Radiation-Modified Atactic Polypropylene as a Sensitizer for Photodegradation of Polyethylene

HIDEKI OMICHI, MIYUKI HAGIWARA, MASAHARU ASANO, and KUNIO ARAKI, *Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Watanuki-machi, Takasaki, Gunma-ken, Japan*

Synopsis

Atactic polypropylene (APP) was dissolved in CCl_4 and irradiated with ^{60}Co gamma rays in various gas atmospheres (air, O_2, N_2, and Cl_2). A small amount of the irradiated APP was blended with polyethylene (PE) as a sensitizer for photodegradation of PE. There was no significant acceleration of decrease in yield strength of PE with UV exposure when oxidized APP or chlorinated APP was used. On the contrary, the use of the APP which was both oxidized and chlorinated caused a considerable acceleration of decrease in both yield strength and elongation. From the fact that the amount of carbonyl groups formed in the matrix PE with UV light exposure was closely related to both the amount of carbonyl groups and the amount of C–Cl bonds existing in the APP before the UV exposure, it was concluded that the combined action of carbonyl groups and C–Cl bonds in the sensitizer is important in the promotion of the photodegradation of the matrix polymer.

INTRODUCTION

Degradation of polymers under sunlight or UV light can be promoted by adding sensitizers such as inorganic metal oxides,[1] carbonyl compounds,[2] quinones,[3] peroxides,[4] nitrogen chromophore compounds,[5] polycyclic hydrocarbons,[6] and dyes.[7] The light energy is primarily absorbed by chromophores of the sensitizers and used for the formation of radicals or singlet oxygens which attack the polymers.[4]

Mostly these sensitizers are compounds of low molecular weight, but polymeric sensitizers may have a practical value because of their stability to heat, chemical agents, solvents, etc.

In our previous paper,[8] the modification of atactic polypropylene (APP) by radiation-induced oxidation and chlorination was studied. In the present work the modified APP was examined as a sensitizer for photodegradation of polyethylene (PE).

EXPERIMENTAL

Materials

A mass of crude APP (Chisso Co.) was pulverized under freeze condition with liquid nitrogen. Commercially available PE (Mitsubishi Petrochem. ZF 36) was used without further purification. A guaranteed reagent-grade carbon tetrachloride (CCl_4) was used as solvent for APP.

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Procedure

About 5 g APP was dissolved in 1 liter CCl_4 and irradiated with ^{60}Co gamma rays at room temperature in various gas atmospheres (air, O_2, N_2, Cl_2, and O_2 + Cl_2). After the irradiation the solution was poured into cold methanol for precipitating the irradiated APP. The precipitate was repeatedly washed with fresh methanol and dried in a vacuum drying oven. Ten phr of the irradiated APP was blended with PE on a mixing roll at 120°C and was pressed at this temperature to make test pieces 1 mm thick. The UV exposure of the samples, which had been cut into the dumbbell shape specified by ASTM D 1822, was carried out with a Suga Test xenon weathermeter, model WE-6X-HC, or with a high-pressure mercury lamp (Iwasaki, 2.3 kW). The yield strength and elongation were measured at 25°C with an Instron tensile tester, model 1130. In order to measure the degree of oxidation occurring in PE molecules, the matrix PE was separated from the blended polymer by dissolving the samples in *p*-xylene at 138°C and pouring the solutions into *n*-hexane. The purity of the precipitates (matrix PE) was examined by measuring the infrared spectra with a Hitachi IR spectrophotometer, model EPI-G2. The distribution of molecular weight was measured with a Waters gel permeation chromatograph, model 200.

RESULTS AND DISCUSSION

Mechanical Strength of Blended PE

The change in mechanical properties due to UV light exposure was first examined for the PE blended with the APP of different degrees of oxidation. The oxidation of APP was carried out in air or in mixed gases of O_2 and N_2 of different ratios under gamma ray irradiation at room temperature. Figures 1 and 2 show that both yield strength and elongation of the blended PE decrease with the exposure time of UV light. However, no significant acceleration of decrease in these properties is observed by blending the oxidized APP as a sensitizer.

