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Characterization of polyethylene terephthalate films coated with thin $Al_xSi_{1-x}O_y$ layers using monoenergetic positron beams

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ABSTRACT

Open spaces in polyethylene terephthalate (PET) coated with aluminum silicate ($Al_xSi_{1-x}O_y$) were probed using monoenergetic positron beams. The energy distributions of the annihilation γ rays and the positron lifetime spectra were measured for 60-nm-thick $Al_xSi_{1-x}O_y$ ($x = 0$–1) deposited on PET using electron-beam evaporation. A clear correlation was obtained between the line-shape *S* parameter of the annihilation γ rays, water vapor, and oxygen transmission rates. The results suggest that open spaces in the $Al_xSi_{1-x}O_y$ layers play an important role in water/oxygen diffusion in $Al_xSi_{1-x}O_y$/PET, where the concentration/size of such spaces showed its minimum value at $x = 0.2$–0.3. The free volume fraction below the interface between $Al_xSi_{1-x}O_y$ and PET (region width = 100–400 nm) was decreased by the deposition of the coating layer, and this region was also considered to act as a barrier against penetrations of gasses and molecules.

1. Introduction

Polymer films coated with thin metallic or ceramic layers have been used extensively in packaging of foods, medical supplies, electronic components, etc. [1,2]. In this structure, polymer films provide excellent mechanical properties such as elasticity and tear resistance, while the coating layers act as barriers to prevent gasses and water vapor permeation. Coated polymer films are, in general, produced in a vacuum chamber with a roll-to-roll configuration, where the coating layers are quickly deposited on moving polymer films [3]. The metallic or ceramic layers can be deposited using various techniques such as thermal, electron beam, sputtering, and chemical vapor depositions. In general, the water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) for polymer films are higher than 10 g/m^2·day and 10^3 ml/m^2·day·MPa, respectively. Using 10–100-nm-thick coating layers can reduce these by one or two orders of magnitude. The permittivity of coated polymer films strongly depends on imperfections of coating layer/polymer structure such as pinholes in coating layers, which could be created by the roughness of polymer surfaces or gas generation from polymers [2,4–6]. The control of morphology of coating layers is also important because their grain boundaries are expected to act as fast pathways of atoms and molecules. When transparent ceramic layers, such as SiO_x, AlO_x and TiO_x, are deposited on polymer films, their atomic configurations are considered to be very different from their thermal equilibrium state because their typical deposition temperature is lower than 100 °C. As a result, atomic scale disorder, vacancy-type defects and open spaces are expected to be introduced with high concentrations, and such defects could play an important role in the diffusion of atoms and molecules in coated polymer films. Positron annihilation is an established technique for investigating defects in solids [7]. This technique has been used to study behaviors of open spaces (free volumes) in amorphous polymers [8,9]. For thin ceramic layers, a monoenergetic positron beam is also useful for evaluating open spaces or defects in such layers [10,11]. In this study, we used monoenergetic positron beams to characterize polyethylene terephthalate (PET) films coated with aluminum silicate ($Al_xSi_{1-x}O_y$) layers.

When a positron is implanted into condensed matter, it annihilates with an electron and emits two 511-keV γ quanta [7]. The energy distribution of the annihilation γ rays is broadened by the momentum component of the annihilating electron–positron pair p_L that is parallel to the emitting direction of the γ rays. The energy of the γ rays is given by $E_\gamma = 511 \pm \Delta E_\gamma$ keV. Here, the Doppler shift ΔE_γ is given by $\Delta E_\gamma = p_L c / 2$, where c is the speed of light. A freely diffusing positron may be localized in a vacancy-type defect or open volumes because of Coulomb repulsion from positively charged ion cores. Because the momentum distribution of the electrons in such defects differs from that of electrons in the bulk material, these defects can be detected by measuring the Doppler broadening spectra of the annihilation radiation. The resultant changes in the spectra are characterized by the *S* parameter, which mainly reflects changes due to the annihilation of positron–electron pairs with a low-momentum distribution. In general, the characteristic value of *S* for the annihilation of positrons due to their trapping by vacancy-type defects is larger than that for positrons

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annihilated from the free-state. The lifetime of positrons trapped by vacancy-type defects increases because of the reduced electrondensity in such defects. Information obtained by measuring the lifetime spectra of positrons is useful for identifying vacancy-type defects [7].

