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STRUCTURE DEPENDENCE OF GAMMA-RAY IRRADIATION EFFECTS
ON POLYETHYLENES STUDIED BY POSITRON ANNIHILATION

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ABSTRACT

The radiation effects on five kinds of polyethylenes (PEs) were studied from the viewpoints of mechanical properties, free radicals and positron annihilation. The degradation of the mechanical strength of samples irradiated by ^{60}Co γ -rays was evaluated based on the elongation at break and the tensile strength. Fully stretched PE with a crystallinity larger than 99% was greatly affected by γ -irradiation. In low-density PEs free radicals were detectable only above 70 kGy, and sharply increased above 100 kGy. A detectable number of free radicals was obtained even at 0.1 kGy in PEs having high crystallinity. At around 100 kGy, the increase in the intensity (I_3) of ortho-positronium (o-Ps), seems to be associated with an increase in the mechanical strength. Contrary to the expectation that the o-Ps seeks intermolecular space holes only in amorphous regions, the I_3 obtained in PEs with nearly 100% crystallinity was almost half that of low-density PEs, and τ_3 had similar values. This suggests that even in crystalline regions the o-Ps seeks intermolecular space holes comparable to those in the amorphous regions.

1. INTRODUCTION

Polyethylenes (PEs) are one of the polymers utilized in many fields such as engineering, medical, and agricultural, and even in our daily lives. Many types of PEs have been produced so as to satisfy requirements for such wide-ranging applications. Generally, these PEs have been classified as high-density PE (HDPE, $\rho > \sim 0.94$) and low-density PE (LDPE, $\rho < \sim 0.94$) (Oka and Yamagata, 1969). Additionally, there are also several types of PEs in HDPE and LDPE. They have different molecular weights, polymer structures and crystallinity, on which the characteristics of the PEs depend.

The γ -irradiation of PEs below a few MGy results in mostly free-radicals formation and cross-linkings, which change the characteristics of polymers. In industry, radiation curing through free-radicals reactions or cross-linkings has been employed to increase the mechanical strength of polymers (Handlos, 1979; Patel, 1979; Ueno, 1990, 1993). However, a suitable total dose is quite essential in order to improve the characteristics. Any further increase in the dose results in a degradation of the properties. PE has been employed as electrical insulating materials, which are often used in radiation environments and facilities: e.g., nuclear power plants and accelerator facilities. For the long-term operation of these facilities, it is essential to investigate the radiation effects on the various insulating materials.

Some fraction of the free radicals formed in the crystalline

region can be trapped in polymer chains and can live very long. However, free radicals which move from the crystalline region to the crystalline-amorphous interface, or which are induced in the amorphous region, disappear with a short period by forming cross-linkings. Both the polymer structure and crystallinity influence the lifetimes of the radicals; generally, free radicals in LDPE have shorter lives and are at smaller concentrations than in HDPE (Fujimura *et al.*, 1979). Since PEs have a fundamental polymer structure, radiation-induced free radicals in PE have been studied extensively by ESR (Ranby and Rabek, 1977).

PE is one of the polymers that are frequently studied by positron annihilation (PA). In polymers, positrons with high energy (e.g. e^+ from a ^{22}Na source; average energy of 210 keV) lose energy through interactions with the surrounding media, and finally annihilate with electrons, subsequently emitting annihilation γ -rays. Some fraction of the positrons form positroniums (Ps), which seek intermolecular space holes, and can reside in them until they annihilate by a pick-off process. The typical PA spectra comprise three different lifetime components; the longest lifetime component has been assigned to *ortho*-positronium (*o*-Ps) (τ_3 : 2 ~ 3 ns), the shortest one to the *para*-positronium (*p*-Ps) (τ_1 : ~ 0.125 ns in vacuum), and the intermediate one the self-annihilation of free positrons (τ_2 : 0.3 ~ 0.4 ns). PA is quite sensitive to any intermolecular space holes, and is a useful tool for studying polymer structures (Kindle 1984; Kindle and Reiter, 1987; Balta Calleja *et al.*, 1985; Jean 1990; Zhang and Ito, 1991; Suzuki *et al.*, 1992).