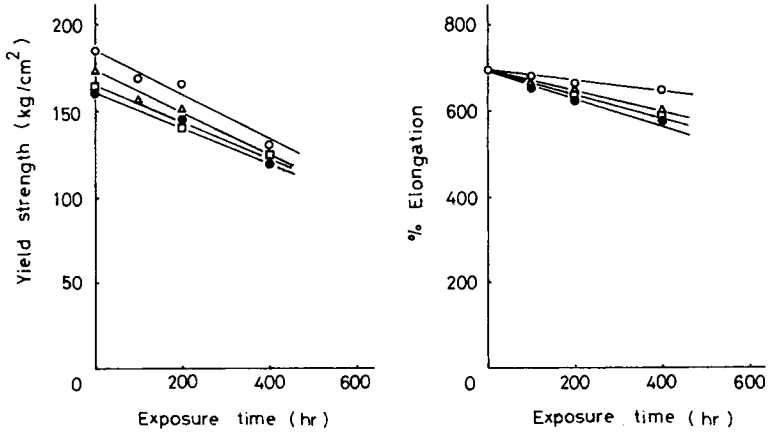


Fig. 1. Effect of UV exposure on yield strength and elongation of PE blended with APP: (○) PE; (△) PE + unirradiated APP; (□) PE + APP irradiated in air up to 20 Mrad; (●) PE + APP irradiated in air up to 50 Mrad.

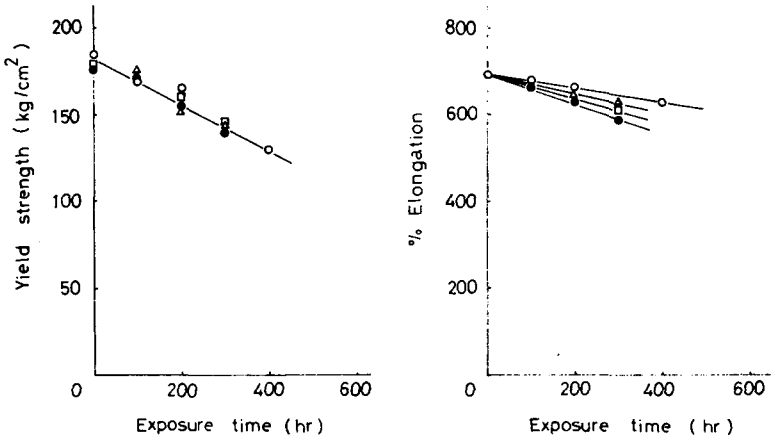


Fig. 2. Effect of UV exposure on yield strength and elongation of PE blended with APP: (○) PE; (△) PE + APP irradiated in N_2; (□) PE + APP irradiated in the mixture of N_2 and O_2 (1:1); (●) PE+ APP irradiated in O_2; irradiation dose, 20 Mrad.

In our previous paper[8] it was found that polyenyl groups as well as C–Cl bonds were introduced into APP by the radiation-induced chlorination. The polyenyl groups in the APP may act as chromophores because polyenyl compounds have high molecular absorption coefficients in a near-ultraviolet region.[4] Figure 3 shows the changes in yield strength and elongation of blended PE with UV exposure. The blending of the chlorinated APP caused no acceleration of decrease in yield strength and only a little acceleration of decrease in elongation. The comparison of Figures 1–3 shows that the chlorinated APP is only marginally better than the oxidized APP. This result suggests that the coexistence of polyenyl chromophores and C–Cl bonds in the sensitizer APP is not so effective for promoting the photodegradation of PE.