For amorphous materials, positronium (Ps: a hydrogen-like bound state between a positron and an electron) may form in open spaces [8]. Ps exhibits two spin states: para-Ps (*p*-Ps) is a singlet state and ortho-Ps (*o*-Ps) is a triplet state. The intrinsic lifetimes of *p*-Ps and *o*-Ps are 0.125 ns and 142 ns, respectively. Ortho-Ps primarily exhibits three-photon (3γ) annihilation that produces a continuous energy distribution from 0 to 511 keV. Because *p*-Ps decays from 2-γ process, the energy of such γ-rays is 511 keV. Thus, an increase in the Ps formation rate increases the *S* value. When *o*-Ps is trapped by open volumes, the positron involved in *o*-Ps may annihilate with an electron of pore interiors to emit two γ rays before 3γ-annihilation (pick-off annihilation). A large open space decreases the probability of this process and increases the *o*-Ps lifetime. Thus, one can estimate the size of open volumes from measurements of the *o*-Ps lifetime [7,12–14].

2. Experiment

The samples investigated were PET films coated with $Al_xSi_{1-x}O_y$ layers. 50-μm-thick biaxially oriented PET films (Toyobo COSMOSHINE: A4100) were used as substrates. WVTR and OTR were measured according to ISO 15106-2 and 15105-2 using PERMATRAN-W Model 3/31 and OX-TRAN Model 2/21 (MOCON, Inc.). WVTR and OTR for the film without the coating layer were 10.8 $g/m^2 \cdot day$ and 280 $ml/m^2 \cdot day \cdot MPa$, respectively. $Al_xSi_{1-x}O_y$ ($x = 0$–1) layers about 60 nm thick were deposited on the PET films using a dual element electron-beam evaporation apparatus at room temperature. The thickness of the coating layer was obtained by using a stylus type step profiler. The deposition technique and film properties are detailed elsewhere [15]. The ratio of Al to Si (x) was controlled by electron beam current for each target and confirmed from measurements of X-ray fluorescence. To characterize an interlayer between $Al_xSi_{1-x}O_y$ and PET without the positron annihilation influencing the $Al_xSi_{1-x}O_y$ layer, the coating layers were removed using dilute HF solution (5%).

With a monoenergetic positron beam, the Doppler broadening spectra of the annihilation radiation were measured with a Ge detector as a function of the incident positron energy *E*. For each incident positron energy *E*, a spectrum with about 1×10^6 counts was obtained. The low-momentum part was characterized by the *S* parameter, defined as the number of annihilation events over the energy range of 511 keV $\pm \Delta E_\gamma$ (where $\Delta E_\gamma = 0.76$ keV) around the center of the peak. The relationship between *S* and *E* was analyzed by VEPFIT, which is a computer program developed by van Veen et al. [16]. The *S*–*E* curve was fitted using

$$S(E) = S_s F_s(E) + \Sigma S_i F_i(E), \quad (1)$$

where $F_s(E)$ is the fraction of positrons annihilated at the surface and $F_i(E)$ is the fraction annihilated in the i-th layer ($F_s(E) + \Sigma F_i(E) = 1$). S_s and S_i are *S* parameters that correspond to the annihilation of positrons on the surface and in the i-th layer, respectively. The lifetime spectrum of positrons was measured using a pulsed monoenergetic positron beam [17]. Approximately 3×10^6 counts were accumulated. The lifetime spectrum of positrons $S_{LT}(t)$ is given by $S_{LT}(t) = \sum \lambda_i I_i \exp(-\lambda_i t)$, where λ_i and I_i are the annihilation rate and intensity of positrons of the i-th component, respectively. The lifetime of positrons τ_i is given by $1 / \lambda_i$. The observed spectra were analyzed with a time resolution of approximately 260 ps (full-width at half-maximum) using the RESOLUTION computer program [18]. The lifetime spectrum can also be represented in a continuous decay form:

$$S_{LT}(t) = \int_0^\infty \lambda \alpha(\lambda) \exp(-\lambda t) d\lambda, \quad (2)$$

where $\alpha(\lambda)$ is the probability density function (PDF) of the annihilation rate. A numerical Laplace inversion technique for the deconvolution of lifetime spectra of positrons was developed by Gregory [19].

