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## Changes in the microstructure of polyvinyl chloride polymer during the process of stress relaxation probed by positron annihilation

C L Wang<sup>††</sup> and S J Wang<sup>‡</sup>

<sup>†</sup> China Centre of Advanced Science and Technology (World Laboratory), PO Box 8730, Beijing 100080, People's Republic of China

<sup>‡</sup> Department of Physics, Wuhan University, Wuhan 430072, People's Republic of China<sup>§</sup>

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**Abstract.** Positron lifetime measurements were performed on poly(vinyl chloride) (PVC) polymer as a function of stress relaxation time ( $t = 0-120$  h). According to the variations in the ortho-positronium (o-Ps) lifetime  $\tau_3$  and intensity  $I_3$ , the relaxation process can be divided into three periods. In the first period ( $t \approx 0-30$  h), the decrease in  $\tau_3$  and the increase in  $I_3$  indicate the segmental orientation and the creation of free-volume holes in the amorphous regions. In the second period ( $t \approx 30-90$  h), the changes in the o-Ps parameters imply the coalescence of holes. Above  $t = 90$  h, both  $I_3$  and  $\tau_3$  reach constant levels, which suggests that the structure of PVC approaches the equilibrium state. These results show that the positron annihilation lifetime is sensitive to the microstructure changes of glassy polymers during the process of stress relaxation.

### 1. Introduction

Investigation of the microstructure of polymers is important for a better understanding of their complicated physical properties [1]. For glassy polymers, the microstructural state can be characterized by the concentration and the average size of free-volume holes [2]. It has been experimentally shown that the free-volume properties, which indicate the segmental motion and local packing density, are directly relevant to some important physical properties of polymers, such as glass transition [3], pressure response [3], physical aging [4] and deformation [5, 6]. As is well known, the positronium (Ps) 'atom' is preferentially localized and annihilated in the free-volume holes of the amorphous region, so positron annihilation spectroscopy (PAS) is able to detect sensitively the properties of atomic-scale free-volume holes in polymers [3].

The relaxation behaviour of polymers is an interesting topic in polymer science. A glassy polymer in a non-equilibrium state will spontaneously approach an equilibrium state. The relaxation behaviour is determined by the structure [7] and is a result of the local conformational rearrangements of molecular segments or of the dynamics of free-volume holes [8]. Conventionally, mechanical experiments are used as a measure of the structural state of glassy polymer. For example, a stress relaxation experiment on glassy poly(vinyl chloride) (PVC) at a small strain shows that, when the relaxation time  $t$  initially increases to 30 h, the stress undergoes an obvious reduction, and then it decreases slowly until it reaches a lower level within the limited time of observation [9]. This behaviour is also

<sup>§</sup> Correspondence address.

confirmed by the measurement of the creep compliance as a function of the creep time [10]. On the other hand, the PAS method was recently used to investigate microstructure changes as a function of the annealing temperature or of the isothermal relaxation time [3, 7, 11]. As for the effect of stress on the physical aging (or volume recovery), some workers have proposed that a large stress does not affect the structure and that the observed effects are due to viscoelastic memory [12]. The object of the present work is to determine whether and how the structure has been affected during the mechanical relaxation processes. In this paper, we report the results of positron lifetime measurements on well-aged PVC glass stretched at a small strain as a function of relaxation time, and we discuss the changes in the structure and in the free-volume properties.

## 2. Experiment

The dumbbell-shaped specimens with a thickness of 2.0 mm and a width of 15 mm were cut from a piece of PVC plate (density =  $1.45 \text{ g cm}^{-3}$ ) which had been aged for several years at room temperature after moulding. The crystallinity of the specimen as deduced from the density is estimated to be 48%. The average molecular weight of the PVC is 44 500, and the glass transition temperature  $T_g$  is 360 K. A mechanical stretching device was used to elongate the specimens and then to fix them at the residual deformation  $\epsilon = 8\%$  at room temperature, as described elsewhere [6]. For the glassy polymer PVC, the stress-strain curve at room temperature shows that its yield point is near  $\epsilon_y = 10\%$  [13]. The specimens in this study were stretched to  $\epsilon = 8\% < \epsilon_y$ , in order to avoid neck formation or chain slippage [1, 6, 13]. After the specimens had been stretched, then the positron lifetime was measured *in situ*.