The effect of APP which had been oxidized and chlorinated under gamma ray irradiation was next examined. Figure 4 shows that both the yield strength and

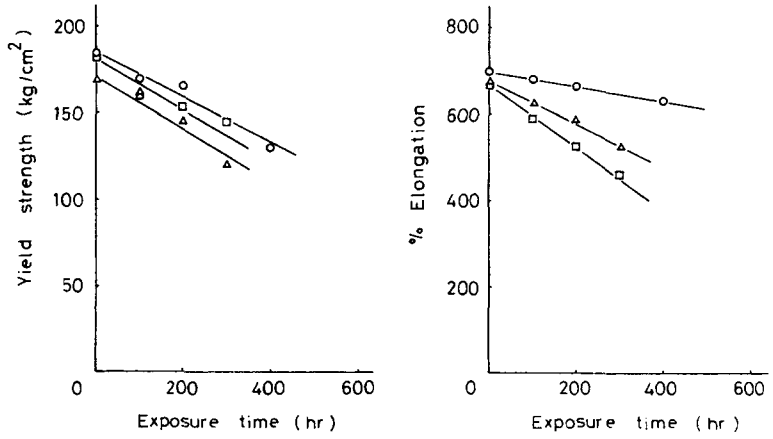


Fig. 3. Effect of UV exposure on yield strength and elongation of PE blended with APP: (○) PE; (△) PE + chlorinated APP (Cl content = 9.3 wt %); (□) PE + chlorinated APP (Cl content = 45.0 wt %).

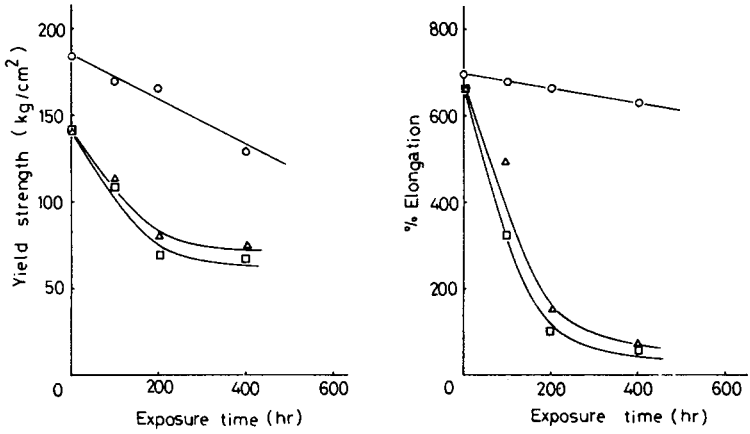


Fig. 4. Effect of UV exposure on yield strength and elongation of PE blended with APP: (○) PE; (△) PE + APP irradiated in Cl_2–O_2 mixture (Cl content in APP = 4.3 wt %); (□) PE + APP irradiated in Cl_2–O_2 mixture (Cl content in APP = 43.5 wt %).

elongation decrease more rapidly than in the former two cases (Figs. 1–3). In the case of oxidized and chlorinated APP the samples exposed to UV light for more than 200 hr became so brittle that further degradation was no longer measured with the tensile tester.

Figure 5 shows the IR spectra of the APP irradiated under vacuum (a), in O_2 (b), and in CCl_4 in the atmosphere of mixed gases of O_2 and Cl_2 (c). The absorptions at 600–800 cm^{-1} are due to C–Cl bonds, and that at 1708 cm^{-1} is due to carbonyl groups. It is clear from these spectra that both carbonyl groups and C–Cl bonds are introduced into APP under the irradiation condition represented by (c). The carbonyl group is well known as a chromophore for near-ultraviolet light.[4] Therefore, the marked acceleration of photodegradation as shown in

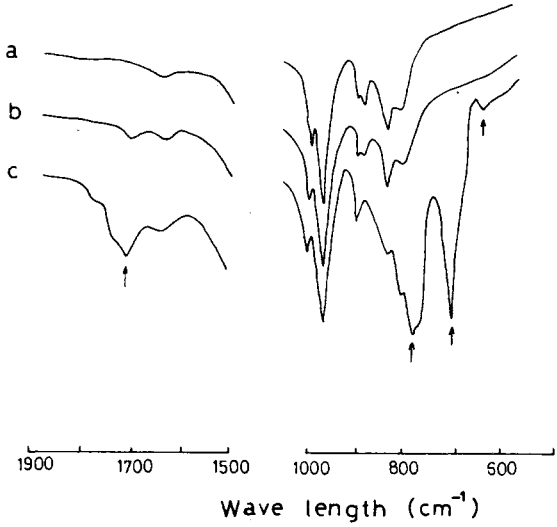


Fig. 5. IR absorption spectra of irradiated APP. Irradiation condition: (a) under vacuum; (b) in O_2; (c) in CCl_4 under the flow of mixed gases of O_2 and Cl_2.

