Durability of Radiation-Sterilized Polymers. I. Estimation of Oxidative Degradation in Polymers by Chemiluminescence

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Synopsis

In relation to sterilization of medical supplies, the degree of degradation by γ-ray and electron beam irradiations of homopolypropylene (HP), copolypropylene (CP, coplymer including 6% of ethylene unit) and polymethylpentene were compared, and chemiluminescence (CL) of irradiated polymers were measured. HP degraded extremely around the sterilization dose (2.5 Mrad) by either γ-ray or electron beam irradiations. In the case of CP and polymethylpentene, stabilities of polymers far differed between γ-ray and electron beam irradiations. The polymethylpentene was more stable than the polypropylenes against irradiation. The counts of CL emitted by recombination of peroxy radical (ROO ·) increased with increasing dose, reflecting degrees of oxidation of polymers. The degradation of polymers was independent of irradiation sources, rather it depended on the degree of oxidation. It was found that CL analysis are favorable for estimation of degradation in irradiated polymers.

INTRODUCTION

Gamma ray irradiation has been used widely for the sterilization of the medical supplies such as syringes and surgery gloves.[1,2] The sterilization of medical supplies with electron beam is carried out in a few countries.[3] In the case of sterilization with electron beam, its application are limited to thin materials such as surgery gloves, since the penetration is very small comparing with γ-ray. However, sterilization technique with electron beam could probably be developed gradually in the near future, because of easy handling of its facility.

Polymers such as polyethylene, polypropylene, and poly(vinyl chloride) have been widely used as materials of medical supplies.[3] It is well known that polypropylene degrades easily during irradiation of γ-ray and storage after irradiation.[4,5] This degradation reaction of γ-irradiated polypropylene is oxidative by the radical mechanism. The radical species formed on isotactic polypropylene by γ-ray irradiation was identified, and potential additives to prevent degradation of γ-irradiated polypropylene have been developed by Williams et al.[4,5]

The degree of the oxidation of the polymer could be estimated by determining the amounts of carbonyl group formed via irradiation with infrared spectrometry and the relationship between concentration of carbonyl group and degradation of the polypropylene were discussed.[6] On the other hand, it has been reported that chemiluminescence (CL) is observed by recom-

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bination of peroxy radical (ROO ·) formed by oxidation.[7,8] Recently, a study on oxidation of blend polymer was carried out using CL analysis by Naito and Kwei.[8] Further, CL analyzer has been used to estimate degree of oxidation on used food oils.[9] However, CL analysis of irradiated polymers and systematic studies on physical properties of polypropylene irradiated with electron beam have not been carried out.

In this paper, degree of the degradation of the isotactic polypropylene by γ-ray and electron beam irradiations were compared. Furthermore, relation between chemiluminescence and degree of degradation of polypropylene was investigated.

EXPERIMENTAL

Materials

Commercial homopolypropylene (HP), copolypropylene (CP, copolymer including 6% of ethylene units), and polymethylpentene were used for irradiation. Dumb bell test pieces 2 mm thick were prepared for tensile strength test by extrusion.

Irradiation

γ-Ray irradiation from Co-60 was carried out at an exposure rate of 1×10^6rad/h. Electron beam irradiation was done at a beam current of 1 mA and acceleration energy of 1 MeV generated by a Cockroft-Walton type accelerator (2Mev, 30 mA). Samples were irradiated by repeating 1 Mrad/pass (0.143 Mrad/sec) to prevent thermal accumulation.

Measurement of Elongation at Break

Elongation at break was determined from stress–strain curves measured by using an Instron Tensometer (Model No. 1130). Selected tension speeds were 50 mm/min for HP, 100 mm/min for CP, and 20 mm/min for polymethylpentene, respectively, after suitable tension speeds to evaluate degradation of irradiated polymers were investigated. The results given in the following section are the average of five readings. The tension test was done within 24 h after irradiation.