In this study, five kinds of PEs irradiated in a vacuum by ^{60}Co γ -rays were used to investigate radiation effects. Radiation-induced free radicals and their mechanical strength were measured. PA was applied to these samples. Based on the viewpoints of intermolecular space holes, the radiation effects on the mechanical strength and free radicals have been discussed. The radiation and crystallinity effects on Ps formation were also studied.

2. EXPERIMENTAL

The samples used in this study were commercially available PEs produced by Mitsui Petrochemical Industries, LTD, and kindly supplied by that company along with certified data. Four kinds of PEs (a high-density PE called Hi-Zex; HZ, a linear low-density PE; LLDPE, a branched low-density PE; BLDPE and an ultra-high molecular-weight PE; UHMWPE) were supplied in the form of 2 or 1 mm thick slabs. The details of characteristics are listed in Table 1. These slabs were cut into the standard mini-dumbbell shape (as described by the Japanese Industrial Standard (JIS) (Fig.1)) for testing the mechanical strength. For PA experiments, 10×20 mm samples were used. A super polyethylene fiber called TEKMIROn, a UHMWPE with nearly 100% crystallinity, can be supplied only as a fiber. For measuring the mechanical strength, a bundle of 10 fibers was used; for a PA experiment, cloths made of the fibers were folded to obtain sufficient thickness ($\sim 0.5 \text{ g/cm}^2$) to stop the positrons from ^{22}Na .

In order to measure the tensile strength and elongation at a break, a material testing machine (INTESCO, model 2005) was employed. The drawing speed was 100 mm/min for fibers and 5 mm/min for mini-dumbbells. The separation of chucks of the testing machine was 100 mm for the former samples and 40 mm for the latter. The number of test samples for each PE was varied between 5 and 10, depending on the difficulty in taking consistent data. For LLDPE, BLDPE, UHMWPE, and TEKMIROn, the measurement errors of these mechanical properties were around 10%. However, for HZ the error was as large as 50%, due to its brittleness.

A positron annihilation lifetime (PAL) technique was employed to study the intermolecular space holes of irradiated and unirradiated PEs. The details concerning the experimental method and the analysis of PAL have been given elsewhere (Suzuki *et al.*, 1988).

Radiation-induced free radicals in irradiated PEs were measured using an ESR spectrometer (JEOL JES-RE3X). Samples weighing 20 ~ 30 mg were cut from the same materials used for PAL.

All PE samples were sealed in glass containers in vacuum for γ -ray irradiation at the Japan Atomic Energy Research Institute (JAERI). The irradiation was performed at room temperature for ten different total doses, ranging from 0.1 kGy to 3 MGy. Four days after the irradiation, PE samples were removed from the containers by breaking the vacuum into a vacuum storage. PAL measurements were continued almost for one week after breaking the vacuum, while other samples were kept in the vacuum storage.

ESR measurements were completed in a few hours after the breaking of vacuum. Although free radicals induced in PE samples decayed insignificantly in vacuum, some of them decayed in short period, when they were exposed in air (see Fig.5). Hence it is important to keep samples in vacuum till the measurement to study the effect of free radicals.

3. RESULTS

3.1 Mechanical Strength

The degradation of the mechanical strength of five kinds of PEs is shown in Figures 2 and 3. Figure 2 shows that, for unirradiated samples, TEKMI-IRON is ca. 30-times stronger than UHMWPE and ca. 100-times stronger than BLDPE, LLDPE and HZ. This result is expected based on the TEKMI-IRON polymer structure, since TEKMI-IRON has nearly 100% crystallinity, and the polymer chains are ordered along the axis. The theoretical shear strength expected for the polyethylene molecule is $1.3 \times 10^5 \text{ kg/cm}^2$ (Oka and Yamagata, 1969). Unirradiated TEKMI-IRON shows almost 15% of the theoretical strength. The ratio of the mechanical strength of unirradiated samples to the strength at 3 MGy was calculated for HZ, LLDPE, UHMWPE, BLDPE and TEKMI-IRON as follows: 0.5, 1.6, 1.9, 0.6, and 11, respectively. Hence, the largest decrease in the strength due to radiation was observed in TEKMI-IRON.

