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Positron Annihilation Lifetime Studies of Free Volume Changes in Polycarbonate under Static Tensile Deformation

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ABSTRACT: Positron annihilation lifetime spectroscopy was used to investigate strain-induced free volume changes in well-aged Bisphenol A polycarbonate. From our previous studies, it appears that the orthopositronium (o-Ps) lifetime, τ_3, yields an estimate of the mean volume, $\langle v_f \rangle$, of o-Ps trapping sites ("holes"), whereas the intensity of the o-Ps decay component, I_3, is proportional to the number density N of holes. Thus the product $I_3\langle v_f \rangle$ is a measure of the fractional free volume, h. A miniature load cell was constructed which enables in situ positron annihilation measurements on polymer samples under well-specified tensile strains. We find that, for well-aged polycarbonate, h increases with strain up to a level of 4%, after which no further change in h occurs. This behavior is consistent with literature observations of strain-enhanced rejuvenation of the mechanical properties of polycarbonate. Upon long-term room-temperature annealing of a polycarbonate specimen held at 3% strain, we find that h gradually decreases to levels below the initial value, suggesting a strain-induced reactivation of physical aging, and hence a closer approach to the equilibrium density.

1. Introduction

A variety of experimental studies[1-11] indicate that positron annihilation lifetime measurements can be used to probe structural disorder (free volume) in amorphous polymers. Most of these investigations have involved observations of changes in orthopositronium (o-Ps) lifetimes, τ_3, and intensities, I_3, which correlate with known changes in free volume, e.g., at the glass transition temperature, T_g,[1-8] or during isothermal annealing in the glassy state below T_g.[7-10] Much remains to be learned, however, about the quantitative aspects. For example, in poly(vinyl acetate) (PVAc), provided we operate at temperatures $T > T_g$, we find[9] an excellent numerical correlation between the Simha–Somcynsky free volume parameter, h, and the product $I_3\langle v_f \rangle$ where $\langle v_f \rangle$ is the average volume of o-Ps trapping sites ("holes"), computed from τ_3. Below T_g, quantitative interpretation of the positron data is rendered more difficult because of the sensitivity to variations in thermal history.[7-11]

Here, we report applications of positron analysis to probe free volume changes in polycarbonate under applied tensile stress. A previous study[8,10] of o-Ps intensities and lifetimes in polycarbonate has appeared. These authors[8,10] found a change in the temperature dependence of τ_3 and I_3 near the β-transition temperature, T_β. The latter is a temperature at which a pronounced sub-T_g relaxation process has been observed in mechanical and dielectric[12,13] properties. This temperature also represents a demarcation between brittle ($T < T_\beta$) and ductile ($T > T_\beta$) response of polycarbonate to large strain deformations.[12,13] It has been noted[12,13] that the observation of a mechanical relaxation process at T_β is highly dependent on thermal history, being much weaker in annealed samples. Hill et al. also investigated[8,10] changes in the positron lifetime parameters on isothermal annealing in the glass. They report decreases in I_3 on annealing, while τ_3 remains fairly constant. This phenomenon has also been observed in other laboratories during physical aging of polystyrene[7,11] and poly(vinyl acetate).[9] An unusual feature of the thermal history used in the study of Hill et al.[8,10] is that thermal conditioning of these samples was performed at 80 °C, i.e., at a temperature substantially below the glass transition temperature (T_g = 150 °C). However, we have carried out[14] positron annihilation studies of polycarbonate under strain-free conditions, using prior thermal conditioning at $T > T_g$, and obtained results similar to the observations of Hill et al.[8,10]

In this paper, we describe an experimental effort designed to investigate the utility of positron annihilation measurements for investigating free volume changes in polymers subjected to large strains. Previous mechanical studies have established[15,16] that the segmental mobility increases; i.e., the viscoelastic relaxation times decrease in polymers subjected to large strains. This observation has been interpreted to indicate[13,14] that large strains increase the free volume and hence reverse or retard the physical aging process ("rejuvenation"). Subsequently, experiments show that physical aging resumes, and there is a progressive decrease in segmental mobility in the deformed material.[15,16] This point of view is controversial however, and it has been suggested,[17] alternatively, that the structure of glassy materials may remain unaltered at large strains and that the apparent change in aging rate is at least partly due to the nonlinear viscoelastic response of the material. Clearly, it is of interest to investigate the structural disorder in polymer glasses subjected to mechanical deformation. We have constructed a small loadframe to permit positron annihilation lifetime experiments in situ on polymer specimens subjected to well-specified tensile strains. We report changes in o-Ps parameters I_3 and τ_3 on polycarbonate samples at incremental tensile strains ranging to 7%, as well as changes during physical aging of a specimen held at a constant 3% strain.

