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Photodegradation of Crosslinked Polyethylene

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ABSTRACT

The photodegradation of crosslinked polyethylene has been studied by ultraviolet (UV) and Fourier transform infrared (FT–IR) spectroscopic techniques and by gel and density measurements. The formation of the diene-type compound as well as of the gel was observed in γ-irradiated polyethylene. The efficiency of photodegradation was estimated from the oxygenated and vinyl group formation observed, and by the change of gel fraction. The photodegradation of crosslinked polyethylene may be initiated by the absorption of a photon by diene-type compounds formed by γ-irradiation. The rate of photo-oxidation and chain scission is faster in crosslinked polyethylene than in uncrosslinked polymer. A photodegradation mechanism for polyethylene crosslinked by γ-irradiation is proposed on the basis of the experimental results.

INTRODUCTION

Polyethylene (PE) is one of the most important commercial polymers and it is widely used in various industrial fields. On irradiating PE with γ-rays in the absence of oxygen, crosslinking is produced in the amorphous region.[1–3] The crosslinked PE has excellent chemical properties such as heat stability and solvent resistance.[4] It has been

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reported that the effect of crosslinking on mechanical properties is to increase modulus and yield stress and to reduce ductility.[5]

Insulation tape, covering materials for electric wires and heat-shrinkable films for packaging have been utilized for commercial products as applications of crosslinked PE. These commercial products are often used under conditions of exposure to terrestrial sunlight. The photochemical behaviour of crosslinked PE, however, has received little attention.

Since crosslinked PE has many excellent chemical and mechanical properties, it is important to clarify its photo-degradation mechanism as a basis for improving the photostability of the polymer.

EXPERIMENTAL

Low density (LD) and high density (HD) polyethylene pellets without any additives were supplied by Ardrich Chemicals Co. Ltd. Spectrograde *n*-hexane, ethanol and special grade *p*-xylene (supplied by Nakarai Chemicals Ltd., Kyoto, Japan) were used as received. Polyethylene (PE) films were prepared by hot-pressing with a pressure of 10 kg/cm^2 for 10 min at (T_m + 10 °C), where T_m is the melting temperature of PE. Polyethylene films thus formed were soaked in *n*-hexane overnight and then dried in air. The thickness of the films used was *ca* 0·1 mm for the experiments other than IR measurements, for which it was *ca* 0·03–0·04 mm. The films were irradiated in air and in vacuum with a Toshiba H-400P medium pressure mercury lamp at a fixed position at which the incident intensity was 1050 J/m^2 s. γ-Irradiation from a ^{60}Co source was carried out in vacuum and in air at room temperature, at a dose rate of $3{\cdot}0 \times 10^5$ rad/h and in doses of $0\text{–}1 \times 10^8$ rad. The ESR and UV absorption spectra of photo-irradiated samples were recorded on a JEOL JES-3BX ESR spectrometer and a Hitachi type 323 spectrophotometer, respectively. Infrared spectra were recorded with a Nicolet MX-1 FT-IR spectrophotometer at the Research Center for Resources and Energy Conservation, Nagoya University. The photoirradiated PE was extracted with *p*-xylene for 24 h by a Soxhlet extractor, washed with ethanol and then dried under vacuum for 24 h. The gel fraction (%) was estimated from the equation:

$$f = (W/W_0) \times 100 \qquad (1)$$

where W_0 is the initial weight of polymer and W is the weight of the fraction of photo-irradiated polymer insoluble in *p*-xylene. The densities of photo-irradiated samples were measured in ethanol–water mixtures by a flotation method.

RESULTS AND DISCUSSION

Gel formation by γ-irradiation

LDPE and HDPE were exposed to γ-rays from a ^{60}Co source in air and in vacuum at room temperature, then left to stand in air for one week, during which the concentration of radicals formed during γ-irradiation decayed to one-tenth of its initial value; it attained a plateau value by the end of this period. The gel fraction (%) of γ-irradiated LDPE and HDPE films in vacuum and in air was then determined from eqn. (1). The results are given in Fig. 1.

The gel did not form in the case of γ-irradiated LDPE and HDPE in air. On the other hand, the gel fraction of LDPE and HDPE γ-irradiated in vacuum increased with the irradiation dose and reached a plateau value. The gel fraction is larger in LDPE than in HDPE for each irradiation time. This result is well explained by the fact that LDPE is more amorphous than HDPE.

