

Investigation of High-Density Polyethylene Film Surface Treated with Chromic Acid Mixture by Use of 2,4-Dinitrophenylhydrazine

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Synopsis

High-density polyethylene films were treated with chromic acid mixture. 2,4-Dinitrophenylhydrazine was reacted on the treated films. The changes in amounts of 2,4-dinitrophenylhydrazones formed in the films were inferred by comparing the absorptions in the ultraviolet spectra. The changes in the film surfaces by chromic acid mixture treatment were investigated by comparing the changes in the amount of the hydrazones with changes in water wettability of the treated films. Scanning electron micrographs of the treated film surfaces were taken. Oxidation of the film surface zone, partial breakdown of polymer in the film surface zone, and oxidation of surface zone bared from the film inner zone seem to have occurred with increase in treatment time. When the treatment temperature was raised, the increase in carbonyl groups in the surface of the high-density polyethylene film with rise in treatment temperature seems to have been prevented by an increase in partial breakdown of polymer in the film surface.

INTRODUCTION

Treatment of polyethylene film surfaces with chromic acid mixture has been carried out to improve the adhesive bonding properties of the surfaces to paints and adhesives.

Examination of oxidation in the polyethylene film surfaces treated with chromic acid mixture has been carried out by measuring wettability with H-bonding liquids on the surfaces generally.

In a previous paper,¹ the change in amount of 2,4-dinitrophenylhydrazones formed in low-density polyethylene films treated with chromic acid mixture had been compared with the change in wettability with water of the treated films.

In this work, the high-density polyethylene films were treated with chromic acid mixture, and 2,4-dinitrophenylhydrazine was reacted on the treated films. The change in amount of 2,4-dinitrophenylhydrazones formed in the treated films was compared with change in wettability with water of the treated films. Scanning electron micrographs of the treated film surfaces were taken. The change in the high-density polyethylene film surfaces by chromic acid treatment was compared with the change in low-density polyethylene film surfaces. The results are reported in this paper.

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

	HDPE High-density polyethylene film	LDPE Low-density polyethylene film
Density, g/ml	0.949	0.926
—CH ₃ /1000 C ^a	1.6	19.9
—CH=CH ₂ /1000 C ^b	0.8	trace amount
—CH=CH—/1000 C ^b	trace amount	trace amount
>C=CH ₂ /1000 C ^b	trace amount	0.2

^a Obtained according to ASTM D 2238-64 T, using infrared spectroscopy.

^b Obtained by using infrared spectroscopy.^{2,3}

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. Densities, methyl group content, and unsaturated group content of the films, according to the specification of the samples received from Showa Yuka Company, are given in Table I.

The HDPE and LDPE crystallinities obtained by x-ray method,⁴⁻⁶ according to the specification of the samples received from Showa Yuka Company, were 80% and 67%, respectively. The HDPE and LDPE crystallinities obtained by using infrared spectroscopy³ were 69% and 44%, respectively. Their 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 prepared from potassium dichromate, sulfuric acid, and water in a ratio of 5:100:8 by weight was used for the treatment of polyethylene films. The following two methods were used: (1) Cleaned polyethylene films were immersed in the chromic acid mixture at 30 °C for different periods of time. (2) Cleaned polyethylene films were immersed in the chromic acid mixture, and heated to different temperatures for 1 min. Then the films were withdrawn from the chromic acid mixture, washed thoroughly with distilled water, and dried in a desiccator.

Powdered high-density polyethylene (received from Showa Yuka Company; no additives) was immersed in the chromic acid mixture at 30 °C for 20 min; the treated powder was then filtered with a glass filter, washed thoroughly with distilled water, and dried at about 40 °C under vacuum for about 10 hr.

Formation of 2,4-Dinitrophenylhydrazones in Treated Polyethylene Film

The reagents were prepared by the method carried out in previous work.⁷ 2,4-Dinitrophenylhydrazine solution was prepared by mixing the reagents at

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 polyethylene films treated with 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 angle meter. The mean of ten measurements was taken in each sample. All measurements were made at about 50% R.H. and $20\text{ }^{\circ}\text{C}$, 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. For infrared spectroscopic measurement of powdered polyethylene, KBr pellets were used.