2. Experimental Section

2.1. Positron Lifetime Spectrometer. The positron annihilation lifetime spectroscopy system consists of a vacuum chamber, BaF_2 and CsF detectors, and a fast–fast coincidence detection system, based on EG&G ORTEC NIM modules. Data were collected on a PCA multichannel analyzer (Tennelec). A uniform sample temperature is maintained by a temperature controller (Model 805, Lake Shore Cryogenics) using two diode sensors, which monitor the temperature at two different surface areas and control fluctuations in temperature during data

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acquisition to within ±0.04 °C. To optimize the time resolution function and the detecting efficiency of the system, a cylindrical cesium–fluoride crystal (1.5 × 1.5 in.) was used as a scintillator to detect the 1.27-MeV γ-ray which functions as the positron "birth" signal and a conical barium–fluoride crystal (0.8 × 1 × 1 in.) to detect the 0.511 MeV γ-ray which serves as the "death" signal. The windows of the constant fraction differential discriminators, which select the energy ranges of the γ-rays, were set using a sodium-22 positron source with a polycarbonate sample. For a 15-μCi ^{22}Na positron source, the count rate was about 300 cps. The source, ^{22}NaCl, was deposited on a thin aluminum foil (1.7 mg/cm^2) within an area of diameter 2.5 mm. The foil was then folded into a 7-mm square shape and sandwiched between two rectangular pieces (1 × 1.3 × 0.4 cm) of the polycarbonate sample. The time resolution function in each experiment was determined in the process of computer fitting of the data and was compared with independent measurements using the prompt γ-rays of ^{60}Co. For ^{60}Co the full width at half-maximum (fwhm) was consistently less than 230 ps. Time calibration was done by several methods. One, based on the random coincidence rate, showed that the channel width of the multichannel analyzer was 10.3 ps. To test this result, we observed the γ-rays from the decay of ^{207}Bi, finding a mean lifetime of 182 ± 5 ps for the 570-keV level of ^{207}Pb, in agreement with the published lifetime of 186 ps.

2.2. Data Analysis of Positron Lifetime Spectra. Each spectrum was fitted to a sum of four exponentially decaying functions convoluted with the resolution function, by means of the program[18] PATFIT-88. The resolution function is approximated as the sum of three Gaussian functions whose statistical weights and full widths at half-maximum are determined by the fitting program to be those that give the best data fit. After the resolution function has been determined for one lifetime spectrum with a given source-sample assembly, the function is assumed to be the same for all subsequent lifetime spectra as long as the assembly remains in place. The resolution function consistently had an fwhm of about 230 ps, equal to that found from the ^{60}Co source. When a new sample is introduced, the resolution function is again found from the fitting procedure; minor changes in the tail of the function are sometimes found, probably because of a change in scattering from one detector to the other when the geometry changes slightly. After the resolution function is found from analysis of the initial run on a sample, the parameters to be determined in each subsequent analysis are the position t_0 for the starting point of each exponential decay and the four intensities (I_s, I_1, I_2, and I_3) and four decay constants (reciprocals of the mean lifetimes τ_s, τ_1, τ_2, and τ_3) for the exponential functions. The source component (I_s, τ_s) results from positrons that are annihilated before they reach the sample;[21] almost all of these stop in the aluminum foil covering the source. From the known foil thickness we calculate that in our experiments about 7% of the positrons were annihilated in the foil. The positron lifetime in aluminum is known to be τ_s = 180 ps; hence, the values of I_s and τ_s can be fixed in the curve-fitting procedure.

The program PATFIT-88 determines the remaining seven parameters, after subtracting the known source component.[18] The starting time t_0, the three mean lifetimes, and two intensities are varied; the third intensity is then determined by requiring the sum of the intensities to be equal to 100%. During physical aging experiments, the two shortest lifetimes show variations that appear to be random; therefore, these two lifetimes are held at their mean values in a subsequent reanalysis of all of the curves, in order to minimize the effects of random fluctuations on the values of τ_3 and I_3. Theoretically, the shortest lifetime component (I_1, τ_1) results from annihilation of parapositronium (p-Ps), whose mean lifetime is known to be approximately 125 ps, while the intermediate component (I_2, τ_2) arises from annihilation of free positrons with lifetime τ_2 = 400 ps. However, the intensity of p-Ps must be proportional to that of o-Ps, and we find that it is not possible to obtain a good fit by keeping τ_1 fixed at 125 ps and using a reasonable intensity for this component ($I_1 = 0.33I_3$). Therefore we allow τ_1 to vary, assuming that this component is the unresolved sum of p-Ps and another positron state in the polymer.