A  $20\mu\text{Ci } ^{22}\text{Na}$  positron source sealed on Ni foil ( $1.7 \text{ mg cm}^{-2}$ ) was placed between the two specimens. Positron lifetime *in-situ* measurements were performed using a fast-coincidence system having a time resolution of 240 ps. Total counts of  $(1.2\text{--}1.5) \times 10^6$  for each spectrum were collected within around 60 min at room temperature. The lifetime spectra were analysed using the PATFIT program [14] with a source correction, as previously described [6].

## 3. Results and discussion

Positron lifetimes in the stretched PVC were measured in the as-received PVC sample and the stretched sample as functions of the relaxation time in the range 0–120 h. Each spectrum of PVC was best fitted with three lifetime components, and the variances ( $\chi^2$ ) of the fits were smaller than 1.2. The longest component ( $\tau_3 = 1.78\text{--}1.88 \text{ ns}$ ;  $I_3 = 6\text{--}7\%$ ) is attributed to ortho-positronium (o-Ps) pick-off annihilation in the free-volume holes of amorphous regions [3]. The second component ( $\tau_2 = 0.37 \pm 0.01 \text{ ns}$ ;  $I_2 \simeq 63\%$ ) is assigned to the annihilation of positrons [15]. For the first component ( $\tau_1 = 0.14\text{--}0.17 \text{ ns}$ ;  $I_1 \simeq 30\%$ ), because  $I_1:I_3 > 1:3$ , the statistical population ratio of para-positronium (p-Ps) to o-Ps atoms, it is not only from the p-Ps annihilation. Since the resolution of the spectrometer is 240 ps, the intrinsic p-Ps lifetime of 125 ps is not expected to be well separated from the short-lifetime component which may come from positron annihilation in PVC [16]. As mentioned above, the o-Ps component is relevant to the free-volume properties, and it is markedly sensitive to the relaxation process; so, in this paper, our main attention is paid to the changes in  $\tau_3$  and in  $I_3$  with the relaxation time.

In the current PAS method, the average radius  $R$  of the free-volume holes is evaluated from the o-Ps lifetime  $\tau_3$  according to the following semi-empirical equation [3]:

$$\tau_3 = \frac{1}{2} \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right]^{-1} \quad (1)$$

where  $\tau_3$  and  $R$  are expressed in nanoseconds and ångströms, respectively.  $R_0$  equals  $R + \Delta R$  where  $\Delta R$  is the fitted empirical electron layer thickness (equal to 1.656 Å). Furthermore, it is considered that the o-Ps intensity  $I_3$ , which reflects the probability of formation of o-Ps atoms, is proportional to the hole concentration [17].

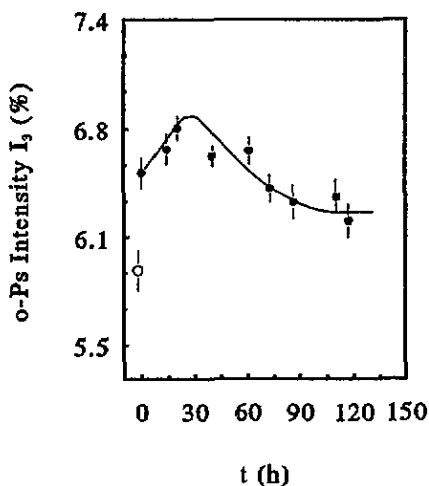


Figure 1. Variation in the o-Ps intensity  $I_3$  in the relaxed PVC (●) versus the stress relaxation time  $t$ , compared with  $I_3$  in the as-received sample (○).

