

Radiation-Induced Oxidative Degradation of Isotactic Polypropylene

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Synopsis

Gas evolution, oxygen consumption, and change of mechanical properties were studied for the γ -ray irradiation of isotactic polypropylene from ^{60}Co under various conditions, such as vacuum, air, and oxygen at room temperature. For irradiation under vacuum, $G(\text{H}_2) = 2.9$ and $G(\text{CH}_4) = 0.09$; the G values for other gases were very small. In the presence of oxygen, $G(\text{H}_2)$ was the same, and the G values for other hydrocarbons were two times those under vacuum. The G values of oxidative products and oxygen consumption were $G(\text{CO}_2) = 2.5$, $G(\text{CO}) = 1.1$, and $G(\text{O}_2) = 50$ at oxygen pressure of 500 torr and were dependent on oxygen pressure. With irradiation under vacuum at 2–3 Mrad, mechanical properties scarcely changes immediately after irradiation but degrade gradually with storage time in air at room temperature.

INTRODUCTION

It is known that ionizing radiation is useful for the sterilization of disposable medical supplies and equipment. Radiation sterilization has been developed to an industry.¹

This article is concerned with the radiation effects on isotactic polypropylene which is widely used for manufacturing disposable syringes. Gas evolution and change in mechanical properties were investigated for irradiation in oxygen and under vacuum. Oxygen consumption is also discussed for irradiation in the presence of oxygen. In general, radiation sterilization is performed in air at room temperature and with a total dose of 2–3 Mrad.¹ It is important to study the G values of the evolved gases since some of them can be toxic. The effect of irradiation conditions (vacuum, air, or oxygen) and the postirradiation effect were investigated.

The radiation chemistry of polypropylene was reported by Black and Lyons,^{2,3} Schnabel and Dole,⁴ and many others. Schnabel and Dole found that the $G(\text{H}_2)$ is 2.7 and $G(\text{CH}_4)$ 0.08. Kondo and Dole⁵ studied the irradiation of isotactic and atactic polypropylene in the presence or absence of N_2O to find that $G(\text{H}_2)$ is 2.63 and $G(\text{CH}_4)$ 0.17 under vacuum and lower in the presence of N_2O . The main chain scission of isotactic polypropylene has been discussed in the reviews by Chapiro,⁶ Charlesby,⁷ and more recently by Dole.⁸ They found that chain scission predominates at low doses. Oxygen accelerates the degradative reactions by peroxidation of the polymer chain followed by decomposition and rearrangement, leaving as a net result on additional chain scission.^{9,10} Dunn et al.¹¹

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studied the radical structure and its role in the oxidative degradation of γ -irradiated polypropylene. They found that the ultimate mechanical degradation in an irradiated sample is independent of the conditions of irradiation (air or vacuum) and of the specific radical species.

EXPERIMENTAL

Materials. The samples were isotactic polypropylene (IPP) powder with average diameter of 0.38 mm of the Sumitomo Chemical Co., Ltd., and sheets 0.5 mm thick molded from the powder at 180°C. The sample does not contain any stabilizer.

Sample Preparation and Irradiation. A known weight of the sample was put in the sample tube shown in Figure 1 and then degassed over 24 hr and sealed. In the case of irradiation in oxygen, the oxygen was introduced into the sample tube with constant pressure after degassing for about 1 hr. The irradiation was carried out with ^{60}Co γ -rays at room temperature at a dose rate of 1 Mrad/hr.

Analysis of Gas Evolution and Oxygen Consumption. After irradiation, the samples were connected to the vacuum line as shown in Figure 1, then the pressure of the total gas was measured with an MKS-Baratron manometer (dynamic range: $10^{-3} \sim 10^3$ torr). The evolved gases and residual oxygen were analyzed by gas chromatography (GC). GC(I) was an Ohkura model 820 with a column of molecular sieve of 5 Å. GC(II) was a Yanagimoto GCG-550 T with a Porapack-S column. Helium as a carrier gas for GC(I) and GC(II) was used with a flow rate of 30 ml/min. GC(I) was used for lighter molecules such as hydrogen, oxygen, methane, and carbon monoxide, and GC(II) was used for carbon dioxide, ethane, and ethylene. The mass spectrometer used for analysis of the gas evolution was a Hitachi-RMU-6, 90° single focusing. The electron energy for ionization was 100 eV, and the acceleration voltage was 3.0 kV. The sample preparation for analysis by mass spectrometry was the same as for gas chromatograph.