Figure 4 may be caused by the coexistence of carbonyl chromophores and C–Cl bonds in the sensitizer APP.

Comparison of the results in Figures 3 and 4 shows that the carbonyl chromophore is more effective than the polyenyl chromophore.

Structure of Matrix PE

Figure 6 shows the changes in GPC curves of the blended PE with UV exposure. When the exposure time is increased, the curve consists of two peaks; peak I corresponds to the original PE and peak II, to the degraded PE. If the curves (b′) and (c′) are obtained as differences between the observed distribution curves (solid lines) and the curves (dotted lines) which are drawn to resemble the distribution curve of the original PE, they can represent the molecular weight distribution of the degraded PE corresponding to peak II. It is clear that the photodegraded PE has a broad molecular weight distribution and its amount increases with increasing the time of UV exposure.

Changes in molecular structure of the blended PE after UV exposure were investigated by IR spectra measurements. Spectrum (a) in Figure 7 was obtained from the PE blended with unirradiated APP, and spectrum (b) was obtained from the matrix PE after separation from the blended polymer. The absorptions at 1168, 998, 973, and 842 cm^{-1} in spectrum (a) are due to the tertiary methyl groups in APP,[9] and those at 1080, 888, and 730 cm^{-1} are due to PE.[10] Spectrum (b) has no absorptions due to APP. Further, by comparing spectrum (b) with spectrum (c) obtained from original PE, it can be said that the separated matrix PE is completely free from APP.

In order to give a measure of the rate of photo-oxidation of the blended PE, the effect of UV exposure time on IR absorption at 1708 cm^{-1} which appeared in the matrix PE was investigated. The APP blended as a sensitizer was previously irradiated with gamma rays in an atmosphere of various O_2 contents. Figure 8 shows that the rate of carbonyl formation in the matrix PE increases with UV exposure time and that the oxidation is accelerated by increasing the O_2 content in the atmosphere for gamma ray irradiation. Since the amount of carbonyl groups in APP can be assumed to increase with increasing O_2 content, the results in Figure 8 demonstrate that the formation of carbonyl groups in the matrix PE is sensitized by the carbonyl groups in APP.

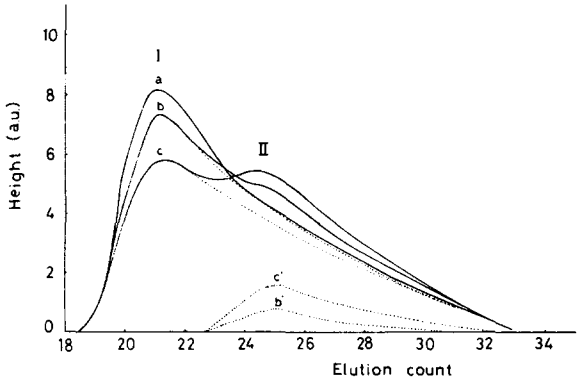


Fig. 6. GPC curves of PE: (a) unexposed; (b) exposed to UV light for 8 hr; (c) exposed to UV light for 15 hr. Dotted lines show the imaginary distribution curves corresponding to peaks I and II.