2.3. Construction of Load Cell. Several initial experiments were carried out, in which prestressed polycarbonate specimens were subjected to positron lifetime measurements, and were largely inconclusive. This led to the decision to construct a small load-frame to enable in situ positron measurements of polymer samples under well-specified strains. This device utilizes a strain transducer consisting of a resistance wire connected to a linear variable differential transformer by means of which the voltage measured across the wire is made proportional to the incremental strain. We have applied this device to carry out positron measurements on polycarbonate under different applied strains.

2.4. Sample Preparation. The Bisphenol A polycarbonate specimens used in this investigation were commercial specimens obtained from Bayer AG Co., Leverkusen, Germany, and Bayer-Mobay, Pittsburgh, PA. GPC analysis of the polymer yielded number- and weight-average molecular weights, M_n = 18 340 and M_w = 43 606. The glass transition temperatures were determined in each case to be 150 °C by differential scanning calorimeter (DSC) at a heating rate of 20 °C/min. The polycarbonate sample on which high-temperature studies were performed changes color when the sample temperature is taken higher than 165 °C, presumably due to chemical degradation, and hence experiments were confined to thermal histories below this temperature. Note that, since the aim of this investigation is to characterize changes of free volume in the polymer glass, an appropriate reference state must be defined, e.g., by controlling the prior thermal or mechanical histories. In the experiments reported here, where we investigate the effect of strain on the as-received and therefore well-aged polycarbonate, we use the initial unstrained specimen as the reference state.

2.5. Calculation of Fractional Free Volume. From the o-Ps intensity, I_3, and lifetime, τ_3, we determine the fractional free volume, h, as the product $h/c = I_3\langle v_f\rangle$, where the average hole volume, $\langle v_f\rangle = 4/3\pi R^3$. R is obtained from τ_3, using an equation developed by Nakanishi et al.,[19] based on a model of Tao[20]

$$\tau_3^{-1} = 2\ (\text{ns}^{-1})[1 - [R/R_0 + 0.159[\sin(2\pi R/R_0)]] \qquad (1)$$

where R is the hole radius and $\Delta R = R - R_0$ is the hole surface electron layer. By measuring o-Ps lifetimes in materials of known hole sizes, e.g., zeolites, it has been determined[19] that ΔR = 0.1656 nm. In our previous study of poly(vinyl acetate)[9] we demonstrated that $I_3\langle v_f\rangle$ is proportional to the fractional free volume, by comparing the temperature variation of the positron free volume h/c with that of the Simha–Somcynsky free volume fraction for poly(vinyl acetate) calculated from P–V–T data.[9] The coefficient c is determined by matching theory and experiment at the glass transition temperature, T_g = 150 °C.

3. Results and Discussion

3.1. Positron Annihilation in the Absence of External Strains. First, we note that I_3 and τ_3 were determined on strain-free polycarbonate as a function of temperature and during annealing in the glassy state. These observations, reported elsewhere,[14] are, within experimental errors, consistent with the published data of Hill et al.,[8,10] despite minor differences in the thermal history. An increase of the temperature in the glass results in an increase in both I_3 and τ_3.[8,10,14] During isothermal annealing following a quench from higher temperatures, τ_3 remains constant while, during the initial annealing period, I_3 decreases monotonically with annealing time.[8,10,14] The initial rate of decrease of I_3 is larger at lower annealing temperatures. All of these phenomena are similar to those described in our similar studies of poly(vinyl acetate)[9] and are qualitatively consistent with our above interpretation of I_3 and τ_3 in terms of relative changes in the matrix free volume. We also note that the positron annihilation lifetime spectrum of the as-received polycarbonate remains constant within experimental error over a period of several days, indicating no evidence of physical or chemical aging.

Thus, in the following sections, where we are dealing with observations of changes in o-Ps annihilation in polycarbonate glasses under isothermal conditions at temperatures well below T_g, we will assume that we can interpret these results in terms of relative variations in free volume.

