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Abstract

Positron irradiation effects on polypropylene (PP) and polyethylene (PE) have been studied using the positron source for positron annihilation (PA) experiments. From the intensities (I_3) of the long-lived component of *ortho*-positronium (*o*-Ps), it has been shown that the irradiation effect is larger in PP than in PE and that the samples with high crystallinity receive larger effect. The positron irradiation effect was compared with the effect of ^{60}Co γ -rays. The decrease in I_3 in 1 MGy γ -irradiated PP was smaller than that of positron irradiated samples, although the latter dose was estimated to be about two orders of magnitude smaller than the former. By decomposing the *o*-Ps component further into two components, it has been found that most of the decrease is concerned with the longest-lived component, indicating that it is mainly the Ps formed in the amorphous region that is affected by radiation.

1. Introduction

Positron annihilation (PA) is a useful technique to investigate characteristics of materials. However, as reported by Welander and Maurer (1992), PA must be carefully applied to study polymers. As positrons emitted from ^{22}Na induce radiation damage, the intensities (I_3) of the long-lived component of *ortho*-positronium (*o*-Ps) decrease gradually with the measurement time. They showed that the decrease depends on the kind of polymers. A large decrease was observed for polypropylene (PP), and it was attributed to free radicals formed by the positron irradiation.

Reactions with free radicals have been considered as one of the quenching processes of *o*-Ps. Several works were published on PA in polymers containing radiation-induced free radicals (Wang et al., 1986, 1988; Hsu and Hadley, 1971; Kindle, 1984). In these works, it was suggested that the intensity of the long-lived component is reduced and its lifetime is shortened due to the presence of free radicals. On the other hand, Jean and Ach (1978) reported that the γ -ray irradiation effects on the intensities and the lifetimes of *o*-Ps can not always be related to free radicals and suggested that structure change must be considered. The present authors also observed a marked decrease in I_3 in 3 MGy irradiated polyethylene where about 100 μmol of free radicals were accumulated. When the radical concentration was reduced by heat treatment at 373 K, however, there was no change in the I_3 value, indicating that there was not direct correlation with I_3 and the radical concentration at 373 K. (Suzuki et al., 1992).

Thus the radiation effect on intensities and lifetimes of *o*-Ps has been discussed from the points of view of both the radicals and the structure changes.

So far, radiation effects on polymers have been studied by PA without paying much attention to the positron irradiation effect on samples. However, if samples being investigated are affected by positron irradiation, experimental results reported must be carefully analyzed. The irradiation dose by e^+ is especially large in angular correlation experiments, in which intense sources of the order of 3.7×10^8 Bq (ca. 10 mCi) are commonly used.

In this work, the radiation effect from the positron source on polymers is positively considered. First, positron irradiation effects on PP and PE are demonstrated in vacuum and in air at 300K. Further decomposing the *o*-Ps component into two by a 4 component analysis, it is shown that the positron irradiation effect occurs mostly in the amorphous regions. Then the effect of ^{60}Co γ -rays is compared with the effect of positron irradiation.

2. Experiments

The PA experiments were conducted with a conventional fast-fast coincidence system having a time resolution of 270 ps full width at half maximum (FWHM). The time spectrometer was composed of two plastic scintillation detectors (40mm ϕ $\times$ 40mm Pilot-U mounted on a Hamamatsu H1949 photomultiplier), two differential

constant fraction discriminators (ORTEC 583): one for start signals from 1.27 MeV γ -rays and the other one for stop signals from 0.511 MeV annihilation γ -rays, a time-to-amplitude converter (ORTEC 457), and a multichannel analyzer with a 1024 conversion gain (SEIKO 7800). The data taking was controlled by a personal computer (NEC-PC).

Positron source was prepared by depositing ca. 1.1 MBq (30 μ Ci) of aqueous $^{22}\text{NaCl}$ on a Kapton foil of 7 μm thickness and 10x10 mm area. After dried, the foil was covered with the same size of the foil and then the edges were glued with epoxy resins. The source was furthermore sealed in a 3 μm Mylar foil and then sandwiched by two identical samples for PA measurements. The diameter of the spot of ^{22}Na source was ca. 1.5 mm ϕ .

