

## Change of Polypropylene Film Surface by Chromic Acid Mixture Treatment

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

### Synopsis

Polypropylene films were treated with chromic acid mixture. The change in the treated films was investigated by comparing change in amount of 2,4-dinitrophenylhydrazones formed in the treated films with their change in wettability with water. 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 seemed to occur with increase in treatment time or with increase in treatment temperature.

### INTRODUCTION

Polyolefin surfaces are chemically inert. As a result of this inertness, printing inks, paints, and adhesives do not adhere to ordinary polyolefin surfaces. Treatment of polyolefin surfaces with chromic acid mixture improves the adhesive bonding properties of the surfaces.

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

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

In this work, the polypropylene films were treated with chromic acid mixture, and 2,4-dinitrophenylhydrazine was reacted on the treated films. The change in the amount of 2,4-dinitrophenylhydrazones formed in the treated films was compared with change in water wettability of the treated films.

### EXPERIMENTAL

#### Polypropylene Films

Polypropylene film (density 0.905 g/ml, thickness 0.064 mm) received from Showa Yuka Company was used in this work. The film contained a small amount of 2,6-di-*tert*-butyl-4-methylphenol and *N*-*n*-octadecyldiethanolamine (less than 1.0 wt-%). The helical content in the film was calculated by using the method suggested by Brader.<sup>2</sup> The helical content was about 75 wt-%.

### Treatment with Chromic Acid Mixture

A chromic acid mixture prepared from potassium dichromate, sulfuric acid, and water in the ratio of 5:100:8 by weight was used for the treatment of polypropylene. Cleaned polypropylene films were immersed, under varying conditions of dipping time and temperature, into the chromic acid mixture. The films were then withdrawn from the chromic acid mixture, washed thoroughly with distilled water, and dried in a desiccator. Powdered polypropylene (polypropylene was received from Showa Yuka Company) was immersed into chromic acid mixture at 30°C for 1 hr; then the treated powder was filtered with glass filter, washed thoroughly with distilled water, and dried at about 40°C under vacuum for about 20 hr.

### Formation of 2,4-Dinitrophenylhydrazones in Treated Polypropylene Film

The reagents were prepared by the method used in the previous work.<sup>3</sup> 2,4-Dinitrophenylhydrazine solution was prepared by mixing the reagents 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 polypropylene films treated with chromic acid mixture were immersed, under varying conditions of dipping time, in the 2,4-dinitrophenylhydrazine solution. The films were then withdrawn from the hydrazine solution, repeatedly washed with ethyl alcohol until the hydrazine absorption at the 1200  $\text{cm}^{-1}$  band in the infrared spectrum had disappeared, and dried.

### 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 polypropylene, KBr pellet was used.

### 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 for each sample. All measurements were made at about 50% R.H. and 20°C, within 10 sec of placing each drop.

### Effect of Time of Reaction between 2,4-Dinitrophenylhydrazine and Treated Films

The polypropylene films were treated with the chromic acid mixture at 45°, 55°, and 65°C for 20 min, and washed and dried. The treated films were immersed in 2,4-dinitrophenylhydrazine solution, removed from the hydrazine solution after different periods of time had elapsed, and washed and dried. The absorption of 2,4-dinitrophenylhydrazones at 365  $\text{m}\mu$  in the films was measured and the change in amount of hydrazones formed in the films was inferred by comparing their absorptions.

### Effect of Treatment Temperature

The polypropylene films were treated in the chromic acid mixture, heated to different temperatures for 20 min, and washed and dried. The contact angles of water on the treated films were measured.

The treated films were immersed in 2,4-dinitrophenylhydrazine solution, removed from the hydrazine solution after 10 min had elapsed, and washed and dried. The absorption of 2,4-dinitrophenylhydrazones at  $365\text{ m}\mu$  in the films was measured.

### Effect of Treatment Time

The polypropylene films were treated with chromic acid mixture at  $60^\circ$  and  $70^\circ\text{C}$  for different periods of time, and washed and dried. The contact angles of water on the treated films were measured.

The treated films were immersed in 2,4-dinitrophenylhydrazine solution, removed from the hydrazine solution after 10 min had elapsed, and washed and dried. The absorption of 2,4-dinitrophenylhydrazones at  $365\text{ m}\mu$  in the films was measured.

