

Formation of 2,4-Dinitrophenylhydrazones in High-Density Polyethylene Film Irradiated with Ultraviolet Light

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Synopsis

Polyethylene films were irradiated in air by ultraviolet light. 2,4-Dinitrophenylhydrazine was reacted on the irradiated films. The changes in amounts of carbonyl groups and 2,4-dinitrophenylhydrazones formed in the films were inferred by comparing their absorptions in the infrared and ultraviolet spectra, respectively. It seems that the contents of carbonyl groups formed in the amorphous regions in the high-density polyethylene films by the irradiation were larger than the contents of carbonyl groups formed in the amorphous regions in the low-density polyethylene films. The decreases in contact angles of water on the high-density polyethylene films by the irradiation were larger than the decreases in the contact angles on the low-density polyethylene films. The amounts of 2,4-dinitrophenylhydrazones formed in the irradiated high-density polyethylene films were less than the amounts of 2,4-dinitrophenylhydrazones formed in the irradiated low-density polyethylene films.

INTRODUCTION

In a previous paper,¹ the formation of 2,4-dinitrophenylhydrazones in low-density polyethylene films irradiated in air with ultraviolet light and the regeneration of carbonyl groups from the 2,4-dinitrophenylhydrazones in the irradiated films were reported. In this work, the high-density polyethylene films were irradiated in air by ultraviolet light, and 2,4-dinitrophenylhydrazine was reacted on the irradiated films, and the changes of the contents of carbonyl groups in the irradiated films, the contact angles of water on the irradiated films, and the amounts of 2,4-dinitrophenylhydrazones formed in the irradiated films were compared with their changes in irradiated low-density polyethylene films. The results are reported in this paper.

EXPERIMENTAL

Films

High-density polyethylene film and low-density polyethylene film (used in a previous work¹) received from Showa Yuka Company were used in this work. The densities, crystallinities, and methyl group and unsaturated group contents in the films, according to the specification of the samples received from Showa

TABLE I
Densities, Crystallinities, and Methyl Group and Unsaturated Group Contents of Samples

	HDPE (high-density polyethylene film)	LDPE (low-density polyethylene film)
Density	0.949 g/ml	0.926 g/ml
Crystallinity ^a	80%	67%
—CH ₃ /1000 C ^b	1.6	19.9
—CH=CH ₂ /1000 C ^c	0.8	trace amount
—CH=CH—/1000 C ^c	trace amount	trace amount
>C=CH ₂ /1000 C ^c	trace amount	0.2

^a Obtained by x-ray method.²⁻⁴

^b Obtained according to ASTM D2238-64T, using infrared spectroscopy.

^c Obtained by using infrared spectroscopy.^{5,6}

Yuka Company, are given in Table I. Their films contained no additives. The HDPE and LDPE thicknesses were 0.087 and 0.10 mm, respectively.

Irradiation of Films

A low-pressure mercury lamp (Ushio UL 2-1SQ) was used which emits more than 90% of its light at 2537 Å. No filter was necessary. Every sample was exposed at a distance of 6 cm from the Ushio lamp in air atmosphere. The temperature in the atmosphere was maintained at about 20°C during the irradiation.

Measurement of Formation of Carbonyl Groups

The films were irradiated for different periods of time. The intensity of absorption at 1715 cm⁻¹ in each film was measured with a Perkin-Elmer Model 180 infrared spectrophotometer. The calculation of absorbance was done by baseline method. The change in the amount of carbonyl groups formed in each film was inferred by comparing their absorptions.

Measurement of Wettability with Water

The films were irradiated for different periods of time. The contact angle of a drop of water placed on each film surface was measured by using an Erma Model G-1 contact angle meter. The mean of ten measurements was taken in each film. All measurements were made at about 50% R.H. and 25°C, within 10 sec of placing each drop.

Measurement of Formation of 2,4-Dinitrophenylhydrazones

The reagents were prepared by the method carried out in a previous work.⁷ 2,4-Dinitrophenylhydrazine solution was prepared by mixing 2,4-dinitrophenylhydrazine, 1 g, hydrochloric acid, 5 ml, water, 5 ml, and ethyl alcohol, 100 ml. The solution was prepared just before use in every experiment.

