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Positron Annihilation Studies of the Free Volumes in Nylon12/PVA Films Treated by Supercritical Carbon Dioxide

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Free volume variations of Nylon12/Polyvinyl alcohol (Nylon12/PVA) blends treated in supercritical carbon dioxide (ScCO$_2$) were investigated using positron annihilation lifetime spectroscopy. It is found that *o*-Ps lifetime τ_3 and the corresponding intensity I_3 in Nylon12/PVA decrease with increase of the PVA content. Being treated in ScCO$_2$ at 50 °C and 20 MPa for 1 h, the free volume holes in Nylon12/PVA blends expand to different extents depending on the weight ratio of PVA. After releasing of CO$_2$, the free volume size decreases as a function of the elapsed time due to the molecular relaxation, and the relaxation time constant depends on the content of PVA in the blends.

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PACS/topics: Nylon12/PVA, ScCO$_2$, positron annihilation, free volume, relaxation

1. Introduction

Supercritical carbon dioxide (ScCO$_2$, $T_c = 31.1\,^{\circ}$C, $P_c = 7.37$ MPa) has been used as a kind of green solvent in polymer synthesis and processing, pharmaceutical extraction, etc. Over the past three decades, numerous polymers [1–8] including bulk materials and thin films, either amorphous or semi-crystalline polymers, have been found to be able to dissolve or swell in ScCO$_2$ with large density fluctuations [9–11]. However, very little is clearly known about the interaction between CO$_2$ and the polymers. In ScCO$_2$ treated polymers, a clear expansion of the free volume due to swelling effect of ScCO$_2$ is observed. Considerable research efforts have been devoted to free-volume relaxation after ScCO$_2$ treatment. Claes et al. reported that the pronounced stability of the enlarged free volume of ScCO$_2$ treated PTMSP at room temperature and a characteristic relaxation time was in the order of ∼ 30 years [12].

Positron annihilation lifetime spectroscopy (PALS) has drawn much attention recently in condensed materials research due to its high sensitivity to vacancies [13, 14], surface and interface defects, free-volume holes [15–17] and pores [18–20]. When an energetic positron is implanted in solid materials, it slows down to thermalized state through collisions with surrounding molecular electrons and molecules. At the end of its track the positron either annihilates directly with an electron or forms an intermediate state, positronium (Ps). The Ps, with a Bohr diameter of 1.06 Å, is a bound state consisting of an electron and a positron. The Ps is typically formed in two states, *ortho*-Ps (*o*-Ps) of spin-parallel triplet state and *para*-Ps (*p*-Ps) of spin-antiparallel singlet state. In vacuum, *o*-Ps, annihilates into 3γ rays, with an intrinsic lifetime of 142 ns, and *p*-Ps, annihilates into 2γ rays, with a much shorter lifetime of 125 ps. The *o*-Ps is of high sensitivity to free-volume voids and prefers to be trapped therein. If *o*-Ps is localized in an atom-sized hole, it can annihilate with electrons on the holes wall via the "pick-off" process and its lifetime is shortened to a few ns. The *o*-Ps lifetime through 2γ pick-off annihilation is well correlated with the holes size, so that the subnanometer-sized free volume can be examined by PALS.

The relation between the *o*-Ps lifetime τ_3 and an equivalent spherical cavity radius R smaller than ∼ 1 nm is described by the Tao–Eldrup equation [21–24]:

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

where R is the average radius of the free volume cavity, $\Delta R = 1.66$ Å is an empirical parameter derived from fitting the observed *o*-Ps lifetimes and free volume sizes in molecular solids. The mean hole free volume V_{FV}, can be calculated from the following equation:

$$V_{FV} = \frac{4\pi R^3}{3}. \quad (2)$$

In the present work, a kind of barrier and active packaging film was prepared by melt blending Nylon 12 and polyvinyl alcohol (PVA). Free-volume relaxation behaviors of ScCO$_2$ treated Nylon 12/PVA blend films with various PVA contents were investigated using PALS.