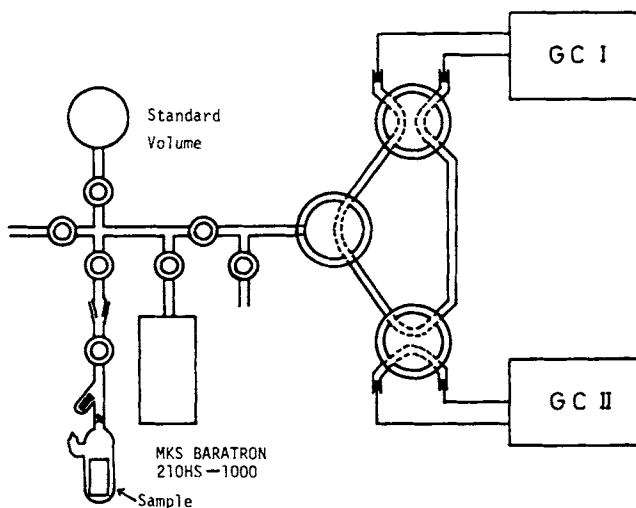


Fig. 1. Schematic diagram for gas analysis.

Measurement of Mechanical properties. The dumbbell-shaped samples were 63 mm long, with a neck 25 mm long and 3 mm wide. The measurements were carried out with an Instron model 1130. The crosshead speed was 5 cm/min. In order to study the postirradiation effect, the samples irradiated up to 2 Mrad under vacuum were kept at various temperatures in air, and the tensile properties were measured.

RESULTS AND DISCUSSION

Gas Evolution and Oxygen Consumption

Figure 2 shows the amounts of gas evolution from IPP powder irradiated under vacuum with different doses. The amount of total gas evolution increases with dose but is inclined to level off at higher doses. Of the total gas evolved, about 95 mole % is hydrogen and about 3 mole % is methane. A small amount of ethane and carbon dioxide is also detected. The amount of gas evolution from the film is nearly the same with the powder.

The G value of each gas is listed in Table I. The CO and CO₂ formations are due to the oxygen remaining in the sample, which is a larger amount in the film samples than in the powder. Our G values agree well with those of Schnabel and Dole.⁴ Another 20 gases approximately were detected by mass spectrometry; their relative amounts are listed in Table II.

Figure 3 shows the amounts of gas evolution and oxygen consumption for IPP powder irradiated under an initial oxygen pressure of 500 torr at room temperature. The amount of hydrogen evolution is the same in the case of vacuum, but the evolution of methane is enhanced about twofold by the presence of oxygen. Carbon dioxide and carbon monoxide evolution increases with the irradiation dose, and the G values are relatively high. The oxygen consumption increases with irradiation dose. The quantity of consumed oxygen per unit dose decreases

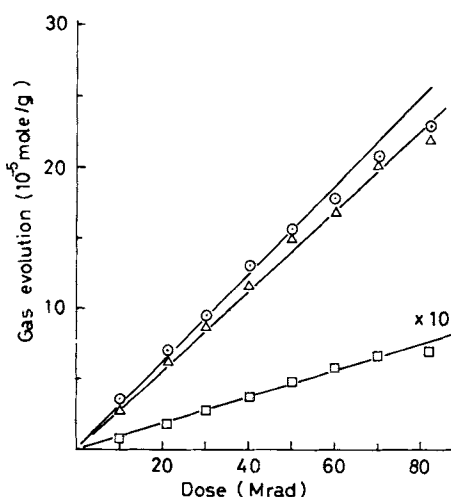


Fig. 2. Gas evolution vs. dose in IPP powder irradiated under vacuum at room temperature: (○) total gas; (Δ) H₂; (□) CH₄.