For TEKMI-IRON, although no significant change was observed up to 10 kGy, the strength decreased along with the dose between 10

and 70 kGy, which may have been due to radiation-induced chain scissions. A recovery of the mechanical strength at around 100 kGy suggests an increase in the cross-linkings, which would compensate for any loss due to scissions. Above 100 kGy, compared with other PEs, the weakening of the strength was significant for TEKMI-IRON, since it has few branches and any chain scission results in a significant loss of strength of the polymer chains. Above 1 MGy, the strength tended to increase for HZ and BLDPE, and to decrease for linear PEs such as LLDPE, UHMWPE, and TEKMI-IRON.

Figure 3 shows the elongation at a break versus the dose. For five PEs, no change in the elongation was observed up to 10 kGy. For TEKMI-IRON, BLDPE and HZ, it decreased along with the dose between 10 and 70 kGy, and recovered at around 100 kGy; for UHMWPE and LLDPE, however, the elongation was almost constant up to 100 kGy. The decrease in the elongation was significant above 100 kGy for five PEs. The ratio of the elongation of unirradiated samples to the elongation at 3 MGy was 25, 17, 13, 5, and 3.5 for HZ, LLDPE, UHMWPE, BLDPE and TEKMI-IRON, respectively. Hence, HZ shows the largest decrease in elongation, which explains its brittleness after 3 MGy irradiation.

The increase in the mechanical strength, the elongation around 100 kGy and the decrease above the dose are considered to be due to the change in the viscoelastic properties induced by cross-linkings and scissions.

3.2 Radiation-Induced Free Radicals

The relative intensities of free radicals in PEs are shown in Figure 4 as a function of the irradiation dose. Normally, two types of free radicals (alkyl and allyl radicals) with different lifetimes, are induced in PEs below ca. 10 MGy. Alkyl radicals decay within 1 day, even at 77K, and also convert to allyl radicals by encountering double bonds (Ranby and Rabek, 1977). On the other hand, allyl radicals trapped in crystalline regions have a lifetime of several months. Since the irradiation was conducted at room temperature, most of the radicals induced by irradiation were considered to be of the allyl type. The lifetimes of free radicals also depend on the form or shape of the materials and the environment (Ranby and Rabek, 1977). When samples with free radicals are stored in a vacuum, the radicals have quite long lifetimes. We found that radicals induced in TEKMIRON had quite shorter lifetimes (about a week) than that of UHMWPE (several months) when they were kept in air at room temperature (Fig.5). This is considered to be due to the shape of the materials; TEKMIRON fiber has a large surface area, which can be exposed to air compared with UHMWPE slabs.

In our low-density PEs (BLDPE and LLDPE), the free radicals were detectable above 30 kGy irradiation, which is the detection limit by a regular ESR measurement. However, in TEKMIRON with high crystallinity, the radicals were observed even at 0.1 kGy irradiation. These findings indicate that detectable free radicals strongly depend on such polymer structures as crystallinity.

Also, the radicals in TEKMIRON show a linear relation to the dose up to 300 kGy. For UHMWPE, detectable free radicals were induced above 1 kGy; these increased almost linearly with dose up to 300 kGy. Above 300 kGy, free-radicals formation in TEKMIRON and UHMWPE showed a slight deviation from a linear relationship.

The linear relation between the free radicals and dose might be useful for estimating the radiation dose based on the concentration of free radicals. When a radiation dose of 90 ± 10 kGy was applied to HZ and UHMWPE by an electron beam, the equivalent γ -ray dose was obtained as 120 and 80 kGy with about a 10% error, respectively. Good agreement was achieved and the usefulness may be improved by encapsulating the samples in a vacuum.

3.3 Positron Annihilation in γ -ray Irradiated Polyethylenes

Although the PAL spectra in PE can be analyzed with four lifetime components, which require more than 4 ~ 5 million events for a reliable analysis, the spectra were analyzed by three components in this experiment because of insufficient statistics. Figures 6 and 7 show τ_3 and I_3 of the o-Ps as a function of the dose, respectively. The results for PA in unirradiated samples versus the crystallinity are also shown in Figure 8.