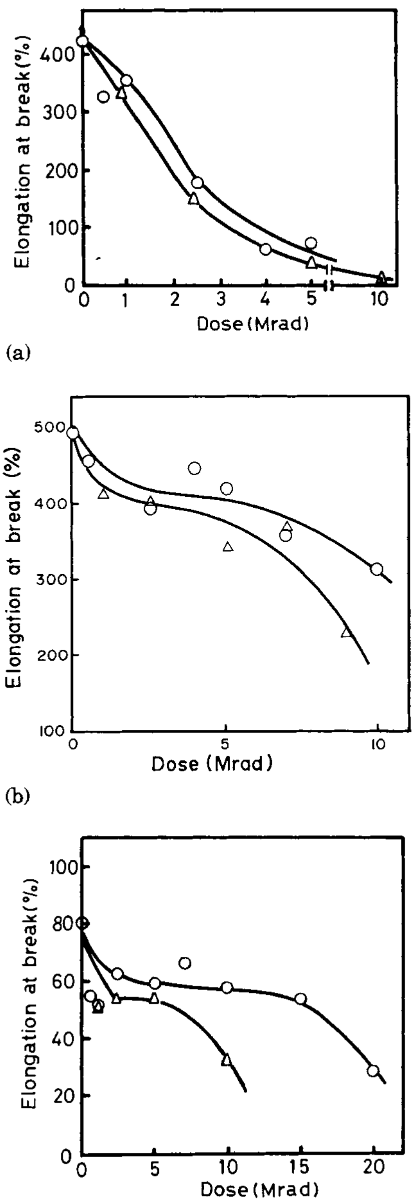
Measurements of Chemiluminescence

Chemiluminescence (CL) of irradiated samples (2×2 cm) were measured by using OX-7 of TOHOKU Denshi Sangyo Co, Ltd. Gate time for CL measurement was 10 s and the CL intensity was normalized as counts/s. The CL measurement was carried out within 24 h after irradiation.

RESULTS AND DISCUSSION

Degradation of Polymers by Irradiation

It is well known that polypropylene degrades by γ-ray irradiation.[10,11] The decrease of elongation at break reflects degradation of polymers. The elongation at break of polypropylene and polymethylpentene irradiated with electron beam and γ-ray are shown in Figure 1. Elongation at break decreased with increasing dose in every polymers. It can be seen that the HP degrades steeply in the lower dose range up to 2.5 Mrad, while degradation of CP by irradiation is small and have a plateau in the range up to around 5 Mrad in comparison with HP. The CP contains ethylene units in the main chain. Polyethylene is a typical crosslinking polymer. Thus, it is ascertained that the ethylene chain apparently retarded degradation of CP by irradiation.



(c)

Fig. 1. Elongation at break of irradiated polymers: (a) homopolypropylene; (b) copolypropylene; (c) polymethylpentene; (△) γ-ray irradiation; exposure rate, 1×10^6 R/h; (○) electron beam; dose rate, 0.143×10^6 rad/s.

Next, it should be noted that γ-ray and electron beam irradiation affects on polymers differently. The samples irradiated with γ-ray were more easily degraded than those irradiated with electron beam, in the case of CP and polymethylpentene. The difference in degradation behavior between the two irradiation method become more remarkable at a higher dose range from 10 to 15 Mrad. The polymethylpentene is more stable in comparison with polypropylene for irradiation. Moreover, it was shown that electron beam irradiation was favorable for sterilization of medical supplies, since degradation by irradiation was smaller than that γ-irradiated polymer. In stress–strain curves, yield stress hardly changed and tensile strength decreased slightly with decrease of elongation against dose in three polymers.

Change of CL by Irradiation Dose

Mendenhall reported that chemiluminescence is emitted from an exicted ketone formed by recombination of peroxy radical in the termination step and the following reaction schemes are presented[12]:

$$2R'O_2\cdot \rightarrow R'OH + R''_2C = O + O_2 \tag{1}$$

$$2R'O_2\cdot \rightarrow P^* \tag{2}$$

$$P^* + Q \rightarrow P + Q \tag{3}$$

$$P^* \rightarrow P + h\nu \tag{4}$$

where P* indicates an exited ketone and Q is a quenching species. Accordingly, the intensity of the luminescence is expected to depend on the concentration of the peroxy radicals.

In order to confirm behavior of degradation on irradiated polymers, the CLs of irradiated polymers were measured. Temperature dependence of CL of irradiated CP with electron beam are shown in Figure 2. From this figure, it can be seen that CL counts increased linearly with increasing temperature. Since the mobility of polymer segments increase with temperature, recombination of peroxy radicals formed in polymers become active. Thus, CL intensity increased with increasing temperature. The apparent activation energy calculated from the result is 13.6 kcal/mol for various doses. This value (13.6 kcal/mol) is smaller than the one data published for the oxlyluminescence of polypropylene in the temperature range of 60–150°C by Schard and Russell (23.3 kcal/mol).[13] It might be attributed to that the apparent activation energy for CL of irradiated polypropylene did not contain the initial step of radical formation.