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2. Experimental

2.1. Sample and preparation

Nylon 12 (L1670) in pellet form with glass transition temperature of 28 °C and melting temperature of 180.0 °C was purchased from Evonik Industries Corporation, Germany. Polyvinyl alcohol (PVA, degree of polymerization is about 2400) with glass temperature of 102 °C and melting temperature of 226 °C was obtained from Taiwan Changchun Petrochemical Company. Prior to to being melted, the Nylon12 pellets and PVA powder were dried in a vacuum oven at 80 °C for 16 h and 12 h, respectively. The weight ratios of PVA in Nylon12/PVA blends are represented as 0, 10, 30, 50 wt%, respectively. The blends were prepared by melting blend in a SHJ-20 double screw extruder at 230 °C using screw speeds of 50 rpm. The thickness of the resulted Nylon12/PVA blend films, prepared by a SJ20/28-BL26 film blowing machine from Wuhan Tongchuang Plastic Machinery Company, is about 40 μm. CO_2 with a purity of 99.99% was used for $ScCO_2$ treatments.

2.2. $ScCO_2$ treatment

A high-pressure reactor from Jiangsu Hong Bo Mechanical Machinery Ltd. (China) with an internal volume of 200 ml was used in combination with a plunger pump. Square pieces with a thickness of 40 μm and side length of 5 cm were cut from the Nylon12/PVA films and placed into the reactor vessel, which was then sealed. First, the reactor vessel was flushed with low-pressure CO_2 for about 1 min before reaching the chosen temperature and pressure. Then, Nylon12 film and Nylon12/PVA blend films samples were kept in the vessel under stable $ScCO_2$ condition of 50 °C and 20 MPa for one hour. After that, the CO_2 pressure was slowly released to ambient atmosphere at 0.5 MPa/min, as higher rate of depressurization could lead to foaming of the polymers. To prevent CO_2 from liquefying during depressurization, the vessel temperature was kept above 35 °C. As a reference, the untreated samples were heat treated in the same vessel but without the presence of CO_2 in ambient atmosphere at 50 °C for one hour.

2.3. PALS measurements

All the PALS measurements in this work were carried out at room temperature in ambient atmosphere by utilizing a conventional fast-fast coincidence system with a time resolution of approximately 280 ps (full width at half-maximum). The lifetime spectra were accumulated with total counts of 1.0 million. During the measurements, two identical samples stacked to ∼ 1 mm in thickness with many pieces of the films were sandwiched around a 20 μCi positron source (^{22}Na) sealed with 7 μm thick Kapton films. The components of the positron annihilation in the source and Kapton films were subtracted using Si single crystal as reference. All of the positron lifetime spectra were evaluated by the LT routine [25] after source correction. All the spectra were decomposed into three lifetime components without fixing any lifetime or intensity, the variances of the fits were in the range of $0.90 \approx 1.05$.

3. Results and discussion

3.1. Free volumes in Nylon12/PVA blends as a function of PVA content

Figure 1 shows the variations of the *o*-Ps lifetime (τ_3), *o*-Ps intensity (I_3) and mean hole free volume size (V_{FV}) for neat Nylon12 and Nylon12/PVA blend films as a function of PVA content. As shown in Fig. 1a, both τ_3 and I_3 for the Nylon12/PVA blend films decrease after blending PVA into the Nylon12 matrix, in comparison to the neat Nylon12 sample, which is interpreted for that the hydrogen bonding between Nylon12 and PVA molecular chains is enhanced with increase of the amount of PVA. PVA with good barrier property against oxygen has strong intramolecular hydrogen bonding, which results in high crystallinity in PVA. On one hand, to a certain extent, the addition of PVA into Nylon 12 matrix suppresses the formation of Ps because of the crystallinity in PVA. On the other hand, the extra intermolecular hydrogen bonding between Nylon12 and PVA act as physical crosslinks, which reduces the free volume size and molecular mobility of Nylon12. Similar result on the decrement in *o*-Ps in a polymer blend (PS-PC) as a function of the addition of semicrystalline PC has been reported [26]. The results show that with increase of PVA, the free volume size and concentration are reduced because of the strong intermolecular interaction and intramolecular hydrogen bonding.