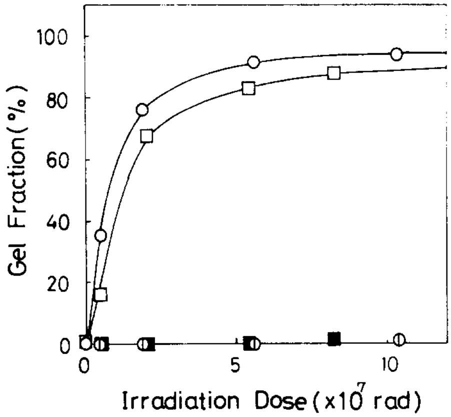


Fig. 1. Changes in the gel fraction of HDPE and LDPE films exposed to γ-rays at room temperature against the irradiation dose. ○, LDPE in vacuum; □, HDPE in vacuum; ◑, LDPE in air; ■, HDPE in air.

In this study, we chose the LDPE exposed to γ-rays to 5×10^7 rad in vacuum as the crosslinked PE sample. The gel fraction of this sample is *ca* 90%. The uncrosslinked LDPE is termed 'native PE' in this paper.

Photo-irradiation of crosslinked PE

On photo-irradiation of crosslinked and native PE in vacuum, the absorption spectra shown in Fig. 2 were obtained. Unirradiated PE has no prominent band in the region of wavelength <400 nm except the bands at wavelengths shorter than 210 nm and near the 230 nm region. The optical densities of these absorption bands show a small increase with increasing photo-irradiation time. New bands with $\lambda_{max} < 210$ nm, at 236 nm and at 285 nm appear with γ-irradiation in vacuum. The band at $\lambda_{max} = 236$ nm disappears and new bands having λ_{max} at 323 nm and 360 nm appear on prolonged photo-irradiation following γ-irradiation. The intensity of the band at $\lambda_{max} = 236$ nm decreases rapidly with increasing photo-irradiation time, as shown in Fig. 3. This band was not observed for the γ-irradiated polymer in air. The species having a band at $\lambda_{max} = 236$ nm can absorb the light

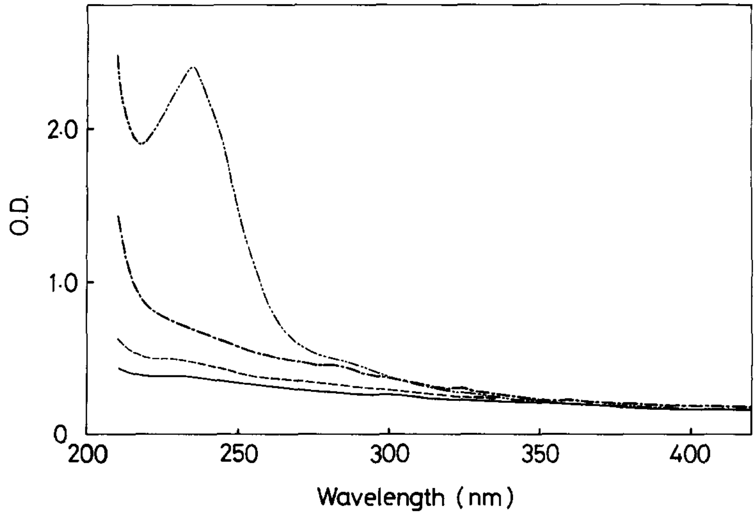


Fig. 2. Absorption spectra of γ- and photo-irradiated LDPE. ——, unirradiated; - - - - -, photo-irradiated for 240 min; — — — —, γ-irradiated to $4{\cdot}95 \times 10^7$ rad; — — —, photo-irradiated for 240 min after γ-irradiation to $4{\cdot}95 \times 10^7$ rad in vacuum.

from a medium pressure mercury lamp and may be responsible for the initiation of the photo-reaction of crosslinked PE. Partridge has assigned a band having λ_{max} at 238 nm to allyl radicals and diene-type compounds.[6] We consider that this band is mainly attributed to the diene-type compound formed by γ-irradiation for the following reason. If this band is attributed to allyl radicals, some changes with heat treatment would occur, e.g. polyene formation and peroxide formation in the absence and presence of O_2, respectively. The crosslinked PE films were heat-treated in air and in vacuum at 86 °C for 10 min. The results are given in Fig. 4. The intensity of band did not decrease with heat treatment either in air or in vacuum. This means that the band having λ_{max} at 236 nm cannot be attributed to allyl radicals, which also have λ_{max} in the same wavelength region. The diene-type compound formed in crosslinked PE decreases in its

