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Effects of deformation on the microstructure of PTFE polymer studied by positron annihilation

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Abstract. The free-volume properties of uniaxially stretched polytetrafluoroethylene (PTFE) have been studied by positron lifetime spectroscopy as a function of residual deformation ϵ in the range of 0–180%. According to the variation of *ortho*-positronium (*o*-Ps) intensity, the stretch process can be divided into three stages, i.e. elastic region ($\epsilon = 0$ –20%), plastic-flow region ($\epsilon = 20$ –80%) and strain-strengthening region ($\epsilon = 80$ –180%). In each stage the free-volume concentration is constant, but it has a step increase at the transition points ($\epsilon = 20\%$ and 80%). The average radius of free-volume holes increases with deformation in the elastic region, has a maximum in the plastic-flow region, and finally tends to a lower level in the strain-strengthening region. These results show that positron annihilation lifetime is a sensitive means to probe the microstructural change of polymers during deformation.

1. Introduction

The correlation between microstructure and macroscopic properties of polymers has been of interest for years [1, 2]. In the amorphous regions of a polymer, structural changes can be characterized in statistical terms such as density fluctuation, or concentration and average size of free-volume holes [3]. Experimental studies have shown that these randomly distributed holes are relevant to macroscopic properties of polymers, e.g. the glass transition [4, 5], pressure response [6], physical aging [3] and solid-state polymerization [7]. Positron annihilation spectroscopy (PAS) has been developed to probe the variations of average size and concentration of free-volume holes [8, 9], on the basis that positronium (Ps) formation is found only in amorphous regions and the Ps 'atom' is preferentially localized in the free-volume holes.

The effect of deformation on microstructure is one of the interesting topics in polymer science. In stress–strain measurements, the yield point ϵ_y of a polymer usually characterizes the different stretching properties [10] and indicates the slippage of chains. When $\epsilon < \epsilon_y$, the deformation of a polymer is reversible under smaller stress, but post-yielding deformation is irreversible and the polymer undergoes some structural changes, such as slippage and orientation of chains, stress-induced crystallization and the production of chain ends, free radicals and cracks [2, 11].

In this paper, the results of positron lifetime measurements on stretched deformation of PTFE as a function of uniaxial residual deformation ϵ are presented, and the variation of the longest-lived component is discussed in terms of the free volume and the separation, orientation, slippage and scission of chains.

2. Experiment

The dumbbell-shaped specimens used in this study were cut from a piece of PTFE plate (density = 2.20 g cm⁻³), and had a thickness of 2.1 mm and a width of 15 mm. A mechanical stretching device was used for fixing two specimens and provides a constant stretch rate of 4% per minute. The residual deformation was obtained according to the formula

$$\epsilon = (l - l_0)/l_0$$

where l_0 and l were the original and present length of the line-marked region in the middle of the PTFE specimen. When ϵ reached a preset value (e.g. 10%, 20%, etc), the stretch was stopped.

A 15 μ Ci ²²Na positron source sealed on Ni foil (1.7 mg cm⁻²) was placed between the two specimens. Positron lifetime measurements were performed using a fast-fast coincident system, which has a resolution of 250 ps, measured from the prompt curve of a ⁶⁰Co source. A million counts were collected for each spectrum in about 60 min at room temperature.

3. Results and discussion

Positron lifetimes in PTFE have been measured as a function of residual deformation ϵ in the range of 0–180%. According to the method used by Kindl and Sormann [12], each spectrum of PTFE was resolved into four positron components using the computer program PATFIT [13], where a positron source correction (7%) in Ni foil has been subtracted. Variances of fits (χ^2) are smaller than 1.18. The shortest component τ_1 is due to *para*-positronium (*p*-Ps) annihilation [5, 14] and positron annihilation in the bulk of the crystalline regions. Considering τ_1 is nearly the same as 125 ps, the *p*-Ps lifetime *in vacuo* [14], we fix $\tau_1 = 0.125$ ns in order to reduce the error bars. The second component ($\tau_2 = 0.32 \pm 0.03$ ns) is assigned to positron annihilation in the crystalline regions [5, 9]. The origin of the third component ($\tau_3 = 0.90 \pm 0.3$ ns) is still the subject of controversy [14]. Here we consider that τ_3 and its intensity I_3 result from the pick-off annihilation of *o*-Ps trapped at the crystal–amorphous interface [14, 15] and in the bulk of the amorphous region. The longest component ($\tau_4 = 3.8$ – 4.2 ns) is attributed to *o*-Ps pick-off annihilation in the free-volume holes of amorphous regions [9], and the *o*-Ps intensity I_4 is directly proportional to the concentration of free-volume holes [16]. The values of τ_4 and I_4 are consistent with literature results [12], and the average radius R of free-volume holes can be evaluated from the *o*-Ps lifetime τ_4 by the free-volume model [9]. The results of positron lifetime measurements are listed in table 1. From table 1 we can see that the population ratio of *p*-Ps and *o*-Ps atoms, i.e. $I_1 = \frac{1}{3}(I_3 + I_4)$, is in good agreement with the measured results in the region of $\epsilon = 80$ – 180% ; but I_1 is slightly larger than $\frac{1}{3}(I_3 + I_4)$ in the region of $\epsilon = 0$ – 80% , which implies that the shortest component has a smaller contribution from positron annihilation in the bulk of the crystalline regions. As shown in table 1, only the fourth component (τ_4, I_4) is particularly sensitive to the deformation, so in this paper the main attention is paid to the changes in τ_4 and I_4 with deformation ϵ .

