Korea Polymer Journal, Vol. 3, No. 1, pp 7-11 (1995)

UV and Thermal Oxidation of Polyethylene Compounded with Photosensitizer

Chang Lim Jun

Department of Industrial Chemistry, Hong Ik University,
Jochiwon, Chungnam, 339-800, Korea

Received August 20, 1994

ABSTRACT: The photoinitiated oxidative degradation was measured in polyethylene films compounded with the photo-sensitizer. The oxidation was monitered by changes of carbonyl formation detected by IR spectroscopy. The disintegration of mechanical properties of polyethylene films was analyzed by change of elongation-at-break which can be associated with a brittleness. The two measurements bring us the same conclusion that the oxidative aging proceedes in the dark, once the oxidation has been initiated by UV-irradiation. These experiments actually mean that a continous oxidative aging of the photo-degradable plastics occurs even after buing under ground.

Introduction

Most of synthetic polymeric materials have poor self-degradability and long life-time, and cause serious solid waste pollution problem. Polyethylene is a major material used for packaging, disposal products and agricultural films, and it is one of the hardest materials to be degraded by nature. In this study, we prepared the films of polyethylene compounded with a photodegradation accelerating additive, and the oxidative degradations of these films by ultraviolet light and heat are studied using infrared spectroscopy and Instron.

The mechanism of polymer oxidation and degradation is complex. Mayo[1] investigated an oxygen induced pyrolysis of polyolefins, Buchachenko[2] reported on the solid phase oxidation of polyolefins, Zsuzsa *et al.*[3] studied the kinetics of the formation of oxygen containing groups during the oxidation of polypropylene, Kawamatsu[4] compared the thermal oxidation of polypropylene with that of polyethylene, Iring *et al.*[5] reported on the change of molecular weight distribution in the thermal oxidation of polyethylene and polypropylene, the same authers[6] examined the formation and decomposition of polyethylene peroxides, Barabas *et al.*[7] identified the volatile products formed in the thermal oxidation of polypropylene, Ivanov *et al.*[8] examined the photo-induced oxidation of rubbers, polybutadiene and polyisoprene, which also occurs with photo-induced mechanism involving hydroperoxides.

The oxidation of polymers, especially polyolefins, autocatalytically proceeds in the presence of oxygen by a free-radical mechanism. The primary product is a hydroperoxide which decomposes to free-radicals that initiate the chain reactions. The hydroperoxide decompositions are accelerated by heat, light and certain metallic impurities.[9]

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \cdot\mathrm{OH}$$
$$2\ \mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{ROO}\cdot + \mathrm{H_2O}$$

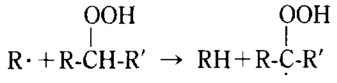
Oxygen may react with polymer substrates, RH, in the absence of radical initiator or hydroperoxide, and results in free-radicals via two different paths.[10]

$$\mathrm{RH} + \mathrm{O_2} \rightarrow \mathrm{R}\cdot + \mathrm{HOO}\cdot$$
$$2\ \mathrm{RH} + \mathrm{O_2} \rightarrow \mathrm{R}\cdot + \mathrm{H}\cdot + \mathrm{ROOH}$$

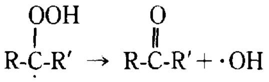
The following reactions may take place by the formed radicals.

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \rightarrow \mathrm{ROO}\cdot$$
$$\mathrm{H}\cdot + \mathrm{O_2} \rightarrow \mathrm{HOO}\cdot$$
$$\mathrm{HOO}\cdot + \mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{H_2O_2}$$
$$\mathrm{ROO}\cdot + \mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{ROOH}$$

The hydroperoxide on decomposition forms alkoxy radicals which abstract hydrogen to produce alcohols or ketons.



$$\mathrm{R}\cdot + \mathrm{R\text{-}}\overset{\mathrm{OOH}}{\overset{|}{\mathrm{C}}}\mathrm{H\text{-}R'} \rightarrow \mathrm{RH} + \mathrm{R\text{-}}\overset{\mathrm{OOH}}{\overset{|}{\underset{\cdot}{\mathrm{C}}}}\mathrm{\text{-}R'}$$



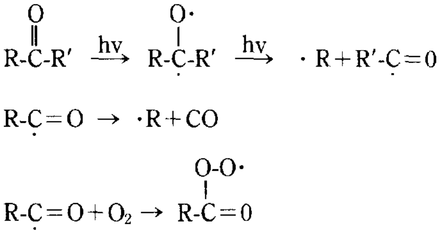
$$R\text{-}\overset{OOH}{\overset{|}{\underset{\cdot}{C}}}\text{-}R' \rightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}R' + \cdot OH$$

