

Durability of Radiation-Sterilized Polymers III. Oxidation Layer Determined by Chemiluminescence

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Synopsis

Chemiluminescence (CL) analysis was used for determining the oxidation layer formed by the irradiation of polypropylene for medical supplies. The depth of the oxidation layer from the surface depended on dose rate and increased with decreasing dose rate. The oxidation occurred remarkably at a region near the surface area of the film where the diffusion of oxygen is more sufficient. On the contrary, there was very little oxidation in the interior portion. The oxidation layers of polypropylene samples irradiated with electron beam showed U-shaped profiles in the cross-section of film as did as a sample irradiated with γ -rays. However, the degree of oxidation by irradiation with electron beam was very small; CL intensity at the surface area was only one-third that for the γ -irradiated samples.

INTRODUCTION

Recently, γ -ray irradiation sterilization has been used widely for disposable medical supplies. However, there is a problem that plastic medical supplies degrade during irradiation (sterilization) and storage because of residual radicals left after irradiation.

In previous papers,^{1,2} it was reported that polypropylene and polymethylpentene irradiated with electron beam were more stable than those irradiated with γ -rays and that the chemiluminescence analyzer is useful for identification of degradation in irradiated polymers. It is well known that polypropylene irradiated in air is degraded by oxidation.^{3,4} Therefore, estimation of the oxidative layer in irradiated polymer is important to clarify the mechanism of degradation. The depth of the oxidative layer in γ -irradiated polyethylene and ethylene-propylene copolymer (EPR) were estimated by measurement of gel fraction and oxygen consumption during irradiation by Seguchi et al.⁵ Furthermore, the oxidation layer was determined by measuring density and penetration in relative hardness of cross-section in the irradiated EPR.⁶

In this study, the oxidative layer of the γ -rays and electron beam-irradiated polypropylene was determined by the chemiluminescence method.

EXPERIMENTAL

Materials

A commercial-grade copolypropylene containing 6% ethylene units was used for measurement of the oxidation layer without removal of antioxidant. In order to prepare the film of various thicknesses, polypropylene chips were pressed under a pressure of 150 kg/cm² for 5 min at 180°C using spacers of various thicknesses after preheating for 5 min. Then, the sample was maintained under a pressure of 50 kg/cm² at room temperature for cooling. Dumbbell test pieces 2 mm thick were prepared for the tensile strength test by extrusion.

Irradiation and Measurement of Elongation at Break

Irradiation of samples and measurement of elongation at break of the irradiated polypropylene were the same as described in the previous paper.¹

Measurement of Oxidative Layer

The chemiluminescence (CL) of irradiated samples (3 × 3 cm) was observed by using the CL analyzer (OX-7) of Tohoku Denshi Sangyo Co. Ltd. The gate time for CL measurement was 10 s, and the CL intensity was normalized as counts per second.

The oxidative layer was determined as follows. First, CL counts from a 1 mm thick of polymer film were measured. Then, CL counts were measured after scraping away 50 μm of surface layer from both sides of the sample. The decrease in CL counts emitted in 50 μm thickness by scraping was plotted as a function of thickness. The CL measurement was carried out at 80°C within 24 h to prevent decay of CL after irradiation.

Measurement of Diffusion Coefficient and Solubility Constant of Oxygen in the Film

The diffusion coefficient D and solubility constant S were determined by measuring the desorption rate of oxygen in the film under normal pressure, after saturating oxygen in the film under a pressure of 10 kg/cm² using an autoclave according to the method of Seguchi and Arakawa.⁷

RESULTS AND DISCUSSION

Oxidative Layer of γ -Irradiated Polypropylene

A few papers on the mechanism of CL in oxidation have been published.^{8,9} The CL is emitted when excited ketone formed in the recombination of peroxy radical (ROO[•]) in organic compounds converts to ketones of the ground state.

As described in the previous paper,¹ CL of irradiated polymer was measured in the range from 25 to 100°C, and its intensity increased with increasing temperature of measurement because the mobility of polymer segments become active. The apparent activation energy of the CL for ir-

radiated polypropylene was 13.6 kcal/mol. For estimation of the oxidative layer, the CL value was determined at 80°C.

