

Formation of 2,4-Dinitrophenylhydrazones in Polyethylene Film Treated with Chromic Acid Mixture

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Synopsis

2,4-Dinitrophenylhydrazones formed by the reaction of 2,4-dinitrophenylhydrazine with carbonyl groups were formed in polyethylene film oxidized with chromic acid mixture. The changes in amount of the hydrazones formed in the films were inferred by comparing the absorptions in the ultraviolet spectra and compared with changes in wettability with water of the films. In the early stage of treatment with chromic acid mixture, the hydrazone amount increased and the contact angle of water decreased. After the early stage of the treatment, the hydrazone amount decreased slightly and increased again thereafter, and the contact angle of water seemed to increase slightly and decreased again thereafter. The hydrazone amount increased with increase in time of the reaction between 2,4-dinitrophenylhydrazine and oxidized polyethylene film. For temperatures of treatment with chromic acid mixture above about 45°C, the hydrazone amount increased with rise in the treatment temperature and rate of the increase increased with rise in the treatment temperature, and the contact angle of water decreased with rise in the treatment temperature, and the rate of the decrease seemed to increase with rise in the treatment temperature.

INTRODUCTION

It has been known¹⁻⁴ that carbonyl groups are formed in polyethylene film when the film is irradiated in air by ultraviolet light or treated with chromic acid mixture. However, the formation of 2,4-dinitrophenylhydrazones in polyethylene film when the film is irradiated in air by ultraviolet light or treated with chromic acid mixture has received relatively little attention. Therefore, in a previous paper,⁵ the formation of 2,4-dinitrophenylhydrazones in polyethylene films irradiated in air by ultraviolet light has been reported. In this paper, the effects of time of treatment of polyethylene film by chromic acid mixture, temperature of treatment of polyethylene film by chromic acid mixture, and time of reaction between 2,4-dinitrophenylhydrazine and treated polyethylene film on the formation of 2,4-dinitrophenylhydrazones in the treated films and a comparison of the change in the amount of 2,4-dinitrophenylhydrazones formed in the treated polyethylene film with change in wettability with water of the treated film are described.

EXPERIMENTAL

Polyethylene Films

Low-density polyethylene film (density, 0.926 g/ml; thickness, 0.10 mm) received from Nippon Olefin Company was used in this work. The film contained no additives.

Treatment with Chromic Acid Mixture

Chromic acid mixtures prepared from potassium dichromate, sulfuric acid, and water at a ratio of 5:100:8 by weight were used for polyethylene treatment. Cleaned polyethylene films were immersed, under varying conditions of dipping time and temperature, into chromic acid mixture, and the films were then withdrawn from the chromic acid mixture, washed thoroughly with distilled water, and dried in a desiccator. Powdered low-density polyethylene (received from Nippon Olefin 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 a previous work.⁶ 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 polyethylene films treated with chromic acid mixture were immersed, under varying conditions of dipping time, in the 2,4-dinitrophenylhydrazine solutions; the films were then withdrawn from the hydrazine solutions, repeatedly washed with ethyl alcohol until the hydrazine absorption at the 1200 cm^{-1} band in the infrared spectrum had disappeared, and dried.

Absorption Spectra

Ultraviolet absorption spectra of all the samples were recorded by means of a Hitachi Model 356 recording ultraviolet spectrometer. The infrared absorption spectrum of the powdered polyethylene was recorded by means of a Perkin-Elmer Model 180 infrared spectrophotometer. For infrared spectroscopic measurement, KBr pellets were 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 in each sample. All measurements were made at about 50% R.H. and 20°C, within 10 sec of placing each drop.

Measurement of Effect of Treatment Time on Formation of 2,4-Dinitrophenylhydrazones

The polyethylene films were treated with chromic acid mixture at 30°C for different periods of time, washed, and dried. The treated films were immersed in 2,4-dinitrophenylhydrazine solutions, removed from the hydrazine solutions after 15 min had elapsed, washed, and dried. The absorptions of 2,4-dinitrophenylhydrazones at 365 $m\mu$ in the films were measured and the change in amount of the hydrazones formed in each film was inferred by comparing their absorptions.

Measurement of Effect of Treatment Time on Wettability with Water of the Treated Film Surface

The polyethylene films were treated with chromic acid mixture at 30°C for different periods of time, washed, and dried. The contact angles of water on the treated films were measured.