TABLE II
Relative Composition of Evolved Gases from IPP Powder during Irradiation under Vacuum and in Oxygen by Mass Spectrography

| Component gas | Relative composition | |
|---------------------------------|----------------------|-----------------|
| | 40 Mrad, vacuum | 50 Mrad, oxygen |
| H ₂ | 100 | 100 |
| CH ₄ | 3.5 | 5.0 |
| O ₂ | — | 1.4 (remaining) |
| N ₂ | — | 1.1 |
| CO ₂ | 0.01 | 31 |
| CO | 0.02 | 14 |
| H ₂ O | — | 1.9 |
| C ₂ H ₆ | 0.01 | 0.19 |
| C ₃ H ₈ | 0.007 | — |
| C ₄ H ₁₀ | 0.048 | 0.17 |
| C ₅ H ₁₀ | — | 0.01 |
| C ₅ H ₁₂ | 0.024 | 0.01 |
| C ₆ H ₁₄ | 0.009 | 0.03 |
| C ₇ H ₁₄ | 0.003 | — |
| C ₇ H ₁₆ | 0.013 | 0.015 |
| C ₈ H ₁₆ | 0.001 | — |
| C ₈ H ₁₈ | 0.003 | — |
| C ₉ H ₁₈ | 0.002 | — |
| C ₉ H ₂₀ | 0.002 | — |
| C ₁₀ H ₂₂ | 0.001 | — |

at high doses. The *G* values of gas evolution and oxygen consumption at an initial oxygen pressure of 500 torr are listed in Table III. Some amount of water was also detected by mass spectroscopy, but it was not analyzed quantitatively.

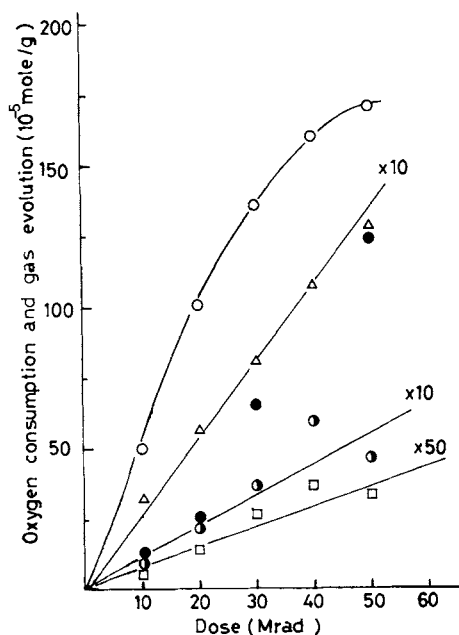


Fig. 3. Oxygen consumption and gas evolution vs. dose in IPP powder irradiated in oxygen at 500 torr of initial pressure: (○) O₂ consumption; (△) H₂; (●) CO₂; (●) CO; (□) CH₄.

TABLE III
G Values of Gas Evolution and Oxygen Consumption on IPP Powder and Film Irradiated in Oxygen (500 torr Initial Pressure) at Different Doses

| | Powder | | | | | Film | | | | |
|---|-------------|------|------|------|------|-------------|------|------|------|------|
| | Dose (Mrad) | | | | | Dose (Mrad) | | | | |
| | 10 | 20 | 30 | 40 | 50 | 10 | 20 | 30 | 40 | 50 |
| <i>G</i> (total) | 10.1 | 9.3 | 11.0 | 6.4 | 8.7 | 9.6 | 8.7 | 4.6 | 4.3 | 4.2 |
| <i>G</i> (H ₂) | 3.0 | 2.8 | 2.5 | 2.6 | 2.5 | 3.1 | 2.6 | 2.5 | 2.5 | 2.3 |
| <i>G</i> (CH ₄) | 0.11 | 0.13 | 0.17 | 0.18 | 0.13 | 0.09 | 0.08 | 0.09 | 0.09 | 0.08 |
| <i>G</i> (CO) | 1.0 | 1.1 | 1.2 | 1.4 | 0.8 | 0.4 | 0.2 | 0.2 | 0.2 | 0.2 |
| <i>G</i> (CO ₂) | 0.93 | 1.1 | 2.1 | — | 2.4 | 0.6 | 0.5 | 0.5 | 0.4 | 0.4 |
| <i>G</i> (O ₂) ^a | 49.0 | 50.0 | 43.0 | 39.0 | 35.0 | 17.0 | 12.0 | 8.0 | 6.0 | 6.0 |
| <i>P</i> (O ₂) ^b | 405 | 314 | 241 | 171 | 38 | 390 | 342 | 357 | 315 | 309 |

^a Oxygen consumption.