The films irradiated for different periods of time were immersed in the 2,4-dinitrophenylhydrazine solution and removed from the hydrazine solution after 5 min had elapsed.

The films irradiated for 8 hr were immersed in the 2,4-dinitrophenylhydrazine solution and removed from the hydrazine solution after different periods of time had elapsed.

Their films were repeatedly washed with ethyl alcohol until the hydrazine absorption at 1200 cm^{-1} band in the infrared spectrum had disappeared, and dried.

The absorptions of 2,4-dinitrophenylhydrazones at $365\text{ m}\mu$ in their films were measured by using a Hitachi Model EPS-3 recording ultraviolet spectrometer. The change in amount of the hydrazones formed in each film was inferred by comparing their absorptions.

RESULTS AND DISCUSSION

Formation of Carbonyl Groups by Irradiation

The infrared spectrum at 1800 to 1700 cm^{-1} in high-density polyethylene film irradiated by ultraviolet light is shown in Figure 1. The absorptions⁸⁻¹² of the C=O stretching vibration appeared at about 1760 to 1700 cm^{-1} . The spectral change in the infrared spectrum shows that carbonyl groups were formed in the molecular chains when the film was irradiated by ultraviolet light.

Plots of A/l of carbonyl groups at 1715 cm^{-1} in the irradiated films versus times of irradiation on the films are shown in Figure 2, where A is the absorbance of the each film and l is the thickness of the film. The absorption in HDPE was larger than the absorption in LDPE at each irradiation time. The amount of amorphous region in LDPE is more than the amount of amorphous region in HDPE. Therefore, it is considered that the content of carbonyl groups formed in the amorphous region in HDPE was larger than the content of carbonyl groups formed in the amorphous region in LDPE.

Matsuda and Kurihara¹² have reported that the increases in absorption at regions of carbonyl stretching vibration in the infrared spectra in high-density polyethylene films were larger than the increases in absorption at regions of

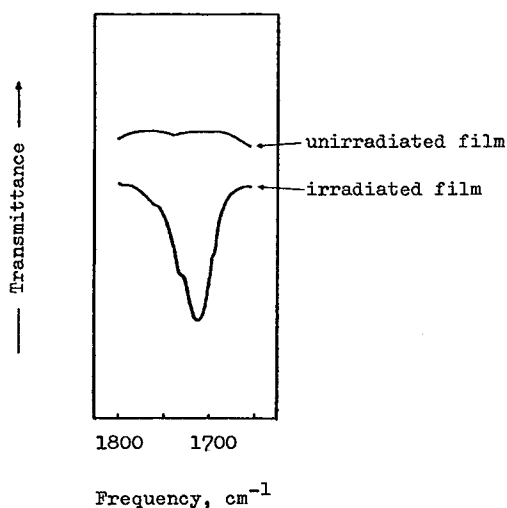


Fig. 1. Carbonyl stretching region of irradiated HDPE.

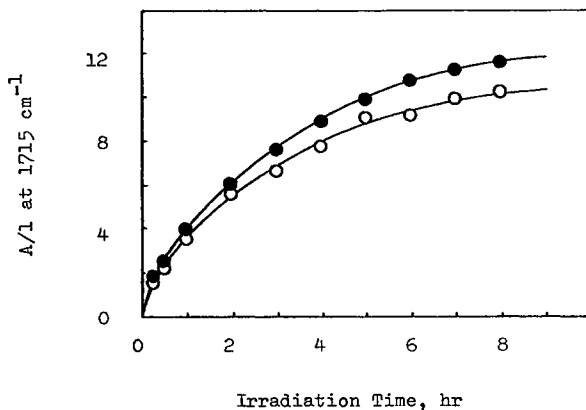


Fig. 2. Plot of A/l for irradiated HDPE (●) and LDPE (○) at 1715 cm^{-1} vs. irradiation time.

carbonyl stretching vibration in the infrared spectra in low-density polyethylene films when the high-density polyethylene films and low-density polyethylene films were irradiated in air by ultraviolet light. The origin of this phenomenon is ascribed to a difference in contents of olefinic double bonds in the polymers between high-density polyethylene polymer and low-density polyethylene polymer. Therefore, in this work, it is within the range of possibility that the difference in contents of carbonyl groups formed in the amorphous region in the films between HDPE and LDPE was caused by a difference in contents of olefinic double bonds in the polymers.