3.2. Strain Dependence of Free Volume in Polycarbonate. Positron annihilation spectra were determined on the as-received polycarbonate specimen at T = 25 °C subjected to increasing tensile strains up to 7%. The results are shown in Figure 1. As shown in parts a and b of Figure 1 applications of strains up to a level of around 4% produces an increase in τ_3, and hence in $\langle v_f \rangle$, but little change in I_3, i.e., in N. Above 4% strain, no further variation in $\langle v_f \rangle$ or in N is apparent. The corresponding free volume fraction h, which, of course, parallels the behavior of $\langle v_f \rangle$, is exhibited in Figure 1c. It is pertinent to remark that the stress–strain curve for our polycarbonate specimen shows typical macroscopic yield behavior at 6% strain.[14]

Several studies of the material properties of polycarbonate show distinctive modifications in the preyielding regime. First, measurements of the bulk volume[22] are reported to show an increase with tensile strain, ϵ, up to 3.5%, at which point the volume begins to level off and decreases with further strain. The initial volume increase is numerically consistent with that anticipated since the Poisson ratio, υ, of polycarbonate, is smaller than 0.5:

$$\Delta V/V_0 = (1 - 2\upsilon)\epsilon \qquad (2)$$

For Bisphenol A polycarbonate, υ = 0.385. We point out here that the relative increase in the fractional free volume with strain, measured by the o-Ps annihilation spectrum, i.e., $\Delta h/h_0$, is substantially larger than the fractional increase in bulk volume, $\Delta V/V_0$, as shown in Figure 2. Thus the increase in the free volume is larger than that produced by an affine expansion of the holes.

Second, a study[16] of the so-called strain-induced rejuvenation or reversal of the physical aging process in the mechanical properties of polycarbonate found characteristic changes when the applied strain reaches 4%. Specifically, the storage and loss tensile moduli, E' and E'' were measured at 10 Hz on well-aged polycarbonate during stress relaxation at static tensile strains from 1.2 to 6.5% at 50 °C. It was observed that E' and $1/E''$ decrease when the static strain is applied and then increase monotonically with time. This behavior was attributed to an initial increase in segmental mobility with applied strain, followed by physical aging. The magnitude of these changes increases uniformly with the applied strain until it becomes 4% and then levels off. Clearly, such an observation suggests that the free volume increases with strain up to 4% and then becomes constant and hence is quite consistent with our positron results.

3.3. Physical Aging in Polycarbonate under Applied Strain. We have carried out a positron annihilation lifetime study of free volume changes in a well-annealed polycarbonate specimen subjected to a static tensile strain of 3.0% at 25 °C. The positron spectrum was recorded at intervals of 3 h during stress relaxation and physical aging following the application of the strain for a total period of 200 h and again periodically every 3 h during further physical aging following release of the load until a total of 340 h had elapsed. In parts a–c of Figure 3, we show respectively the variation of I_3, τ_3, and the fractional free volume h during this experiment. The horizontal line indicates the initial values of the unstrained specimen. Application of strain causes an initial increase of τ_3, and hence $\langle v_f \rangle$, while I_3, and hence N, remains constant within experimental error. During the physical aging process which accompanies stress relaxation, the fractional free