^b Remaining oxygen pressure, in torr.

Under these experimental conditions, the oxygen pressure in the sample tube is not constant during the irradiation because the oxygen is consumed by the oxidation as shown in Table III.

Figure 4 shows the oxygen consumption and gas evolution from IPP film irradiated in oxygen with initial pressure of 500 torr at room temperature. Hydrogen and methane evolution increase linearly with dose. The carbon dioxide and carbon monoxide evolution and oxygen consumption increase with the irradiation dose and level off at higher dose. The amount of oxygen consumption is less than that in the powder sample because of the slow oxygen diffusion in to the film, and the oxidation does not proceed well inside the film. The G values of gas evolution and oxygen consumption on IPP film are listed in Table III. Figures 5 and 6 show the oxygen consumption and gas evolution from the powder and film irradiated at 20 Mrad as a function of oxygen pressure. The oxygen consumption obviously increases with oxygen pressure. The dependence of oxygen consumption on pressure is more remarkable for the film samples than the powder. These phenomena are also due to slow diffusion of oxygen in the case of film samples.

For irradiation of IPP powder in oxygen, the oxygen consumption G value is about 50 at low doses, while that of the oxygen components in evolved gases is only about 3. This indicates that most of the consumed oxygen converts to the oxidative products of IPP. Decker et al.¹² reported that the G values of the oxygen consumption on IPP at 45°C are 132 and 85 at a dose rate of 3.9×10^4 and 1.05×10^5 rad/hr, respectively. The difference from our G values may be due to the experimental methods and irradiation conditions. They¹² reported that the $G(O_2)$ decreases to about 35 by increasing the dose rate to 1 Mrad/hr.

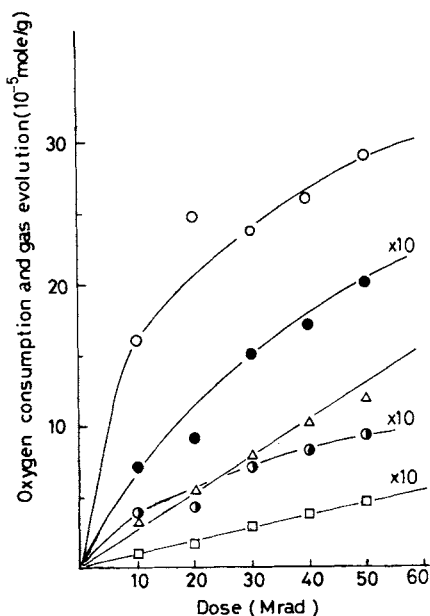


Fig. 4. Oxygen consumption and gas evolution vs. dose in IPP film irradiated in oxygen at 500 torr of initial pressure. Symbols as in Fig. 3.

TABLE IV
G Values of Gas Evolution and Oxygen Consumption on IPP Powder and Film Irradiated at 20 Mrad in Oxygen at Various Pressures

| | Powder | | | | | | Film | | | | | |
|---------------------------------|--------------------------------|------|------|------|------|------|--------------------------------|------|------|------|------|------|
| | Initial oxygen pressure (torr) | | | | | | Initial oxygen pressure (torr) | | | | | |
| | 300 | 400 | 500 | 700 | 700 | 700 | 150 | 300 | 400 | 500 | 700 | 700 |
| G(Total) | 9.2 | 8.5 | 9.3 | 7.0 | 7.0 | 7.0 | 3.0 | 7.6 | 8.2 | 8.7 | 7.0 | 7.0 |
| G(H ₂) | 2.9 | 3.1 | 2.8 | 3.3 | 3.3 | 3.3 | 2.5 | 2.7 | 2.7 | 2.9 | 3.3 | 3.3 |
| G(CH ₄) | 0.17 | 0.22 | 0.13 | 0.15 | 0.15 | 0.15 | 0.05 | 0.11 | 0.11 | 0.11 | 0.11 | 0.11 |
| G(CO) | 1.2 | 1.5 | 1.1 | 1.0 | 1.0 | 1.0 | 0.1 | 0.2 | 0.17 | 0.18 | 0.20 | 0.20 |
| G(CO ₂) | 2.5 | 2.6 | 2.5 | 2.2 | 2.2 | 2.2 | 0.21 | 0.34 | 0.33 | 0.43 | 0.47 | 0.47 |
| G(O ₂) ^a | 37 | 42 | 50 | 58 | 58 | 58 | 4.2 | 8.0 | 10.0 | 12.1 | 11.5 | 11.5 |
| P(O ₂) ^b | 11 | 58 | 314 | 337 | 337 | 337 | 101 | 200 | 283 | 342 | 594 | 594 |

^a Oxygen consumption.

