

Investigation of High-Density Polyethylene Film Surface Treated with Chromic Acid Mixture by Use of 2,4-Dinitrophenylhydrazine. II. Film Surfaces Treated at 70°C

KOICHIRO KATO, *Material Division, Industrial Products Research Institute, Tokyo, Japan*

Synopsis

High-density polyethylene films were treated with chromic acid mixture at 70°C. The treated films were then reacted with 2,4-Dinitrophenylhydrazine. The changes in the amounts of carbonyl groups and 2,4-dinitrophenylhydrazones formed in the films were estimated by comparing their absorptions in the infrared and ultraviolet spectra, respectively. Scanning electron micrographs of the treated film surfaces were taken. Oxidation of the film surface zone, etching of the film surface zone, and oxidation of surface zone bared from the film inner zone seem to have occurred with increase in treatment time. High-density polyethylene film surfaces were oxidized to a greater extent than low-density polyethylene film surfaces; however, the rate of etching of the low-density polyethylene film surface zone was larger than that of the high-density polyethylene film surface zone.

INTRODUCTION

In a previous paper,¹ high-density polyethylene film surfaces treated with chromic acid mixture at 30°C for different periods of time and surfaces treated with chromic acid mixture heated to different temperatures in a range of 30° to 70°C had been compared with low-density polyethylene film surfaces produced by the chromic acid mixture treatment.

Industrially, treatment of polyethylene film surfaces with chromic acid mixture is frequently carried out at a high temperature, that is, at about 70°C, to strengthen the adhesive bonds of the films to paints and adhesives.

In this work, high-density polyethylene films were treated with chromic acid mixture at 70°C, and 2,4-dinitrophenylhydrazine was allowed to react with the treated films. The changes of content of carbonyl groups in the treated films, the contact angles of water on the treated films, and the amount of 2,4-dinitrophenylhydrazones formed in the treated films were compared with comparable changes in treated low-density polyethylene films. Scanning electron micrographs of the treated film surfaces were taken. 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 of the high-density polyethylene (HDPE) and low-density polyethylene (LDPE) films were 0.949 g/ml and 0.926 g/ml, respectively. The HDPE and LDPE crystallinities obtained by the x-ray method²⁻⁴ according to the specifications of the samples received from Showa Yuka Company were 80% and 67%, respectively. The HDPE and LDPE crystallinities obtained by using infrared spectroscopy⁵ were 69% and 44%, respectively. The unsaturated group content of the films obtained by infrared spectroscopy^{5,6} (according to the specifications of the samples received from Showa Yuka Company) are as follows:

	HDPE	LDPE
$-\text{CH}=\text{CH}_2/1000 \text{ C}$	0.8	trace amount
$-\text{CH}=\text{CH}_2- /1000 \text{ C}$	trace amount	trace amount
$\text{>C}=\text{CH}_2/1000 \text{ C}$	trace amount	0.2

These films contained no additives. The HDPE and LDPE thicknesses were 0.087 mm and 0.10 mm, respectively.

Treatment with Chromic Acid Mixture

Chromic acid mixture was prepared by mixing a 10% aqueous solution of potassium dichromate with a solution prepared from sulfuric acid (97%) and water at a ratio of 30:10 by volume. Cleaned polyethylene films were immersed in the chromic acid mixture at 70°C for different periods of time. The films were then withdrawn from the chromic acid mixture, washed thoroughly with distilled water, and dried in a desiccator.

Formation of 2,4-Dinitrophenylhydrazones in Treated Polyethylene Film

The reagents were prepared by methods carried out in previous work.⁷ 2,4-Dinitrophenylhydrazine solution was prepared by mixing 1 g 2,4-dinitrophenylhydrazine, 5 ml hydrochloric acid, 5 ml water, and 100 ml ethyl alcohol. The solution was prepared just before use in every experiment. The polyethylene films treated with the chromic acid mixture were immersed in the 2,4-dinitrophenylhydrazine solution for 15 min. The films were then withdrawn from the hydrazine solution, repeatedly washed with ethyl alcohol until the hydrazine absorption at the 1200 cm^{-1} band in the infrared spectrum had disappeared, and dried.

