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The evolution of microstructure of polystyrene following pressure relaxation: a positron study

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Positron annihilation lifetime spectra on polystyrene (PS) have been measured as a function of pressure relaxation time ($t = 0$–100 h) under the initial uniaxial pressure $P = 0, 25$ and 50 MPa, respectively. In order to extract the information on the variations in the microstructure and free-volume hole as a function of pressure relaxation time t, we first considered the inhibition of *ortho*-positromium (o-Ps) formation by positron-irradiation induced free-radicals; second we evaluated the quantity $\Delta I_3(t)$, i.e. the difference in the o-Ps formation probability between $P = 25$ (or 50) and 0 MPa. We observed that $\Delta I_3(t)$ dramatically increases with t up to a characteristic time (≈ 5 and 12 h for $P = 25$ and 50 MPa, respectively) and then tends to a constant level. This result is explained by the evolution of microstructure and free-volume holes in PS during pressure relaxation. Copyright © 1996 Elsevier Science Ltd.

(Keywords: positronium formation probability; free-volume hole; pressure relaxation)

INTRODUCTION

Polymers are widely utilized as engineering materials with various mechanical properties. It is of interest to investigate the mechanical response of polymers when subjected to various loading[1]. Usually polymers show a strong time- or temperature-dependent behaviour under deformation (including compression and extension). Moreover, the deformed and aged polymers usually exhibit some differences in time-dependent mechanical and thermal properties as compared with the non-deformed ones[2–4]. Therefore, detecting the change of microstructure *versus* the elapsed time for the deformed polymers is an important factor for understanding the time-dependent macroscopic properties.

As a sensitive probe of atom-scale free-volume holes of polymers, positron annihilation lifetime spectroscopy (PALS) has been used to monitor the evolution of microstructure in various physical processes, such as physical aging, deformation and tensile stress relaxation[5–7]. This technique involves using a positron source (e.g. ^{22}Na) to emit positrons into the sample. After a positron enters into a polymer, most of its energy is transferred to the host, and then is thermalized within a few picoseconds and may form a positronium (Ps) atom with an electron of macromolecules. There are two kinds of Ps atoms. The *para*-positronium (p-Ps), in which the spins of positron and the electron are anti-parallel (χ_{00} state), has a lifetime of 0.125 ns by self-annihilation in vacuum; while the *ortho*-positronium (o-Ps, χ_{1M} states, where $M = 1, 0, -1$) has a longer lifetime of

142 ns in vacuum[8,9]. In polymers, the o-Ps lifetime is shortened to 1–5 ns, and due to that, it is localized in a region of lower electron density, i.e. the free-volume hole[8,9], where it undergoes a pick-off annihilation with an electron of surrounding molecules[8,9]. There is a semi-quantitative relation between the o-Ps lifetime and the average free-volume size[8,10]. On the other hand, the o-Ps intensity (or the o-Ps formation probability) gives information on both the chemical environment where the o-Ps is formed and the concentration of free-volume holes[5–9,11]. In spite of recent observation of the effect of positron irradiation on the o-Ps formation probability[12–14], in this work we will compare the measured o-Ps intensities $I_3(t)$ in the as-received sample and the compressed one and subtract the positron irradiation effect from the $I_3(t)$ in the compressed sample. So the evolution of free-volume holes in the pressure relaxation process can be extracted from PALS measurements.

The relaxation behaviour of compressed polymers at the post-yielding stage is one example of viscoelastic properties[3]. Generally, a glassy polymer in a non-equilibrium state will gradually approach an equilibrium or more precisely, a quasi-equilibrium state. It is proposed that the relaxation behaviour is correlated with the local conformational rearrangements of molecular segments or the dynamics of free-volume holes[2]. Conventionally, the dilatometry or the mechanical tests are used as a measure of the structural state of glassy polymer[3]. However, direct evidence of microstructure changes during the relaxation of compressed polymers is lacking. In this paper we will present the results of PALS measurements on the uniaxially compressed polystyrene (PS), and discuss the microstructural and free-volume hole changes along the pressure relaxation of PS.

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EXPERIMENTAL

In this study we used a commercial grade of PS which has been aged for over 2 years at room temperature after moulding. The as-received board was cut into discs with a thickness of 4.24 mm and a diameter of 11.30 mm. The specimens were compressed under an uniaxial and apparent pressure of $P = 25$ and 50 MPa, respectively, using a mechanical compressor. The residual deformation was measured to be $\epsilon = 34\%$ and 50% for $P = 25$ and 50 MPa, respectively. About 15 min later the pressure was removed, and a positron source was immediately sandwiched between the two identical specimens and PALS measurement began as a function of elapsed time. The positron source was ^{22}Na with an activity of about 20 μCi, deposited in an area of about 10 mm^2 and sealed on two Al foils (1.4 mg cm^{-2}). For the sake of comparison, we also measured the positron annihilation lifetime spectra of the as-received sample (i.e. at $P = 0$) as a function of source exposure time at room temperature.