In the presence of metallic catalysts, the reactions can be accelerated as follows.

$$ROOH + M^{n-} \rightarrow RO\cdot + M^{(n+1)+} + OH^-$$
$$ROOH + M^{(n+1)+} \rightarrow ROO\cdot + M^+ + H^-$$

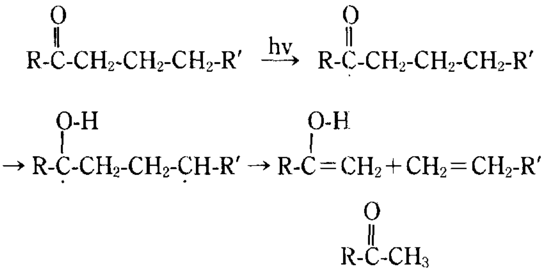
The oxidative chain reaction is the degradation agency responsible for deterioration in properties of the polymer during the usage even under general conditions. Chain scission may occurs in the polymer containing keton groups by two types; Norrish I and II.[11]

Norrish I



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}R' \xrightarrow{hv} R\text{-}\overset{O\cdot}{\overset{|}{\underset{\cdot}{C}}}\text{-}R' \xrightarrow{hv} \cdot R + R'\text{-}\underset{\cdot}{C}=0$$
$$R\text{-}\underset{\cdot}{C}=O \rightarrow \cdot R + CO$$
$$R\text{-}\underset{\cdot}{C}=O + O_2 \rightarrow R\text{-}\overset{O\text{-}O\cdot}{\overset{|}{C}}=0$$

NOrrish II

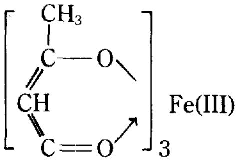


$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R' \xrightarrow{hv} R\text{-}\overset{O}{\overset{\|}{\underset{\cdot}{C}}}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}R'$$
$$\rightarrow R\text{-}\overset{O\text{-}H}{\overset{|}{\underset{\cdot}{C}}}\text{-}CH_2\text{-}CH_2\text{-}\underset{\cdot}{C}H\text{-}R' \rightarrow R\text{-}\overset{O\text{-}H}{\overset{|}{C}}=CH_2 + CH_2=CH_2\text{-}R'$$
$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

Many scientists have studied various photosensitizers for accelerating oxidative degradation inducrd by UV light. Researchers of Exxon,[12] ICI[13] and Badishe[14] used benzen and naphthalene derivative as photosensitizer and thio-compounds have been also studied.[15] Scott *et al.*[16] reported effective agents; transition metal complex of acetate, oleate, acetylacetonate etc.

Experimentals

Materials. We synthesized ferric acetylacetonate as follows; the mixture of the methanol solution of acetylacetonate and the aqeuous solution of ferric (III) chloride with small amount of sodium acetate is heated at 90~100 ℃, and cooled to room temperature, then red fine crystals are obtained by recrystallization in refrigerator. The product is washed with deionized water and dried in vacuum oven.



Film Preparation. Low density polyethylene was compounded with 0.35% of the prepared ferric acetylacetonate by Brabender (plasti-corder) at 150 ℃, 50 rpm for 50 minutes, and PE films with average thickness 0.3 mm are prepared by simple press method.

Irradiation and Measurements. The prepared films are treated by UV light (Japan Eye Cure Light, 1 Kw, length 25 cm) for 30 minutes, 2 and 5 hours, and these pre-treated films are aged at different temperatures (20, 40, 70 ℃), and the changes of carbonyl formation are detected on the first day, 5th days, 9th days and 17th days by IR spectrophotometer Bio-Lab model FTS-60M. The change of the mechanical properties (the elongation-at-break..) of films were measured by Instron under the cross-head speed 50 mm/min. Average of five tests was taken to report.

Results and Discussion

Figure 1 shows four spectra. The first spectrum is that of ferric acetylacetonate. The second is of pure polyethylene. The third is of the polyethylene compounded with ferric acetylacetonate. This spectrum show that the peak placed at 1570 cm^{-1} of ferric acetylacetonate (first spectrum) is added to that of pure polyethylene (second spectrum). The last spectrum shows two features. That is the peak at 1570 cm^{-1} assigned to the photosesitizer have been disappeared, and the one at 1710 cm^{-1} has been increased, indicative of some oxidations during compounding process at high temperature(150 ℃) with the aid of ferric acetylacetonate as initiator. But the polyethylene films without photosensitizer do not show much change in spite of UV radiation for untill 5 hours as shown in Figure 2.