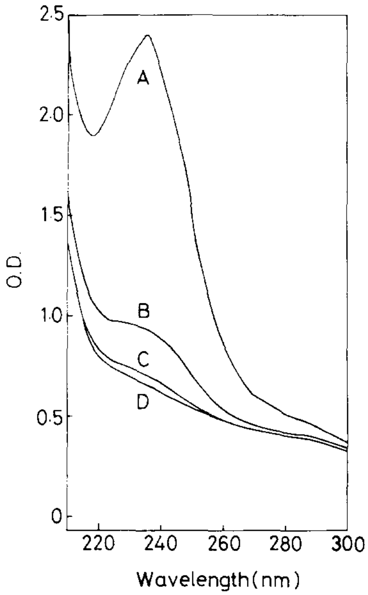


Fig. 3. Absorption spectra of photo-irradiated LDPE after γ-irradiation to $4{\cdot}95 \times 10^7$ rad in vacuum. A, unirradiated; B–D, photo-irradiated for (B) 30 min, (C) 60 min, (D) 240 min.

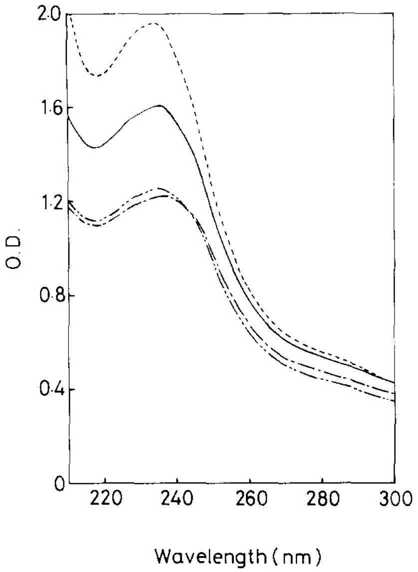


Fig. 4. Changes of absorption spectra of LDPE by heat treatment after γ-irradiation to $4{\cdot}95 \times 10^7$ rad in vacuum. ——, No heat treatment in vacuum; - - - - -, heat treated at 86 °C for 10 min in vacuum; — — — —, heat treated at 86 °C for 10 min in air; — - —, no heat treatment in air.

concentration by photo-irradiation, as already shown in Fig. 3. This indicates that the diene-type compound can absorb the light from a medium pressure mercury lamp and initiate the photochemical reaction of crosslinked PE. The formation of new species in PE by γ-irradiation would be responsible for the photosensitivity of crosslinked PE. This will be discussed later.

The bands having λ_{max} at 285 nm, 323 nm and 360 nm can be assigned to dienyl, trienyl and tetraenyl radicals, respectively.[7]

Chemical changes in crosslinked PE by photo-irradiation

Much useful information is gained by the analysis of IR spectra of photo-irradiated PE. The FT–IR method is a powerful tool for detecting and analysing small changes produced in PE samples by photo-irradiation. The IR spectrum of photo-irradiated crosslinked PE in air is shown in Fig. 5. A similar IR spectrum was observed in the photo-irradiation of native PE.

The changes in the intensities with photo-irradiation at 1720 cm^{-1} ($\nu_{C=O}$)[8], 909 cm^{-1} ($\nu_{CH=CH_2}$), 720 cm^{-1} (amorphous region + crystalline region) and 730 cm^{-1} (crystalline region)[9,10] are larger in the crosslinked PE than in native PE. These differences are clearly demonstrated by the difference spectrum between photo-irradiated

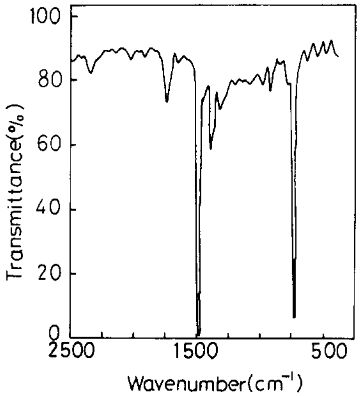


Fig. 5. IR spectra of crosslinked PE photo-irradiated for 180 min in air and 10 cm away from the light source.

