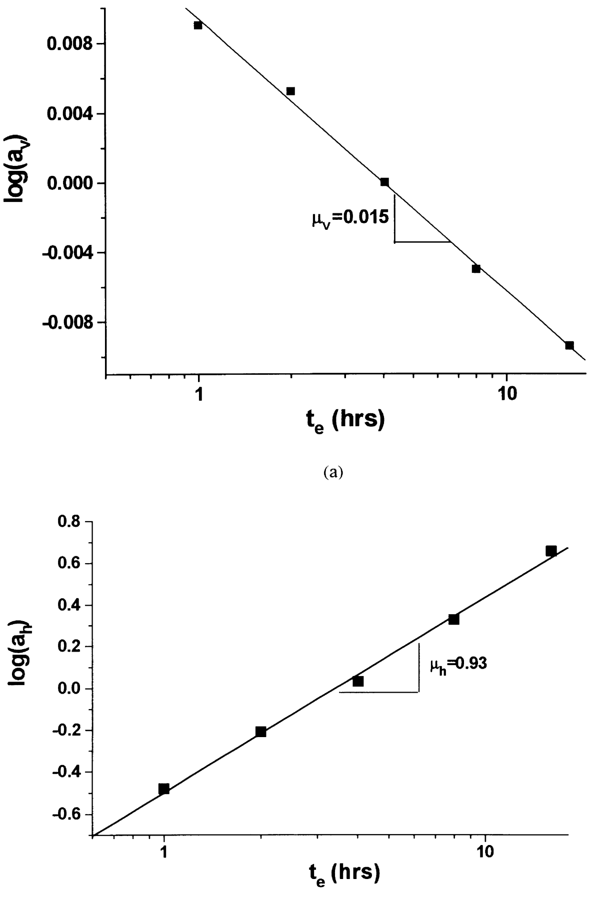
(b)

Figure 9 Sample creep data for an oriented PS (f = 0.10) at 60°C showing (a) the shrinkage-corrected creep curves and (b) the master curve obtained by horizontal and vertical shifting of each curve to a reference ageing time of 4 h refererence time for the shifting was 4 h. Notice that there were some 'imperfections' in the overlap which are believed to be a result of noise in the initial creep curves, error during shrinkage correction (particularly due to the assumption of a linear form for the slope correction), and error incurred during the horizontal and vertical shifting. That this is attributable to noise and shifting error is particularly true since the overlap error occurred randomly for different samples and different orientation functions. For cases where the overlap error is large and cannot be attributed to shifting error, then one must be careful in the interpretation since thermorheological simplicity no longer applies. Fortunately, this latter scenario was not a problem in this study. Finally, the vertical and horizontal shift factors are plotted as a function of ageing time in *Figure 10*. From these plots, μ_v and μ_h can be determined from the slopes of the curves.

Shift rate data for PC and PS. The resulting horizontal shift factors as a function of ageing time for different values of *f* are shown in *Figure 11* for both polymers. The slopes represent the horizontal shift factors which are seen to decrease slightly with increasing orientation. The horizontal shift factors, μ_h, for PS, as determined from *Figure 11b*, are plotted in *Figure 12a* as a function of *f*. Similar values for the PC samples are shown in *Figure 12b*. The vertical shifting rates for PC did not change significantly with *f* and had a value of 0.010 ± 0.004. This is in reasonably good agreement with the value of 0.008 obtained by O'Connell and McKenna under similar test conditions[30]. Nevertheless, it is noted that the whole concept of vertical shifting is still controversial. Work by Bradshaw and Brinson[31] indicates that horizontal shifting alone is best for most polymers (and under most test conditions), although they note that a few polymers still require vertical shifting for good fitting. In this study, attempts at using only horizontal shifting consistently resulted in poor master curves for PC so vertical shifting was always included. For PS, the values for μ_v were more erratic with some of the curves requiring no vertical shifting and some having shift rates of up to 0.02. It is uncertain why this variability exists although sample curvature may have been partly responsible.

For both polymers, μ_v was not found to be a function of orientation within the accuracy of the measurements so only the horizontal shift rate data will be interpreted. With that in mind, the data in *Figure 12* imply that the ageing rates *from a mechanical standpoint* decrease upon stretching the sample, but do not vary with *f*. This step change in μ_h upon stretching is similar to what was seen with the volume relaxation rate β, except that the mobility trend is in the opposite direction. The trend in μ_h is also in qualitative agreement with predictions based on the free volume theory.