The true stress σ of PTFE was continuously measured as a function of deformation ϵ at room temperature with a stretch rate of 150% per minute, as shown in figure 1. As is well known, the whole stretch process of a polymer can be divided into three stages according to the variations of σ and $\partial\sigma/\partial\epsilon$ [2]. From figure 2 the yield point is easily determined

Table 1. The results of positron lifetime measurements on PTFE as a function of deformation ϵ .

ϵ (%)	τ_2 (ps)	τ_3 (ps)	τ_4 (ns)	I_1 (%)	I_2 (%)	I_3 (%)	I_4 (%)	χ^2
0	323 ± 7	997 ± 70	3.828 ± 0.04	14.31 ± 0.81	53.99 ± 0.77	14.27 ± 0.83	17.43 ± 0.45	1.05
10	321 ± 6	1021 ± 73	3.896 ± 0.05	13.50 ± 0.83	56.12 ± 0.70	12.96 ± 0.72	17.42 ± 0.45	1.07
20	316 ± 7	984 ± 60	3.947 ± 0.05	11.93 ± 0.86	55.53 ± 0.72	14.48 ± 0.80	18.06 ± 0.37	1.17
30	330 ± 8	959 ± 76	3.931 ± 0.04	15.60 ± 0.79	52.43 ± 0.89	12.93 ± 1.00	19.04 ± 0.41	0.97
40	327 ± 7	1019 ± 74	4.054 ± 0.05	13.40 ± 0.79	55.10 ± 0.73	13.01 ± 0.80	18.49 ± 0.43	0.91
60	337 ± 6	1140 ± 90	4.276 ± 0.06	16.16 ± 0.70	52.97 ± 0.61	12.10 ± 0.56	18.77 ± 0.51	1.01
70	326 ± 7	1015 ± 78	4.089 ± 0.05	14.59 ± 0.78	53.47 ± 0.72	12.51 ± 0.78	19.43 ± 0.43	0.93
80	289 ± 7	811 ± 53	4.013 ± 0.04	9.29 ± 0.80	58.35 ± 0.96	13.00 ± 1.28	19.36 ± 0.28	0.95
90	312 ± 8	892 ± 68	3.937 ± 0.04	10.57 ± 0.92	54.98 ± 0.94	13.49 ± 1.16	20.96 ± 0.35	1.05
100	317 ± 8	911 ± 70	3.937 ± 0.04	11.76 ± 0.79	54.02 ± 0.94	12.86 ± 1.12	21.36 ± 0.37	0.97
110	326 ± 7	1030 ± 90	3.990 ± 0.04	11.46 ± 0.79	56.31 ± 0.72	10.90 ± 0.75	21.33 ± 0.41	0.96
120	320 ± 7	960 ± 80	3.982 ± 0.04	12.14 ± 0.84	54.52 ± 0.83	11.95 ± 0.95	21.39 ± 0.41	1.00
140	302 ± 8	884 ± 62	3.982 ± 0.03	10.31 ± 1.00	54.10 ± 0.87	13.90 ± 1.08	21.69 ± 0.33	1.04
160	297 ± 8	830 ± 63	3.867 ± 0.03	9.48 ± 1.07	55.14 ± 1.00	13.59 ± 1.30	21.79 ± 0.31	0.97
180	285 ± 9	852 ± 74	3.973 ± 0.03	9.10 ± 1.24	52.25 ± 1.18	16.23 ± 1.60	22.42 ± 0.25	1.09