CL of Various Irradiated Polymers

In Figure 3, the CL amounts measured at 80 and 100°C were ploted as a function of dose. It can be seen that the CL amounts vary with kind of polymers. The CL of polymethylpentene is the largest in the three polymers, indicating irradiated polymethylpentene is more easily oxidized than other two polymers. The CL of irradiated polymers may be depended on physical

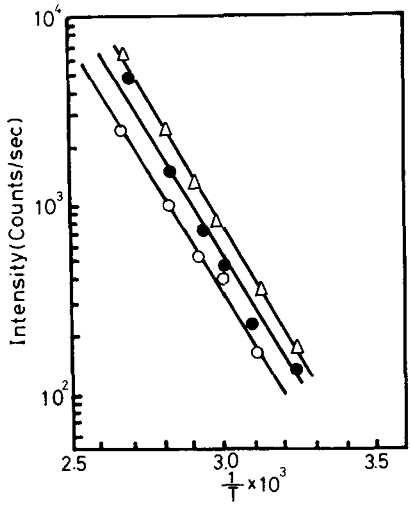


Fig. 2. Effect of dose on chemiluminescence of copolypropylene in electron beam irradiation: (○) 2.5 Mrad; (●) 5.0 Mrad; (△) 10 Mrad.

and chemical properties such as molecular mobility, crystallinity, T_g, and structure of polymer. Since structure and crystallinity of polymethylpentene having pendant chain [—CH_2—$CH(CH_3)_2$] differ from polypropylene, it is suggested that the polymethylpentene was oxidation more easily than polypropylene in the same irradiation dose.

Figure 4 shows change of CL amounts of polymer irradiated with γ-ray and electron beam. At a lower dose range up to 2.5 Mrad, the difference of CL amounts of polymer between γ-ray and electron beam irradiations are relatively small, while in higher doses such as 5.0 and 10 Mrad, CL

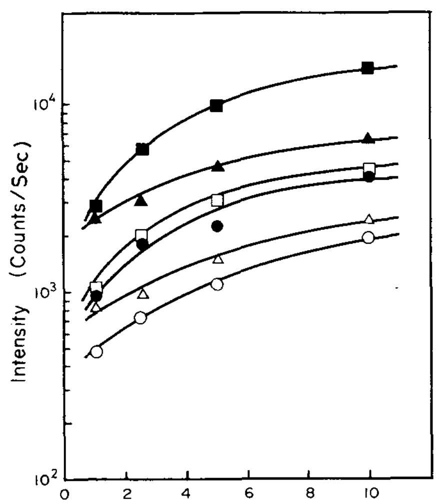


Fig. 3. Chemiluminescence of various polymers irradiated with electron beam. Measurements temp 80°C: (○) homopolypropylene; (△) copolypropylene; (□) polymethylpentene. 100°C: (●) homopolypropylene; (▲) copolypropylene; (■) polymethylpentene.

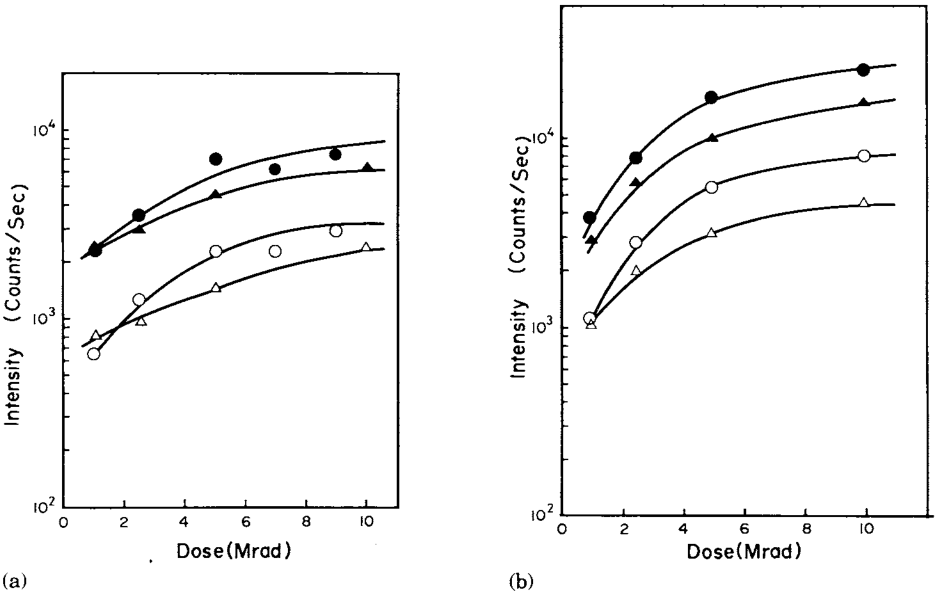


Fig. 4. Comparison of chemiluminescence in polymers irradiated with γ-ray and electron beam. (a) copolypropylene; (b) polymethylpentene. Measurement temp.: electron beam: (△) 80°C; (▲) 100°C; γ-ray: (○) 80°C; (●) 100°C.

amounts are far different between two irradiation method. The CL amounts of γ-irradiated samples are always larger than those of ones irradiated with electron beam. This fact indicates that peroxy radicals are more easily formed in γ-irradiated polymers comparing with electron beam irradiated ones. In case of γ-ray irradiation, the effect of diffusion of oxygen into polymer films during irradiation is large, because samples are exposure for long times such as 5.0 and 10 h for given dose. On the contrary, in the case of electron beam irradiation, the effect of oxygen in polymer is relatively small, because irradiation time is so short as several seconds, even for 5.0 and 10 Mrad. Accordingly, γ-irradiated polymer would be more easily degraded than electron beam irradiated polymer. Thus, the CL can be used to estimate degrees of oxidation in irradiated polymers.