Measurement of Wettability with Water of Treated Film Surfaces

A drop of distilled water was carefully placed on the surface of the sample, and the contact angle of the drop was measured by using an Erma Model G-1 contact

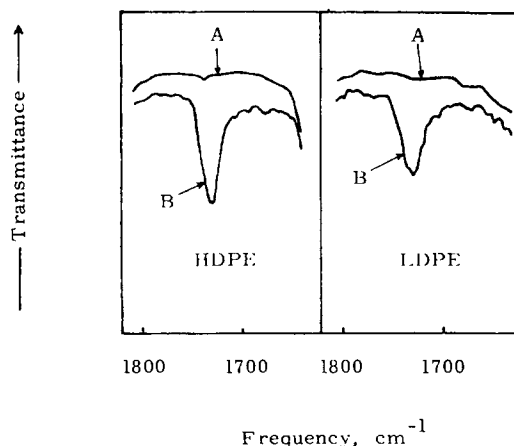


Fig. 1. Carbonyl stretching region of polyethylene films treated with chromic acid mixture: (a) original films; (b) treated films.

angle meter. The mean of ten measurements was taken with each sample. All measurements were made at about 50% R.H. and 20°C, within 10 sec of placing each drop.

Absorption Spectra

Ultraviolet absorption spectra of the samples were recorded by means of a Hitachi Model 356 recording ultraviolet spectrometer. Infrared absorption spectra of the samples were recorded by means of a Perkin-Elmer Model 180 infrared spectrophotometer.

Scanning Electron Microscopy

The scanning electron micrographs of the polyethylene film surfaces were taken with a Hitachi-Akashi Model MSM-4 scanning electron microscope.

RESULTS AND DISCUSSION

The infrared spectra of the polyethylene films treated with chromic acid mixture at 70°C showed that the absorptions⁸⁻¹¹ of the C=O stretching vibration appeared at about 1750 to 1700 cm^{-1} , as shown in Figure 1. The spectral changes in the infrared spectra show that carbonyl groups were formed in the molecular chains when the polyethylene films were oxidized at 70°C by chromic acid mixture.

The ultraviolet spectra of the chromic acid-treated polyethylene films allowed to react with 2,4-dinitrophenylhydrazine showed absorptions^{12,13} of 2,4-dinitrophenylhydrazones near 365 nm, as shown in Figure 2 (where HDPE-DNPH is the abbreviation for the HDPE reacted with 2,4-dinitrophenylhydrazine and LDPE-DNPH is the abbreviation for the LDPE reacted with 2,4-dinitrophenylhydrazine). The spectral change in the ultraviolet spectra shows that 2,4-dinitrophenylhydrazones were formed in the polyethylene films by the re-

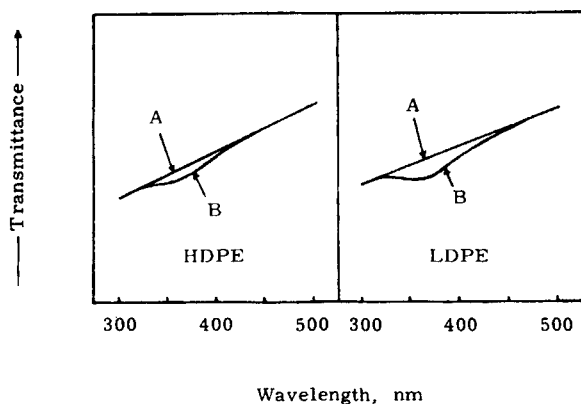


Fig. 2. Ultraviolet spectra of HDPE-DNPH and LDPE-DNPH: (a) films treated with chromic acid mixture; (b) films treated with chromic acid and then reacted with 2,4-dinitrophenylhydrazine (HDPE-DNPH and LDPE-DNPH).

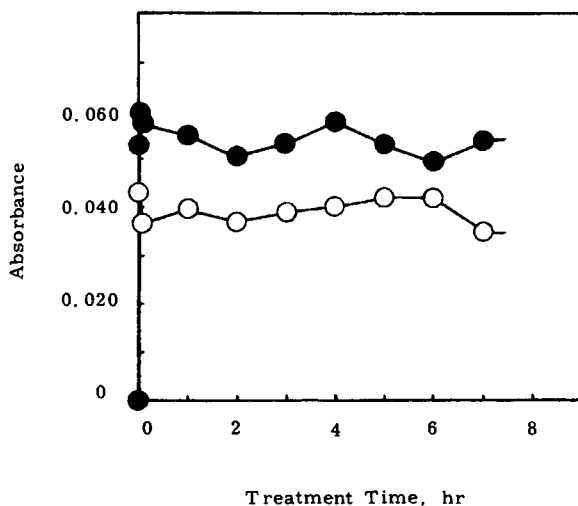


Fig. 3. Plots of absorbances at 1730 cm^{-1} in treated HDPE (●) and LDPE (○) vs treatment time.

action of 2,4-dinitrophenylhydrazine with the carbonyl groups in the polymer chains when the 2,4-dinitrophenylhydrazine was reacted with the films oxidized by chromic acid mixture.