Scanning Electron Microscopy

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

RESULTS AND DISCUSSION

Absorption Spectra

The infrared spectrum of high-density polyethylene powder when the polyethylene powder was treated with chromic acid mixture at $30\text{ }^{\circ}\text{C}$ showed that

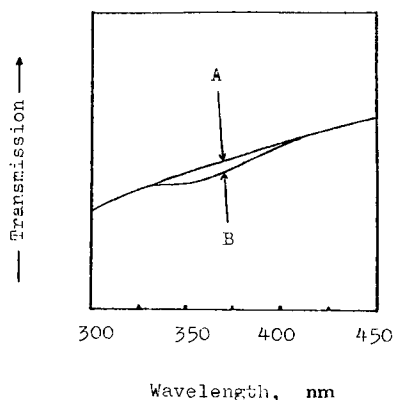


Fig. 1. Ultraviolet spectrum of HDPE-DNPH: (A) HDPE oxidized with chromic acid mixture; (B) HDPE-DNPH.

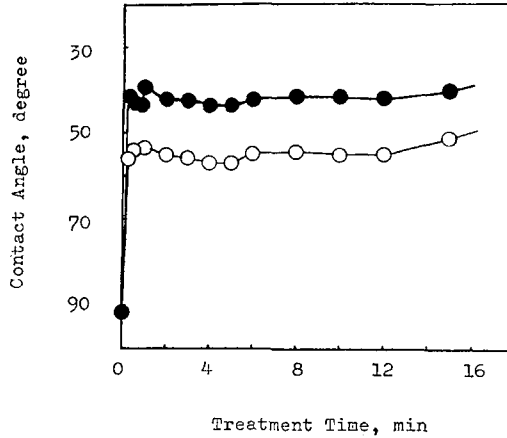


Fig. 2. Contact angles of water on HDPE (●) and LDPE (○) treated with chromic acid mixture vs. time of treatment of the films with chromic acid mixture.

absorptions⁸⁻¹¹ of C=O stretching vibration appear at about 1740 to 1710 cm^{-1} . The spectral change in the infrared spectrum shows that carbonyl groups were formed in the molecular chains when the polyethylene powder was oxidized by chromic acid mixture.

The ultraviolet spectrum of HDPE when 2,4-dinitrophenylhydrazine was reacted on the film treated with chromic acid mixture showed that the absorptions^{12,13} of 2,4-dinitrophenylhydrazones appeared at about 355 to 365 nm as shown in Figure 1, where HDPE-DNPH is the abbreviation for the HDPE reacted with 2,4-dinitrophenylhydrazine. The spectral change in the ultraviolet spectrum shows that 2,4-dinitrophenylhydrazones were formed in the 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 oxidized by chromic acid mixture.

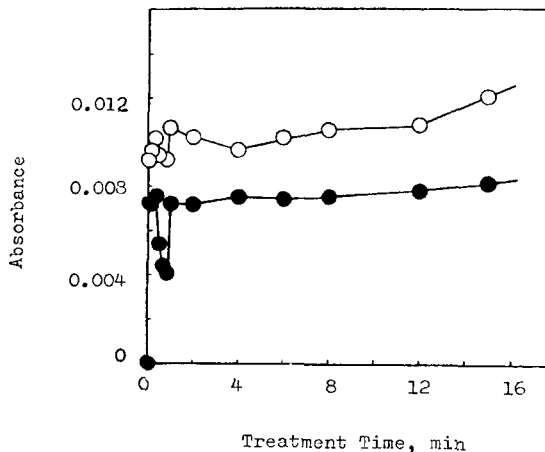


Fig. 3. Absorbances at 365 nm in HDPE-DNPH (●) and LDPE-DNPH (○) vs. time of treatment of the films with chromic acid mixture.

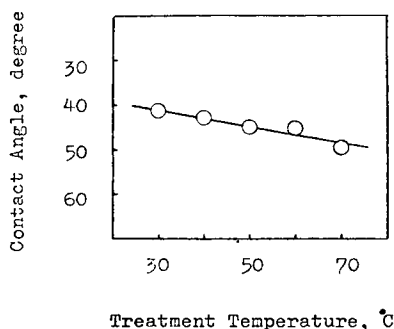


Fig. 4. Contact angles of water on HDPE treated with chromic acid mixture vs. temperature of treatment of HDPE with chromic acid mixture

Effect of Treatment Time

Plots of contact angles of water on treated polyethylene films versus times of treatment of the polyethylene films with chromic acid mixture are shown in Figure 2. Plots of absorbances at 365 nm in HDPE-DNPH and LDPE-DNPH versus times of treatment of the polyethylene films with chromic acid mixture are shown in Figure 3, where LDPE-DNPH is the abbreviation for the low-density polyethylene film reacted with 2,4-dinitrophenylhydrazine. In the early stage of the treatment, the absorbances at 365 nm increased with increase in treatment time, and the contact angles of water decreased with increase in treatment time. These phenomena show that the polyethylene film surfaces are oxidized in the early stage of the treatment.