The PALS measurements were performed using a fast–fast spectrometer[8] with a time resolution of 270 ps. A positron lifetime spectrometer can measure the time interval between the two incidents of positron emission from the source and its annihilation in materials. Two detectors were used to monitor the start signal (a 1.28 MeV γ-ray characterizing the emission of positron from source) and the stop signal (a 0.511 MeV γ-ray characterizing the positron annihilation in materials). In a fast–fast coincident system, each time pick-off unit is a constant fraction differential discriminator (CFDD), which can generate the time information and determine the energy ranges of start and stop γ-signals simultaneously[15]. A sketch of the fast–fast coincident spectrometer is presented in ref. 8.

In this work the lifetime spectrum was collected at 1–2 h intervals at the beginning of relaxation (i.e. $t < 10$ h) at room temperature and at 10–16 h intervals at the longer relaxation time (i.e. $t > 10$ h). The time intervals of PALS measurement at different initial pressure conditions were identical for the purpose of comparison. Each spectrum contained approximately 10^6 counts, was measured twice and the results have good repeatability.

RESULTS AND DISCUSSION

The lifetime spectra were resolved into three components using the PATFIT program[16] with a source and background correction as previously described[6,7]. After we fixed the first component $\tau_1 = 125$ ps in order to reduce the error bars of positron parameters, the variances of fits (χ^2) were smaller than 1.2. The two short components, $\tau_1 = 125$ ps and $\tau_2 \approx 400$ ps were assigned to *para*-positronium (p-Ps) atoms and 'free' positron annihilation. The longest component ($\tau_3 \approx 2.0$ ns, $I_3 = 30$–36%) is attributed to the o-Ps pick-off annihilation and correlated with the free-volume holes of amorphous regions[8]. The variations of o-Ps intensity in PS as functions of the initial pressure and the elapsed time are shown in *Figure 1*. In contrast the o-Ps lifetime appears constant (≈ 2.0 ns), independent of the elapsed time and the initial pressure.

Positron irradiation effect

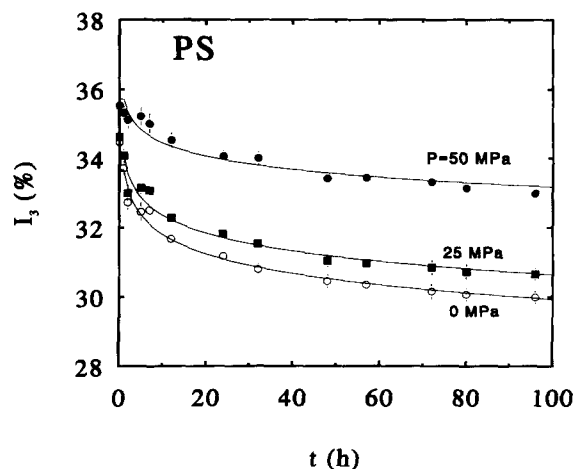Before we investigate the change in free-volume

Figure 1 The variation of o-Ps intensity I_3 in the compressed (■,●) and as-received (○) PS samples vs the relaxation time. The solid lines are drawn to guide the eyes

properties in PS during the pressure process, it is necessary to discern the irradiation effect of positrons on the microstructure of polymers from the pure free-volume relaxation effect. As shown in *Figure 1*, the o-Ps intensity I_3 in the as-received sample ($P = 0$) decreases with source exposure time and approaches a saturation level at $t \approx 80$ h. This fact cannot be simply attributed to the structural relaxation, since the tested sample has been aged for over 2 years. A similar phenomenon has also been found in some glassy polymers such as polycarbonate (PC, the glass transition temperature $T_g \approx 355$ K), and polytetrafluorethylene (PTFE, $T_g \approx 388$ K) and even in some polymers at a rubber state such as polyethylene (PE, $T_g \approx 240$ K) and polypropylene (PP, $T_g \approx 285$ K)[12–14]. It has been also found that the decrease of I_3 is strongly dependent on the positron source activity[12,13]. This observation may be explained by the positron irradiation induced chemical modifications[17–19]. In fact, after positrons with an initial average energy of about 200 keV enter into polymers, they lose most of their energy by collision with the molecules. In addition, the energy of a part of the resultant 1.28 and 0.511 MeV γ-rays will be absorbed by the sample. The lost energy of positron and γ-rays leads to the production of the positively-charged free radicals[18], which can reduce the Ps formation for the following reasons: (i) the free radicals have a positive electron affinity, which can absorb the residual electrons in the positron spur and the Ps formation is therefore inhibited[11,20]; (ii) the Ps-molecular[8] or Ps-free radical species may be formed. On the other hand, free radicals in the amorphous regions of polymers can decay by recombination with the non-saturated bond or by the gas evolution[18]. In glassy polymers, the lifetime of free radicals may become extremely long and is essentially determined by the temperature, i.e. the polymer temperature is further below its T_g, the longer the lifetime τ of the free-radicals[18]. Therefore, we can establish a rate equation for the free-radical number $n(t)$ vs the elapsed time in the sample by considering the competition between the creation and decay mechanisms of free-radicals, i.e.