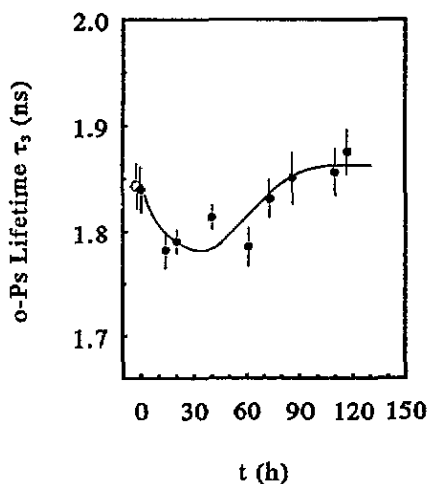


Figure 2. Variation in the o-Ps lifetime  $\tau_3$  in the relaxed PVC (●) versus the stress relaxation time  $t$ , compared with  $\tau_3$  in the as-received sample (○).

The measured o-Ps intensity  $I_3$ , the lifetime  $\tau_3$  and the average radius  $R$  of free-volume holes in the stretched PVC as functions of the relaxation time are shown in figures 1, 2 and 3, respectively. We have also measured the positron lifetimes in the as-received sample for comparison with the stretched sample. As shown in figure 1,  $I_3$  at the beginning of relaxation is larger in the stretched PVC than in the as-received PVC, which suggests that the stress can induce the creation of new free-volume holes [6], and the structure of the as-received sample is closer to that of the equilibrium state than that of the stretched sample at  $t = 0$  h is.

From figure 1, we observe that the o-Ps intensity  $I_3$  in the stretched PVC increases with increasing relaxation time up to  $t \approx 30$  h; then it monotonically decreases and reaches a lower level above  $t \approx 90$  h. Therefore, the stress relaxation process can be divided into three periods, which is consistent with the variation in the o-Ps lifetime  $\tau_3$  shown in figure 2. According to equation (1), the hole radius is calculated and plotted in figure 3 from which we can see that the hole radius  $R$  decreases from 2.70 to 2.64 Å for  $t = 0-30$  h; then it increases to 2.71 Å for  $t = 30-90$  h and remains constant at 2.72 Å above 90 h. In the first period  $t \approx 0-30$  h, the results indicating an increase in the hole concentration and a decrease in the hole size imply the creation of new free-volume holes and the segmental orientation [4, 6], respectively. In the amorphous region of glassy polymer at a small strain, owing to

the anchorage of crystallites and the entanglements of chains [18], slippage of chains is impossible; stress can lead to the separation of some chains from others and therefore to the creation of new free-volume holes. In the initial stage of stress relaxation, the local stress distribution along the segments is non-uniform [18]; under larger stresses, some segments tend to be oriented and have more order arrangement, which may reduce the average size of free-volume holes [4, 6], as indicated by the variation in  $R$  in figure 3.

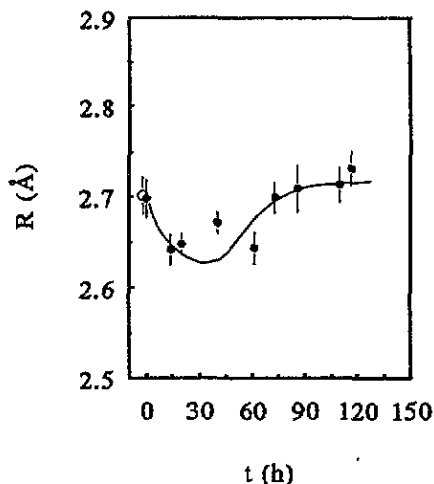


Figure 3. Variation in the hole radius  $R$  in the relaxed PVC (●) versus the stress relaxation time  $t$ , compared with  $R$  in the as-received sample (O).