3. Results and discussion

Fig. 1 shows the *S* values as a function of incident positron energy *E* for the PET films coated with $Al_xSi_{1-x}O_y$ layers ($x = 0$, 0.4, and 1). The *S*–*E* relationship for uncoated PET is also shown. For all samples, the measured *S* values saturated at $E \cong 20$ keV, suggesting that almost all positrons implanted with this energy region annihilate in the PET film. For uncoated PET, the *S* value was decreased with decreasing *E* (<1 keV). The formation mechanism of Ps in polymers can be explained by the spur model [20]. This model treats a reaction between a thermal or an epithermal positron and excess electrons created in the terminal positron spur. After a the positron creates a terminal spur both the positron and spur electrons diffuse, while slowing down to near thermal energy, this can result in the formation of Ps in open spaces. The observed behavior of *S*, therefore, can be attributed to the diffusion of positrons toward the surface and the suppression of the Ps formation due to the decrease in spur electrons in low *E* region [9].

For $Al_{0.4}Si_{0.6}O_y$/PET, the *S* values were almost constant at $E = 0.5$–2.5 keV, which can be attributed to the annihilation of positrons in the $Al_{0.4}Si_{0.6}O_y$ layer. The *S* value started to decrease above 2.5 keV, and reached its minimum value at $E = 4$–5 keV. Similar behavior of *S* was observed for other coated samples. Fig. 2 shows the *S*–*E* relationships for the coated samples after the removal of the $Al_xSi_{1-x}O_y$ layers. Mean implantation depth of positrons x_m is shown in the upper horizontal axis, which was calculated by using the relation: $x_m = (A / \rho) E^r$, where $A = 2.75$ μg cm^{-2} keV^{-r}, $r = 1.7$, and ρ is density [7]. The uncoated PET film was characterized before and after the HF treatment, and we confirmed that the HF treatment does not affect the *S* value for PET. As shown in Fig. 2, the *S* values in the subsurface region ($E = 1$–4 keV) were found to be decreased by the deposition of the coating layers. The solid curves are fittings of the diffusion equation for positrons to the experimental data. The obtained results are shown in Fig. 3. For $Al_{0.4}Si_{0.6}O_y$/PET, for example, the region width with small *S* value was 370 nm, and this can be attributed to the modification of PET due to the deposition of the coating layer. The *S*–*E* curves for the coated sample (Fig. 1) can be reasonably fitted using the depth distribution of *S* shown in Fig. 3, and we found that the derived *S* values for the $Al_xSi_{1-x}O_y$ layers were close to those measured at $E = 1$–2 keV.

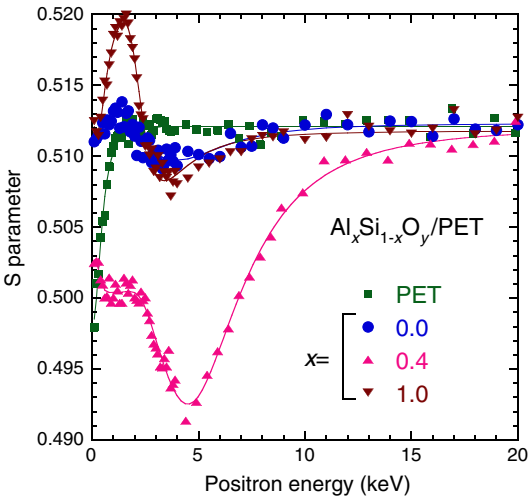

Fig. 1. *S* parameters as a function of incident positron energy *E* for the PET films coated with $Al_xSi_{1-x}O_y$ layers ($x = 0$, 0.4, and 1). Result for the PET film without coating is also shown. The solid curves are fittings of the diffusion equation for positrons to the experimental data. The *S* values at $E < 2$ keV correspond to the annihilation of positrons in the $Al_xSi_{1-x}O_y$ layers.