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Investigation of polymer deformation by positron annihilation

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ABSTRACT

Positron lifetimes in polytetrafluoroethylene (PTFE) and polyethylene (PE) have been measured as a function of residual deformation ϵ . For PTFE, the variation of o-Ps intensity shows a three-stage processes: the elastic region ($\epsilon=0-20\%$), plastic-flow region ($\epsilon=20-80\%$) and strain-strengthening region ($\epsilon=80-180\%$). The changes of free-volume hole size and concentration suggest the separation, scission and orientation of segments. For PE, the o-Ps parameters are sensitive to the elastic and plastic regions. Particularly, the hole concentration decreases linearly with ϵ , which indicates the crystallization during deformation.

1. INTRODUCTION

The correlation between microstructure and macroscopic properties of polymers has been of interest for many years [1]. It was found that the tensile strengths and Young's moduli of polymers are rather lower than the expected values, and different mechanisms have been proposed on the deformation of semi-crystalline polymers [2]. In order to discern the different physical processes during deformation, we performed the positron lifetime experiment on the glassy PTFE and rubbery PE at room temperature as a function of ϵ .

2. EXPERIMENT

The dumbbell-shape specimens were cut from two pieces of PTFE and PE plates. A mechanical stretching device provides a stretch rate of $4\% \text{ min}^{-1}$ and fixed the elongated specimens. When the ϵ reaches a preset value (i.e., 10%, 20%, etc), the stretch was stopped. Immediately a $15\mu\text{Ci } ^{22}\text{Na}$ positron source sealed on Ni foil (1.7mg cm^{-2}) was placed between the two specimens. Positron lifetime measurements in situ were performed using a fast-fast coincident system which has a time resolution of 250ps. A million counts were collected for each spectrum within about 1 hour.

3. RESULTS AND DISCUSSION

(1). Microstructural changes in PTFE

Positron spectrum of PTFE has been best resolved into four components by using PATFIT program [3,4]. We observed that the longest component τ_4 is particularly sensitive to ϵ , where τ_4 is from o-Ps annihilation in the free-volume holes of amorphous regions [6], and its intensity is proportional to the hole concentration.

There is a good correlation between the o-Ps intensity I_4 and the true stress σ of PTFE. We have measured the true stress-deformation curves of PTFE (the stretch rate is 150% per min.), which clearly shows three deformation stages and $\epsilon=10\%$ is the yield point [7]. In Fig.1 the variation of I_4 indicates the three stages of PTFE deformation, i.e., the elastic ($\epsilon=0-20\%$), plastic-flow ($\epsilon=20-80\%$) and the strain-strengthening region ($\epsilon=80-180\%$). The yield point indicated by I_4 , i.e. $\epsilon=20\%$, is somewhat retarded in comparison with that indicated by stress-deformation curve. This fact can be interpreted by relaxation effects. Mechanical experiments [10] have shown that the decrease of stretch rate can retard the yield point. For PAS measurement the stretch rate is 4% per minute, which is smaller than 150% per minute for σ - ϵ measurement; and when ϵ reaches a preset value the stretch was stopped for 1 hour in order to acquire data. So the PTFE chains have enough time to rearrange themselves and chain slip is retarded.

As shown in Fig.1 and 2, in the elastic region ($\epsilon=0-20\%$), we observed the hole concentration is nearly constant, while its size has a slight increase with ϵ . It indicates a small separation of segment without the hole creation. At the end of elastic stage ($\epsilon=20\%$), the larger stresses can induce the separation of segments and the creation of holes and lead to the increases of I_4 and τ_4 .

In the plastic-flow stage ($\epsilon=20-80\%$), the microstructure undergoes dramatic changes. Due to inter-molecular friction force [10], the stress can be transferred from one chain to another and results in the slip, separation and orientation of chains. The constant I_4 suggests that no new holes are expected to be created, and the separation of segments only induces the enlargement of holes in the period of $\epsilon=20-60\%$. When $\epsilon=60-80\%$, the dramatic decrease in o-Ps lifetime τ_4 is due to the orientation of segments. In polymers the free-volume hole is an unoccupied space, around which the segments are arranged disorderly. Under a larger stress, the segments tend to align and have more order arrangement [7,10], which would effectively reduce the hole size in the region of $\epsilon=60-80\%$.

At the end of plastic-flow stage ($\epsilon=80\%$), a step increase in I_4 is observed, probably resulting from the scission of chains and the creation of more free-radicals and chain ends. Since PAS experiment is performed at $T < T_g$ ($T_g=388K$ for PTFE), the PTFE is in glassy state and the scission of chains is possible due 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, both I_4 and τ_4 have no obvious changes. The possible reasons are: 1). There is a dynamic balance between production and diminution of free-volume holes due to the active motion of chain ends and free-radicals [9]; 2). The orientation degree of segments reaches a saturation level. When $\epsilon > 160\%$, I_4

begins to increase again until PTFE is broken at $\epsilon=185\%$.

(2). Microstructural changes in PE

The measurement of stress vs ϵ shows a three-stage processes, namely, the elastic ($\epsilon=0-20\%$), strain-softening ($\epsilon=20-40\%$) and plastic-flow ($\epsilon=40-190\%$). Lifetime spectrum of PE is resolved into three components, in which the longest-lived τ_3 is from o-Ps annihilation in free-volume holes in amorphous regions, and the intermediate τ_2 is from positron annihilation in the defects of crystalline regions. In the elastic region, the increases of size and concentration of free-volume holes in the amorphous region may result from the scission of chains [9] and the increase of crystalline-amorphous interfaces. Near the yield point ($\epsilon=20\%$), the maximum in hole size and concentration provides an experimental evidence for the free-volume theory on deformation [8]. The increases in I_2 and τ_2 shown in Fig.3-4 coincide with the structural changes from the spherulites to the microfibril and the generation of grain boundaries [1]. While the maximum τ_2 at $\epsilon=20\%$ indicates the coalescence of defects under high stress. In the strain-softening stage, the nearly constant I_3 and τ_3 imply that the microstructural changes take place mainly in the crystalline regions [9]. In the plastic-flow stage, the decrease of I_3 arises from the stress-induced crystallization, while the nearly constant τ_3 may be related to the constant stress vs ϵ . In this stage, τ_2 reveals a continuous decrease but I_2 increases with ϵ , which shows the rearrangement of chains in the crystalline regions.

Fig.1 The plot of o-Ps intensity vs. ϵ

Fig.2 The plot of o-Ps lifetime vs. ϵ

Fig.3 The plot of positron intensity I_2 vs. ϵ for PE

Fig.4 The plot of positron lifetime τ_2 vs. ϵ for PE

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