^b Remaining oxygen pressure, in torr.

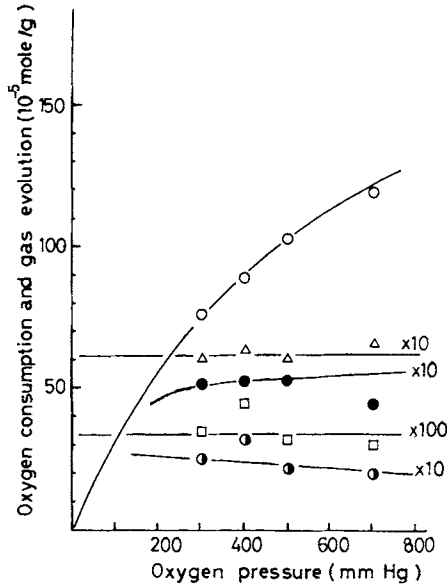


Fig. 5. Oxygen consumption and gas evolution vs. oxygen pressure in IPP powder irradiated up to 20 Mrad in oxygen. Symbols as in Fig. 3.

When IPP film is irradiated in air, the extent of oxidation will be the same as that when the film is irradiated in oxygen under 150 torr corresponding to the partial oxygen pressure in air. The amount of gas evolution and oxygen consumption at 2 ~ 3 Mrad at which medical supplies are sterilized can be estimated from our results by extrapolation.

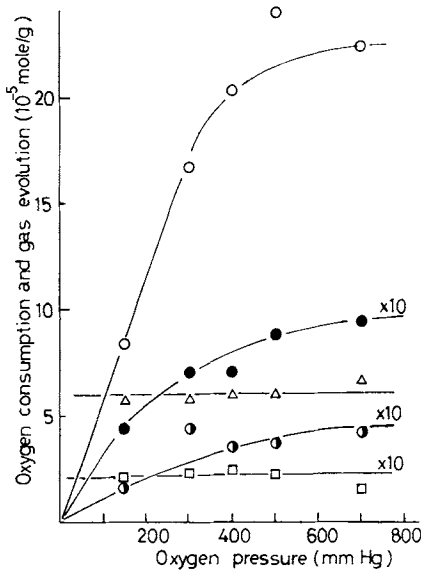


Fig. 6. Oxygen consumption and gas evolution vs. oxygen pressure in IPP film irradiated up to 20 Mrad in oxygen. Symbols as in Fig. 3.

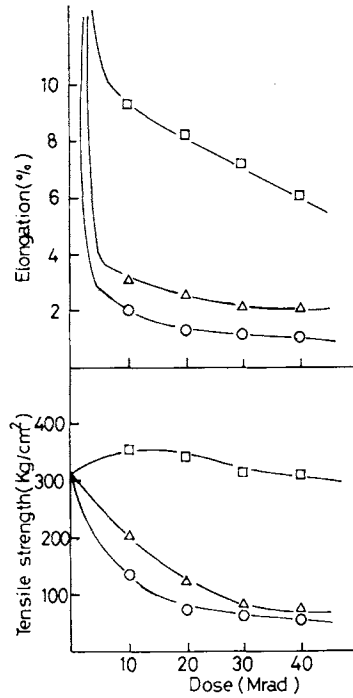


Fig. 7. Elongation and tensile strength at break of irradiated IPP vs. dose: (□) irradiated under vacuum; (Δ) irradiated in air; (○) irradiated in oxygen.