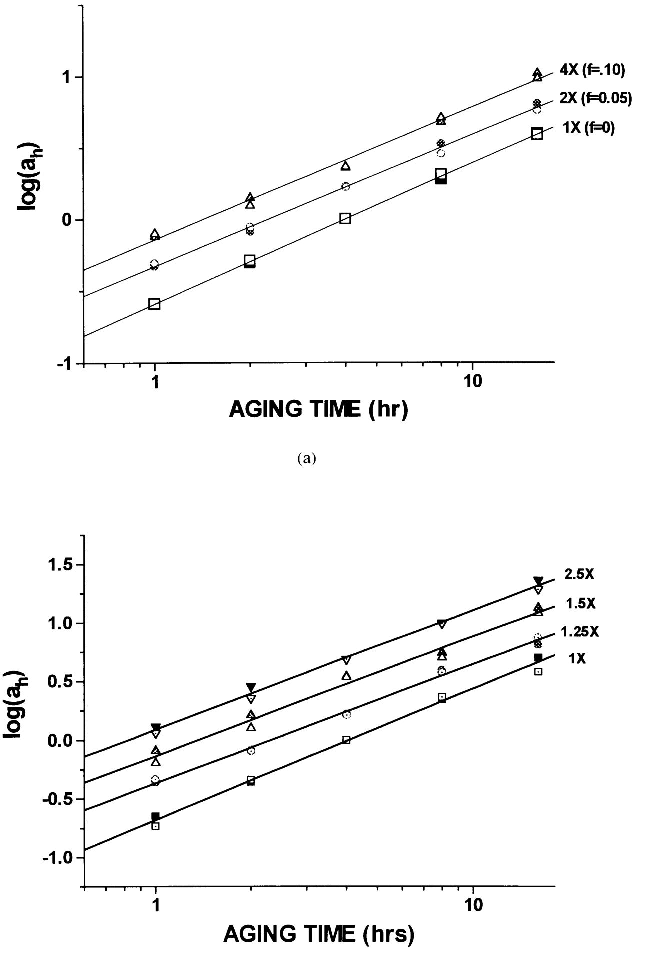
Comparison of iso-ageing time compliance curves. Compliance curves for PS and PC at an iso-ageing time, t_e, equal to 4 h and varying values of *f* are compiled in *Figure 13a* and *Figure 13b*, respectively. Each of these



(a)

(b)

Figure 10 Vertical (a) and horizontal (b) shifting data for the oriented PS sample in *Figure 13*



(a)

(b)

Figure 11 Horizontal shift factors for (a) PS at 60°C and (b) PC at 90°C. Vertical scale corresponds to 1 × samples only. Other curves have been offset for clarity