Measurement of Effect of Time of Reaction Between 2,4-Dinitrophenylhydrazine and Treated Polyethylene Film on Formation of 2,4-Dinitrophenylhydrazones

The polyethylene films were treated with chromic acid mixture at 20° and 50°C for 1 min, washed, and dried. The treated films were immersed in 2,4-dinitrophenylhydrazine solutions, removed from the hydrazine solutions after different periods of time had elapsed, washed, and dried. The absorptions of 2,4-dinitrophenylhydrazones at 365 $m\mu$ in the films were measured, and the change in amount of the hydrazones formed in each film was inferred by comparing their absorptions.

Measurement of Effect of Treatment Temperature on Formation of 2,4-Dinitrophenylhydrazones

The polyethylene films were treated in chromic acid mixture, heated to different temperatures for 1 min, washed, and dried. The treated films were immersed in 2,4-dinitrophenylhydrazine solutions, removed from the hydrazine solutions after 15 min had elapsed, washed, and dried. The absorptions of 2,4-dinitrophenylhydrazones at 365 $m\mu$ in the films were measured, and the change in amount of the hydrazones formed in each film was inferred by comparing their absorptions.

Measurement of Effect of Treatment Temperature on Wettability with Water of the Treated Film Surface

The polyethylene films were treated in chromic acid mixture, heated to different temperatures for 1 min, washed, and dried. The contact angles of water on the treated films were measured.

RESULTS AND DISCUSSION

The infrared spectrum at 1800 to 1700 cm^{-1} in polyethylene powder treated by chromic acid mixture is shown in Figure 1. The absorptions⁷⁻¹⁰ of the C=O stretching vibration appeared at about 1740 to 1710 cm^{-1} . The spectral change in the infrared spectrum shows that carbonyl groups

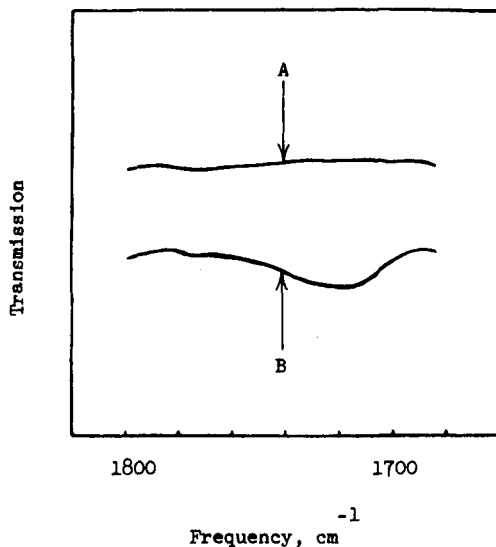


Fig. 1. Infrared spectrum at 1800 to 1700 cm^{-1} in polyethylene oxidized by chromic acid mixture: (A) unoxidized polyethylene; (B) oxidized polyethylene.

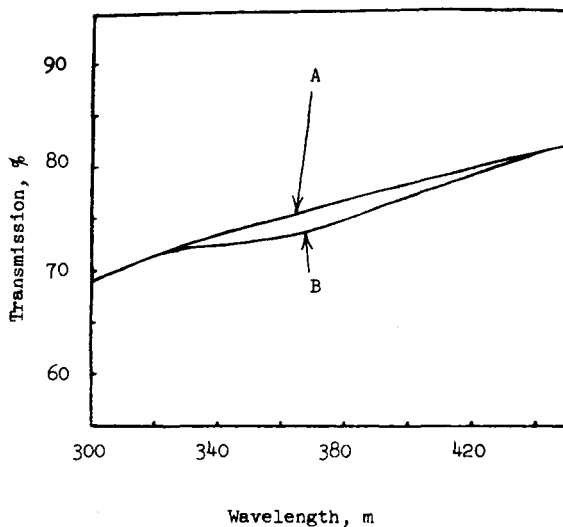


Fig. 2. Ultraviolet spectrum of PE-DNPH: (A) polyethylene film oxidized with chromic acid mixture; (B) PE-DNPH.

were formed in the molecular chains when the polyethylene powder was oxidized by chromic acid mixture.

The ultraviolet spectrum of polyethylene film when 2,4-dinitrophenylhydrazine was reacted on the film treated with chromic acid mixture showed that the absorptions^{11,12} of 2,4-dinitrophenylhydrazones appear at 365 $m\mu$ as shown in Figure 2, where PE-DNPH is the abbreviation for the polyethylene film 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.