The absorptions at 1715 cm^{-1} in the films increased with increase in the irradiation time, and rates of the increases of the absorptions gradually decreased with increase in irradiation time. It seems that carbonyl groups increased with increase in the irradiation time and rates of the increases of carbonyl groups decreased with increase in the irradiation time.

Wettability on Surface of Irradiated Film

Plots of contact angles of water on irradiated films versus times of irradiations on the films are shown in Figure 3. The decreases in the contact angles on HDPE surfaces by irradiation were larger than the decreases in contact angles on LDPE surfaces by irradiation. It is within the range of possibility that the difference of rates of oxidation of polymers in the surfaces of the films between HDPE and LDPE was caused by difference of contents of olefinic double bonds in the polymers.

The contact angles of water on the films decreased with increase in irradiation time in the early stage of the irradiation, and the rates of the decreases decreased with increase in irradiation time. The rates of the decreases of the contact angles were low after the early stage of the irradiation. It seems that the greater part of the oxidation in the surfaces of the films occurred in the early stage of the irradiation.

Formation of 2,4-Dinitrophenylhydrazones in Irradiated Film

The ultraviolet spectrum of high-density polyethylene film when 2,4-dinitrophenylhydrazine was reacted on the film irradiated with ultraviolet light showed

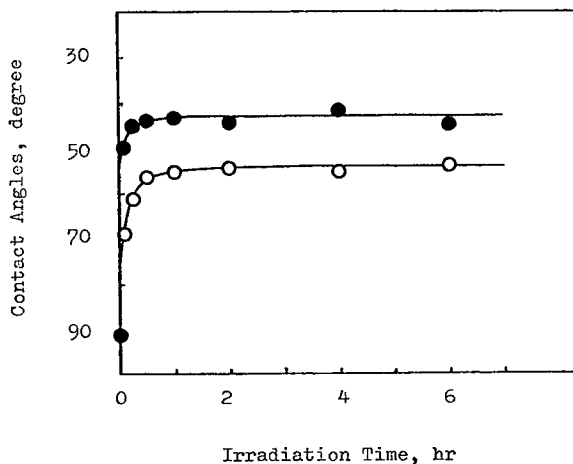


Fig. 3. Contact angles of water on irradiated HDPE (●) and LDPE (○).

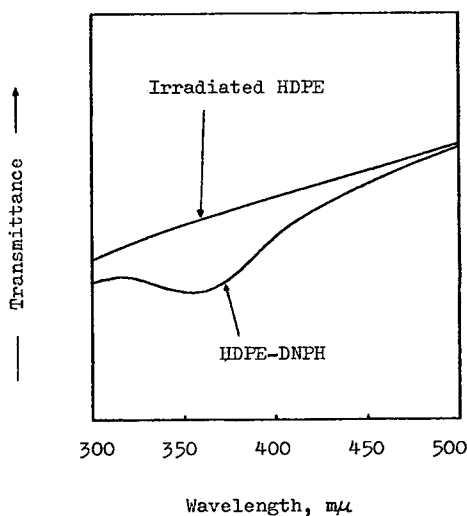


Fig. 4. Ultraviolet spectra of irradiated HDPE and HDPE-DNPH.

that the absorptions^{13,14} of 2,4-dinitrophenylhydrazones appear near 365 $m\mu$, as shown in Figure 4, where HDPE-DNPH is the abbreviation for the high-density polyethylene film reacted with 2,4-dinitrophenylhydrazine. The spectral change in the ultraviolet spectrum shows that 2,4-dinitrophenylhydrazones were formed in the high-density polyethylene film by reaction between 2,4-dinitrophenylhydrazine and the carbonyl groups in the polymer chains, when the 2,4-dinitrophenylhydrazine was reacted on the film irradiated by ultraviolet light.

