

# Direct evidence of positron trapping at polar groups in a polymer-blend system

Y. Nagai and T. Nonaka

*The Oarai Branch, Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan*

M. Hasegawa

*The Oarai Branch, Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan  
and Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

Y. Kobayashi and C. L. Wang

*National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan*

W. Zheng and C. Zhang

*Shanghai Institute of Nuclear Research, Chinese Academy of Sciences, Shanghai 201800, China*

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Energy spectra of positron annihilation radiation were measured in polymer blends of polyethylene and ethylene vinyl acetate copolymer (E/VA) by means of the coincidence Doppler broadening technique. Positron annihilation with the core electrons of oxygen was appreciably increased by the addition of small amounts of E/VA to polyethylene and was detected with a sensitivity one order of magnitude higher than would be expected from the number density of the oxygen atoms in the polymer blends. This clearly shows that the positron is sensitively trapped by the polar acetate group of E/VA and demonstrates the usefulness of positrons as a sensitive chemical probe for polar structures in a nonpolar polymer matrix with high positron mobility. [S0163-1829(99)00941-8]

In metals and semiconductors, positrons are sensitively trapped by open-volume-type defects. The trapped positrons annihilate with the surrounding electrons, conveying useful information on the local electronic environment around the defects. The high sensitivity of positrons to open-volume defects is well documented.<sup>1-4</sup>

Recently, it was found that not only such defects but also defect-free nanoparticles embedded in materials can act as trapping centers for positrons, provided that the positron affinity of the particles is higher than that of the host material.<sup>5</sup> Thus the sites that attract positrons are not restricted to defects. One may expect the negatively charged parts of polar groups in molecular substances to act as trapping centers as well.

Positron trapping at polar groups in polymers has been suggested by Kobayashi *et al.*<sup>6</sup> They measured positron mobility in polymer blends of polyethylene and ethylene vinyl acetate copolymer (E/VA) by observing the Doppler shift of the annihilation  $\gamma$  rays as a function of external electric field. The addition of a small amount of E/VA to polyethylene resulted in a drastic reduction in mobility, which strongly suggests that positrons are being captured by the polar acetate group of E/VA.

In this study, we directly confirmed this positron trapping effect by using the coincidence Doppler-broadening (CDB) technique, which has recently been developed to identify the chemical element with which the positron annihilates.<sup>7-12</sup> CDB spectra were measured for the same types of samples used in a previous study:<sup>6</sup> polymer blends of polyethylene and E/VA. Positron annihilation with the core electrons of the oxygen contained in the acetate group of E/VA was detected with a sensitivity one order of magnitude higher than would be expected from the number density of the oxygen in the polymer blends, thus confirming the positron trapping effect.

Polyethylene (low-density polyethylene) and E/VA (random copolymer) were obtained from UBE Industries, Ltd. and Beijing Organic Chemical Factory, respectively. The vinyl acetate content of the E/VA was about 14 wt %. Thus 1/20 of the vinyl group was accompanied by a polar acetate group and the number density of the oxygen atoms in E/VA was about 1.6%. Polyethylene and E/VA were mixed at 130–140 °C with a roller and then pressed into sheets with a thickness of about 2 mm at 140 °C using a liquid press machine. Samples with E/VA concentrations of 0, 3, 6, 15, 36, and 100 wt % were studied. The immiscible nature of the blends over the entire composition range was demonstrated by differential scanning calorimetry (DSC).<sup>6</sup>

CDB spectra were measured using two Ge detectors. The energies of annihilating  $\gamma$ -ray pairs (denoted by  $E_1$  and  $E_2$ ) were simultaneously recorded by the two detectors located at an angle of 180° relative to each other. The difference in energies of the two  $\gamma$  rays  $\Delta E = E_1 - E_2$  is expressed as  $cp_L$  and the total energy  $E_t = E_1 + E_2$  is expressed as  $2m_0c^2 - E_B$  (neglecting the thermal energies and chemical potentials), where  $p_L$  is the longitudinal component of the positron-electron momentum along the direction of the  $\gamma$ -ray emission,  $c$  is the speed of light,  $m_0$  is the electron rest mass, and  $E_B$  is the electron binding energy.<sup>11</sup> Selection of coincidence events that fulfilled the condition  $2m_0c^2 - 2.4 \text{ keV} < E_t < 2m_0c^2 + 2.4 \text{ keV}$  resulted in a significant improvement in the peak to background ratio (by three orders of magnitude) over conventional one-detector measurement, which enabled us to observe element-specific high-momentum positron annihilation with core electrons.