The decreases in the contact angles on HDPE surfaces produced by chromic acid mixture treatment were larger than the decreases in contact angles on LDPE surfaces produced by chromic acid mixture treatment. This phenomenon shows that the HDPE surfaces were oxidized more 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 olefins. It is within the range of possibility that the difference in rates of oxidation of polymers in the

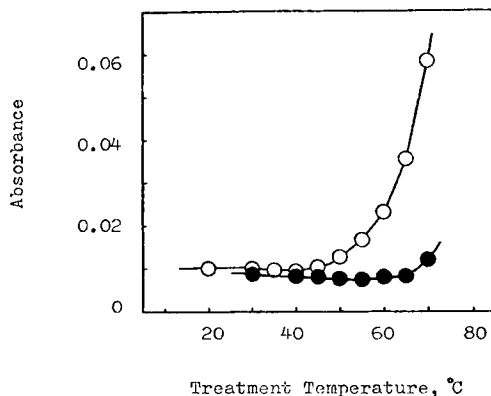


Fig. 5. Absorbances at 365 nm in HDPE-DNPH (●) and LDPE-DNPH (O) vs. temperature of treatment of the films with chromic acid mixture.

surfaces of the films between HDPE and LDPE was caused by a difference in the contents 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. 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 the hydrazine solution into spaces among the molecular chains in LDPE, because the amorphous region in HDPE was smaller than the amorphous region in LDPE.

When the polyethylene films were treated with chromic acid mixture in the range of about 30 to 50 sec, the absorbances at 365 nm in HDPE-DNPH and LDPE-DNPH decreased, as shown in Figure 3, and the contact angles of water on the HDPE surfaces seem to have increased, as shown in Figure 2. It has been reported¹⁶ that polyethylene film weight decreased because of partial breakdown of the polymer in the film surface zone when the film was treated with chromic acid mixture. Therefore, the following changes may have occurred in the polyethylene film surfaces when the films were treated in the range of about 30 to 50 sec. Partial breakdown of the polymers in the film surface zones increases with increase in treatment time. Consequently, the inner zones of the films are bared. Therefore, the amount of carbonyl

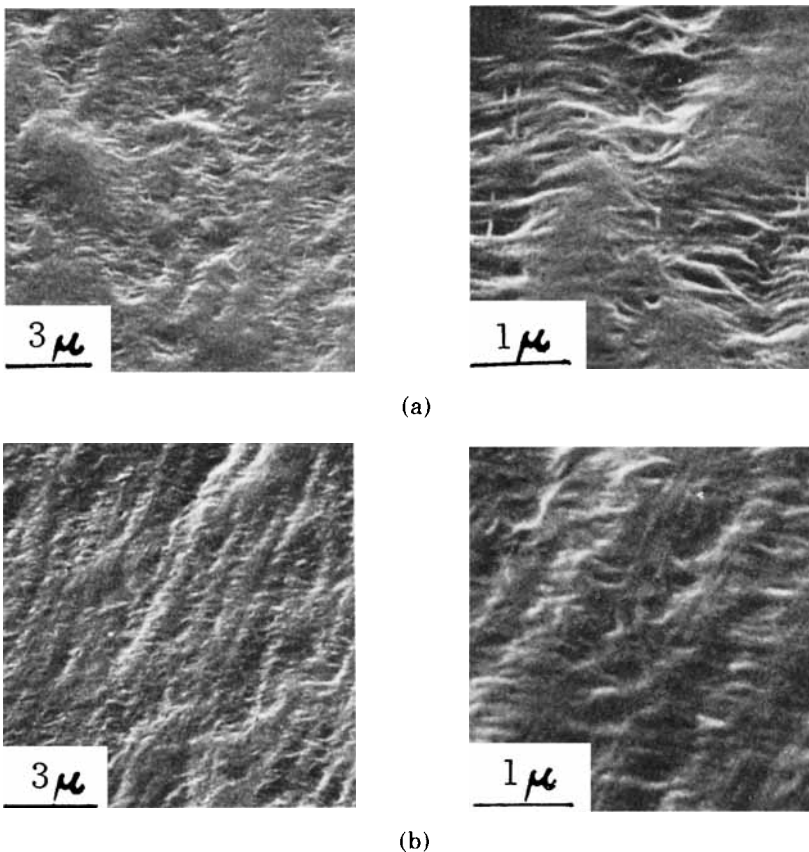


Fig. 6 (continued)