## RESULTS AND DISCUSSION

The infrared spectrum at  $1800$  to  $1700\text{ cm}^{-1}$  in polypropylene powder treated by chromic acid mixture is shown in Figure 1. The absorptions<sup>4,5,6</sup> of the C=O stretching vibration appeared at about  $1740$  to  $1710\text{ cm}^{-1}$ . The spectral change in the infrared spectrum shows that carbonyl groups were formed in the molecular chains when the polypropylene powder was oxidized by chromic acid mixture.

The ultraviolet spectrum of the polypropylene film when 2,4-dinitrophenylhydrazine was reacted on the film treated with chromic acid mixture showed that the absorption<sup>7,8</sup> of 2,4-dinitrophenylhydrazones appears at about  $365\text{ m}\mu$  as shown in Figure 2, where PP-DNPH is abbreviation for the polypropylene film reacted with 2,4-dinitrophenylhydrazine. The spectral change in the ultraviolet spectrum shows that 2,4-dinitrophenylhydrazones were formed in the polypropylene 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.

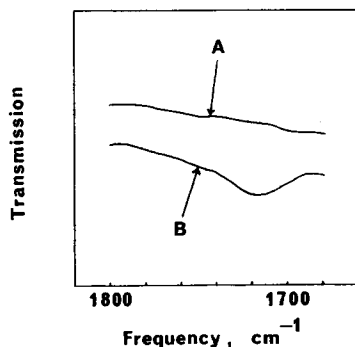


Fig. 1. Infrared spectrum at  $1800$  to  $1700\text{ cm}^{-1}$  in polypropylene oxidized by chromic acid mixture: (A) unoxidized polypropylene; (B) oxidized polypropylene.

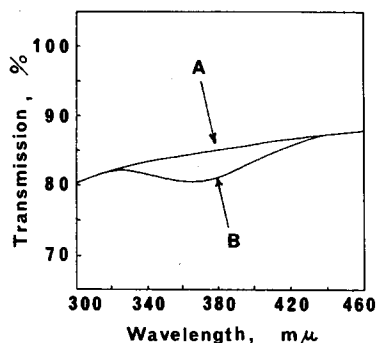


Fig. 2. Ultraviolet spectrum of PP-DNPH: (A) polypropylene film oxidized with chromic acid mixture; (B) PP-DNPH.

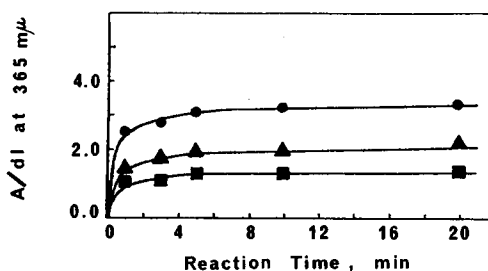


Fig. 3. Plot of  $A/dl$  at  $365\text{ m}\mu$  in PP-DNPH vs. time of reaction between 2,4-dinitrophenylhydrazine and polypropylene films oxidized with chromic acid mixture.

### Effect of Time of Reaction between 2,4-Dinitrophenylhydrazine and Treated Films

Plots of  $A/dl$  at  $365\text{ m}\mu$  in PP-DNPH versus time of reaction between 2,4-dinitrophenylhydrazine and polypropylene films treated with chromic acid mixture at  $45^\circ$ ,  $55^\circ$ , and  $65^\circ\text{C}$  are shown in Figure 3, where  $A$  is the absorbance at  $365\text{ m}\mu$  in the each film,  $d$  is the density of the film, and  $l$  is the thickness of the film. The absorptions at  $365\text{ m}\mu$  increased with rise in temperature of the treatment. The absorption at  $365\text{ m}\mu$  increased with increase in treatment time, and the rates of the increase of absorption at  $365\text{ m}\mu$  decreased with increase in treatment time. The rates of increase of absorption at  $365\text{ m}\mu$  were low after the treated films were immersed in 2,4-dinitrophenylhydrazine solution for about 10 min.

### Effect of Treatment Temperature

Plots of  $A/dl$  at  $365\text{ m}\mu$  in PP-DNPH versus temperatures of treatment of polypropylene films by chromic acid mixture are shown in Figure 4. Plots of contact angles of water on surfaces of treated polypropylene films versus temperatures of treatments of polypropylene films by chromic acid mixture are shown in Figure 5.