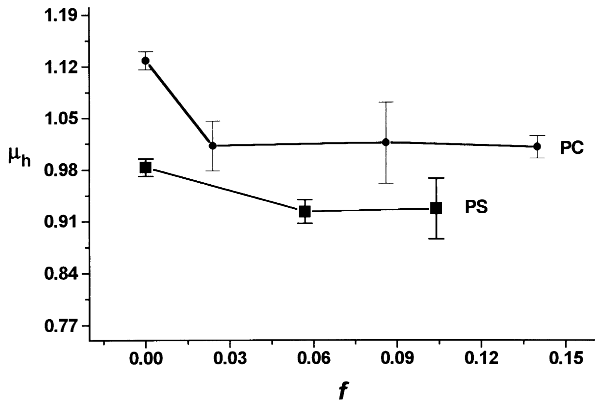
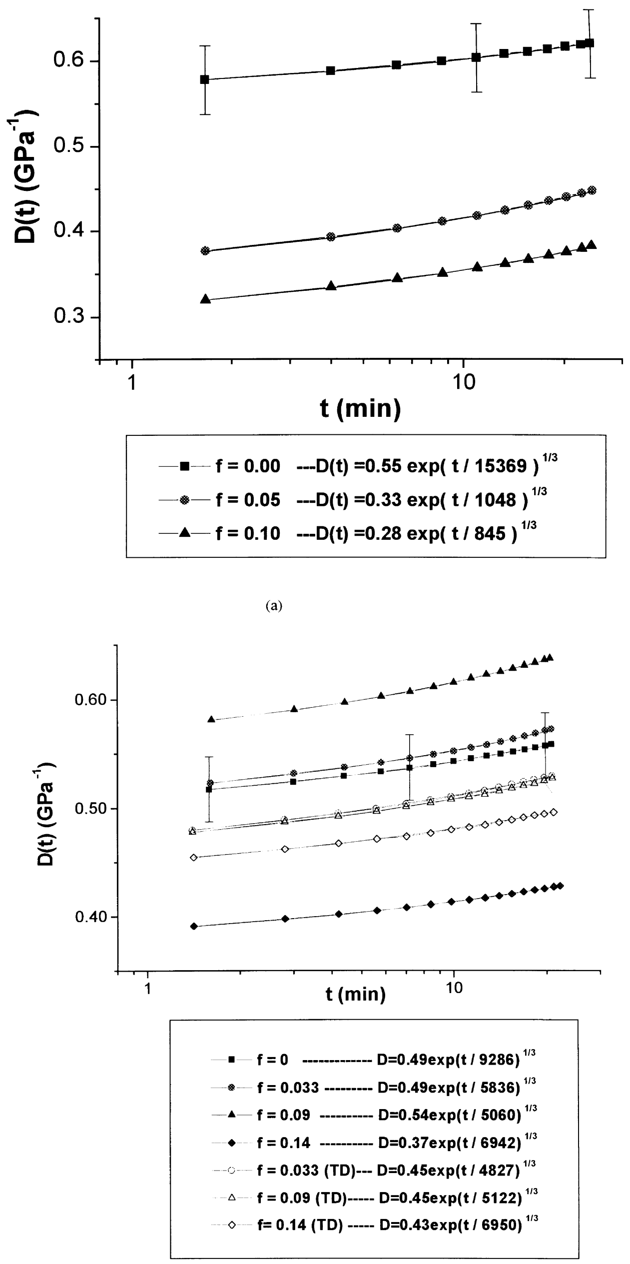


Figure 12 Mechanical shift rates as a function of f for (a) PS at 60°C and (b) PC at 90°C



(a)

(b)

Figure 13 Compliance curves after 4 h for (a) PS at 60°C and (b) PC at 90°C. Stretched exponential fits are shown below the curves. Error bars are representative of all of the samples

curves—for a given value of f—is the average of two or three separate runs. Notice that there is a slight difference in retardation behaviour for the oriented and isotropic PS samples. The oriented samples, in addition to having a lower initial compliance, also increase in compliance at a faster rate (i.e. greater upward curvature). For the PC, this curvature is not as pronounced although still present. Also, the drop in compliance does not become significant until the highest value of f. It is uncertain whether this trend is real or the result of the compliance errors described in the Experimental section. It does, in some ways, mimic the trend in density data where the density initially decreases then increases with f. Regardless, the PC compliance appears to be much less sensitive to orientation effects than PS even though PC is more highly oriented (based on changes in f).

The compliance curves in *Figure 13* were fit to Struik's creep equation[1]

$$D(t) = D_0 \exp(t/\tau)^{\gamma} \qquad (8)$$

where D_0 is the instantaneous compliance, τ is the retardation time, and γ is the 'stretching' exponent, so named because of the way it alters the effective retardation spectrum. All of the curves were fit to this equation while initially allowing D_0, τ and γ to vary. Because of the equation's inherent non-linearity, the goodness-of-fit is less sensitive to slight changes in γ, although these changes bring about even larger changes in τ. To minimize this variability, the curves were then refit while keeping γ fixed at a value of 0.33. This value was obtained by averaging over the previous fitting results, and turned out to be the same for both PC and PS. Even with the constrained γ, excellent agreement between the experimental and fitted curves was obtained with R^2 (i.e. goodness-of -fit) values typically being in excess of 0.99. These equations for the fitted curves are tabulated in the legends of *Figure 13*. Values for τ obtained from the curve fitting are displayed as a function of f in *Figure 14*.