The polyethylene films compounded with ferric acetylacetonate are exposed to UV radiation for 0, 1/2, 2, 5 hours before aging under heat.

The aging of UV-pretreated the polyethylene films is carried out under various temperatures (20,

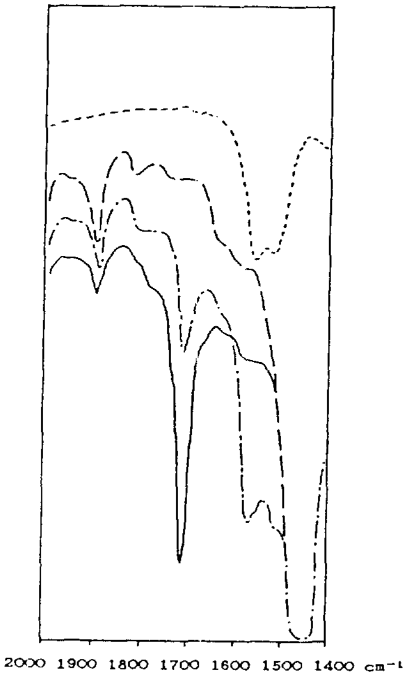


Figure 1. I.R. spectra of pure ferric acetyacetonate (----), of pure polyethylene (— —), of PE film compounded with ferric acetyl acetonate (— -), and of the film let in shade for one night (——).

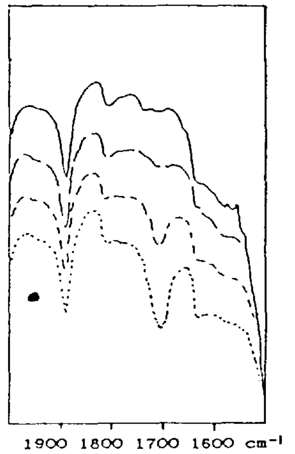


Figure 2. I.R. spectra of PE films without photosensitizer (——) and changes on irradiation by ultraviolet light for 30 minutes (— —), 2 hourse (----), and 5 hours (··········).

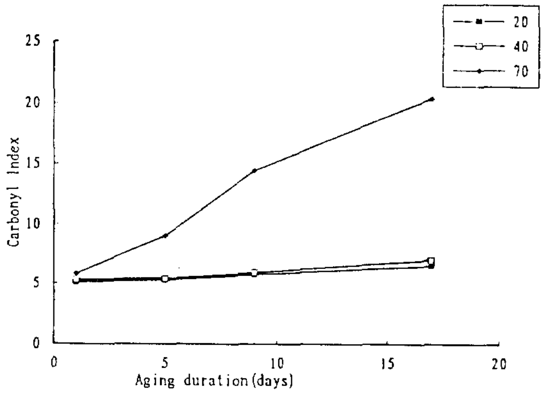


Figure 3. Post thermal aging test of the UV-untreated polyethylene films compounded with the photosensitizer under different temperatures(20, 40, 70 deg.C).

40, 70 ℃) in shade for 17 days. The evaluation of the oxidative degradation by IR spectroscopy was done by following an increase in carbonyl absorbance peak at 1710 cm^{-1} during thermal aging. A peak at 1895 cm^{-1} characteristic of the polyethylene itself due to C-H deformation was used as a reference peak. The results were expressed by carbonyl index defined as [Area of a peak at 1710 cm^{-1} Area of a peak at 1895 cm^{-1}].

Figure 3 shows the changes of carbonyl index of the 3 kinds of the samples untreated by UV light as a function of aging time at 20, 40, 70 ℃. No significant changes are detected for low temperatures(20, 40 ℃). At high temperature, we can see some increase of carbonyl index due to a post thermal oxidation.

Figures 4, 5, 6 also show the change of carbonyl index of the polyethylene films which were UV-treated for 0.5, 2, 5 hours. Much higher carbonyl index and higher rate of carbonyl formation are monitered with longer UV-pretreatment and higher aging temperature.

Figure 6 shows the rate of carbonyl formation is small even for 5 days. The reason is to be associated with the formation of a stable keton radical and a carboxylic acid salt by a chain scisson of polyethylene.