τ_3 of LLDPE and BLDPE with low crystallinity were almost constant up to 3 MGy, whereas τ_3 of HZ, UHMWPE and TEKMIRON with high crystallinity decreased above 1 MGy. The lifetimes are often considered to be related to the size of the intermolecular space holes in which Ps are trapped until they annihilate.

Hence, the findings concerning τ_3 for PEs with low crystallinity suggest that the size of the holes do not significantly change up to 3 MGy. It is expected that PEs irradiated larger dose than 1 MGy undergo structure changes due to scissions, radiation induced double bonds and highly developed cross-linkings, resulting in the brittle materials. These structure changes seem to be significant for PEs with high crystallinities and reduce the size of holes located in the amorphous regions, which is observed as the decrease in τ_3 .

Figure 7 shows I_3 of o-Ps formed in five samples. The I_3 were almost equal for BLDPE and LLDPE, and were larger than those of HZ, TEKMIRON and UHMWPE. This is considered to be due to the polymer structures of the low-density polyethylenes with less crystalline regions. I_3 for all samples increased at around 100 kGy, then decreased above this dose and increased at slightly above 1 MGy, except for HZ.

4. DISCUSSION

Ps formation is affected by many factors: the chemical structures, polymer structures, crystallinity, free radicals, thermal motion, etc. (Ito, 1988). Once a Ps is formed, the o-Ps seeks intermolecular space holes formed in amorphous regions and crystal-amorphous interfaces (Balta calleja *et al.*, 1985, Conso-lati and Quasso, 1990). Hence, I_3 has been expected to be very small in PEs with 100% crystallinity. However, contrary to our expectation, I_3 in TEKMIRON with a crystallinity greater than 99%

was ca. 12%, which is half of the I_3 of low-density PEs; τ_3 is ca. 2.12 ns (Fig. 8), which is similar to its value in amorphous regions. This suggests that the Ps is formed and trapped even in crystalline regions. Tao (1972) has shown that τ_3 is related to the spherical hole radius (R) as $\tau_3 = 0.5 \times [1 - (R - \Delta R)/R + 1/(2\pi) \times \sin\{2\pi \times (R - \Delta R)/R\}]^{-1}$ where ΔR is the thickness of the electron layer; $\Delta R = 0.166$ nm was assigned to fit experimental values (Nakanishi and Jean, 1988). From this equation, the diameter of the hole obtained above is expected to be 0.6 nm. Since, in the crystalline regions the distance between C atoms is 0.3 ~ 0.5 nm and, considering the H atoms, the linear dimension of the space is on the order of 0.1 ~ 0.3 nm (Oka and Yamagata, 1969), it seems that there is not sufficient space for spherical holes with a diameter of 0.6 nm. This result suggests several possibilities: (1) even in the crystalline regions, many defects or intermolecular space holes with similar sizes to those in the amorphous regions may be created among the disordered parts or between ends of main chains, resulting from a C-C main chain scissions; (2) after Ps seeks intermolecular space holes in the crystalline regions, it enlarges the size; and (3) although the area of the amorphous regions is negligibly small in PEs with a crystallinity higher than 99%, there are a large number of gaps of the non-crystalline parts between the crystalline regions or crystalline lamellar, and, thus, it may be possible that the Ps are efficiently trapped in these gaps.

The reactions of the Ps with free radicals are listed as one

of the inhibition and quenching processes. Hence, for HZ, UHMWPE and TEKMIRON the gradual decrease in I_3 with increasing dose up to 70 kGy (Fig.7) is considered to be caused by free radicals. The application of radiation cross-linkings in industries has been conducted in the dose range between 100 and 300 kGy, suggesting that cross-linkings are effectively induced by irradiation at around 100 kGy (Oka and Yamagata, 1969; Patel, 1979; Ueno, 1990,1993). Our experimental result, that free radicals increase sharply at around 100 kGy, which is associated with an increase in the cross-linkings, is consistent with applications at industries. These cross-linkings seem to have a close connection with the increase in both I_3 and the mechanical strength (or viscoelastic properties). Hence, any structure changes through cross-linkings at around 100 kGy may have a greater effect on I_3 than free radicals.