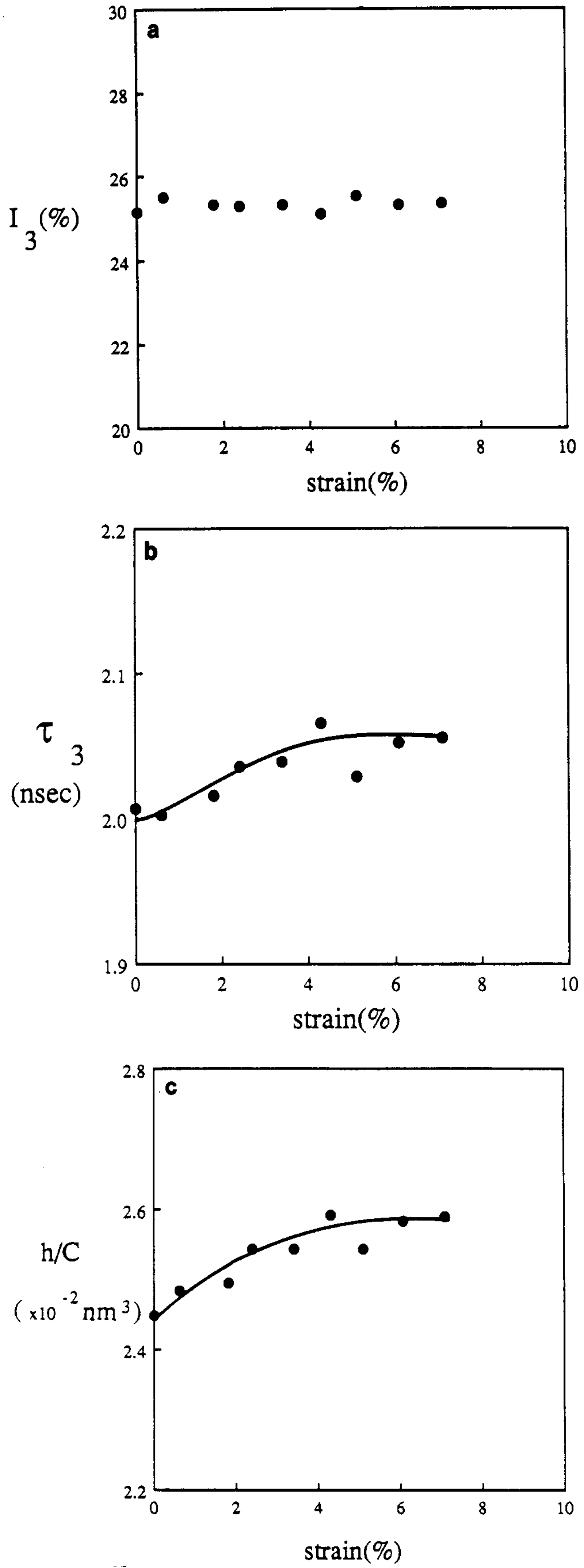

Figure 1. Positron lifetime parameters of polycarbonate as a function of sequential incremental tensile strain: (a) o-Ps intensity, I_3; (b) o-Ps lifetime, τ_3; (c) free volume $h/c = I_3\langle v_f \rangle$. Lines drawn for orientation purposes only.

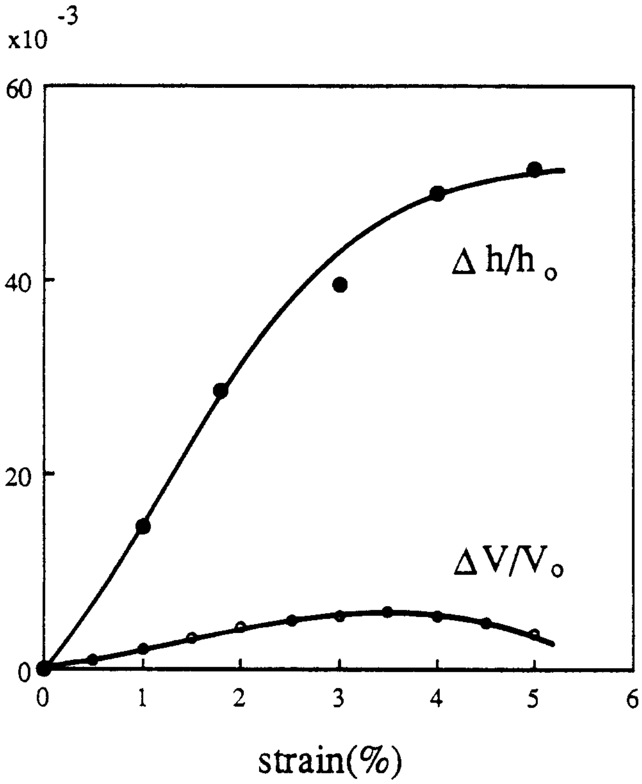

Figure 2. Incremental increase in o-Ps fractional free volume, $\Delta h/h_0$, as a function of applied strain compared to the fractional increase in bulk volume, $\Delta V/V_0$, from ref 25.

volume h decreases, due to decreases in both $\langle v_f \rangle$ and N. Upon release of strain, a further decrease of h occurs throughout the duration of the experiment until, after 340 h, h is smaller than the initial value. Evidently, the application of strain to this well-annealed polycarbonate specimen has reactivated the aging process. The mechanism by which the fractional free volume decreases to levels below those of a well-annealed polycarbonate is unclear. It is interesting to note, however, that Legrand et al.[23] have reported a decrease in the bulk volume of a polycarbonate specimen subjected to a very similar aging history at 3% strain and subsequent strain recovery. The implication of these observations is that prolonged tensile strain permits a loss of free volume through a progressive reorientation and more efficient packing of chains. In this regard, it is relevant to remark that in cold-drawn polycarbonate, both the density[24] and the density fluctuations[25] increase. Also, despite the densification, the free volume shows an enhanced rate of relaxation. It was inferred that cold drawing results in an increase in the free volume fraction. It has also been suggested[24] that the densification reported[22] at strains above 3.5%, but below the yield point in polycarbonate, may be due to local chain orientation.