Shard and Rusell¹⁰ reported that CL emitted on the surface of the polymer is observed in the oxidized form at a higher temperature, 150°C. In order to confirm penetration of CL emitted within the irradiated polymer, CL was measured after covering the irradiated polypropylene with an unirradiated polypropylene sheet of various thicknesses. The results are shown in Figure 1. The CL counts are almost same as those without cover. The CL is observed even through the covered film, which is as thick as 3 mm. This indicates that CL can penetrate the polypropylene sheet, as shown in Figure 1. Thus, it was concluded that CL emitted from the irradiated polypropylene of 1 mm thickness could be detected. Figure 2 shows the effect of dose on CL counts. The CL intensity increases clearly up to 150 μm and become constant at thicknesses greater than 200 μm in any dose. The effect of dose rate on CL intensity of samples of various thicknesses is shown in Figure 3. It can be seen that a inflection point appears clearly at any dose rate and that the thickness at inflection points varies with dose rate. If oxidation of a sample during irradiation proceeds homogeneously, CL intensity should increase with increasing thickness of polymer films. However, since such a phenomenon is not recognized, it should be concluded that the degree of oxidation is less in the deeper regions than the inflection point. It is well known that oxidation of polymers proceeds from the outer area to the inner, because oxygen diffuses from the surface of the polymer into the inner part.⁵ Thus, it is ascertained that the inflection point shows the depth of the oxidative layer from the surface of the polymer and that the polymer at the interior portion is hardly oxidized. The depth of the oxidation layer is approximately 150 μm at 1×10^6 rad/h, 250 μm at 2×10^5 rad/h, and 350 μm at 5×10^4 rad/h. Thus, the depth of the oxidative layer varies with dose rate. Since the oxidation occurs mainly from both sides (surface) of the polymer film, the depth of the oxidative layer from one side is half of the inflection point. The profiles of the oxidative layer for a film of 1 mm thickness irradiated at 2×10^5 rad/h and 1×10^6 rad/h are shown in Figure 4. From these results, it is evident that oxidation occurs more easily around the surface than inside polymer film. The oxi-

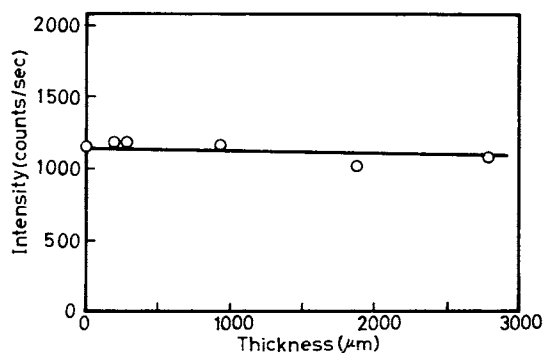


Fig. 1. Relation between the CL intensity and thickness of the covered film. Dose rate, 1×10^6 rad/h; total dose, 3 Mrad.

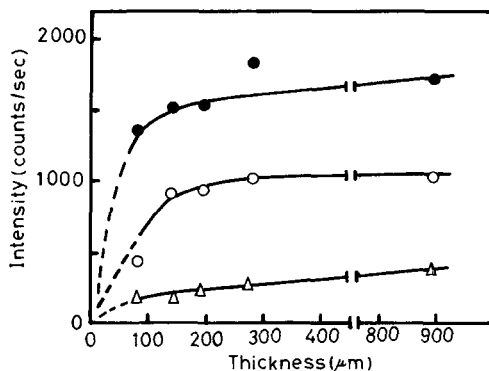


Fig. 2. Effect of dose on CL of γ -irradiated polypropylene: (Δ) 1 Mrad, (\circ) 3 Mrad, (\bullet) 5 Mrad.

dation of the polymer occurs mainly around the surface at a higher dose rate of 1×10^6 rad/h, and it proceeds even deeper from the surface for a lower dose rate, such as 2×10^5 rad/h. The depth of the oxidative layer estimated from the profile shown in Figure 4 is $200 \mu\text{m}$ at 1×10^6 rad/h and $300 \mu\text{m}$ at 2×10^5 rad/h. These values are slightly larger than the inflection points in Figure 3. This might be due to that one unit of scraped layer ($50 \mu\text{m}$) from the surface by which the oxidative layer is estimated is a slightly large. As shown in Figures 3 and 4, the oxidized layer of irradiated polymer increased with decreasing dose rate. This is attributed to the presence of enough oxygen (air) during irradiation to diffuse gradually to the interior of the polymer film, because irradiation times become longer with decreasing dose rates for a given dose. The degree of oxidation of the interior portion (around the center) of the film is very small compared with