A sharp decrease of 3% in I_3 at around 30 kGy was observed for LLDPE and BLDPE, although radiation-induced free radicals were marginally detectable. The elongation of BLDPE was nearly constant up to 30kGy, and at 100kGy increased to twice as large as the value at around 30 kGy, indicating that low-density PEs with a large fraction of the amorphous part are easily subject to cross-linkings by irradiation; the viscoelastic properties then undergo a change. This change seems to be prominent for the branched-type LDPE. In this case, Ps formation (or I_3) in PE is considered to be affected by two factors: free radicals and the change of the polymer structures induced by cross-linkings. Considering the increase in I_3 at around 100 kGy, it seems that

structure changes induced by an irradiation dose of less than about 100 kGy contribute to the increase in I_3 , which may be due to the development of network structures. Hence, the decrease at between 30 and 70 kGy is suspected to be mainly due to free radicals; the structure changes may have a smaller effect on I_3 than the free radicals in the dose range. The intensities of free radicals is marginally detectable on the order of $5 \times 10^{-3} \mu\text{M}/\text{cm}^3$, and the separation between free radicals is estimated to be within ca. 50 nm, assuming a uniform distribution. Since the terminal spur created by e^+ at the end of the track is considered to have a diameter of ca. 80 nm (Byakov et al., 1983), several free radicals may have a chance to be contained in the spur, resulting in a reduction of Ps formation.

I_3 and τ_3 versus the crystallinity for unirradiated PEs are summarized in Figure 8. Although these values are expected to decrease linearly with increasing the crystallinities (Serna et al., 1989), UHMWPE shows the deviation from the linearity. UHMWPE has a linear structure with molecular weights (MW) of ca. 4 millions, while other PEs: LLDPE, BLDPE, and HZ, have MW less than 0.1 millions (Table 1). In order to achieve the high MW, the linear main chains of UHMWPE are tightly packed so as to reduce the intermolecular space holes in the amorphous regions. Hence I_3 and τ_3 of UHMWPE are considered to be reduced due to the packing structures and became smaller than the values of HZ which has a higher crystallinity than UHMWPE. This indicates that molecular structures which are formed to attain the large MW affect I_3 and τ_3 . Also the tightly packed structure of the

amorphous regions seems to affect the variation of I_3 versus γ -ray dose (Fig.7) and the increase in I_3 around 100 kGy became smaller than that of other PEs.

5. CONCLUSION

The radiation effects on five kinds of PEs were studied from the viewpoints of the mechanical strength, positron annihilation and radiation-induced free radicals. PEs are easily affected by radiation, resulting in cross-linkings and scissions. To investigate the effects of these microscopic changes in polymer structures on the macroscopic properties, intermolecular space holes probed by the PAL technique and free radicals by ESR were measured. Our findings show that the microscopic characteristics have a relation to the macroscopic features of the mechanical properties.

It was also found that mechanical properties recovered at around 100 kGy for most PEs. At this radiation level, the free-radicals concentration also drastically increases in low-density polyethylenes; the intensity of o-Ps (the number of intermolecular space holes) also increases. Our results are consistent with the application of radiation cross-linkings in industries, where irradiation doses of between 100 and 300 kGy are employed.

Although Ps formation is expected to be very small in PEs with 100% crystallinity, I_3 in TEKMIRON with a crystallinity greater than 99% is ca. 12% and τ_3 is ca. 2.12ns, which indicate the possibility of that Ps is formed even in crystalline

regions and many intermolecular space holes with sizes comparable to the holes located in the amorphous regions may exist also among C-C main chains in the crystalline regions.

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Table and Figure Captions

Table 1,

Characteristics of five kinds of polyethylenes

Figure 1,

Mini-dumbbell shape of samples for mechanical tests, which was determined by the Japanese Industrial Standard (JIS).

Figure 2,

Mechanical (tensile) strength in kg/cm^2 at the break versus total dose. The symbols are explained in the abbreviation of Table 1.