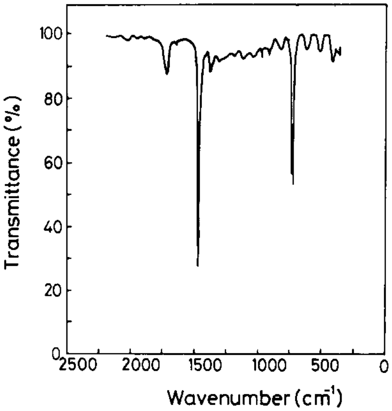


Fig. 6. Difference IR spectra of photo-irradiated crosslinked PE and native PE. Photo-irradiation time, 180 min; null wavenumber, 1643 cm^{-1}.

crosslinked PE and native PE, which is shown in Fig. 6. The changes in the intensities of the C=O group with irradiation time are shown in Fig. 7. The intensity at $\lambda_{max} = 1720\ cm^{-1}$ is given as OD_{1720}/OD_{1463} to remove the effect of film thickness, where OD_{1720} and OD_{1463} are the absorbances at $1720\ cm^{-1}$ and $1463\ cm^{-1}$, respectively. The ratio OD_{1720}/OD_{1463} increases in both cases with an increase in irradiation time, indicating that carbonyl group formation is enhanced by γ-irradiation of PE.

The vinyl group has its absorption maximum at $909\ cm^{-1}$. The changes in the intensities of the vinyl group with irradiation time are shown in Fig. 8, where OD_{909} is the absorbance at $909\ cm^{-1}$. The concentration of vinyl groups increases slightly with an increase of photo-irradiation time in native PE. On photo-irradiating the crosslinked PE film, the concentration of vinyl groups increases significantly with irradiation time and this concentration is higher in crosslinked PE after prolonged irradiation. This behaviour shows that photo-oxidation (formation of carbonyl groups) and chain scission (increase of vinyl groups) are accelerated in γ-irradiated PE.

The gel fraction of photo-irradiated crosslinked PE was measured as a function of irradiation time (Fig. 9). This result also indicates that chain scission by photo-irradiation takes place in this case.

As already described, the ratio of the optical density at $730\ cm^{-1}$ to that at $720\ cm^{-1}$, OD_{730}/OD_{720}, may be used for measuring the degree of crystallinity.[10] Changes in this value with irradiation time are shown in Fig. 10. The ratio OD_{730}/OD_{720} tends to increase with

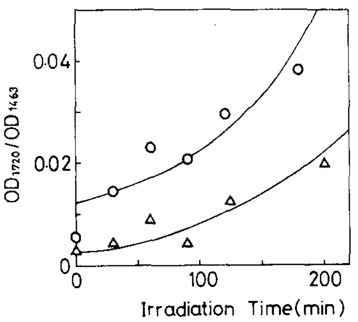


Fig. 7. Changes of OD_{1720}/OD_{1463} against photo-irradiation time. ○, Crosslinked PE; △, native PE.

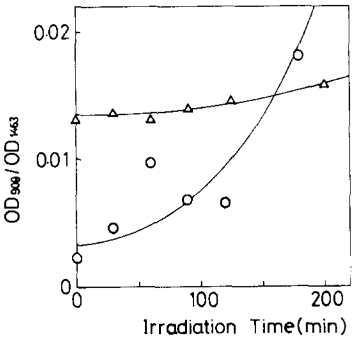


Fig. 8. Changes of OD_{909}/OD_{1463} against photo-irradiation time. ○, Crosslinked PE; △, native PE.

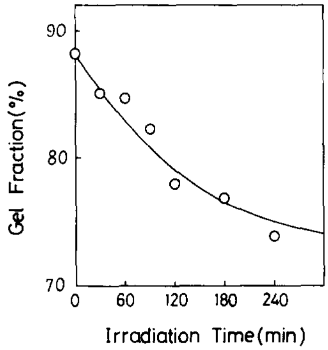


Fig. 9. Changes in gel fraction of crosslinked PE against irradiation time.

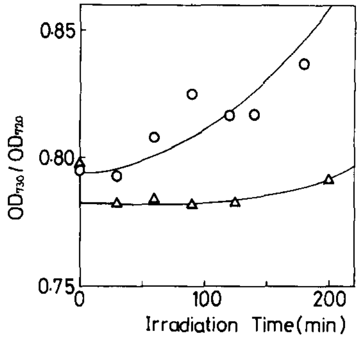


Fig. 10. Changes of OD_{730}/OD_{720} against photo-irradiation time. ○, Crosslinked PE; △, native PE.

increasing irradiation time. This indicates that the degree of crystallinity of PE increases during photo-irradiation. The change of OD_{730}/OD_{720} with irradiation time is greater in crosslinked PE than in native PE.