Inspection of *Figure 14* shows that the effective retardation time decreases upon stretching but then plateaus with further orientation. This is the same trend seen earlier with the β and μ data. The PC sample exhibits a smaller drop in τ relative to the PS and even appears to have a slight upturn at the higher stretch ratios. Surprisingly, the MD and TD retardation times for PC are almost identical functions of f. Thus, the only difference between the two material directions, based on the curve fitting, appears to be in the instantaneous compliance.

The step drop in τ with stretching implies an enhanced mobility in the oriented samples in agreement with the dilatometry data presented earlier. Interestingly, however, the trend in mobility is in the opposite direction of the creep μ data, even though the two results were extracted from the same set of measurements. That the mechanical and volumetric data follow different trends is not a new concept. Simon and co-workers[32] found that the enthalpy and creep time scales were the same for polyetherimide during down-jumps, yet volume relaxation occurred at a faster rate. McKenna and co-workers[33,34], performing both up- and down-jumps with epoxy glasses, found that time to

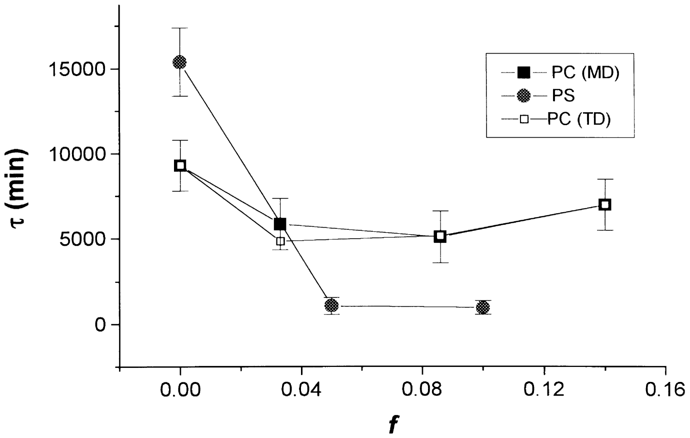


Figure 14 Creep compliance retardation time τ plotted as a function of f for both PC at 90°C and PS at 60°C after 4 h of ageing. The stretching exponent γ is constrained to be 0.33 for both polymers

equilibrium was faster for volume relaxation in the up-jumps, but slower in the down-jumps, relative to mechanical relaxation rates. While this is opposite to the trend seen by Simon, it is possible that these differences are due to the nature of the polymers tested.

DISCUSSION

The increase in density at high f (*Figure 2*) implies that the mean free volume decreases with stretching for both polymers. While for PC one notes a slight increase in free volume at low f, it is speculated that this transitional behaviour is due to competing effects. At low stretch ratios, the deformation follows conventional continuum mechanics and, initially, expansion occurs due to the Poisson effect. As extension is increased, however, the chains begin to pack better and the resulting densification begins to dominate.

If one assumes that the free volume theory is applicable, then the mobility and physical ageing rate are expected to decrease with orientation (at high f) due to the increasing density. Inspection of the dilatometric data, however, clearly proves otherwise. Consequently, the free volume theory, in its current form, seems to be of little use in predicting the changes occurring in these oriented samples. This is not surprising since free volume theories are generally found to be inadequate for predicting physical ageing. Nevertheless, their conceptual simplicity and ease of use make them ideal for comparative purposes.

It is interesting that the dilatometric data show a 50% increase in volume relaxation rate with orientation, and that almost all of this contraction occurs in the stretch direction. It is peculiar, however, that once oriented, the value for β changes very little with further stretching (i.e. a step change followed by a plateau). This is true even for the biaxially oriented sample. It is as if the process of orientation itself, and not the degree of orientation (at least in the range studied here), is responsible for the higher relaxation rates. *It is again important for the reader to realize that the oriented samples are undergoing higher rates of volume relaxation even though they have less free volume initially.* This in many ways resembles the findings of Colucci and co-workers[35] for sub-yield compression/tensile testing of PC. They found that the volume relaxation rate increased with increasing strain regardless of the mode of deformation. This was true even for compression, where hydrostatic pressure caused a decrease in the nominal free volume. Similarly, for large tensile strains, the resulting increase in volume relaxation rate would overwhelm any free volume increase due to Poisson expansion resulting in a net decrease in free volume. This phenomenon has been given the name ‘implosion’.