$$\frac{\mathrm{d}n(t)}{\mathrm{d}t} = \frac{AE}{\epsilon} - \frac{n(t)}{\tau} \tag{1}$$

and the initial condition is

$$n(0) = 0 \qquad (2)$$

where A is the activity of positron radiation source, E is the energy transferred to the sample from one positron and the corresponding γ-rays, and ϵ is the formation energy of one free-radical. On combining equation (1) with (2)

$$n(t) = \frac{AE\tau}{\epsilon}\left[1 - \exp\left(\frac{-t}{\tau}\right)\right] \qquad (3)$$

From equation (3), we see that when $t < \tau$, the number $n(t)$ of free-radicals increases with t, which results in the decrease of the o-Ps formation probability with the elapsed time. At $t \approx \tau$, the $n(t)$ tends to a saturation level, i.e. $n_s = AE\tau/\epsilon$. In our case, $A \approx 8 \times 10^5\,\mathrm{s}^{-1}$, $\tau \sim 2 \times 10^5\,\mathrm{s}$, $E \sim 300\,\mathrm{keV}$ and $\epsilon \sim 10\,\mathrm{eV}$[18] and the volume of sample irradiated by the positron source is about $0.1\,\mathrm{cm}^3$, so we estimate the number density of free-radicals is of the order of $10^{17}\,\mathrm{cm}^{-3}$. From the viewpoint of Ps or electron capture cross-section[21], the free-radicals with a number density of about $10^{17}\,\mathrm{cm}^{-3}$ can effectively reduce the Ps formation probability. Moreover, if one uses a positron source with a larger activity, the saturation level n_s of the free-radical number will become larger and the saturated level of o-Ps intensity will be diminished. This indication has been confirmed by the PALS measurement for the glassy PS[14].

For a polymer in the rubbery state, the micro-Brownian motion of the segments is more active than the glassy state, which will increase the rate of recombination of free-radicals and the unsaturated bonds with temperature, so the lifetime τ and the number density of free-radicals will dramatically decrease with temperature[17,18]. The number density of free-radicals is probably too low to effect the Ps formation if the sample temperature is higher than the T_g. However, a decrease of o-Ps intensity I_3 was also observed with the elapsed time for PP and PE in the rubbery state[12,14]. This fact may be explained by the irradiation-induced cross-linking and degradation of polymers[17,22]. At the initial stage, due to the irradiation of positrons and γ-rays, the unsaturated bonds can combine together to form the cross-linking which may suppress the Ps formation[17,19]. As time goes on, the main-chain scission in the polymers due to irradiation becomes more dominant and is equalized by the cross-linking effect, therefore the o-Ps intensity I_3 tends to a saturation level. However, the increase of the saturation level of I_3 with the testing temperature for PP and PE[12,14] above T_g mainly arises from the creation of free-volume holes[23].

The accumulation of PALS data for a series of polymers[12–14,17,19] suggests to us that (i) the o-Ps intensity in a glassy polymer is correlated with both the number of free-radicals and free-volume holes; (ii) for a rubbery polymer, the saturation value of I_3 at longer measurement time may reflect the microstructural state and the level of hole concentration[13].

The evolution of free-volume concentration

As mentioned above, the o-Ps intensity $I_3(P, t)$ for the glassy polymer PS contains information about both the free-radicals and the free-volume holes, but what we are most interested in is the variation of free-
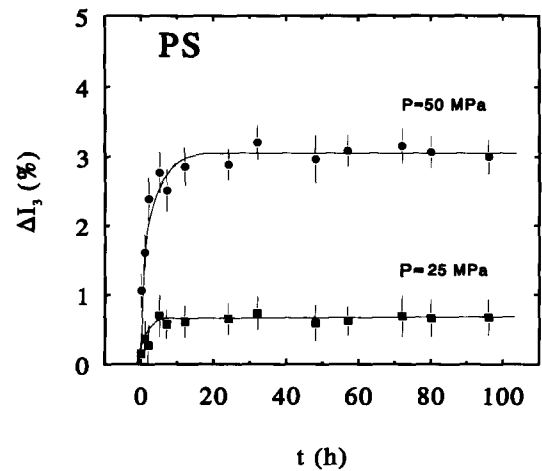