Effect of Time of Treatment with Chromic Acid Mixture

Plots of A/dl at 365 $m\mu$ in PE-DNPH versus times of treatment of polyethylene films by chromic acid mixture are shown in Figure 3, where A is the absorbance at 365 $m\mu$ in the each film, d is the density of the film, and l is the thickness of the film. Plots of contact angles of water on treated polyethylene films versus times of treatments of polyethylene films by chromic acid mixture are shown in Figure 4.

In the early stage of the treatment, the absorption of 2,4-dinitrophenylhydrazones at 365 $m\mu$ increased with increase in treatment time, and the contact angle of water on the film surface decreased with increase in treatment time. It is probable that the amount of carbonyl groups in the surface zone of the film increased with increase in treatment time in the early stage of the treatment.

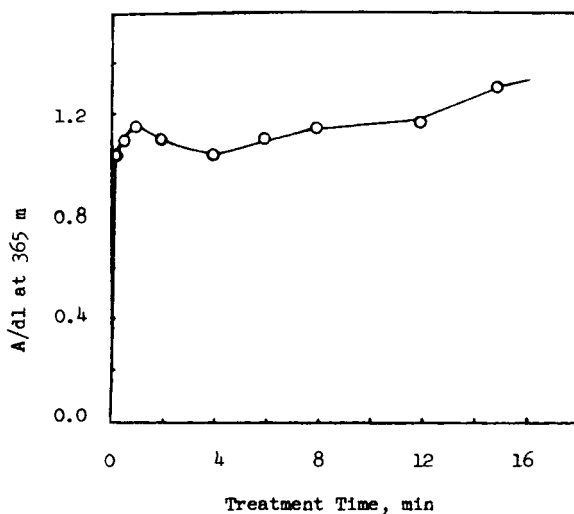


Fig. 3. Plot of A/dl at 365 $m\mu$ in PE-DNPH vs. time of treatment of polyethylene films with chromic acid mixture.

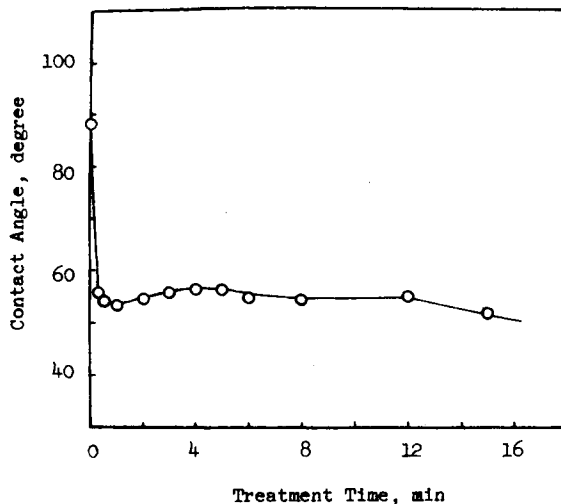


Fig. 4. Contact angles of water on polyethylene films treated with chromic acid mixture vs. time of treatment of the films with chromic acid mixture.

After the early stage of the treatment, the absorption at $365\text{ m}\mu$ decreased slightly and increased again thereafter, and the contact angle of water on the film surface seemed to increase slightly and to decrease again thereafter.

It has been reported⁴ 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, it can be considered that the following changes occurred in the surface zone of the treated polyethylene film. Partial breakdown of the polymer increases with increase in treatment time in the surface zone, so that the inner zones of the film are bared; therefore, the amount of carbonyl groups in the surface zone decreases after the early stage of the treatment. Consequently, after the early stage of the treatment, the amount of 2,4-dinitrophenylhydrazones formed in the film decreases slightly and the contact angle of water on the film surface increases slightly. Thereafter, when the bared surface is oxidized by chromic acid mixture, the amount of hydrazones formed in the film increases again and the contact angle of water on the film surface decreases again.

Effect of Time of Reaction of 2,4-Dinitrophenylhydrazine with Treated Polyethylene Film

Plots of A/dl at $365\text{ m}\mu$ in PE-DNPH versus time of reaction of 2,4-dinitrophenylhydrazine and polyethylene films treated with chromic acid mixture at 20° and 50°C are shown in Figure 5. The absorption at $365\text{ m}\mu$ of the films oxidized at 50°C was larger than the absorption at $365\text{ m}\mu$ of the films oxidized at 20°C . The absorption at $365\text{ m}\mu$ increased with increase in reaction time, and the rate of the increase of the absorption