PP and PE slabs of 2mm thickness were cut into pieces of the size 10x20 mm. Two kinds of isotactic PPs: polypropylene normal (PPN,55%) and polypropylene with high crystallinity (PPHC,66%), and three kinds of PEs: high density PE (HDPE,66%), low density PE (LDPE,34%), and ultra-high molecular weight PE (UHMWPE,54%), were employed for PA experiments. The numbers in the parentheses show the crystallinity determined by X-ray measurements. These samples were kindly offered by Mitsui Petrochemical Industries, LTD.

The data taking was started within a minute from the time at which the positron source was placed between two samples. PA spectra were automatically saved every hour and the next run was started. About 2 million events were collected in each spectrum and the measurements were continued for about 70 h. The PAL

spectra were analyzed using POSITRONFIT EXTENDED (Kirkegaard and Eldrup, 1974).

When the samples were kept in a vacuum cell, two counters had to be separated by 20 mm and the counting rate was low. When the samples with ^{22}Na sources were removed from the cell and directly sandwiched by two counters, the separation between the two counters was 5 mm and the counting rate was increased to 7 to 8 million events in 1 h. Thus a PA spectrum with high statistics was obtained and the o-Ps component becomes resolvable into two components.

In order to compare with the effect of γ -ray irradiation, the samples were sealed in glass-tubes under vacuum and irradiated at room temperature at the ^{60}Co γ -ray irradiation facility, Japan Atomic Energy Research Institute (JAERI). The concentration of the radicals induced in the samples was measured by an Electron Spin Resonance spectrometer (ESR, JEOL JES-RE3X).

3. Results

Figure 1 shows the intensities (I_3) and the lifetimes (τ_3) of o-Ps versus the time after the positron source was sandwiched by two identical PE samples. Figure 2 shows the same for PP. The decreases in I_3 (ΔI_3) are summarized in Table 1.

It is seen that I_3 of PP and PE decreases with time, which is consistent with the previous results by Welander and Maurer (1992), and ΔI_3 in air is larger than that in vacuum. Although ΔI_3 of PP was similar to that of HDPE in the previous results,

the ΔI_3 in PP is twice as large as that in PE in our case.

Figure 2 shows that I_3 s of PPN and PPHC decrease clearly with two different rates: the fast decay is observed within 6 h and then slow decay follows. These two decays can be seen even in I_3 of UHMWPE but after the fast decay I_3 becomes almost constant. However for LDPE the decrease was as small as 1%. It is noteworthy that the decreasing rate, $\Delta I_3/h$, of the slow decay component of PP is almost the same as that of HDPE and the large difference between PP and HDPE is due to the decrease in the fast decay component.

The data of Figures 1 and 2 are rearranged in Figure 3 in terms of normalized I_3 : $I_3(t)/I_3(1)$, where $I_3(1)$ is the first data at 1 h. The decrease in I_3 depends on the crystallinity and the kind of polymers. At $t = 1$ h, the I_3 value in vacuum is larger for the samples with lower crystallinity, since LDPE ($I_3=27\%$) > HDPE (20.2%) > UHMWPE (18.0%) for PE and PPN (20.5%) > PPHC (19.4%) for PP. The decrement of I_3 after 60 h is as follows: UHMWPE, HDPE > LDPE for PE and PPHC > PPN for PP. Hence ΔI_3 is larger for the samples with higher crystallinity.

Contrary to I_3 , τ_3 is not much affected by positron irradiation for both PPs and PEs irrespective of whether air was present or not. This suggests that, even if I_3 is affected by free radicals or others produced by positron irradiation, the hole sizes remain unchanged.

Figure 4 (5) shows I_3 and τ_3 of PE (PP) irradiated by ^{60}Co γ -rays. For three PE samples, there was no significant change in τ_3 up to 1 MGy and then it slightly decreased. The decrease in

I_3 within 1 MGy is summarized in Table 1.