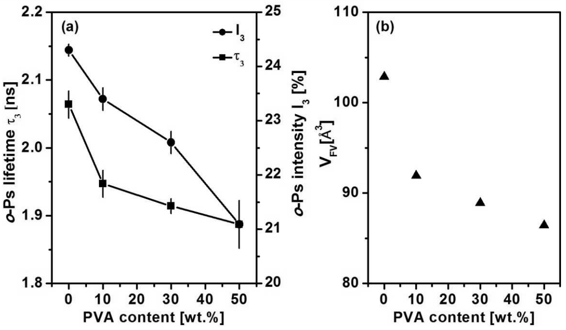

Fig. 1. (a) *o*-Ps lifetime (τ_3) and intensity (I_3), (b) mean free volume (V_{FV}) as a function of PVA content in Nylon 12/PVA blend films.

3.2. Free volume variations in $ScCO_2$ treated Nylon12

Figure 2 shows the variation of the *o*-Ps lifetime(τ_3), *o*-Ps intensity(I_3) and V_{FV} for $ScCO_2$ treated Nylon12 at 50 °C and 20 MPa for 1 h as a function of elapsed time after CO_2 depressurization. To a certain extent, free volume is enlarged after $ScCO_2$ treatment as indicated by the change of τ_3, and V_{FV} for $ScCO_2$ treated Nylon12 shows an increment of ∼ 7.5%, compared with the untreated Nylon12. It means that CO_2 molecules adsorbed in the polymer matrix enhance the segmental mobility [27, 28] of Nylon12 during $ScCO_2$ treatment, because of the adsorbed CO_2 molecules act as active plasticizers. After CO_2 depressurization, the τ_3 in $ScCO_2$

treated Nylon12 is found to decrease as a function of elapsed time, which seems to follow a single exponential trend down within 10 h to the initial value of 2.06 ns of untreated Nylon12. The fitting exponential function is described as follows:

$$\tau_3(t) = \Delta\tau \exp(-t/t_0) + \tau_3^0, \qquad (3)$$

where $\Delta\tau$ is the increment of *o*-Ps lifetime in Nylon12/PVA blends due to ScCO$_2$ treatment, t_0 is the relaxation time constant after CO$_2$ depressurization, and τ_3^0 is the *o*-Ps lifetime in Nylon12 without ScCO$_2$ treatments. The relaxation time constant of ScCO$_2$ treated Nylon12 is determined to be ∼ 1.8 h. Accordingly, it takes *o*-Ps lifetime τ_3 of ScCO$_2$ treated Nyolon12 around 10 h to approach the equilibrium value for untreated sample. The *o*-Ps intensity provides information about the relative probability of *o*-Ps formation in the current Nylon12 system and is likely related to the free volume concentration in Nylon12. The *o*-Ps intensity in ScCO$_2$ treated Nylon12 is lower than that in the untreated sample, and it increases slowly within ∼ 10 h to its initial value. The results in Nylon12 without ScCO$_2$ treatment indicate that the expanded free volumes could reach to their initial states after CO$_2$ depressurization, and it takes the molecular chains of ScCO$_2$ treated Nylon12 ∼ 10 h to reach the equilibrium value.

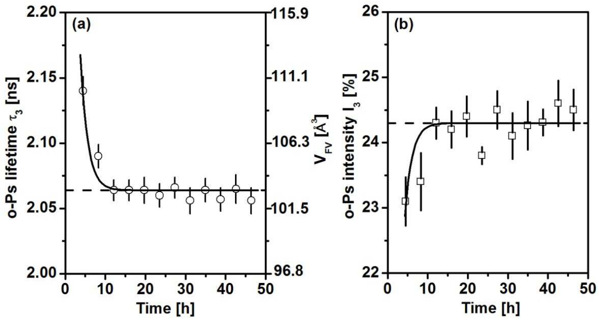

Fig. 2. (a) *o*-Ps lifetime (τ_3), mean hole free volume (V_{FV}) and (b) intensity (I_3) for ScCO$_2$ treated Nylon12 sample at 50 °C and 20 MPa for one hour versus elapsed time after CO$_2$ depressurization. The dashed line represents the *o*-Ps lifetime τ_3 and intensity I_3 of the untreated sample, whereas the solid line represents the fitting relaxation curve.