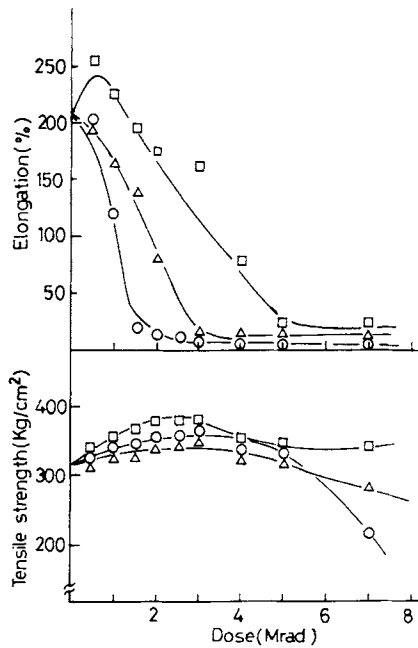


Fig. 8. Elongation and tensile strength at break of irradiated IPP vs. dose at lower dose. Symbols as in Fig. 7.

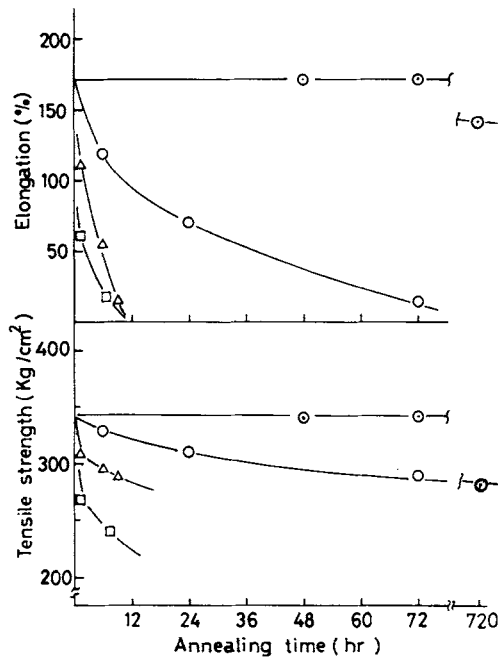


Fig. 9. Elongation and tensile strength at break of IPP irradiated under vacuum up to 2 Mrad vs. annealing time in air at various temperatures: (○) room temperature; (○) 100°C; (△) 120°C; (□) 140°C.

Mechanical Properties of Irradiated IPP

Figure 7 shows the changes of tensile strength (T_b) and percent elongation at break (E_b) of IPP film with irradiation under different conditions at room temperature. The decreases in T_b and E_b are much enhanced in the presence of oxygen. This means that the oxygen accelerates the degradation. The tensile properties of the sample irradiated at a lower dose are shown in Fig. 8. The E_b is remarkably changed, but the T_b is not. The rate of decrease in E_b is largest for irradiation in oxygen and smallest under vacuum.

Dunn et al.¹⁰ reported recently that there is a postirradiation effects on polypropylene and that the ultimate mechanical degradation is independent of the irradiation conditions (air and vacuum). Figure 9 shows the change in T_b and E_b versus time at various temperatures in air after irradiation with 2 Mrad under vacuum. The rate of decrease in both T_b and E_b increases with temperature. It is noted that T_b and E_b become nearly constant after seven days at room temperature, and after one month they decreased to 280 kg/cm² and 140%, respectively. From these data we can presume that the T_b and E_b of the sample irradiated with 2 Mrad under vacuum decrease to similar values as the samples irradiated in air or oxygen when the sample is kept at higher temperature in air.

The decreases of elongation at various temperatures in Figure 9 can be expressed empirically by first-order kinetics. The temperature coefficient of the rate of decrease in the elongation was calculated to be 9 kcal/mole from the Arrhenius equation. We can estimate the elongation after ten months at room temperature will decrease to 50%.

CONCLUSIONS

The evolution of carbon monoxide, carbon dioxide, methane, and other hydrocarbons is increased in the presence of oxygen, but the evolution of hydrogen is not changed. The $G(\text{O}_2)$ of IPP powder has some dependence on the oxygen pressure, and the film sample has a larger dependence due to the slow oxygen diffusion through the polymer matrix.

The mechanical properties of IPP degrade to a large extent with irradiation of a sterilizing dose (2–3 Mrad). The addition of antioxidant is necessary for its practical use with medical supplies.

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