Figure 1 shows CDB spectra of polyethylene and E/VA. In the present measurements the energy resolution of the apparatus was  $\sim 1.1 \text{ keV}$  full width at half maximum (FWHM). The sample-detector distance was 20 cm, which

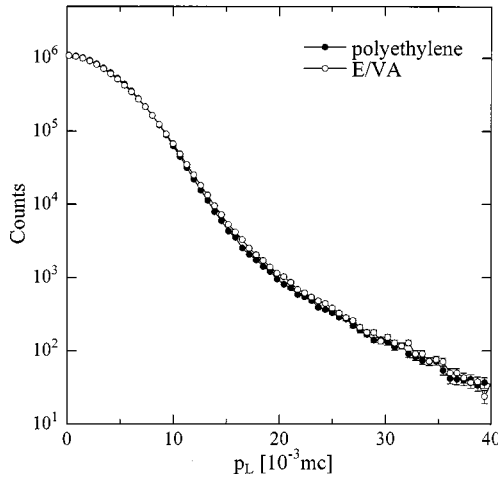


FIG. 1. CDB spectra of polyethylene and E/VA. Each spectrum is normalized to the same total counts.

was long enough to avoid any increase in the background due to  $3\gamma$  annihilation of the triplet state of positronium (Ps), the bound state between a positron and an electron.<sup>13</sup> Each spectrum was normalized to the same total counts. We can see that the momentum density distribution  $N_{EVA}(p_L)$  of E/VA is slightly larger than that of polyethylene  $N_{PE}(p_L)$  in the high-momentum region ( $>15 \times 10^{-3} m_0 c$ ), although the two spectra are similar in shape.

In order to highlight the difference between the two spectra, we obtained the curve  $R_{EVA/PE}(p_L)$  defined as the ratio of the spectrum for E/VA to that of polyethylene:

$$R_{EVA/PE}(p_L) = N_{EVA}(p_L) / N_{PE}(p_L). \quad (1)$$

As is seen from Fig. 2, the ratio curve rapidly increases in the range between 7 and  $16 \times 10^{-3} m_0 c$ , decreases in the region  $16-25 \times 10^{-3} m_0 c$ , and is constant above  $25 \times 10^{-3} m_0 c$  (within the limits of experimental error).

In the high-momentum region, the momentum density distribution  $N_{PE}(p_L)$  of polyethylene is approximately proportional to that of carbon  $N_C(p_L)$ ,

$$N_{PE}(p_L) \propto N_C(p_L), \quad (2)$$

because hydrogen has no core electrons.  $N_{EVA}(p_L)$  is expressed as

$$N_{EVA}(p_L) \propto (1-x)N_C(p_L) + xN_O(p_L), \quad (3)$$

where  $N_O(p_L)$  is the momentum density distribution of oxygen. The parameter  $x$  can be interpreted as the average fraction of oxygen atoms at the site where positron annihilation takes place. Thus the ratio curve becomes

$$R_{EVA/PE}(p_L) \propto (1-x) + xR_{O/C}(p_L), \quad (4)$$

where  $R_{O/C}(p_L) = N_O(p_L) / N_C(p_L)$ . The obvious peak around  $16 \times 10^{-3} m_0 c$  in  $R_{EVA/PE}(p_L)$  suggests a large contribution of positron annihilation with the core electrons of oxygen in E/VA; if there was no oxygen contribution, the ratio curve should have been constant throughout the high-momentum region as would be expected from Eq. (4) when  $x=0$ .

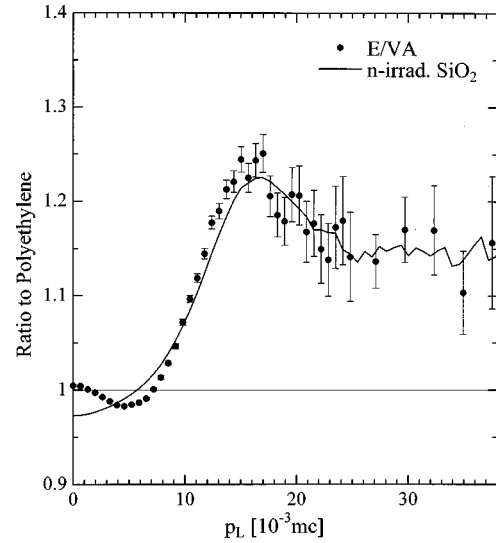


FIG. 2. Ratio curve  $R_{EVA/PE}$  of the CDB spectrum for E/VA relative to polyethylene. The solid line shows the modified ratio curve  $\tilde{R}_{SiO_2/PE}(p_L) = (1-x) + xR_{SiO_2/PE}(p_L)$  with  $x=0.15$  for neutron-irradiated amorphous  $SiO_2$ .