4. Discussion

During the spur processes, Ps formation takes place in the positron terminal spur where electron-ion recombination and scavenging and trapping of electron and/or positron are competing (Ito, 1988). Thus the Ps formation process is strongly affected by many factors as free radicals, chemical functional groups, polymer structures, and so on. Okamoto et al. (1993) showed that Ps formation in various polyimides depends on the electron affinity due to the chemical structures. Inhibition of Ps formation was observed in benzene solutions of various molecules (Wild and Ache, 1976), and we also observed that the inhibition effect by carbonyl groups in polyethylenes becomes stronger at low temperatures ~ 100 K (Suzuki et al., 1993). The role of crystallinity is also important in the positron annihilation (Serna et al., 1989) and the decrease in Ps formation due to radiation effect is larger for the samples with high crystallinity as shown in the last chapter.

Positron irradiation effects on PP and PE

In the irradiation of PE in vacuum, main reaction process is considered to be free radical formation and these radicals easily form cross-linkings. Lawton et al. (1958) reported G-values for total hydrogen productions: $G(\text{H}_2)=4.3$. Main chain scissions are

expected to be very small (Keller and Ungar, 1983). Hence for PE main radiation effect is free radical formation and cross-linkings, which are possibly related to the change in I_3 (Fig.1) in vacuum.

For PP, main chain scissions are expected to occur more than cross-linkings: G values of cross-linkings, $G(X)=0.18$, and scissions $G(S)=0.27$ (Quirk and Alsamarraie, 1988). This is believed to be due to the existence of methyl groups, $[-CH_2-C(CH_3)-CH_2-]_n$, that introduce strain into the main chain (Ichi-kawa, 1992). Main-chain scissions for PP are expected to reduce I_3 because the methyl groups ($-CH_3$) located at the end of branches created by scission are subject to the thermal activation of the rotation and have been considered to act as efficient site for inhibition of Ps formation (Levay et al., 1989; Reiter and Kindle, 1990; Zhang and Ito, 1992; Suzuki et al., 1993). Thus we temporarily ascribe the two decay components in PP as follows: the fast decay component is ascribed to formation of the new $-CH_3$ groups and the slow decay component to formation of free radicals.

The difference in the effects in air and in vacuo irradiation may be due to radiation induced oxidation, which forms carbonyl groups in polymers. The carbonyl groups have electron affinity and may reduce Ps formation in polymers (Suzuki et al., 1993).

The constancy of τ_3 even after the sharp decrease in I_3 may be explained as follows. Above glass transition temperature ($T_g \sim 243$ K for PE (Suzuki et al., 1993), $T_g \sim 256$ K for PP (Quirk

and Alsamarraie, 1989)), polymers are rubbery and micro structures in the amorphous region can move easily like liquid. Ps, which seeks and digs holes in the amorphous region, expands the hole size like forming bubbles in liquid, resulting in the almost constant hole sizes, i.e., constant τ_3 . The longer τ_3 of LDPE than HDPE can be explained by larger holes created in the amorphous region of LDPE.

Total dose deposited by positron irradiation and radiation effect

It is necessary to calculate the mass of irradiated part in order to estimate the total dose Joule/kg (=Gy, 1Gy=100Rad) deposited by positron irradiation. A positron mass absorption coefficient, α^+/ρ , is about $3 \text{ m}^2/\text{kg}$ ($30 \text{ cm}^2/\text{g}$) (Paulin, 1983). With $\rho=900 \text{ Kg/m}^3$ (0.9 g/cm^3) for PP, α^+ becomes $2.7/\text{mm}$. The diameter of the ^{22}Na sources was ca. $1.5 \text{ mm}\phi$ and most positrons were deposited in a volume of 0.65 mm^3 (mass $\sim 0.6 \text{ mg}$).

^{22}Na source of 1.1 MBq emits 2.4×10^{11} positrons with average energy of 216 keV during 60 h , which stop in the small volume obtained above and deposit 0.008 Joules . Since 50% of positrons stop in one side of the samples, the total dose deposit is estimated to be ca. 7 kGy .