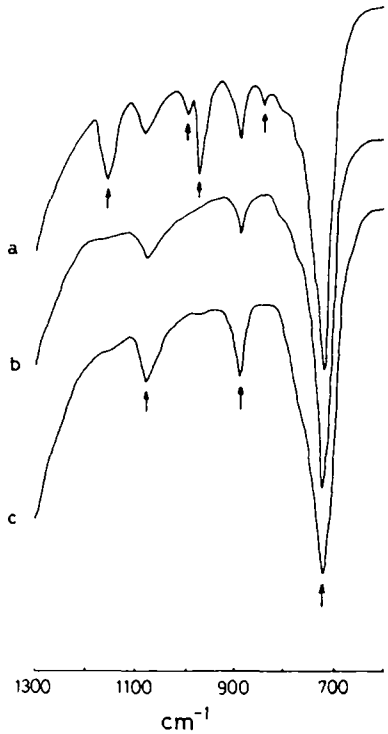


Fig. 7. IR absorption spectra of (a) PE blended with APP before the procedure of separation, (b) PE after the procedure of separation, and (c) original PE.

Figure 9 shows the plot of IR absorption due to carbonyl groups in the blended PE against the chlorine content in the sensitizer APP. The absorption increases from the values shown by the lower curve to those of the upper curve with UV exposure. The net amount of carbonyl groups produced in the matrix PE increases with increasing chlorine content in the sensitizer APP.

The results in Figures 8 and 9 show that both carbonyl groups and C–Cl bonds existing in the sensitizer APP contribute to the promoted formation of carbonyl groups in the matrix PE. The effect of these groups, however, may differ. The

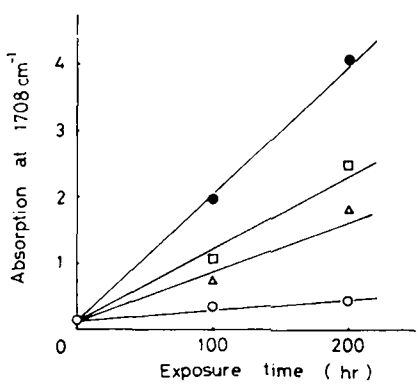


Fig. 8. Influence of UV exposure on increase in absorption at 1708 cm^{-1} in matrix PE. Symbols are the same as in Fig. 2.

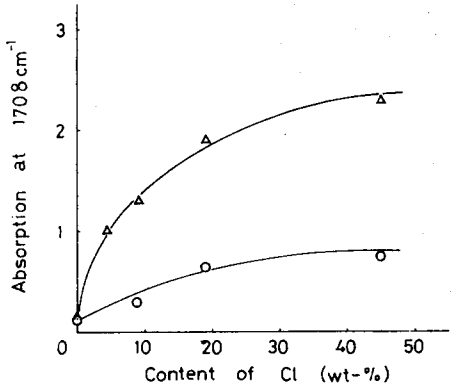


Fig. 9. Influence of Cl content in APP on increase in absorption at 1708 cm^{-1} of PE blended with APP: (○) unexposed; (△) exposed to UV for 16 hr.

energy of near-ultraviolet light may primarily be absorbed by carbonyl groups and produce a certain amount of radicals which are able to attack the matrix PE. If C–Cl bonds coexist with the carbonyl groups in the sensitizer APP, the absorbed light energy may produce chlorine radicals which are more reactive and mobile than the radicals from simply oxidized APP. Thus, the combination of the two functional groups of different action may exert its effect on absorbing the light energy and consuming it for producing reactive radicals. The results in Figure 4 exactly show that this combination is effective for the photodegradation of PE when it is used as a sensitizer.

Degradation Mechanism

A number of works have been reported on the photodegradation mechanism of polymers.[4,11–22] Some workers[14,18,21] studied the effect of sample thickness on the extent of photo-oxidation. Adams[22] studied the composition of functional groups produced in the photodegraded polyethylene and polypropylene. Sitek et al.[15] clarified the difference in efficiency of initiation between backbone carbonyl group and side-chain ketone group when they were introduced in polyethylene. Wiles et al.[12–14] reported that the decomposition route (Norrish type I or type II) of polyketone which was produced in polypropylene depended on the polyketone structure. Kwei[19] clarified the polyketone structure of oxidized poly(vinyl chloride) and suggested a plausible degradation mechanism.