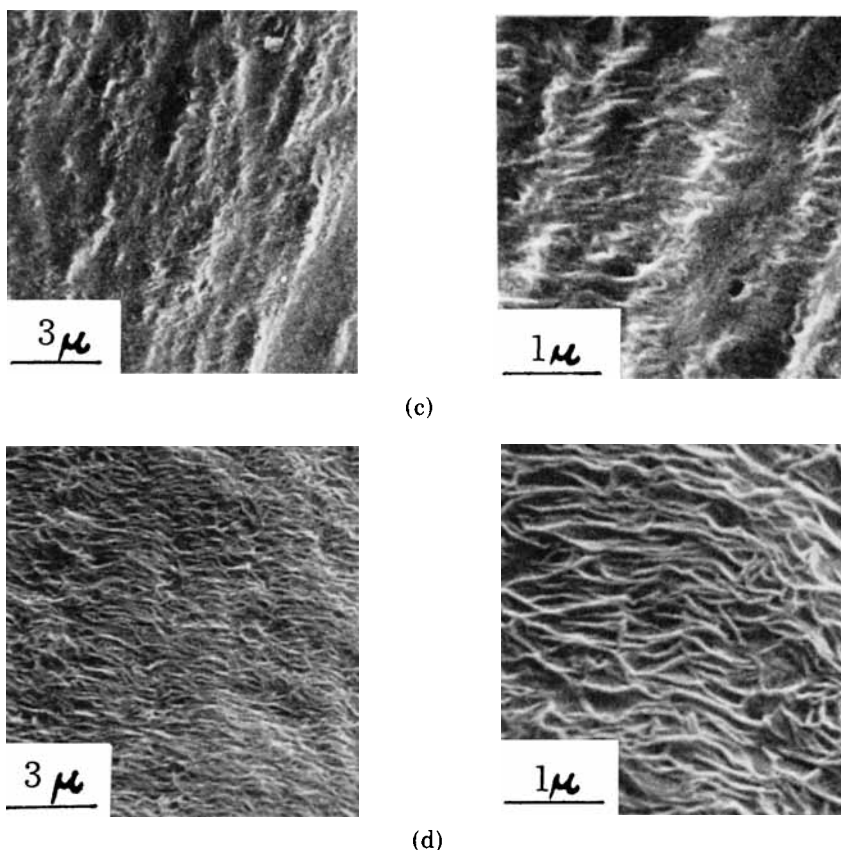


Fig. 6. Scanning electron micrographs of the surfaces of HDPE treated with chromic acid mixture. (a) Untreated film surface. (b) Film surface treated at 30°C for 40 sec. (c) Film surface treated at 30°C for 5 min. (d) Film surface treated at 70°C for 1 min.

groups in the film surface zones decreases. Consequently, the amount of 2,4-dinitrophenylhydrazones formed in the film surface zones decreases and the contact angles of water on the film surfaces increase when the films are treated in the range of about 30 to 50 sec.

However, when the polyethylene films were treated with chromic acid mixture in the range of about 30 to 50 sec, the decreases in absorbances at 365 nm in HDPE-DNPH were larger than the decreases in absorbances at 365 nm in LDPE-DNPH, and the contact angles of water on the LDPE surfaces seem not to have increased. It is within the range of possibility that the extent of partial breakdown of polymer in HDPE surface zones by oxidation was larger than the partial breakdown of polymer in LDPE surface zones by oxidation.

When the polyethylene films were treated with chromic acid mixture above about 1 min, the absorbances at 365 nm in the films varied with increase in treatment time, and the contact angles of water on the film surfaces seem to have varied with increase in treatment time. However, the variations of the absorbances and contact angles after about 1 min were smaller than the variations of the absorbances and contact angles in the range of about 30 to 50 sec. The following changes may have occurred in the polyethylene films.

The polymers that break easily are contained in the film surfaces. The polymers in the film surfaces break partly in the range of about 30 to 50 sec when the films are treated with chromic acid mixture. When the films are treated above about 1 min, the partial breakdown of the polymers in the film surfaces is decreased by a decrease of the polymers that break easily. Consequently, the variations of absorbances at 365 nm and contact angles of water after about 1 min are smaller than the variations of the absorbances at 365 nm and the contact angles of water within the range of about 30 to 50 sec when the polyethylene films are treated with chromic acid mixture for more than about 1 min.