The absorption at  $365\text{ m}\mu$  increased with rise in temperature of the treatment at about  $40^\circ$  to  $60^\circ\text{C}$ ; however, the contact angle of water seemed not to decrease when the treatment temperature was raised from about  $40^\circ$  to  $60^\circ\text{C}$ . It is probable that penetration of chromic acid mixture in the film surface zone

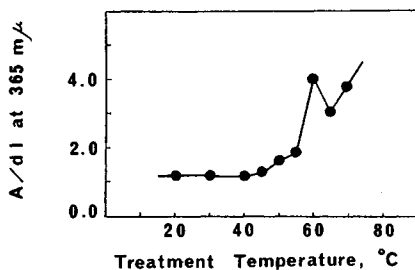


Fig. 4. Plot of  $A/dl$  at  $365\text{ m}\mu$  in PP-DNPH vs. temperatures of treatment of polypropylene film by chromic acid mixture.

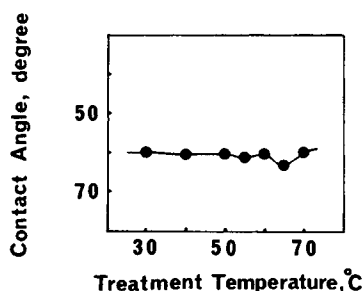


Fig. 5. Contact angles of water on polypropylene film treated with chromic acid mixture vs. temperature of treatment of polypropylene film by chromic acid mixture.

increased with rise in the treatment temperature, therefore the amount of carbonyl groups in the surface zone of the film increased with rise in the treatment temperature.

The absorption at  $365\text{ m}\mu$  in the film treated at  $65^\circ\text{C}$  was less than the absorption at  $365\text{ m}\mu$  in the film treated at  $60^\circ\text{C}$ . The contact angle of water increased when the film was treated at  $65^\circ\text{C}$ .

It has been reported<sup>9</sup> that the polymer in the surface zone of the polypropylene film was eliminated partly because of partial breakdown of the polymer when the film was treated with chromic acid mixture. Therefore, it can be considered that the following changes occurred in surface zone of the treated polypropylene film. When the film was treated at about  $65^\circ\text{C}$ , the partial breakdown of the polymer is increased, and therefore the inner zones of the film are bared; therefore, the amount of carbonyl groups in the surface zone decrease. Consequently, the amount of the hydrazones formed in the film decreased and the contact angle of water on the film increased when the film was treated at  $65^\circ\text{C}$ .

When the film was treated at  $70^\circ\text{C}$ , the absorption at  $365\text{ m}\mu$  in the film increased again and the contact angle of water decreased. It is considered that the oxidation of the bared film surface increased.

#### Effect of Treatment Time

Plots of  $A/dl$  at  $365\text{ m}\mu$  in PP-DNPH versus times of treatment of polypropylene film with chromic acid mixture are shown in Figures 6 and 7. Plots of contact angles of water on treated polypropylene films versus time of treatment of the polypropylene films with chromic acid mixture are shown in Figures 8 and 9.

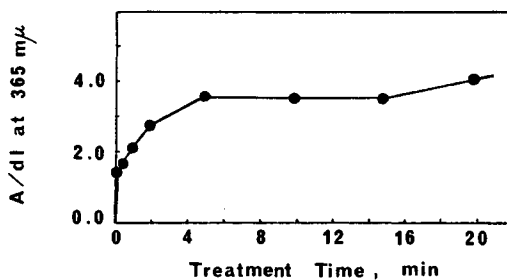


Fig. 6. Plot of  $A/dl$  at  $365\text{ m}\mu$  in PP-DNPH vs. time of treatment of polypropylene film at  $60^\circ\text{C}$ .

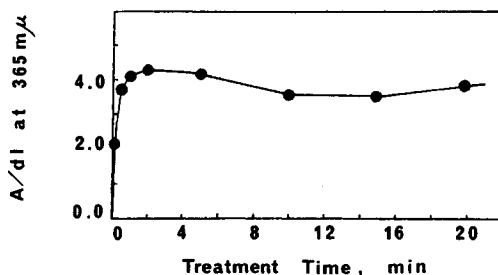


Fig. 7. Plot of  $A/dl$  at  $365\text{ m}\mu$  in PP-DNPH vs. time of treatment of polypropylene film at  $70^\circ\text{C}$ .