Another interesting dilatometric trend exists in the case of PS and relates to the presence of an ‘induction time’ as seen in *Figure 4*. The lag time before significant volume relaxation is longer in the unoriented sample (*ca.* 4000 s as opposed to 1000 s for the oriented sample), indicating that stretching somehow accelerates the initiation of the relaxation process. In effect, orientation causes a decrease in the net relaxation time of the system. Although this lag time is not visible in the polycarbonate data, it may have occurred at much shorter times before thermal equilibrium was established.

The tests on oriented samples also resemble in many ways the stress-induced rejuvenation/acceleration experiments in the literature[1,36–38]. Although the exact mechanism is controversial, it has been found that sufficiently high stresses applied to an aged sample will increase the effective mobility. This increase is believed to be caused by the stress either erasing the physical ageing through free volume formation (i.e. rejuvenation), or by actually increasing the effective ageing rate without changing the current ageing state (i.e. acceleration). The step increase in volume relaxation rate for the oriented samples is in agreement with the enhanced mobility although the applied stress level was obviously well past the yield point. Considering that the free volume decreased in the oriented samples upon stretching, and that the samples were unaged initially (they were stretched above T_g), our data seem to better support the concept of ‘acceleration’.

Contrary to the dilatometric results, the mechanical creep data show a *decrease* in physical ageing rate with increasing f based on the horizontal shift behaviour alone. The shift rate μ_h undergoes a slight drop upon stretching and then changes little with further increases in f. While opposite in direction, this is similar to the ‘step-plateau’ trend seen with the volume relaxation data. As was discussed earlier, this difference may not be unreasonable in light of the findings by Simon *et al.*[32] and McKenna *et al.*[33] that volume and creep occur over different time scales. Clearly, the molecular structure may impact the volumetric and mechanical relaxation responses differently.

It is uncertain why the creep data are in disagreement with Struik's data for rigid PVC[1]. One possibility is the potential formation of strain-induced crystallinity in the PVC. Another is the fact that the scatter in Struik's data is higher than shown here. This is not surprising considering the corrections required to account for shrinkage. A large number of tests were performed in the present study in order to reduce the error bars sufficiently for accurate comparison.

This decrease in horizontal shift rate indicates that the retardation spectrum for an isotropic sample shifts to longer times at a faster rate than for an oriented sample. This implies that an isotropic sample should lose ductility more quickly than an oriented sample, everything else being equal. Nevertheless, it says nothing about how the orientation alters the initial retardation spectrum. To gain this information, one must look at the retardation times in *Figure 14*. Here it is seen that orientation causes a significant drop in the retardation time and, as with the μ_h and volume relaxation data, the values do not change significantly upon further stretching. So, in addition to the oriented relaxation spectra showing a lower shift rate, they also start with a much shorter effective retardation time.

Next, it remains to try and determine the cause for the unusual step-plateau relaxation behaviour with stretching. It may be possible that stretching actually raises the polymer chains to an activated state (which might be independent of f over the range studied). But what produces this activated state? It might be a result of internal stresses brought about by stretching—the internal stresses due either to distortion of the van der Waals' bonds (glassy distortional stresses), or entropic stresses brought about by orientation. In this study, the former should be small in magnitude or absent since the material was hot-drawn. The presence of entropic stresses in the glassy state is still controversial. The whole concept behind rubber elasticity and entropic stresses hinges on the idea that the chains are rapidly rearranging and deviations from the most probable distribution cause the stress. If a chain is then frozen in place, as with a glass, there is no basis for the force to exist. Struik[15] argues that glassy polymers *do* exhibit entropic stresses because motion is never completely frozen. That is, the thermal motions of the glassy segments are still large enough to produce the entropic stresses. This theory is also supported by the sub-T_g shrinkage in *Figure 3* and the fact that almost all of the volume relaxation occurs in the stretch direction (*Figure 8*). It is doubtful that this shrinkage was caused by glassy distortional stresses since these should have relaxed considerably immediately after hot drawing (but prior to the sample being quenched into the glass).