Figure 7 shows the remarkable change. This figure includes two spectra of the UV-pretreated polyethylene film compounded with photosensitizer before thermal aging and the one aged at 70 ℃ for 17 days. This spectrum shows a great shoulder at 1780 cm^{-1} on the main peaks at 1710 cm^{-1}. These changes are regarded as excessive oxidations, and the oxidized polymeric chains progressed up to chain scissions. The chain scissions of polyolefin with carbonyl groups generally form unsaturated terminal groups,[17] and some carboxylic terminations.[18] The peaks at 1780 cm^{-1} ought to be assi-

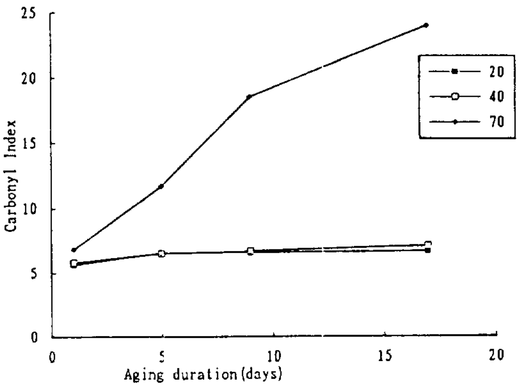


Figure 4. Post thermal aging test of the polyethylene films UV-treated for 30 minutes under different temperatures (20, 40, 70 deg.C).

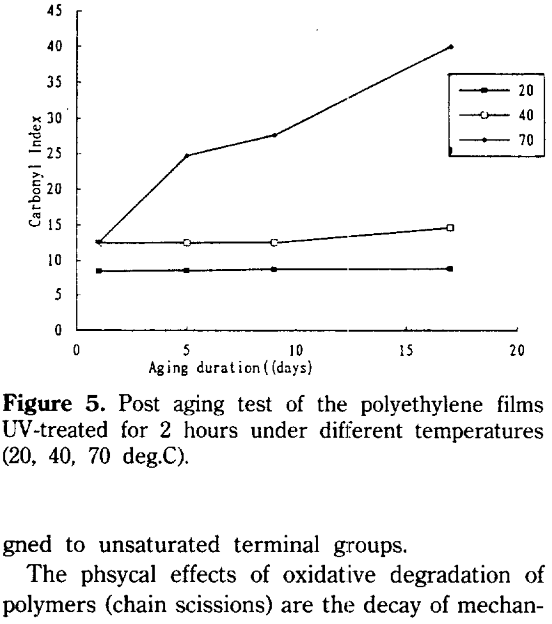


Figure 5. Post aging test of the polyethylene films UV-treated for 2 hours under different temperatures (20, 40, 70 deg.C).

gned to unsaturated terminal groups.

The phsycal effects of oxidative degradation of polymers (chain scissions) are the decay of mechanical properties (strenth, elongation, etc.) and discoloration (mainly yellowing).[19] Especially, elongation-at-break is notably dropped following oxidation and degradation in the case of polyethylene.[20] It eventually becomes brittle, as evidenced by the change in elongation-at-break of polyethylene films, in the course of being oxidized and degraded.[21]

Figure 8 shows the change in elongation-at-break of the polyethylene films compounded with photosensitizer and treated by UV light for different time as a function of aging temperature for 17 days. Untreated polyethylene film and the film treated for 30 minutes by UV light show no significant change

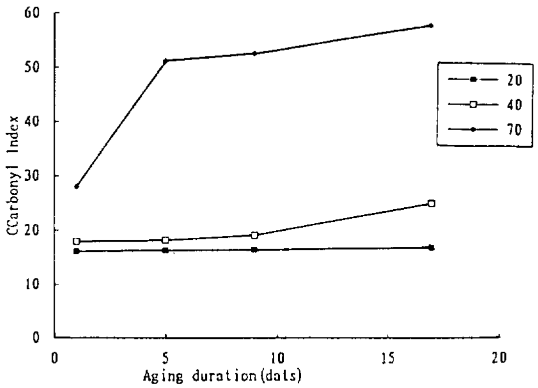


Figure 6. Post aging test of the polyethylene films UV-treated for 5 hours under different temperatures (20, 40, 70 deg.C).

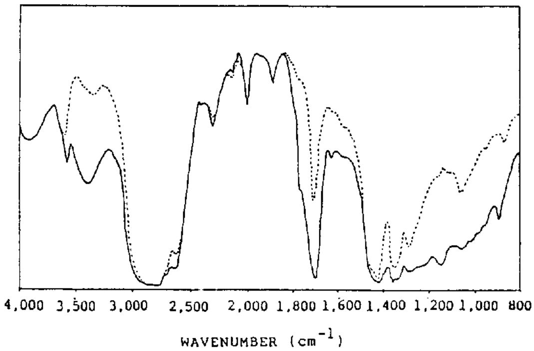


Figure 7. I.R. spectra of PE films, compounded and UV treated for 5 hours, before (----) and after (——) aging at 70 ℃ for 17 days.