The radiation effect on PE and PP seems different between positron and γ -ray irradiation (Table 1). Comparing the effect of 1 MGy γ -ray irradiation with that of 60 h positron irradiation ($\sim 7 \text{ kGy}$), the decrease in I_3 was 6.2% (γ -ray) and 2.8% (e^+) for HDPE, and it was 2.6% (γ -ray) and 6.0% (e^+) for PPHC.

Apparently the effects of γ -rays and positrons are reversed for HDPE and PP, suggesting that they can not be compared simply in terms of the absorbed dose and the radiation effect depends strongly on chemical structures of polymers and a kind of radiation. The sharp decrease in I_3 in PP irradiated low dose by positrons seems to indicate that positrons induce radiation effects more effectively than γ -rays. Since it is considered that e^+/e^- have similar interactions in matter with γ -rays, the reversed result can not be explained well. Further experimental work to investigate the radiation effect of e^+/e^- and γ -rays on PP and PE is under consideration.

Effect of free radicals on positronium formation

Free radicals produced in the amorphous regions may disappear quickly by forming cross-linkings. In polymers with high crystallinity, some fraction of the radicals formed in the crystalline region migrate to the crystal-amorphous interface and are considered to form cross-linkings, resulting in the disappearance of free radicals. The rest of the radicals are often trapped in the crystalline regions and live very long.

The concentration of free radicals produced by positron irradiation can be estimated using their G values: $G(R)=2 \sim 4$ for PE and PP (Hill *et al.*, 1989). Assuming $G(R)=3$, the number of free radicals after 60h irradiation is estimated to be 8×10^{14} in our experiment. If the concentration of free radicals accumulated in the sample is proportional to the crystallinity, 5×10^{14}

free radicals may have long lifetimes in the sample with ca. 66% crystallinity. If these radicals are formed uniformly in the small volume obtained above, the distance between two free radicals is estimated to be of the order of 10 nm.

The shape of the crystalline regions is considered to be a rectangular prism (or lamella) with various size in a range of 10 ~ 20 nm (Oka and Yamagata, 1969). In polymers with high crystallinity like HDPE, the linear dimension of amorphous regions between the crystalline regions is estimated to be a few nm. Within the irradiated volume the number of free radicals obtained above seems to be the same order with the number of crystalline regions. Hence most of crystalline regions is possibly occupied by a few radicals.

Positrons after losing their energies during the slowing down process form the terminal spur at the end of the tracks and produce ca. 30 ion-electron pairs inside the spur (or "blob") (Byakov and Stepanov, 1993), whose diameter is estimated to be 7 nm or less for water (Kaplan and Miterev, 1987) and ca. 80 nm for hydrocarbons (Byakov *et al.*, 1983). Hence, in the case of PE and PP, a few hundreds of radicals are considered to overlap with the spur and electrons in the spur have a chance to encounter the radicals, resulting in the suppression of Ps formation. Thus free radicals accumulated in the crystalline regions can be one of the causes of the decrease in I_3 .

In the samples with low crystallinity (LDPE), there are large amorphous regions and most free radicals produced by irradiation below 70 kGy can not live long (Suzuki *et al.*, 1991). The

slight decrease in I_3 , which is ca. 1 % or less within 60 h positron irradiation, is considered to be due to the small number of free radicals accumulated in the crystalline regions.

Four component analysis for PPN in air

Radiation induced cross-linkings have been well studied about polyethylenes. But still it is not well understood where the cross-linkings are formed (Lihua *et al.*, 1990; Luo *et al.*, 1985). Patel and Keller (1975) found that these were developed outside crystalline regions. However Cackovic *et al.* (1974) reported cross-linkings in crystalline regions. Recent work using solid state ^{13}C NMR (O'Donnel and Whittaker, 1992), demonstrates that these reactions occur mainly in the amorphous regions and the crystal-amorphous interfaces.