Plots of absorbances at 1730 cm^{-1} in treated polyethylene films versus treatment times of the films with chromic acid mixture are shown in Figure 3. Plots of contact angles of water on the treated polyethylene films versus treatment times of the films with chromic acid mixture are shown in Figure 4. Plots of absorbances at 365 nm in HDPE-DNPH and LDPE-DNPH versus treatment times with chromic acid mixture are shown in Figure 5. In the early stages of the treatment, the absorbances at 1730 cm^{-1} and 365 nm increased with increase in treatment time, as shown in Figures 3 and 5, and the contact angles of water decreased with increase in treatment time, as shown in Figure 4. These phe-

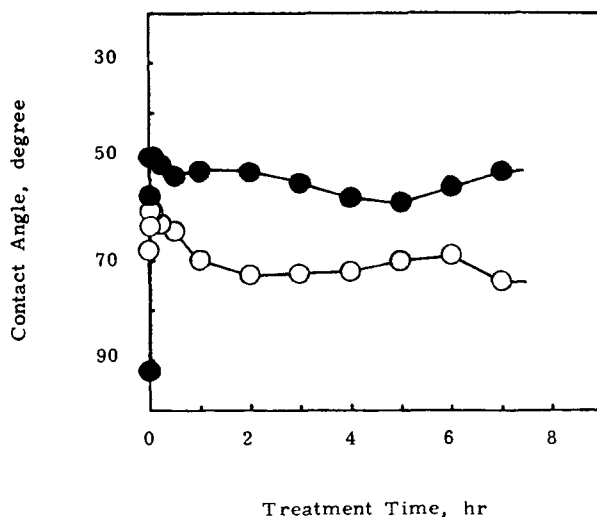


Fig. 4. Plots of contact angles of water on treated HDPE (●) and LDPE (○) vs treatment time.

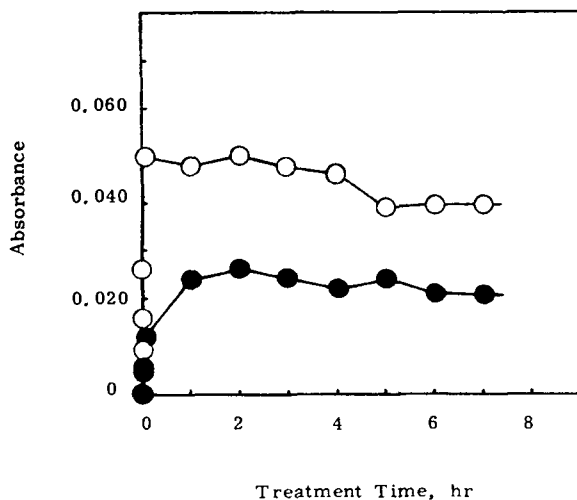


Fig. 5. Plots of absorbances at 365 nm in HDPE-DNPH (●) and LDPE-DNPH (○) vs treatment time.

nomena show that the polyethylene film surfaces are oxidized in the early stages of the treatment. The rate of increase of absorbance at 365 nm in HDPE-DNPH with increase in treatment time was lower than the rate of increase of the absorbance in LDPE-DNPH with increase in treatment time, as shown in Figure 5. The crystalline region in HDPE is larger than the crystalline region in LDPE. Therefore, it is possible that hindrance to 2,4-dinitrophenylhydrazine penetration into spaces between molecular chains in the HDPE surface is larger than the hindrance to 2,4-dinitrophenylhydrazine penetration into spaces between the molecular chains in LDPE surfaces, until partial breakdown of the molecular chains in the HDPE surface increases.