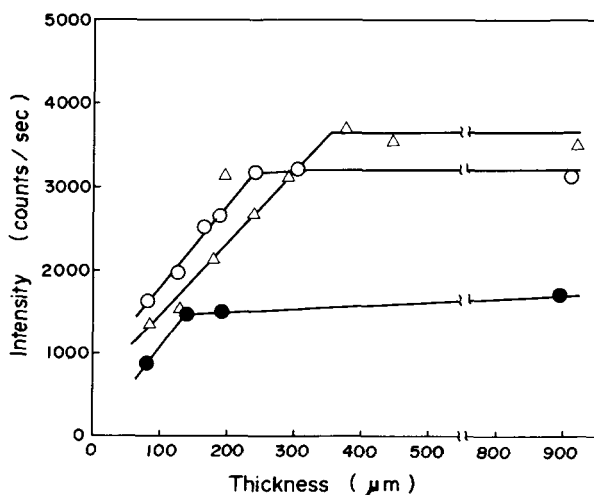


Fig. 3. Effect of dose rate on CL of γ -irradiated polypropylene. (\bullet) 1×10^6 rad/h, (\circ) 2×10^5 rad/h, (Δ) 5×10^4 rad/h. Total dose, 5 Mrad.

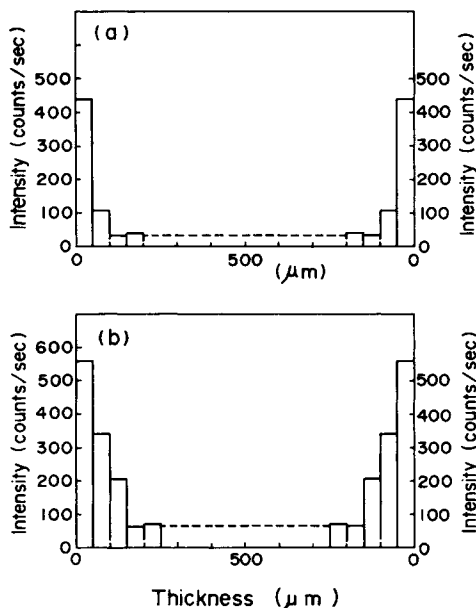


Fig. 4. Profile of the oxidative layer of the γ -irradiated polypropylene. (a) 1×10^6 rad/h, (b) 2×10^5 rad/h. Total dose, 5 Mrad.

that in the outer region. This may reflect that oxidation in the center area is caused only by oxygen already solubilized, owing to the slow diffusion of oxygen from the outer to the inner areas.

The radiation-induced oxidation of polyethylene and EPR has been studied in relation to cable insulation used at the radiation field of a nuclear reactor.⁵⁻⁷ Seguchi et al.⁵ demonstrated that the depth of the oxidative layer, which was estimated by measuring the gel fraction of the irradiated film, corresponded well with the oxygen penetration range calculated from eq. (1):

$$L = \left(\frac{\psi I}{2 D S P} \right)^{1/2} \quad (1)$$

where L (cm) is the oxidative layer of one side in the irradiated film, I (rad/s) the dose rate, S (mol/g-atm) the solubility constant of oxygen, P (atm) the oxygen pressure on the film, D (cm^2/s) the diffusion coefficient of oxygen in the film, and ψ (mol/g-rad) the oxygen consumption during irradiation. The oxidative layers of γ -irradiated polyethylene samples were 400 μm for 3×10^5 rad/h and 250 μm for 1×10^6 rad/h.⁷ The oxidative layers of the polypropylene are estimated from Figure 3 as 125 μm for 2×10^5 rad/h and 75 μm for 1×10^6 rad/h. These values are about one-third of those of polyethylene. This is due to a large difference in the diffusion coefficient D between the polyethylene and polypropylene. That is, D is 6.5×10^{-8} cm^2/s for polypropylene and 5.6×10^{-7} cm^2/s for

polyethylene, with S (3.7×10^{-6} mol/g-atm) of the former not largely different from the latter (2.2×10^{-6} mol/g-atm). Since D of polypropylene is about one-ninth that of polyethylene, the oxidative layer of the polypropylene would be roughly one-third that of polyethylene, according to eq. (1). The oxidized layers of EPR sheet irradiated at doses as high as 175 and 297 Mrad was measured with two methods, density and penetration in relative hardness changes in the cross-section.⁶ The results showed a U-shaped profile as in the case determined by CL analysis. The depth of the oxidative layer was 500–600 μm for 6.7×10^5 rad/h. This value is approximately five times that of the oxidative layer obtained in the present study (polypropylene). Since the D of ethylene-propylene copolymer (1.6×10^{-6} cm/s) is about 25 times that of polypropylene, the ratio of the oxidative layer of the EPR with polypropylene observed by CL analysis agrees almost exactly with that estimated from D using eq. (1).