3.3. Relaxation behaviors of molecular chains in Nylon12/PVA blends

Figure 3 shows the variations of the *o*-Ps lifetime (τ_3), *o*-Ps intensity (I_3) and mean hole free volume size (V_{FV}) for ScCO$_2$ treated Nylon12/PVA blend films as a function of elapsed time after CO$_2$ depressurization. As mentioned above, the free volumes of all ScCO$_2$ treated samples are expanded, and they relax as a function of elapsed time after CO$_2$ depressurization. The free-volumes as a function of elapsed time are fitted with a single exponential function, and the fitted relaxation time constant is 6.6, 10.5, and 22.5 h ScCO$_2$ treated Nylon12/PVA blends with PVA contents of 10, 30, and 50 wt%, respectively, as shown in Fig. 3. In comparison to the ScCO$_2$ treated Nylon12 sample, the enlarged free volume sizes in the ScCO$_2$ treated blends show various longer relaxation times to reach the equilibrium values depending on the weight ratios of PVA. Much longer relaxation time is found for Nylon12/PVA with higher PVA weight ratio, which means that it is difficult for the blends to reach the equilibrium state with increase of the PVA content. As shown in Fig. 3, the free-volume sizes reach their equilibrium values in ∼ 20, ∼ 30, and ∼ 50 h for the blends containing various PVA contents of 10, 30, and 50 wt%, respectively. This is due to the stronger intermolecular interaction between Nylon12 and PVA in the blends with more PVA, which has a relative higher T_g of 102 °C. The addition of PVA into Nylon12 reduces chain mobility of the blends. Thus, for the ScCO$_2$ treated blends, it is rational to observe a longer relaxation time for the blends at room temperature. Meanwhile, it can be also found that the *o*-Ps intensity I_3 for the ScCO$_2$ treated blends increase gradually after CO$_2$ depressurization, although its variation is not significant. As the *o*-Ps lifetime, it takes essentially I_3 the same time to increase to the initial values of the untreated samples. The results demonstrate that the molecular relaxation after CO$_2$ depressurization relies on the weight ratio of PVA, which is attributed to the strong intermolecular interaction between Nylon12 and PVA.

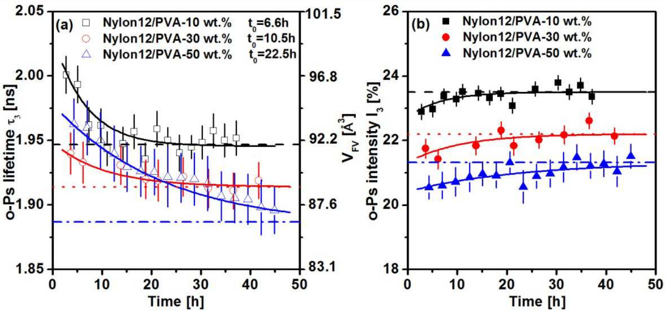

Fig. 3. (a) *o*-Ps lifetime (τ_3), mean hole free volume (V_{FV}) and (b) intensity (I_3) for ScCO$_2$ treated Nylon 12/PVA blend films at 50 °C and 20 MPa for one hour versus elapsed time after CO$_2$ depressurization. The dashed lines, dotted lines and dashed dotted lines in (a) and (b) represent the *o*-Ps lifetime τ_3 and intensity I_3 of the untreated films with the PVA content of 10, 30, and 50 wt%, respectively. The solid lines represent the fitting relaxation curves of the three samples.

4. Conclusion

In this study, the PALS results show that both *o*-Ps lifetime and intensity for Nylon12/ Polyvinyl alcohol (Nylon12/PVA) blend films decrease with increasing the PVA content. Being treated in ScCO$_2$ at 50 °C and 20 MPa for one hour, the free volumes in Nylon12/PVA blends expand. After CO_2 depressurization, the expanded free volume size decreases as a function of the elapsed time due to the molecules relaxation. In comparison to the $ScCO_2$ treated Nylon12, the enlarged free volumes in the $ScCO_2$ treated Nylon12/PVA blends show various longer relaxation times depending on the weight ratios of PVA. The results show that the molecular relaxation of Nylon12/PVA blends after CO_2 depressurization relies on the weight ratio of PVA, which is attributed to the strong intermolecular hydrogen bonding between PVA and Nylon12 molecular chains.

Acknowledgments

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