Relation between Degradation and CL Amounts of Polymers

Figure 5 shows the relationships between the elongation at break and CL amounts of various polymers irradiated with electron beam. The HP degrades at the lowest CL amounts in the three polymers used here. On the other hand, polymethylpentene is relatively stable for high CL amounts (high dose). This corresponds well to the results in Figure 1. Relationships between the elongation at break and CL amounts of CP irradiated with γ-ray and electron beam are shown in Figure 6. The degradation of polymer is independent on kind of irradiation by γ-ray and electron beam for CL amounts. Critical CL amounts for degradation is shown in every polymers. In the case of polymethylpentene, the value of critical CL amounts was larger than that of polypropylene. This fact indicates that degradation of polymethylpentene by oxidation in irradiation of γ-ray and electron beam

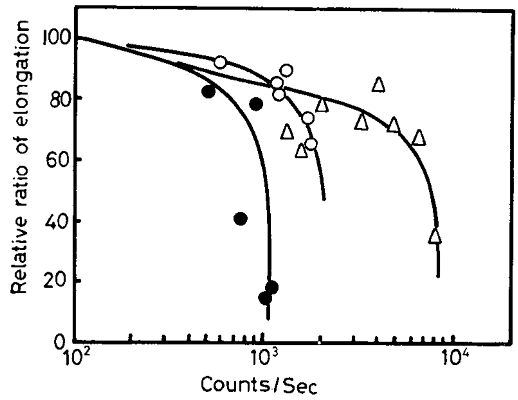
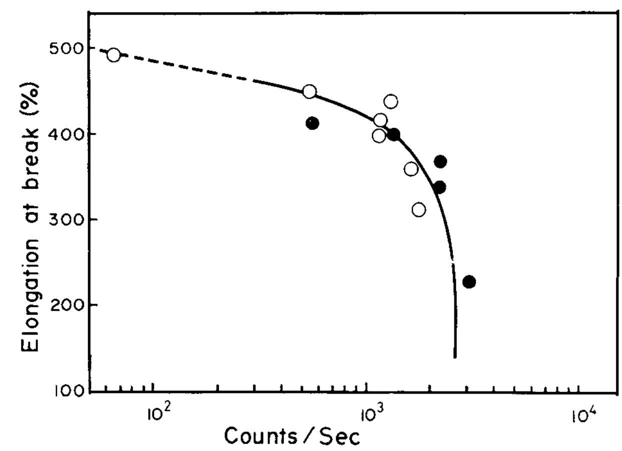
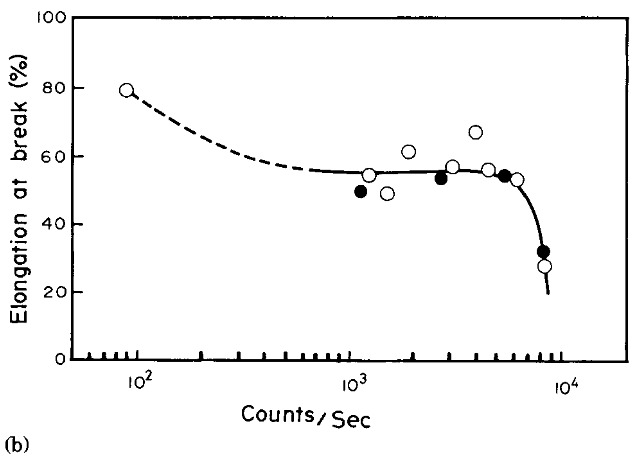


Fig. 5. Relationships between elongation at break and chemiluminescence of various polymers irradiated with electron beam: (●) homopolypropylene; (○) copolypropylene; (△) polymethylpentene. Measurement of chemiluminescence, 80°C.



(a)



(b)

Fig. 6. Relationship between elongation at break and chemiluminescence of various polymers irradiated with γ-ray and electron beam: (a) copolypropylene; (b) polymethylpentene; (○) electron beam; (●) γ-ray; measurement of chemiluminescence, 80°C.

was smaller than that of polypropylene. The CL amounts of irradiated polymethylpentene is much larger than that of irradiated polypropylene. The reason is not clear. However, it was ascertained that CL analysis is favorable for estimation degree of degradation in irradiated polymers. Thus, CL analysis may be possibly applicable to the quality control of sterilized medical supplies by irradiation.

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