In the second period ( $t = 30\text{--}90$  h), the decrease in o-Ps intensity  $I_3$  and the increase in the o-Ps lifetime  $\tau_3$  with increasing relaxation time are attributed to the coalescence of free-volume holes. Since the free-volume hole in the stretched polymer is relevant to the local stress along the chain [18], the sizes of free-volume holes should change under the relaxed stress. In this period, the stress along the chain is relieved and the oriented chains in the first period gradually take more favourable conformations [1]; so the sizes of free-volume holes are enlarged, which can provide larger open spaces for the segmental rearrangement [13, 19].

In the last period (above 90 h), both the o-Ps lifetime  $\tau_3$  and the intensity  $I_3$  are nearly constant, as shown in figures 1 and 2. As time goes on, the local rearrangement of small segments will be slowed down by the viscous drag [1] and the stress distribution gradually becomes uniform; the microstructures of amorphous regions approach closely the equilibrium states [2]. So, in this stage, we observed that both  $\tau_3$  and  $I_3$  are basically unchanged.

Another important parameter is the fractional free-volume  $F_v$ , which is expressed by the product of  $V_f$  and  $I_3$ , namely  $F_v = CV_f I_3$ , where  $V_f \approx 4\pi/3R^3$  is the average volume of the free-volume holes (assuming spherical geometry) and  $C$  is a constant [5, 17]. For convenience, we define a relative fractional free-volume  $F_r$  to reflect the level of fractional free-volume [19]:

$$F_r = V_f I_3. \quad (2)$$

The variation in  $F_r$  also provides some interesting information on the structure changes of the relaxed PVC. We have evaluated  $F_r$  in PVC based on equation (2), and the result

is shown in figure 4. Evidently, the relative fractional free-volume  $F_r$  in the stretched PVC at the beginning of relaxation is higher than that in the as-received PVC, suggesting that cavitation damage may be induced by the stress in the stretched sample [6]. In the stress relaxation process ( $t = 0-120$  h),  $F_r$  remains constant. This observation is greatly different from the facts that the fractional free-volume decreases in the process of isothermal relaxation [3, 11] and increases in the process of heating at  $T > T_g$  [19]. In comparison with the rubbery polymer, the rearrangement of segments in the glassy polymer is more difficult and it needs a longer time; we cannot expect to see the obvious variation in the fractional free-volume in PVC within a limited time of observation. It also deserves mentioning that  $I_3$ ,  $\tau_3$  and  $F_r$  for the relaxed PVC at  $t = 120$  h are all higher than those for the as-received sample; therefore, the equilibrium state of the as-received sample is not the same as that of the equilibrium or, more appropriately, of the quasi-equilibrium state of the well relaxed sample.

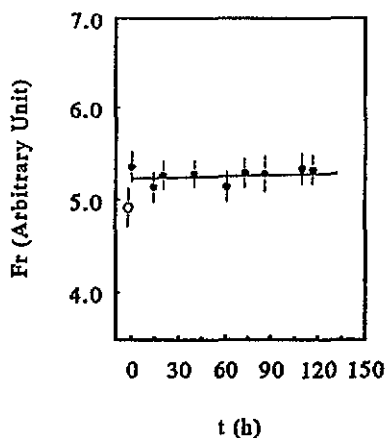


Figure 4. Variation in the relative fractional free-volume  $F_r$  in the relaxed PVC (●) versus the stress relaxation time  $t$ , compared with  $F_r$  in the as-received sample (○).

#### 4. Conclusion

We have performed positron lifetime measurements so as to study the changes in free-volume properties in the stretched PVC polymer during the stress relaxation time  $t = 0-120$  h. The relaxations of the free-volume size and concentration in PVC span a period of about 90 h. The variations in the o-Ps lifetime and intensity show the detailed process of the free-volume relaxation towards an equilibrium or, more appropriately, a quasi-equilibrium state. The constancy of the fractional free-volume versus the relaxation time implies that the rearrangement of segments in the glassy polymer is more difficult than in the rubbery polymer.

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