4. Conclusions

Our positron annihilation lifetime measurements on strain-free polycarbonate are numerically in good agreement with the previous study of Hill et al.[8,10] We find that the apparent free volume level of polycarbonate increases on application of static tensile strains up to 4%, after which it levels off. This is consistent with observed enhancement of the aging rate of the mechanical properties in the presence of large strains. Finally, the o-Ps spectrum of polycarbonate subjected to long-term aging at 3% strain, followed by further aging during strain recovery indicates a negative change in free volume which is consistent with

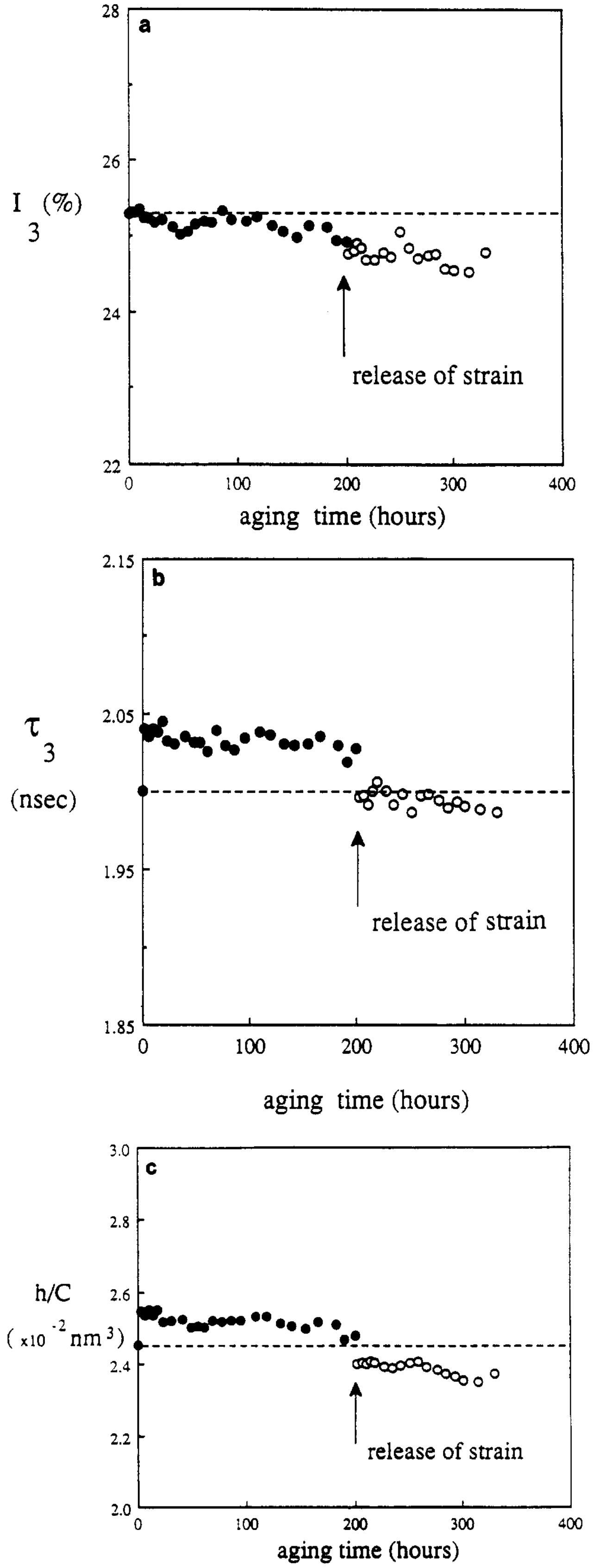

Figure 3. Time evolution of positron lifetime parameters of polycarbonate during isothermal physical aging at 24 °C and 3% applied tensile strain: (a) o-Ps intensity, I_3; (b) o-Ps lifetime, τ_3; (c) free volume parameter $h/c = I_3\langle v_f \rangle$. Closed circles represent data taken under the applied strain; open circles are values after the release of strain; the horizontal broken line indicates that initial values of the various quantities prior to the application of strain.

literature observations of a negative increment in bulk volume of specimens subjected to a similar mechanical history.

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