PA lifetime spectra in PE (Kindle and Reiter, 1987; Reiter and Kindle, 1990; Suzuki *et al.*, 1992) and PP (Uedono *et al.*, 1992) can be resolved into four components. The two short lifetime components, (I_1 and τ_1) and (I_2 and τ_2), are due to self-annihilation of *para*-positronium (*p*-Ps) and free positron annihilation, respectively, with $\tau_1 \sim 125$ ps in vacuum and $\tau_2 \sim 300$ ps. The two long-lived components (I_{3S} , τ_{3S} and I_{3L} , τ_{3L}) are ascribed to the pick-off annihilation of *o*-Ps. The longest-lived component, with $\tau_{3L} \sim 2$ to 3 ns at room temperature, has been assigned to *o*-Ps annihilation in voids or holes in amorphous regions. However the assignment of the shorter one (the second longest-lived component, $I_{3S} \sim 7$ % and $\tau_{3S} \sim 1$ ns) is

still under controversy (Consolati and Cuasso, 1990) and several works have suggested that this may be ascribed to Ps trapped in voids at the crystal-amorphous interface (Balta Calleja *et al.*, 1985; Kindle and Reiter, 1987)

The largest decrease is observed in PPN irradiated in air (Fig.3), while the decrease in I_3 of PE is quite small. Hence, in order to investigate the large decrease for PPN in air, large number of events (ca. 8 million) were collected as described in the experimental section to decompose the spectra into four components without any constraint. The results (Fig.6) show that I_{3L} decreases by 8 % and the decrease in I_{3S} is less than 2 %, while τ_{3L} and τ_{3S} are almost constant. Hence the large decrease in I_{3L} suggests that positron irradiation affects the longest-lived component of *o*-Ps, which is formed in the amorphous region, where main chain scissions are expected to create $-\text{CH}_3$ groups at the end of the branches.

The low sensitivity of I_{3S} to radiation may have something in common with the data obtained by Kindle and Reiter (1987), Reiter and Kindle (1990), Suzuki *et al.* (1992) and Uedono *et al.* (1992), where I_{3S} was reported to remain constant while I_{3L} varied as a function of temperature.

Structure effects on positronium formation

Above 1 MGy, I_3 increased by 1% for LDPE and decreased slightly for HDPE, whereas it was almost constant for UHMWPE. The results listed in Table 1 suggest that the decrease for PE due to ^{60}Co

γ -ray irradiation is larger than that for PP. For PP above 1 MGy, I_3 s of PPHC and PPN increase by 1.8% and 0.6%, respectively, even though the concentration of free radicals increases with dose. If free radicals affect Ps formation, I_3 should decrease. We measured the mechanical strength of irradiated PPN and PPHC by ^{60}Co γ -ray. The elongation at break decreased with increasing γ -ray dose up to 1 MGy and then that of the 3MGy-irradiated samples became larger, which indicates the change in the viscoelastic properties of the samples irradiated large dose above 1 MGy. In such samples, a large number of scissions are expected to occur, resulting in the increase in amorphous regions. Hence, the effect of free radicals on Ps formation seems smaller than that of structure changes.

5. Conclusions

Positron irradiation effects (dose; ca. 7 kGy) on PP and PE have been demonstrated and PPs are shown to receive larger effect on I_3 than PEs. However the effect of γ -ray irradiation (dose; 1 MGy) is larger for PE than that for PP (Table 1), suggesting that radiation effect can not be compared simply in terms of the absorbed dose. The large decrease in I_3 in PP is considered to be due to the degrading-type polymer structure and methyl groups are subject to the thermal activation of rotation at the end of chains created by main chain scissions, resulting in the inhibition of Ps formation.

For PE, the main reaction induced by radiation is considered

to be free radical formation and cross-linkings. Hence the decrease in I_3 is caused mainly by the accumulation of free radicals in the crystalline regions. From the results of positron irradiation experiments, it seems that structure changes formed by cross-linkings in amorphous regions do not affect apparently the Ps formation due to the small dose. If the large dose is applied to samples, scissions may affect Ps formation through the change of viscoelastic properties of polymer structures.