It is also possible that the activated energy state is a result of the net change in the intermolecular force fields (e.g. the Lennard–Jones potential) brought about by the molecular rearrangement and flow. The density is changing with f so interatomic distances must also be changing, even if only slightly. In addition, the changes in interatomic distance are not the same in the MD and the TD, with the TD distances being slightly smaller on average. This was recently confirmed by Jean and co-workers from this laboratory by means of positron annihilation and two-dimensional angular correlation (2D-ACAR) measurements on similarly stretched polycarbonate samples[39]. They observed that the shape of the free volume sites became more elliptical with stretching. This is also in agreement with Lunn and Yannas' infra-red study of PC where the nominal 2971 cm^{-1} absorption peak shifted to a greater extent for parallel *versus* perpendicular polarization in oriented samples.

Assuming that an activated state is responsible, how does it produce the changes in volumetric and mechanical behaviour? If we consider bond rotation and molecular rearrangement, in general, to involve an activation energy barrier, then the effect of the activated energy state will be to lower that barrier. In the case of volume relaxation, lower barriers will result in more rapid segmental rearrangement so denser chain packing is more easily facilitated. This increase in the rate of segmental rearrangement will also reduce the creep retardation time (*Figure 14*). The decrease in μ_h is more difficult to explain, assuming the decrease is significant. It is tentatively hypothesized that the activated state of the oriented chains somehow offsets the shifting of the retardation spectra to longer times. In other words, the relaxation mechanism for the oriented polymer chains is less affected by the changes brought about by ageing (i.e. decreased free volume, increased cooperative motions, etc.). This insensitivity to ageing of the oriented samples is apparent in the volume sensitivity data shown in *Figure 15* for both PS and PC, where S drops significantly for the oriented samples. Referring back to equation (4), the change in mobility for a given change in free volume is lower in the oriented samples. It may be that only a portion of the retardation spectrum is affected but the net effect is still an apparent reduction in the shifting rate.

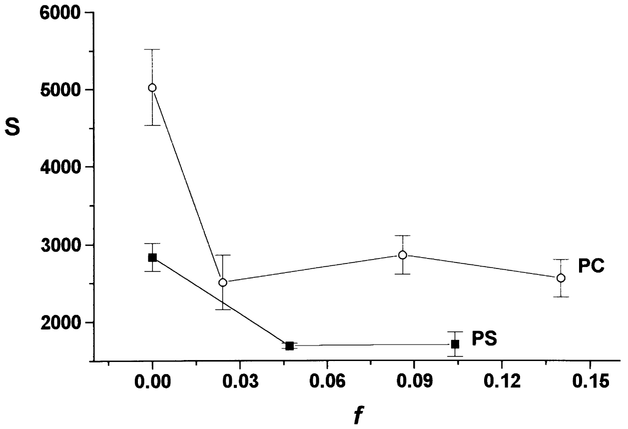


Figure 15 Volume sensitivity data as a function of f for PC aged at 90°C and PS aged at 60°C

SUMMARY

It has been shown that orientation has an effect on physical ageing, although the magnitude of this effect varies with the measurement method. Dilatometric data show an increase in ageing rate in oriented samples with length contraction occurring only along the stretch direction. This is in agreement with previous dilatometric studies of cold-drawn PC although the latter show a larger ageing rate enhancement upon stretching[8,9].

Creep/mechanical shift rates, on the other hand, show a slight decrease with drawing. In both cases, however, it is not the magnitude of the orientation function that matters, only the fact that the polymer has been stretched. Further analysis of the creep compliance data shows that the effective retardation time decreases significantly with stretching. This implies that the chain segments are able to reorganize more quickly in the oriented samples, which may explain the faster volume relaxation rates. The volume sensitivity, S, also decreases with f so the stretched samples are less sensitive to free volume relaxation than their unoriented counterpart.

It is speculated that the unusual orientation–ageing behaviour observed in this study is a result of the strain-induced formation of an activated energy state—this state being independent of the degree of molecular orientation for the range studied. The mechanism for the formation of the activated energy state is uncertain although a few possibilities have been suggested. These include internal (entropic) stresses, anisotropy in the net intermolecular force field, and free volume redistribution.

Future papers will be aimed at characterizing the local molecular structure and relaxation behaviour and will help to determine which, if any, of these mechanisms is best at describing the unusual ageing phenomena. These studies will also address such issues as the localized free volume determined from positron annihilation measurements and the effect of orientation on both the dynamic mechanical relaxation strength and the solid-state nuclear magnetic resonance spin relaxation time.

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