From these data, it was ascertained that the oxidative layer depends largely on the D of oxygen and that the depth of the oxidative layer decreases with decreasing D . The oxidative layers vary with polymers and decrease in the order polypropylene < polyethylene < ethylene-propylene copolymer.

Effect of Oxidation on Elongation at Break

As described in the previous section, oxidation of the polymer depended largely on the dose rate and the polymer is oxidized more easily at lower dose rates. Table I shows the effect of dose rate on the elongation at break. A decrease in the elongation at break obtained from the stress-strain curve reflects the degree of degradation. As can be seen in Table I, the deterioration of the polymer increases with lowering dose rates or an increase in the depth of the oxidative layer. Thus it is concluded that the determination of oxidative layers gives a useful measure for the estimation of physical properties of irradiated materials.

Oxidative Layer of Polypropylene Irradiated with Electron Beam

In the previous paper¹ it was reported that, since the oxidation of polypropylene irradiated with electron beam was less than that γ -rays, the degradation was less in comparison with the case irradiated with γ -rays. The effect of dose rate on CL intensity is shown in Figure 5. The CL counts increase proportionally with thickness up to 200 μm ; over 250 μm the

TABLE I
Relationship Between the Elongation at Break and Dose Rate (Total Dose, 5 Mrad)

Dose rate (rad/h)	Elongation at break (%)
Unirradiated	304
1×10^6	282
2×10^5	213
5×10^4	18.3

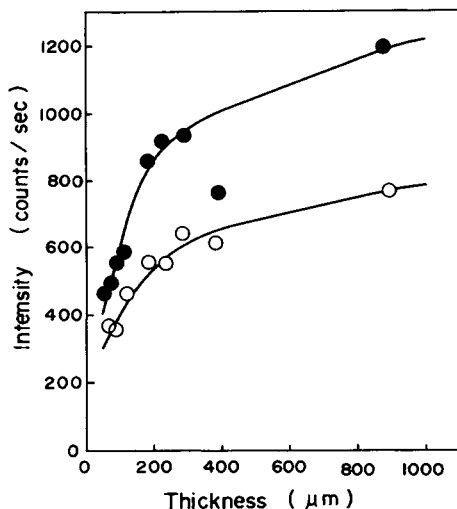


Fig. 5. Effect of dose rate on CL of polypropylene irradiated with electron beam. Dose rate (●) 0.29×10^5 rad/s, 0.2 mA; (○) 1.43×10^5 rad/sec, 1 mA. Total dose, 5 Mrad.

increase in CL counts is depressed. These results differ from those obtained in the case of γ -irradiated samples, and the inflection point that indicates the oxidative layer is not clear. This may be attributed to a temperature rise in the sample during electron beam irradiation. However, it would be more reasonable to conclude that oxidation occurs within $250 \mu\text{m}$ from the surface of the polymer film because an increase in CL counts is remarkably retarded in thicknesses over $300 \mu\text{m}$. Figure 6 shows the profile of the oxidative layer of the sample irradiated with electron beam. The CL intensity at film surface area is only one-third that for the γ -irradiated sample (Fig. 4). It is similarly U-shaped as obtained for the sample irradiated with γ -rays. From these data, it was ascertained that the oxidative layer is formed an electron beam-irradiated polymer as well as a γ -irradiated polymer.

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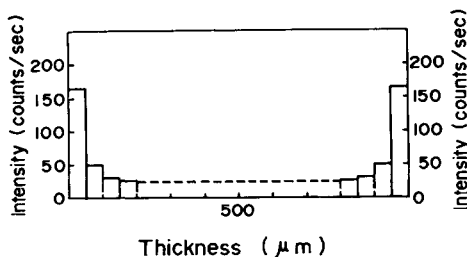


Fig. 6. Profile of the oxidative layer of polypropylene irradiated with electron beam. Dose rate, 1.43×10^5 rad/s (1 MA). Total dose, 5 Mrad.

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