Effect of Treatment Temperature

When the temperature of treatment of HDPE was raised from about 30° to 60 °C, the contact angle of water on the HDPE surface seems to increase with rise in treatment temperature, as shown in Figure 4, and the absorbance at 365 nm in HDPE-DNPH decreased slightly with rise in temperature of the treatment at about 30° to 55 °C and increased slightly with rise in temperature of the treatment at about 55° to 70 °C, as shown in Figure 5. It is probable that the following changes occurred in the polyethylene films. The par-

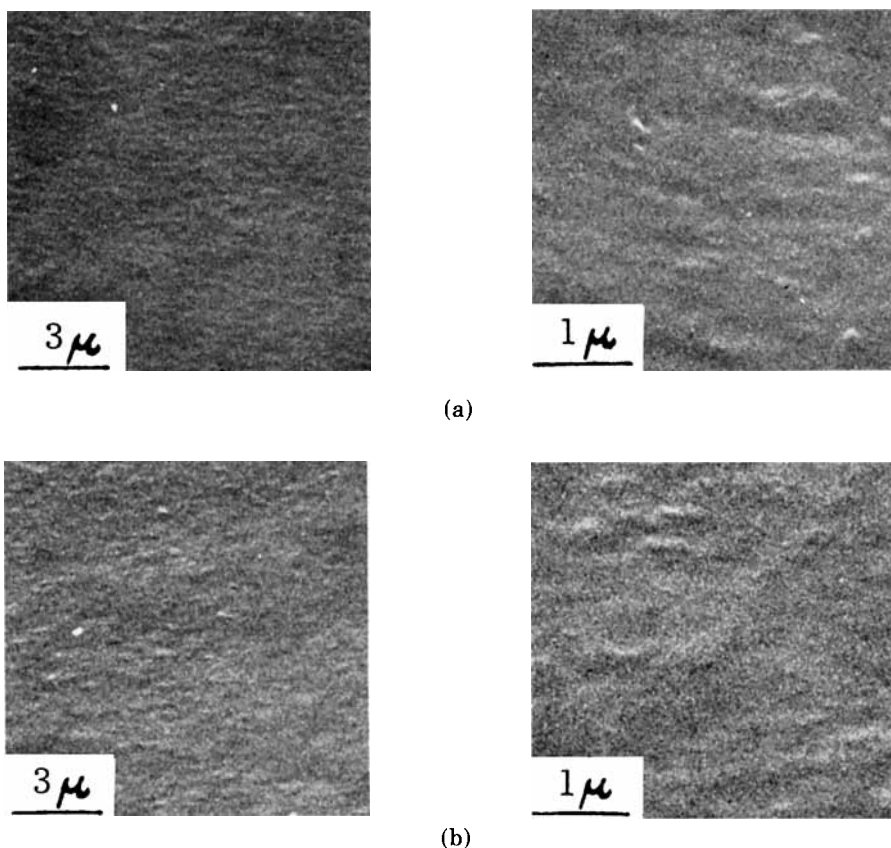


Fig. 7 (continued)