Figure 2 The variation of $\Delta I_3(t)$ vs the pressure relaxation time. The solid lines are drawn to guide the eyes

volume hole concentration during pressure relaxation. In order to extract the variation of hole concentration with the relaxation time and eliminate the positron irradiation effect on the o-Ps intensity, we calculated and plotted the difference of o-Ps intensity between the compressed and as-received samples in *Figure 2*, i.e. $\Delta I_3(t) = I_3(P, t) - I_3(P = 0, t)$ for $P = 25$ and $50\,\mathrm{MPa}$, which is expected to represent the change in the hole concentration with t.

In *Figures 1* and *2*, we observe that the o-Ps intensity at $t = 0$ in the compressed samples at $P = 25$ or $50\,\mathrm{MPa}$ is higher than that in the as-received sample, implying the creation of new free-volume holes in the sample subjected to the compressive stress. At $P = 25$ or $50\,\mathrm{MPa}$, since the residual deformation is higher than the yielding point $\epsilon\,(\approx 5\%)$[24], some segments will undergo plastic deformation for the reason that the local stress may exceed the critical value for shearing[1,4]. So some shear microbands are formed[25], in which some new holes are created to allow the plastic flowing of segments[6]. It should be mentioned here that our observation is very different to that of Wang *et al.*[26], i.e. the decrease of o-Ps intensity in an epoxy resin with increasing static pressure. For the piston-and-cylinder apparatus in ref. 26, the decreases in the size and concentration of holes can be induced by static pressure. But in our experiment, the sample undergoes an uniaxial compression which is expected to result in the formation of localized shear microbands and the creation of new holes in PS[1,25].

The information on the microstructure changes following the pressure relaxation can be inferred from the quantity ΔI_3 in *Figure 2*. At the initial pressure $P = 25\,\mathrm{MPa}$, $\Delta I_3(t)$ increases with the relaxation time t and tends to a constant level at $t \approx 5\,\mathrm{h}$, demonstrating that some new holes are created up to $t \approx 5\,\mathrm{h}$ and then the microstructure approaches a quasi-equilibrium state. At the shorter relaxation time ($t < 5\,\mathrm{h}$), the internal stress is not uniformly distributed and some segments are rearranged to suit the non-uniformed internal stress, therefore the number of free-volume holes becomes larger to accommodate the segmental rearrangement. With the elapse of time, the residual stress distribution gradually becomes uniform, the sample tends to the equilibrium state and no new holes are expected to be

created. On the one hand, $\Delta I_3(t)$ at $P = 50$ MPa reaches a constant level up to $t \approx 12$ h, which is longer than $t \approx 5$ h at $P = 25$ MPa. This fact probably results from the fact that the number of shear microbands formed under 50 MPa is more than that under 25 MPa, and the departure from the quasi-equilibrium state at the short relaxation time under 50 MPa is more obvious than at 25 MPa.

Some other interesting facts are suggested from *Figures 1* and *2*. First, after the removal of external pressure ($P = 25$ or 50 MPa), we still observed hole creation with relaxation time. Since the residual deformation ϵ at $P = 25$ or 50 MPa is larger than the yielding deformation ϵ_y, we reach the conclusion that the hole creation process following the pressure relaxation is microscopically irreversible[1,6]. Second, the constant level of $\Delta I_3(t)$ under $P = 25$ MPa is 0.7%, which is smaller than the constant level of 3.0% under $P = 50$ MPa. This observation indicates that the quasi-equilibrium state of the compressed sample under $P = 25$ MPa is not the same as that under $P = 50$ MPa. Third, based on *Figure 2*, the fractional free-volume[7] will increase with the relaxation time following the pressure relaxation, which is very different from the constancy of fractional free-volume during the tensile stress relaxation[7]. In comparison with the tensile stress relaxation, the shear microband in the pressure relaxation is probably easier to form under large deformation, so we can see the obvious increase in the fractional free-volume in PS sample following pressure relaxation.

CONCLUSIONS

We have carried out PALS measurement on polystyrene under pressure relaxation at initial pressures of $P = 25$ and 50 MPa. After considering the positron irradiation effect on the o-Ps intensity, we obtained information on the creation of new free-volume holes with relaxation time up to a characteristic time of $t \approx 5$ h for $P = 25$ MPa and $t \approx 12$ h for $P = 50$ MPa. This result is interpreted by the formation of shear microbands and segmental rearrangement. The present work demonstrates that PALS is a sensitive means to monitor the evolution of the microstructure of glassy polymers during pressure relaxation.

ACKNOWLEDGEMENTS

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