Crystallinity is also an important factor for radiation effect and the samples with high crystallinity receive larger effect. Irradiation conditions were studied and I_3 of samples irradiated in air decreased larger than that in vacuum, which is considered to be caused by the formation of carbonyl groups.

Investigating two long-lived components of o -Ps, most of the decrease was observed in the longest lifetime component (I_{3L} , τ_{3L}) which is related to the Ps annihilation in amorphous regions. This result suggests that Ps formed in the amorphous region is affected by irradiation more than that in the crystal-amorphous interface, where Ps annihilation is considered to be associated with the second longest lived component (I_{3S} , τ_{3S}).

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Figure captions

Figure 1,

Positron irradiation effects on τ_3 and I_3 for three kinds of polyethylenes: high density (HDPE), low density (LDPE) and ultra-high molecular weight (UHMWPE). τ_3 values of HDPE (in air and in vacuum) and UHMWPE are the same. The details of these samples are shown in the experimental section.

Figure 2,

Positron irradiation effects on τ_3 and I_3 for two kinds of isotactic polypropylenes: polypropylene normal (PPN) and polypropylene with high crystallinity (PPHC). The details of these samples are shown in the experimental section.

Figure 3,

Normalized I_3 ($=I_3(t)/I_3(1)$) shown in Figures 1 and 2, where $I_3(1)$ is the value at 1 h.

Figure 4,

^{60}Co γ -ray irradiation effects on τ_3 and I_3 for three kinds of polyethylenes. The abbreviation of samples are shown in the caption of Figure 1.

Figure 5,

^{60}Co γ -ray irradiation effects on τ_3 and I_3 for two kinds of polypropylenes. The abbreviation of samples are shown in the

caption of Figure 2.

Figure 6,

Two long-lived components for polypropylene normal (PPN) taken in air for 24 h. The lifetime spectra were analyzed with four components. The longest-lived component and the second one are represented by subscripts of L (long) and S (short), respectively. The intensity and the lifetime of the longest-lived component are commonly represented by I_4 and τ_4 , respectively.

Table caption

Table 1 Summary of ΔI_3 due to positron irradiation (PI) and γ irradiation (GI)

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and γ irradiation (GI)

	PPN	PPHC	HDPE	LDPE	UHMWPE
PI in 60 h (Vacuo)	-5.7%	-6.0%	-2.8%	-0.8%	-3.0%
PI in 60 h (Air)	-7.8%		-4.0%		
GI of 1MGy (Vacuo)	-3.7%	-2.6%	-6.2%	-4.5%	-5.0%

PI: positron irradiation

GI: γ irradiation

Figure 1, Positron irradiation effects on τ_3 and I_3 for three kinds of polyethylenes: high density (HDPE), low density (LDPE) and ultra-high molecular weight (UHMWPE). τ_3 values of HDPE (in air and in vacuum) and UHMWPE are the same. The details of these samples are shown in the experimental section.

Figure 2, Positron irradiation effects on τ_3 and I_3 for two kinds of isotactic polypropylenes: polypropylene normal (PPN) and polypropylene with high crystallinity (PPHC). The details of these samples are shown in the experimental section.

Figure 3, Normalized I_3 ($=I_3(t)/I_3(1)$) shown in Figures 1 and 2, where $I_3(1)$ is the value at 1 h.

Figure 4,
 ^{60}Co γ -ray irradiation effects on τ_3 and I_3 for three kinds of polyethylenes. The abbreviation of samples are shown in the caption of Figure 1.

Figure 5,
 ^{60}Co γ -ray irradiation effects on τ_3 and I_3 for two kinds of polypropylenes. The abbreviation of samples are shown in the caption of Figure 2.

Figure 6,
Two long-lived components for polypropylene normal (PPN) taken in air for 24 h. The lifetime spectra were analyzed with four components. The longest-lived component and the second one are represented by subscripts of L (long) and S (short), respectively. The intensity and the lifetime of the longest-lived component are commonly represented by I_4 and τ_4 , respectively.