For more quantitative discussion, a suitable reference sample for positron annihilation with oxygen is required. For this purpose, we employed neutron-irradiated ( $\sim 8.3 \times 10^{18}$  n/cm<sup>2</sup>) vitreous silica. Previous studies showed that the angular correlation of the annihilation radiation (ACAR) curves of this sample reflects the momentum distribution of the electrons of oxygen,<sup>14,15</sup> indicating that positrons annihilate with the electrons of oxygen rather than those of silicon. Thus  $N_O(p_L)$  is well approximated by the momentum density distribution of neutron-irradiated silica in the high-momentum region. Figure 3 shows the curve  $R_{SiO_2/PE}(p_L)$  as the ratio of the CDB spectrum for the silica sample to that for polyethylene. The shape of the ratio curve is very similar to that of the E/VA curve in Fig. 2. The solid line in Fig. 2 corresponds to the modified ratio curve  $\tilde{R}_{SiO_2/PE}(p_L) = (1-x) + xR_{SiO_2/PE}(p_L)$  with  $x=0.15$ . It reproduces well the  $R_{EVA/PE}(p_L)$  data, implying that about 15% of the positrons in E/VA annihilate with the electrons of oxygen.

The above results are only possible in the presence of positron and/or Ps trapping at the acetate group, because a rate of  $\sim 15\%$  positron annihilation with oxygen is one order of magnitude higher than the number density ( $\sim 1.6\%$ ) of the oxygen atoms in E/VA. If Ps capture by the acetate group is present, the longest positron lifetime in E/VA should be much shorter than that in polyethylene because of the chemical quenching of the triplet state Ps (ortho-Ps). However, no such shortening of positron lifetime was observed.<sup>6</sup> Thus the Ps reaction in E/VA is excluded, evidencing positron trapping at the acetate group. The trapping seems to be a loose localization of the positron around the acetate group rather than strong binding to the oxygen atom because the fraction of positrons that annihilate with oxygen is  $\sim 15\%$ ; some positrons still annihilate with carbon atoms.

The CDB spectra of the polymer blends of E/VA and polyethylene at E/VA concentrations of 3, 6, 15, 36, wt % were also measured. Here we introduce the  $W$  parameter, which is defined as the ratio of the counts in the high mo-

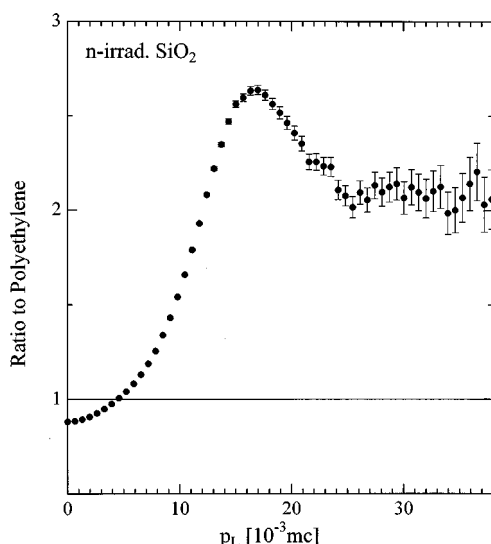


FIG. 3. Ratio curve  $R_{\text{SiO}_2/\text{PE}}$  of the CDB spectrum for neutron-irradiated ( $\sim 3.5 \times 10^{-2}$  dpa) amorphous  $\text{SiO}_2$  relative to polyethylene.

mentum ( $15 \times 10^{-3} m_0 c < |p_L| < 30 \times 10^{-3} m_0 c$ ) region to the total counts contained in the entire region. The  $W$  parameter is a measure of the fraction of positron annihilation with oxygen in this case; a larger contribution of oxygen to the CDB spectrum will result in a larger  $W$  parameter (Fig. 2). Figure 4 shows the  $W$ -parameter as a function of E/VA concentration. The rapid increase in the  $W$  parameter at lower E/VA concentrations shows that positron annihilation with oxygen is sensitively enhanced by the addition of small amounts of E/VA to polyethylene. Obviously the sensitive effect of E/VA is related to the high positron mobility in polyethylene.<sup>6,16</sup>