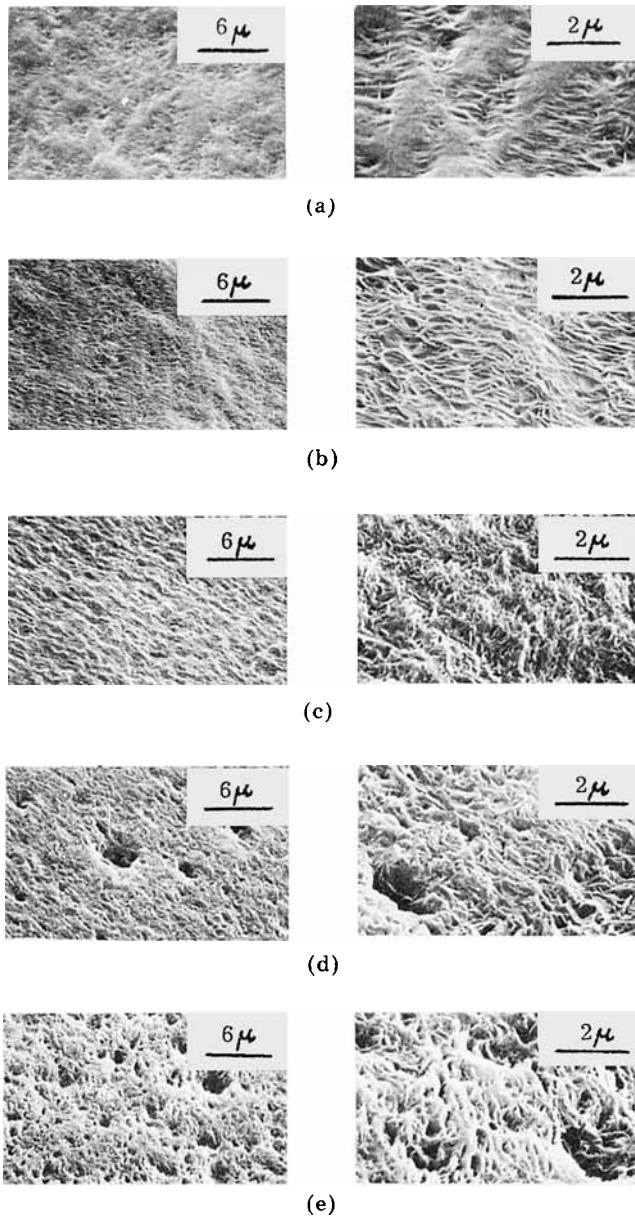


Fig. 6. Scanning electron micrographs of the surfaces of HDPE treated with chromic acid mixture.

The absorbances at 1730 cm^{-1} in HDPE were larger than the absorbances at 1730 cm^{-1} in LDPE, as shown in Figure 3. The decreases in the contact angles on HDPE surfaces produced by chromic acid treatment were larger than the decreases in the contact angles on comparably treated LDPE surfaces, as shown in Figure 4. These phenomena show that the HDPE surfaces were oxidized to a greater extent than the LDPE surfaces. It has been known^{14,15} that the rate of oxidation of olefins is affected by the content of olefinic double bonds in the

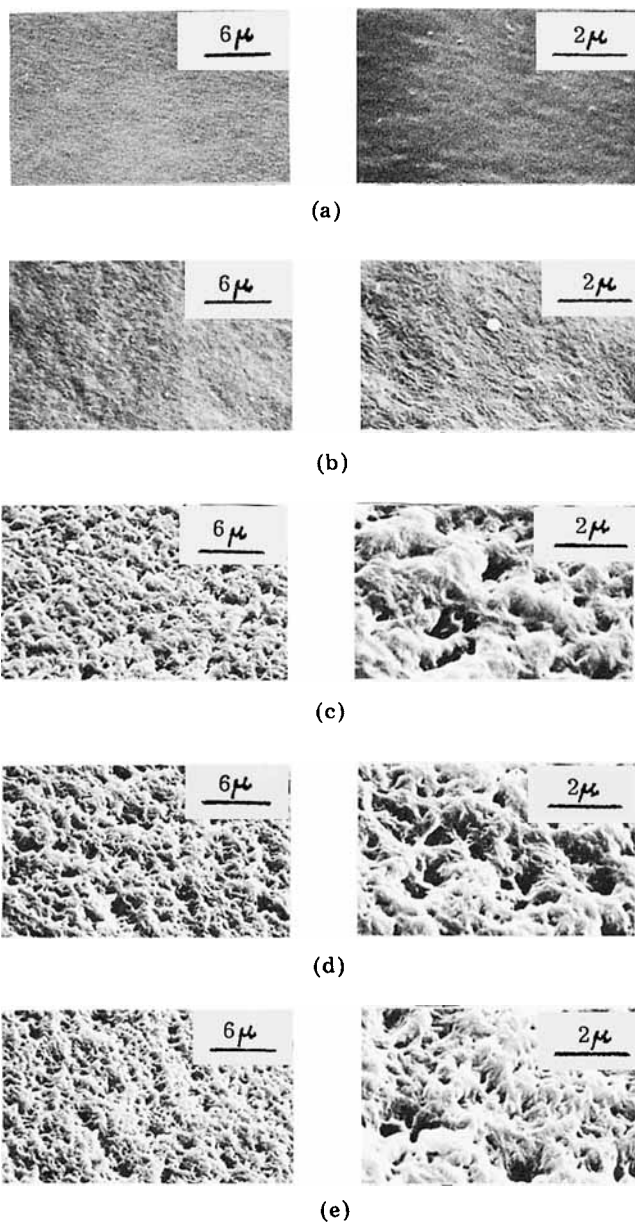


Fig. 7. Scanning electron micrographs of the surfaces of LDPE treated with chromic acid mixture.

olefins. It is within the range of possibility that the difference between HDPE and LDPE in the rate of oxidation of the respective polymer film surface was caused by a difference in the content of olefinic double bonds in the polymers.