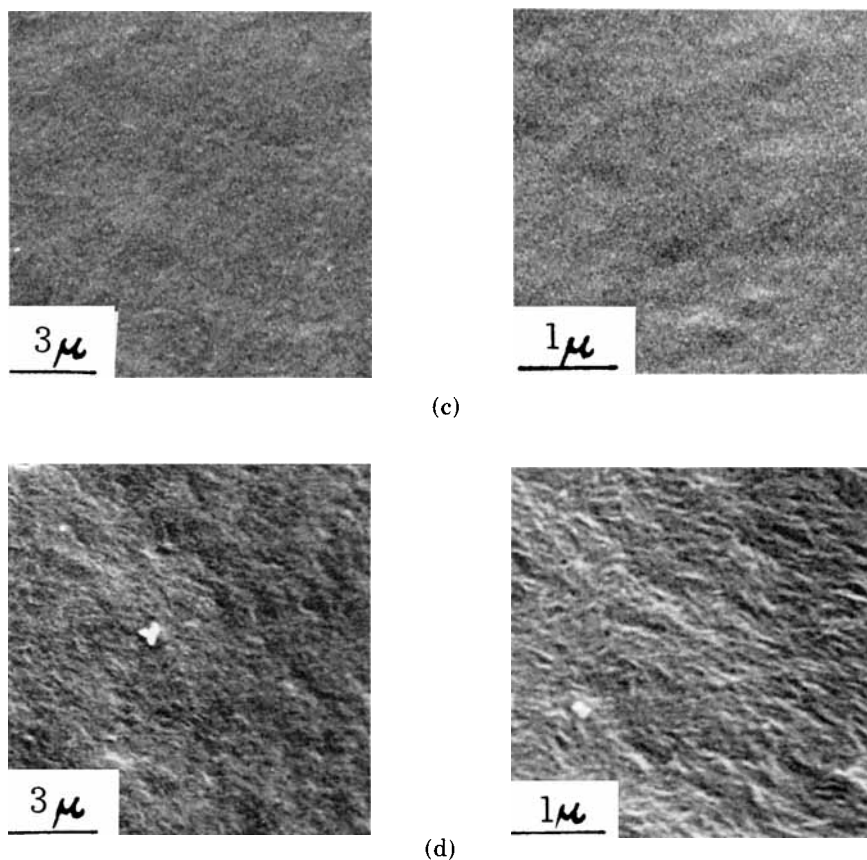


Fig. 7. Scanning electron micrographs of the surfaces of LDPE treated with chromic acid mixture. (a) Untreated film surface. (b) Film surface treated at 30°C for 40 sec. (c) Film surface treated at 30°C for 5 min. (d) Film surface treated at 70°C for 1 min.

tial breakdown of polymer in the film surface increases with rise in treatment temperature; therefore, the surfaces bared from the film inner zone increase with rise in treatment temperature. The crystal region in the surface bared from inner zone in HDPE is large because the crystal region in HDPE is large. The reaction of chromic acid mixture with polymer in the crystal region is hindered. Consequently, the increase of carbonyl groups in the HDPE surface with rise in treatment temperature is prevented when the treatment temperature is raised.

The scanning electron micrographs of polyethylene films treated with chromic acid mixture are shown in Figures 6 and 7. When the polyethylene films were treated at 30 °C, the distinguishable partial breakdowns of polymers in the film surfaces seem not to have occurred. However, when the polyethylene films were treated at 70 °C, lamella packets were apparent in the LDPE surfaces and were clearly apparent in the HDPE surfaces. It is probable that the partial breakdown of polymer in the film surfaces was too fine to observe when the films were treated at 30 °C. It is considered that lamella packets were bared from the film inner zones by the increase in breakdown of polymers in the film surfaces when the films were treated at 70 °C. It is probable

that lamella packets were clearly apparent in the HDPE surface because the crystal region in HDPE is large. It is probable that chromic acid mixture was hindered from reacting with polymer in the crystal region bared from the film inner zone.

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References

1. K. Kato, *J. Appl. Polym. Sci.*, **18**, 3087(1974).
2. L. H. Cross, R. B. Richards, and H. A. Willis, *Disc. Faraday Soc.*, **9**, 235(1950).
3. E. Cernia, C. Mancini, and G. Montaudo, *Polym. Lett.*, **1**, 371(1963).
4. S. Krimm and A. V. Tobolsky, *J. Polym. Sci.*, **7**, 57(1951).
5. I. Nitta and H. Tadokoro, *Kobunshi*, **5**, 296(1956).
6. I. Nitta and H. Tadokoro, *Kobunshi*, **5**, 345(1956).
7. K. Kato, *J. Appl. Polym. Sci.*, **15**, 2115(1971).
8. F. M. Rugg, J. J. Smith, and R. C. Bacon, *J. Polym. Sci.*, **13**, 535(1954).
9. J. P. Luongo, *J. Polym. Sci.*, **42**, 139(1960).
10. H. C. Beachell and G. W. Tarbet, *J. Polym. Sci.*, **45**, 451(1960).
11. M. Ōki, *Infrared Spectra*, Tokyo University, Tokyo, 1967, p. 80.
12. L. A. Jones, J. C. Holmes, and R. B. Seligman, *Anal. Chem.*, **28**, 191(1956).
13. C. J. Timmons, *J. Chem. Soc.*, 2613(1957).
14. Y. Kamiya, *Oxidation of Organic Compound*, Gihodo, Tokyo, 1973, p. 295.
15. T. Nozoe, *Chemical Experiment*, Vol. II, Chap. 4, Kawaide Shobo, Tokyo, 1942, p. 105.
16. Y. Kumagai, M. Ono, C. Nagasawa, and T. Ouchi, 8th Symposium on Adhesion and Adhesives, Ōsaka, Japan, 1970.

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