Plots of A/l at 365 $m\mu$ in HDPE-DNPH and LDPE-DNPH versus irradiation times are shown in Figure 5, where LDPE-DNPH is the abbreviation for the low-density polyethylene film-formed 2,4-dinitrophenylhydrazones. The rates of increases of absorptions at 365 $m\mu$ after about 1 hr were higher than the rates of increases of absorptions at 365 $m\mu$ within about 1 hr. It can be assumed^{1,15} that 2,4-dinitrophenylhydrazine solution penetrated easily into spaces among molecular chains in the amorphous regions in the irradiated films because car-

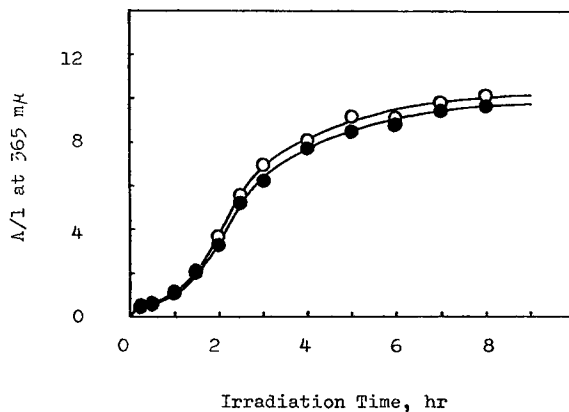


Fig. 5. Plot of A/l for HDPE-DNPH (●) and LDPE-DNPH (○) at $365\text{ m}\mu$ vs. irradiation time.

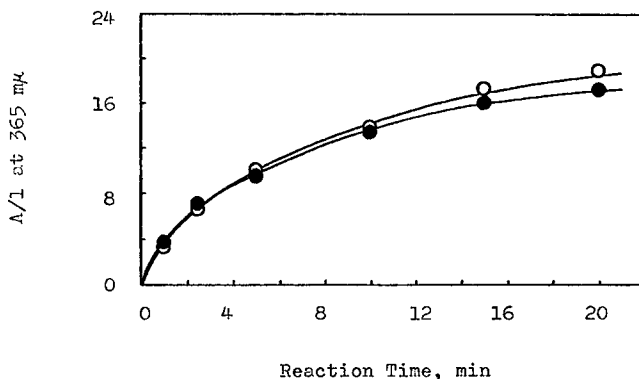


Fig. 6. Plot of A/l at $365\text{ m}\mu$ in HDPE-DNPH (●) and LDPE-DNPH (○) vs. reaction time between 2,4-dinitrophenylhydrazine and irradiated HDPE and LDPE.

bonyl, carboxyl, and ester groups increased on the molecular chains when the films were irradiated above about 1 hr. The rates of increases in the absorptions at $365\text{ m}\mu$ decreased when the films were irradiated above about 4 hr. The absorption of LDPE-DNPH was larger than the absorption of HDPE-DNPH at each irradiation time. It is probable that the hindrance to penetration of 2,4-dinitrophenylhydrazine solution into spaces among the molecular chains in HDPE was larger than the hindrance to penetration of 2,4-dinitrophenylhydrazine solution into spaces among the molecular chains in LDPE, because the content of amorphous region in HDPE was less than the content of amorphous region in LDPE.

Plots of A/l at $365\text{ m}\mu$ in HDPE-DNPH and LDPE-DNPH versus times of reaction between 2,4-dinitrophenylhydrazine and the irradiated films are shown in Figure 6. The absorptions at $365\text{ m}\mu$ increased with increase in reaction time and the rates of the increases of the absorptions gradually decreased with increase in reaction time. The absorptions in LDPE-DNPH were larger than the absorptions in HDPE-DNPH.

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