Figure 3,

Elongation at a break versus the total dose. The symbols are explained in the abbreviation of Table 1.

Figure 4,

Relative intensities of radiation-induced free radicals measured by ESR. The symbols are explained in the abbreviation of Table 1.

Figure 5,

Decay of radiation-induced free radicals after γ -ray irradiated polyethylenes were exposed in air. Intensities are normalized to the first measurements. The symbols are explained in the abbreviation of Table 1.

Figure 6,

Lifetimes (τ_3) of the longest-lived component of the positronium. The symbols are explained in the abbreviation of Table 1.

Figure 7,

Intensities (I_3) of the longest-lived component of the positronium. The symbols are explained in the abbreviation of Table 1.

Figure 8,

τ_3 and I_3 versus crystallinity.

The symbols are explained in the abbreviation of Table 1.

Table 1, Characteristics of five kinds of polyethylenes

	HZ	UHM	LLD	BLD	TEK
Density(g/cm ³) ^a	0.968	0.935	0.920	0.927	0.96
Melting point(°C) ^a	134	136	120	114	148
Crystallinity ^b	0.66	0.54	0.34	0.43	>0.99
Molecular weight	$\sim 6 \times 10^4$	$\sim 4 \times 10^6$	$\sim 5 \times 10^4$	$\sim 8 \times 10^4$	$(7 \sim 8) \times 10^5$
Polymer structure: type branches (-CH ₃ /100C) ^c	linear a few, 1.5	linear few, <<1.0	linear many, 2.8	branched many, 3.5	linear few, <<1.0
Sample form supplied size (mm ³) and diameter	plate 10x20x2 ^d	plate 10x20x1 ^d	plate 10x20x2 ^d	plate 10x20x2 ^d	fiber 38 μ m ^e

a Quoted from production catalogues of each samples, Mitsui Petrochemical Ind. Ltd.

b Crystallinities were determined by X-ray measurements.

c The number of methyl branches per 100 C are estimated using a graph of melting temperatures versus branches (Oka and Yamagata, 1969; Richardson et al., 1963).

d These sizes were used for positron annihilation experiments.

e TEKMIROn is supplied only as a fiber and the diameter is listed in the catalogues.

Abbreviation

HZ - Hi-Zex, High density polyethylene (HDPE)

UHM - Ultra-high molecular weight polyethylene (UHMWPE)

LLD - Linear low density polyethylene (LLDPE)

BLD - Branched low density polyethylene (BLDPE)

TEK - TEKMIROn, A super PE fiber; one of UHMWPE and ideally stretched PE

Figure 2,
Mechanical (tensile) strength in kg/cm² at the break versus total
dose. The symbols are explained in the abbreviation of Table 1.

- A : Total length ----- 60 F : Radius ----- 12 ± 1
 B : Width ----- 12 ± 1 G : Length of testing part ----- 12 ± 0.5
 C : Length of parallel part ----- 16 ± 1 H : Length between holder ----- 40 ± 2
 D : Width of parallel part ----- 3 ± 0.2 I : Thickness ----- 1 ~ 3
 E : Radius ----- 7 ± 0.5

unit : mm

Figure 1,
Mini-dumbbell shape of samples for mechanical tests, which was
determined by the Japanese Industrial Standard (JIS).

Figure 4, intensities of radiation-induced free radicals measured by ESR. The symbols are explained in the abbreviation of Table 1.

Figure 3, Elongation at a break versus the total dose. The symbols are explained in the abbreviation of Table 1.

Figure 6, Lifetimes (τ_3) of the longest-lived component of the positronium. The symbols are explained in the abbreviation of Table 1.

Figure 5, radiation-induced free radicals after γ -ray irradiated polyethylenes were exposed in air. Intensities are normalized to the first measurements. The symbols are explained in the abbreviation of Table 1.

Figure 8, τ_3 versus crystallinity. τ_3 and I_3 are explained in the abbreviation of Table 1.

Figure 7, I_3 of the longest-lived component of the positronium. The symbols are explained in the abbreviation of Table 1.