The absorbances at 365 nm in LDPE-DNPH were larger than the absorbances at 365 nm in HDPE-DNPH, as shown in Figure 5. It is probable that the hindrance to 2,4-dinitrophenylhydrazine penetration into spaces between the mo-

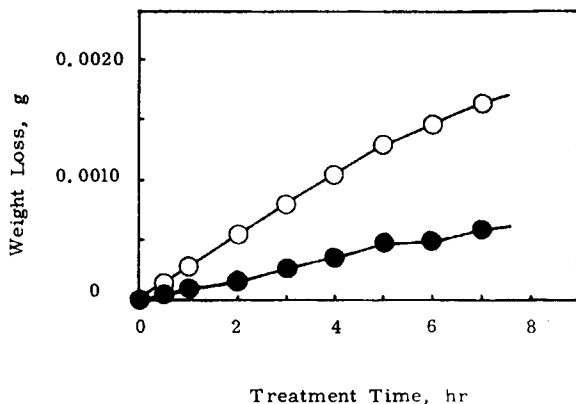


Fig. 8. Plot of weight loss of HDPE (●) and LDPE (○) per 2 cm² of film area vs treatment time.

lecular chains in HDPE was larger than the hindrance to hydrazine penetration into spaces between the molecular chains in LDPE, because the amorphous region in HDPE was smaller than the amorphous region in LDPE.

After the early stages of treatment, the absorbances at 1730 cm⁻¹ and 365 nm in the films decreased slightly and thereafter seemed to repeat the slight decrease and the slight increase of the absorbances with increase in treatment time, as shown in Figures 3 and 5. The contact angle of water on the HDPE surface increased slightly and the contact angle of water on the LDPE surface seemed to increase with increase in treatment time over about 2 hr. Thereafter, the contact angles on the films seemed to repeat the slight decrease and the slight increase of the contact angles with increase in treatment time, as shown in Figure 4.

In order to look at the film surfaces produced after the early stages of the treatment, scanning electron micrographs of the treated film surfaces were taken. The scanning electron micrographs of the treated film surfaces are shown in Figures 6 and 7. When the polyethylene films were treated with chromic acid mixture for 1 min, lamellar packets were apparent in the LDPE surface and clearly apparent in the HDPE surface. It is probable that lamellar packets were bared from the film inner zones by the increase in breakdown in the polymer film surfaces. It is probable that lamellar packets were clearly apparent in the HDPE surface because the crystalline region in HDPE is large. It is suggested that the chromic acid mixture was hindered from reacting with the polymer in the crystalline region bared from the film inner zone.

When the polyethylene films were treated for 1 hr, numerous voids were observed on the LDPE surface, but clear voids were not observed on the HDPE surface. Clear voids were observed on the HDPE surfaces treated for 5 hr. The weight of the films decreased with increase in treatment time, and the weight loss of LDPE was larger than the weight loss of HDPE, as shown in Figure 8. These phenomena show that the polyethylene film surfaces were etched with increase in treatment time and that the rate of etching of the LDPE surface by chromic acid was larger than the rate of etching of the HDPE surface. It is within the range of possibility that this difference in rate of etching of the film surfaces was caused by a difference in the amounts of amorphous regions in the films.

From these results, it can be assumed that the decrease in absorbance at 1730

cm⁻¹ and 365 nm and the increase in contact angle of water after the early stages of the treatment were caused by a decrease in the amount of carbonyl groups in the film surfaces caused by an increase in the surfaces bared from the inner zones in the films. The large decrease in contact angle of water on the LDPE surface after the early stages of the treatment may have been caused by large etching of the LDPE surface.

It can be inferred that the surfaces bared from the inner zones in the films are oxidized and that, thereafter, the etching and oxidation of the film surfaces are repeated. It is probable that repeated absorbances at 1730 cm⁻¹ and 365 nm and contact angles of water slightly increase and slightly decrease, respectively, with increase in treatment time because of the above-mentioned changes in the films.

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