at $\epsilon = 10\%$. After the yield point the slope $\partial\sigma/\partial\epsilon$ has a smaller value below $\epsilon = 80\%$ and then increases more rapidly. So the stretch process of PTFE can be divided into three stages, i.e. elastic ($\epsilon \leq \epsilon_y = 10\%$), plastic-flow ($10\% < \epsilon \leq 80\%$) and strain-strengthening ($80\% < \epsilon \leq 180\%$) stages, respectively. In the elastic stage, the stress increases linearly with deformation ϵ . Above ϵ_y , the increase of stress σ slows down, which shows that PTFE continues to extend uniformly [10]. In the strain-strengthening stage, the value of $\partial\sigma/\partial\epsilon$ continuously increases with ϵ , which means that the Young's modulus increases with ϵ .

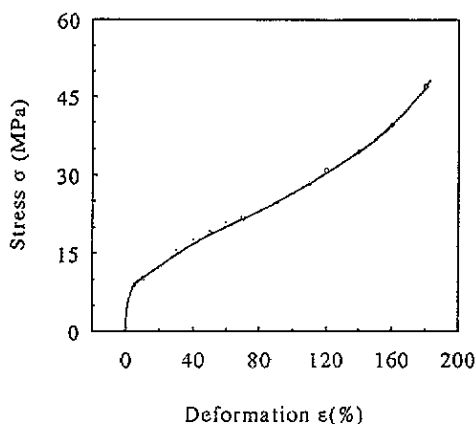


Figure 1. True stress σ versus the residual deformation ϵ for PTFE at room temperature. The stretch rate is 150% per minute.

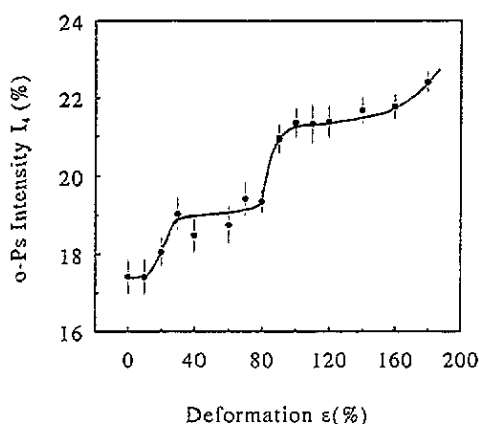


Figure 2. The variation of *o*-Ps intensity I_4 with the residual deformation ϵ in PTFE.

The measured *o*-Ps intensity I_4 , lifetime τ_4 and the average radius of free-volume holes R in PTFE as a function of ϵ are shown in figures 2–4. From figure 2 we have observed that the *o*-Ps intensity I_4 has three plateaux, corresponding to the elastic ($0 < \epsilon \leq 20\%$), plastic-flow

(20% < $\epsilon \leq 80\%$) and strain-strengthening (80% < $\epsilon \leq 180\%$) stages, respectively, and I_4 has a step increase with deformation at the transition points ($\epsilon = 20\%$, 80%). The yield point $\epsilon_y = 20\%$ measured by PAS is somewhat retarded in comparison with $\epsilon_y = 10\%$ in figure 1. This fact can be interpreted in terms of a relaxation effect. Mechanical experiments [10] have shown that the decrease in stretch rate can retard the yield point. For PAS measurements the stretch rate is 4% per minute, which is smaller than the 150% per minute for the σ - ϵ measurement; and when ϵ reaches a preset value the stretch was stopped for 1 h in order to acquire data. So the PTFE chains have enough time to rearrange themselves and chain slippage is retarded.

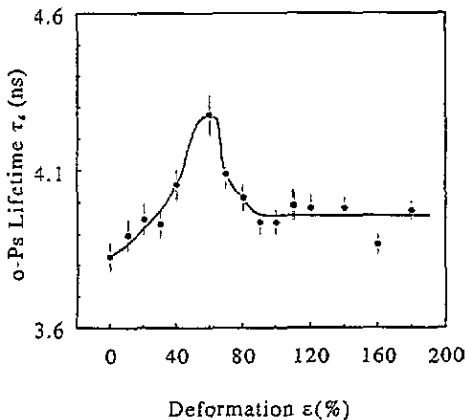


Figure 3. The variation of *o*-Ps lifetime τ_4 with the residual deformation ϵ in PTFE.