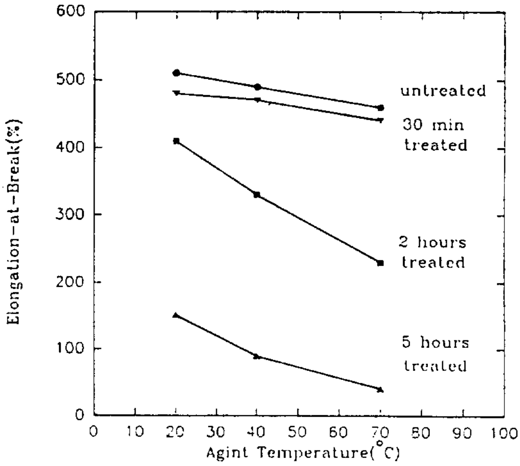


Figure 8. Elongation-at-break of the aged films UV-pretreated.

in elongation-at-break. But the longer treated films by UV irradiation show a much drop(150% for 20, 90% for 40, 40% for 70 ℃) in elongation-at-break to be brittle. The samples of UV-pretreated for 5 hours present notable drop in elongation properties, which is well agreed with the IR spectrum in Figure 6 and Figure 7.

Conclusion

Oxidative degradation of the polyethylene has been accelerated by compounding with photosensitizer, and shown some amount of carbonyl groups in polymer chains. And oxidative degradation of the photo-initiated polyethylene is followed even in shade (without UV light). This result can be applied on the development of self-degradable materials in natural condition, that is, the oxidative degradation of polymeric materials can be initiated by sunlight and developed by underground heat.

Acknoledgement. It is gratefully acknoledged that this work is supported by the research grant of the year 1993 from Hong Ik University.

References

(1) F. R. Mayo, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 713 (1976).
(2) A. L. Buchachenko, *J. Polym. Sci., Polym. Symp.*, **57**, 299 (1977).
(3) L. H. Zsuzsa, M. Iring, G. Balint, T. Kelen, and F. Tudos, *Magy. Kem. Foly.*, **83**, 257 (1977).
(4) S. Kawamatsu, *NKK HDH*, **12**, 65 (1977).
(5) M. Iring, L. H. Zsuzsa, T. Kelen, F. Tudos, L. Fuzes, G. Samay, and G. Bodor, *J. Polym. Sci., Polym. Symp.*, **57**, 55 (1977).
(6) M. Iring, L. H. Zsuzsa, K. Barbas, T. Kelen, and F. Tudos, *Eur. Polym. J.*, **14**, 439 (1978).
(7) M. Barbas, M. Iring, Z. S. Laszlo-Hedvig, TKelen, and F. Tudos, *Magy. Kem. Foly.*, **84**, 344 (1978).
(8) V. B. Ivanov, S. G. Butyagin, and V. Ya. Shlyapintokh, *Kinet. Katak.*, **20**, 1330 (1979).
(9) S. S. Stivala, J. Kimura, and S. M. Gabbay, "*Degradation and Stabilization of Polyolefins*", Ed. by N. A. Allen, Appl. Sci. Pub., England, 1983.
(10) L. Reich and S. S. Stivala, "*Elements of Polymer Degradation*", McGraw-Hill, New York, 1971.
(11) F. Gugumus, *Makromol, Chem., Macromol. Symp.*, **27**, 25-84 (1989).
(12) U.S. Patent 4,037,034 (1977).
(13) U.S. Patent 3,978,033 and 3,994,869 (1976).
(14) G.B. Patent 1,412,877 (1975).
(15) G.B. 2,187,193 A (1989).
(16) U.S. Patent 3,454,510 and 4,067,836 (1978).
(17) H. Kubota, K. Takahashi, and Y. Ogiwara, *Polym. Degrad. Stab.*, **24**, 201-211 (1987).
(18) H. Omichi and M. Hagiwara, *Polymer Photochemistry*, **1**, 15-23 (1981).
(19) D. W. Van Krevelen, "*Properties of Polymers*", p. 470, Elsevier England, 1976.
(20) E. G. Bobalek, J. N. Henderson, T. T. Serafini, and J. R. Shelton, *J. Appl. Polym. Sci.*, **2**, 210 (1959).
(21) P. Vink, "*Degradation and Stabillisation of polyolefins*", p. 213, Ed. by N. S. Allen, Appl. Sci. Publ., England, 1983.