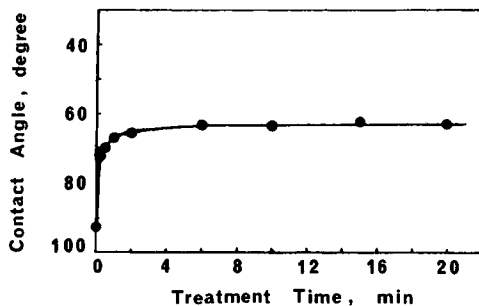


Fig. 8. Contact angles of water on polypropylene film treated with chromic acid mixture at  $60^\circ\text{C}$  vs. time of treatment of the film with chromic acid mixture.

In early stages of the treatment, the absorption at  $365\text{ m}\mu$  increased with increase in treatment time, and the rate of the increase of the absorption in film by treatment at  $70^\circ\text{C}$  was higher than the rate of the increase of the absorption in film by treatment at  $60^\circ\text{C}$ . The absorption at  $365\text{ m}\mu$  in film treated at  $70^\circ\text{C}$  for 2 min was larger than the absorption at  $365\text{ m}\mu$  in film treated at  $60^\circ\text{C}$  for 5 min. The rate of the decrease of the contact angle of water on film treated at  $70^\circ\text{C}$  was higher than the rate of the decrease of the contact angle of water on film treated at  $60^\circ\text{C}$ . It is probable that the rate of formation of carbonyl groups in polypropylene film by treatment at  $70^\circ\text{C}$  was higher than the rate of formation of carbonyl groups in the film by treatment at  $60^\circ\text{C}$ , and the amount of carbonyl groups in the film treated at  $70^\circ\text{C}$  for 2 min was more than the amount of carbonyl groups in the film treated at  $60^\circ\text{C}$  for 5 min.

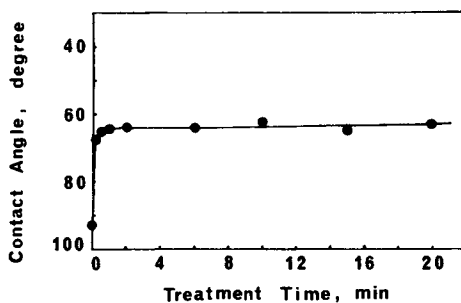


Fig. 9. Contact angle of water on polypropylene film treated with chromic acid mixture at 70°C vs. time of treatment of the film with chromic acid mixture.

The absorption at 365  $m\mu$  decreased slightly when the film was treated at 70°C within the range of about 2 to 10 min. The absorption at 365  $m\mu$  seemed to decrease when the film was treated at 60°C for about 5 to 10 min. It is probable that partial breakdown of polymer in the film surface zones was increased with increase in treatment time, and therefore the inner zones of the film were bared. The contact angle of water seemed not to decrease after the early stage of the treatment. It is probable that the bared surfaces of the films were oxidized quickly.

The absorptions at 365  $m\mu$  increased again when the films were treated upward of about 10 min. It is considered that the bared surfaces of the films were oxidized by chromic acid mixture, and therefore the amount of carbonyl groups formed in the films increased again.

### References

1. K. Kato, *J. Appl. Polym. Sci.*, **18**, 3087 (1974).
2. J. J. Brader, *J. Appl. Polym. Sci.*, **3**, 370 (1960).
3. K. Kato, *J. Appl. Polym. Sci.*, **15**, 2115 (1971).
4. F. Kurihara, *Degradation of Polymers*, Nikkan Kogyo Press, Tokyo, 1970, p. 123.
5. K. Nakao, *Nippon Setsuchaku Kyokaishi*, **6**, 283 (1970).
6. M. Ōki, *Infrared Spectra*, Tokyo University, Tokyo, 1967, p. 80.
7. L. A. Jones, J. C. Holmes, and R. B. Seligman, *Anal. Chem.*, **28**, 191 (1956).
8. C. J. Timmons, *J. Chem. Soc.*, 2613 (1957).
9. S. Yajima and T. Kanbe, *Kinzoku Hyomen Gijutsu*, **23**, 380 (1972).

Received July 17, 1974

Revised November 17, 1974