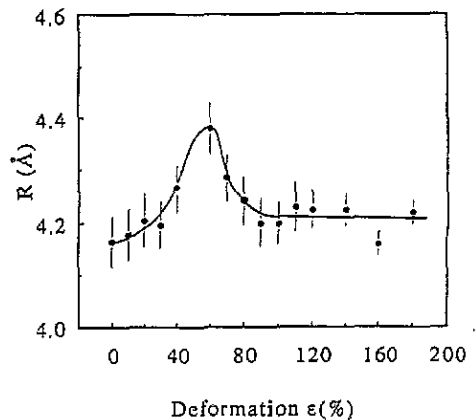


Figure 4. The variation of average radius of free-volume holes with the residual deformation ϵ in PTFE.

From the variations of I_4 and τ_4 shown in figures 2 and 3, information on the microstructural changes in amorphous regions can be obtained. The free-volume holes are formed due to the packing irregularities of segments, chain ends and free radicals [1], and hole concentration and size could be changed during deformation. In the elastic region ($0 < \epsilon < 20\%$), because the crystalline regions and segmental entanglements can impede the slippage of chains, the small elastic deformation in the amorphous region is mainly caused by the displacement of bond lengths and rotation on bond angles [11]; therefore, no new holes are produced and the concentration of free-volume holes is constant (i.e. $I_4 = 17.5\%$). The slight increase of τ_4 with deformation implies a small separation of segments. At the end of the elastic stage ($\epsilon = 20\%$), the local environment and stress distribution in amorphous regions are changed from place to place; the larger stresses can induce the separation of segments, which can lead to the step increase of free-volume concentration.

In the plastic-flow stage ($20\% < \epsilon < 80\%$), the microstructure undergoes dramatic changes. Owing to intermolecular friction force [11], the stress can be transferred from one chain to another and results in the slippage, separation and orientation of chains. The results in this work show that I_4 is nearly constant in this stage and τ_4 increases from 20% and has a maximum at $\epsilon = 60\%$. These observations suggest that no new holes are expected to be created, and the separation of segments only induces the enlargement of holes in the range of $\epsilon = 20$ –60%. When $\epsilon = 60$ –80%, a dramatic decrease in *o*-Ps lifetime τ_4 is observed, which is due to the orientation of segments. In polymers the free-volume hole is an unoccupied space, around which the segments are arranged in a disorderly way. Under

a larger stress, the segments tend to align and have more ordered arrangement [17], which would effectively reduce the hole size in the region of $\epsilon = 60\text{--}80\%$. At the end of the plastic-flow stage ($\epsilon = 80\%$), a step increase in I_4 is observed. Since the PAS experiment is performed at $T < T_g$ (the glass transition temperature $T_g = 388$ K for PTFE), the PTFE is in the glassy state and the scission of chains is possible owing to the anchorage of entanglements and crystallites. Based on the step increase in I_4 at $\epsilon = 80\%$, the scission of chains takes place and more chain ends and free radicals are produced, so a larger number of new free-volume holes are created.

In the strain-strengthening stage ($80\% < \epsilon < 180\%$), both o -Ps annihilation parameters I_4 and τ_4 have no obvious changes. This result suggests that the free-volume concentration and size are unchanged in the strain-strengthening stage. The possible reasons are as follows: (i) There is a dynamic balance between production and diminution of free-volume holes owing to the active motion of chain ends and free radicals. (ii) The degree of orientation of segments reaches a saturation level, so the hole size is not changed in this stage. When $\epsilon > 160\%$, I_4 begins to increase again. This fact implies that the increase of free-volume concentration may be the precursor of PTFE fracture.

4. Conclusion

Positron lifetimes in stretched PTFE have been measured as a function of residual deformation ϵ in the range 0–180%. From the variation of o -Ps intensity I_4 the stretch process can be divided into three stages, i.e. elastic stage ($0 < \epsilon \leq 20\%$), plastic-flow stage ($20\% < \epsilon \leq 80\%$) and strain-strengthening stage ($80\% < \epsilon \leq 180\%$). The variations of I_4 and τ_4 are very sensitive to the microstructural changes in amorphous regions of PTFE during deformation. At smaller deformation (i.e. $\epsilon \leq 60\%$), the separation of chains is observed, while orientation begins from $\epsilon = 60\%$ and scission of chains may occur at larger deformation (i.e. $\epsilon \geq 80\%$). These results indicate the possibility of cavitation damage for stretched PTFE and the free-volume holes may be the precursors of polymer fracture.

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