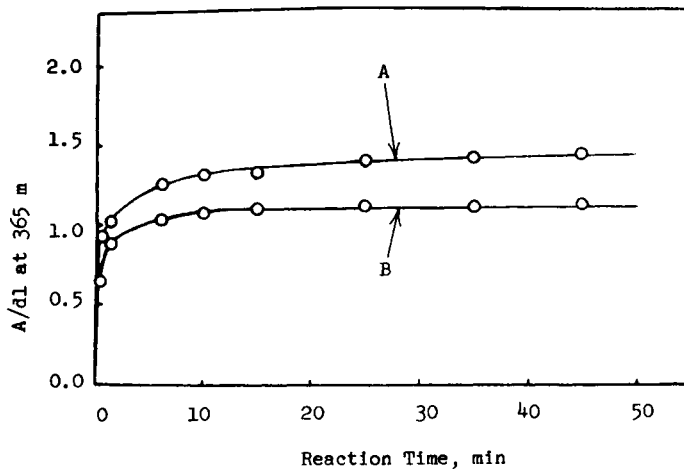


Fig. 5. Plot of A/dl at $365\text{ m}\mu$ in PE-DNPH vs. times of reaction between 2,4-dinitrophenylhydrazine with polyethylene films oxidized with chromic acid mixture: (A) polyethylene films oxidized at 50°C ; (B) polyethylene films oxidized at 20°C .

decreased with increase in reaction time. The rate of increase of absorption at $365\text{ m}\mu$ in the film was low after the treated film was immersed in 2,4-dinitrophenylhydrazine solution for about 15 min.

Effect of Temperature of Treatment with Chromic Acid Mixture

Plots of A/dl at $365\text{ m}\mu$ in PE-DNPH versus temperature of treatment of polyethylene films with chromic acid mixture are shown in Figure 6.

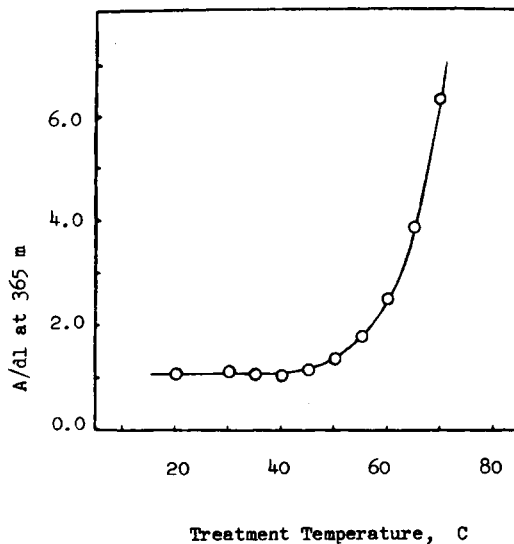


Fig. 6. Plot of A/dl at $365\text{ m}\mu$ in PE-DNPH vs. temperature of treatment of polyethylene films with chromic acid mixture.

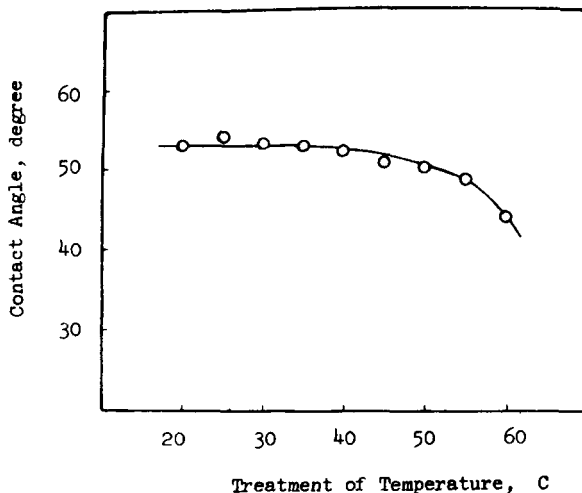


Fig. 7. Contact angles of water on polyethylene films treated with chromic acid, mixture vs. temperature of treatment of polyethylene films with chromic acid mixture.

Plots of contact angle of water on surface of oxidized polyethylene films versus temperature of treatment of polyethylene films with chromic acid mixture are shown in Figure 7. The absorption at $365\text{ m}\mu$ increased with rise in temperature of treatment above about 45°C , and the rate of the increase of absorption at $365\text{ m}\mu$ increased with rise in treatment temperature. The contact angle of water decreased with rise in the treatment temperature above about 45°C , and the rate of the decrease of the contact angle seemed to increase with rise in treatment temperature. It is probable that carbonyl groups in the surface zone of the polyethylene film increased with rise in treatment temperature above about 45°C and the rate of the increase increased with rise in treatment temperature.

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