These experimental results are supported by density measurements for photo-irradiated PE, which are shown in Fig. 11. The density of photo-irradiated PE increases slightly with irradiation time in both cases. The increase of density corresponds to an increase in the packing density of PE molecules, i.e. an increase in crystallinity.

The above results may be summarized as follows

(1) The degree of crystallinity of crosslinked PE increases with photo-irradiation time.

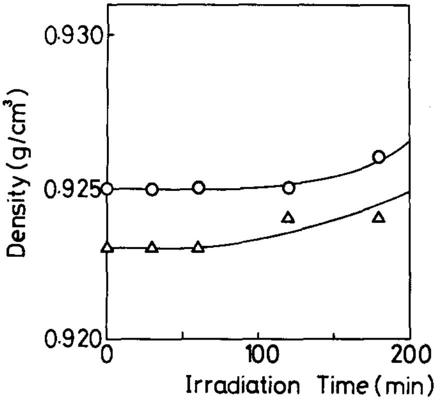
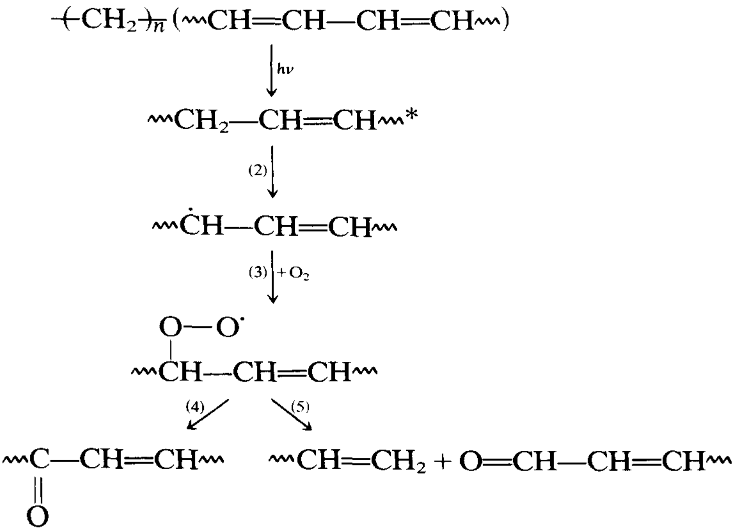


Fig. 11. Changes of the density of PE against photo-irradiation time. ○, Crosslinked PE; △, native PE.

(2) Chain scission of crosslinked PE takes place during photo-irradiation, and increases with irradiation time.

Although at first sight conclusions (1) and (2) seem to conflict with each other, they may be reconciled as follows. The crosslinking of PE takes place only in the amorphous regions because the radicals formed in the crystalline region by γ-irradiation cannot move freely and contribute to crosslinking under our experimental conditions (irradiation was carried out at room temperature). Chain scission in crosslinked PE by photo-irradiation may also take place in the amorphous regions and contribute to a decrease in the gel fraction. The increase in density corresponds to an enhancement in the regularity of the molecular chains. The chain scission in crosslinked PE in the amorphous regions makes the polymer chain more mobile, because the chain lengths of PE molecules become shorter. This causes the degree of crystallinity to increase due to closer packing of the smaller chains. A similar argument has been given for the oxidation of PE by nitric acid:[11] as the reaction proceeds, the degree of crystallinity is substantially increased as a result of both the removal of the amorphous material by oxidation and also the continued crystallization of chains thereby freed from entanglement.

The following reaction scheme can reasonably explain the photodegradation of the crosslinked PE films. Since the mechanism for γ-ray-induced crosslinking of PE is well known, we will not repeat it here.[12]



Processes (4) and (5) have been proven by FT–IR measurements. Diene formation has been identified by UV absorption measurements. The photosensitive behaviour of PE crosslinked by γ-irradiation may arise from the formation of photosensitive groups in PE molecules such as dienes. As already mentioned in the introduction, since crosslinked PE has many excellent mechanical and chemical properties, the photostabilization of crosslinked PE is an important problem. It is important to prevent the formation of photosensitive groups in PE during γ-irradiation. The formation of photosensitive groups such as dienes may be prevented by removing their precursors such as allyl and dienyl radicals. This is probably achieved by annealing γ-irradiated PE. The photostability of crosslinked PE will be improved by such procedures. A further study along these lines is now in progress in our laboratory.

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