Although products such as polyketones formed in polymer play a main role at the advanced stages of photo-oxidation, the sensitizers can have a significant influence on the initial stage.[11] The light energy is primarily absorbed by chromophores of the sensitizers and used for the formation of reactive radicals or singlet oxygens which attack the polymer. The blending of radiation-modified APP with PE was aimed at such a sensitizing effect of the functional groups in APP. The results in Figures 1 and 2, however, show that the effect of oxidized APP is negligibly small. The APP which contains both polyene and C–Cl bond is also not very effective (Fig. 3), while the APP which contains both carbonyls and C–Cl bonds is evidently effective in the photodegradation of PE, as shown in Figure 4. This indicates that the combination of carbonyl chromophore and C–Cl bond in the sensitizer is useful for the initiation of photooxidation.

Thus, the reaction mechanism in this case may be as follows: When PE is blended with the sensitizer APP and exposed to UV light, the absorption of light energy primarily occurs at the carbonyl groups in the sensitizer. The energy is transferred to C–Cl bonds in the neighborhood of the carbonyl groups and used for the elimination of reactive chlorine atoms. These steps may be schematically represented as follows:

$$\mathrm{APP}(>\mathrm{C{=}O},\ \mathrm{C{-}Cl}) \xrightarrow{h\nu} \mathrm{APP}^*(>\mathrm{C{=}O}^*,\ \mathrm{C{-}Cl}) \tag{1}$$

$$\mathrm{APP}^*(>\mathrm{C{=}O}^*,\ \mathrm{C{-}Cl}) \rightarrow \mathrm{APP}^*(>\mathrm{C{=}O},\ \mathrm{C{-}Cl}^*) \tag{2}$$

$$\mathrm{APP}^*(>\mathrm{C{=}O},\ \mathrm{C{-}Cl}^*) \rightarrow \mathrm{APP}^{\cdot} + {}^{\cdot}\mathrm{Cl} \tag{3}$$

where APP (>C=O, C–Cl) denotes APP containing both carbonyl groups and C–Cl bonds in the molecule and APP* denotes the photoexcited APP. This scheme is based on the fact that aliphatic ketones have an absorption maximum in the range of 270–290 nm and that the light energy of this range (100 kcal/mole) is large enough to break C–Cl bonds (78 kcal/mole).

The reactive chlorine atom produced by reaction (3) abstracts hydrogen atom from the matrix PE to produce PE radical, which is oxidized and degraded as follows:

$$\mathrm{PH} + {}^{\cdot}\mathrm{Cl} \rightarrow \mathrm{P}^{\cdot} + \mathrm{HCl} \tag{4}$$

$$\mathrm{P}^{\cdot} + \mathrm{O_2} \rightarrow \mathrm{POO}^{\cdot} \tag{5}$$

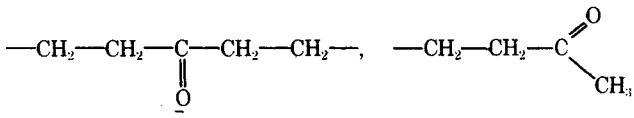
$$\mathrm{POO}^{\cdot} + \mathrm{PH} \rightarrow \mathrm{POOH} + \mathrm{P}^{\cdot} \tag{6}$$

$$\mathrm{POOH} \xrightarrow{h\nu} \mathrm{PH}(>\mathrm{C{=}O}) + \mathrm{H_2O} \tag{7}$$

$$\mathrm{PH}(>\mathrm{C{=}O}) \xrightarrow{h\nu} \text{degraded polymer} \tag{8}$$

where PH and P· are the matrix PE and its radical, respectively. Reaction (4) is supported by the fact that the carbonyl content in matrix PE is increased with increasing C–Cl content in the sensitizer APP (Fig. 9).

Reaction (8) may proceed either via a Norrish type I or Norrish type II reaction according to the polyketone structure of PH(>C=O).[4,11] The wide molecular weight distribution of degraded PE (Fig. 6) indicates that a variety of polyketone structure such as those given below are possibly produced through reactions (4) through (7):



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