Since the polymer blends are immiscible, as stated above, the E/VA domain in blends with low concentrations of EVA is dispersed in the polyethylene matrix. In addition, the electric-field dependence of the intensity of the ortho-Ps component in the lifetime spectrum suggests that the average domain size of the E/VA phase is less than the Onsager radius ( $\sim 20$  nm).<sup>6</sup> In the blend sample with 3% E/VA, for example, we can estimate the number density of the E/VA domain to be on the order of  $10^{16} \text{ cm}^{-3}$ ; the enhancement of the  $W$  parameter points to positron confinement in the E/VA domain. Once a positron diffusing in polyethylene phase reaches the E/VA domain, it will find it difficult to escape from the domain because of trapping at the acetate group.

The intensities of ortho-Ps in the lifetime spectra of all measured blends are between 26 and 29%<sup>6</sup> i.e., more than 1/3 of the positrons form Ps before annihilation. As mentioned above, Ps is not captured by the polar acetate group.

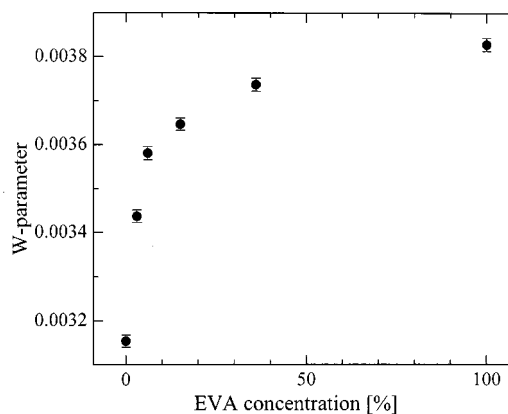


FIG. 4. Dependence of  $W$  parameter on E/VA concentration. The  $W$  parameter is defined as the fraction of the counts in the high momentum ( $15 \times 10^{-3} m_0 c < |p_L| < 30 \times 10^{-3} m_0 c$ ) region relative to the total counts contained in the entire momentum region of the CDB spectrum.

The difference in behavior between Ps and the positron is attributed to the charge neutrality of the Ps atom. Ps prefers large open spaces to a polar group. Thus the contribution of pick-off annihilation of ortho-Ps with the core electrons of oxygen to the high momentum region of the CDB spectrum is thought to be very small; it merely reflects the number density of oxygen atoms in E/VA ( $\sim 1.6\%$ ). Therefore the probability that a free (non-Ps) positron will annihilate with the electrons in oxygen is much larger than 15%.

For many years, Ps has been recognized as a unique probe for nm-size free volume holes in polymers. Meanwhile, little attention has been paid to the process of free positron annihilation in polymers, though it is the major mode of positron annihilation. The present work suggests that free positrons may serve as sensitive chemical probes for polar groups in nonpolar polymers with high positron mobility.

In conclusion, coincidence Doppler broadening of positron annihilation radiation was measured for polymer blends of polyethylene and ethylene vinyl acetate copolymer (E/VA). Positron annihilation with core electrons of oxygen (which is contained only in the acetate group of E/VA) was detected with a sensitivity one order of magnitude higher than would be expected from the number density of the oxygen atoms in the polymer blends. This is clear evidence of positron trapping at the acetate group and suggests that the positron can act as a sensitive chemical probe of polar structures in nonpolar polymers.

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- <sup>15</sup>In Ref. 14, the neutron dose dependence of the ACAR spectra for amorphous SiO<sub>2</sub> is studied in detail. The ACAR curves decompose well into two Gaussian components: a narrow component and a broad component. The former is due to self-annihilation of singlet-state Ps (para Ps) formed in “intrinsic” structural voids, while the latter arises from pick-off annihilation of ortho-Ps and annihilation of free positrons with valence electrons in bulk and defects introduced by neutron irradiation. The FWHM of the broad component is about  $10.6 \times 10^{-3} m_0 c$ , which is much larger than that for divacancies in silicon (about  $8.5 \times 10^{-3} m_0 c$ ). In addition, the FWHM of the broad component is unchanged by irradiation (only its intensity increases with increasing neutron dose). These results strongly suggest that regardless of the neutron irradiation dose, positrons annihilate with electrons of the same character—electrons associated with oxygen atoms.
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