

NOTES

Modification of Permeation and Wettability in Polyethylene Film by Photochlorosulfonation

INTRODUCTION

There have been several patents¹⁻³ of surface treatment of polyethylene with chlorine and sulfur dioxide gas under ultraviolet light. However, these patents deal only with improving bonding of polyethylene film to adhesives, lacquers, or pigments and give no further investigation into the effect of permeation properties of film by photochlorosulfonation treatment. Recently Olsen and Osteraas⁴ have shown by wettability measurement that the surface of polyethylene can be modified with atomic sulfur generated by the pyrolysis of carbonyl sulfide and by the photolysis of carbonyl sulfide and other sulfur compounds. On the other hand, a U. S. patent⁵ refers to the improvement of heat sealability, impermeability, and printability of polyolefin films by coating such a surface of chlorosulfonated polyolefin.

For the purpose of developing useful films for packaging, this note describes the improvement of oxygen gas permeability and wettability (this directly correlates with printability and adhesion) of polyethylene film by treatment with chlorine and sulfur dioxide gas under ultraviolet light; the infrared data of the modified films were also obtained.

In the preparatory experiment, it was found that the diffusion constants of chlorine and sulfur dioxide gas to polyethylene are very low (3.73×10^{-8} and 8.65×10^{-8} cm²/sec respectively), although their sorption in polyethylene is large (1.45×10^{-2} and 1.83×10^{-2} cc (S.T.P.)/cc·cm Hg).

From these facts it is conceivable that this photochlorosulfonation treatment has no effect on the favorable bulk physical properties of polyethylene because the chlorosulfonated layer is expected to be restricted only to the surface.

EXPERIMENTAL

Low-density (sp. gr. 0.918) polyethylene film with a melt index 4.0, degree of crystallinity 50.0%, thickness 0.03 mm, and containing only a very small amount of lubricant was obtained from Mitsubishi-Yuka Co.

Samples of polyethylene film were placed into a radiation cell which has a quartz window (2 mm in thickness) through which ultraviolet light was transmitted. A radiation source (Toshiba mercury lamp SHL-100 UV, 75 W) was mounted 7 cm from the film surface. Then the gas mixture (1:1 by volume) of sulfur dioxide and chlorine was admitted into the radiation cell until the whole pressure reached 1 atm, and the film was exposed to the light for definite times at about 20°C.

Permeability constants were determined at 20°C by the ordinary high-vacuum technique, originally developed by Barrer.⁶

Wettability was measured by using a telescopic cathetometer equipped with a circular protractor. The contact angles of the water drop thus obtained were averaged over five measurements.

RESULTS AND DISCUSSION

As shown in Figure 1, the chlorine and sulfur contents of photochlorosulfonated polyethylene film rapidly increased with increase in reaction time and approached

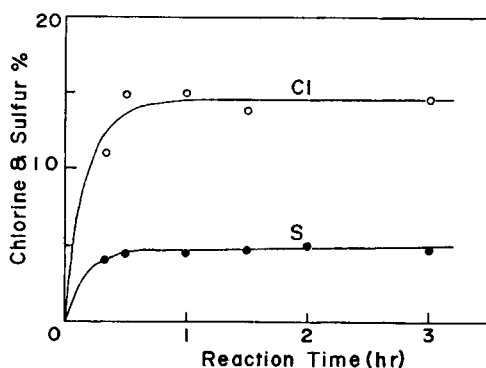


Fig. 1. Chlorine and sulfur contents of photochlorosulfonated polyethylene film vs. reaction time.

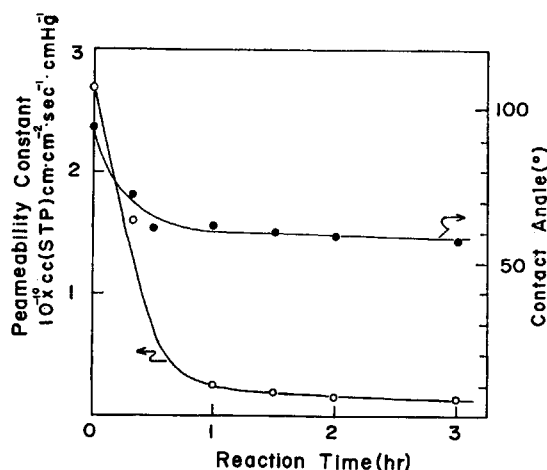


Fig. 2. Oxygen gas permeability constant and contact angle of water drop of photochlorosulfonated polyethylene film vs. reaction time.

asymptotic values (Cl, 14.5%; S, 5.0%) above about 0.5 hr. This indicates that the reaction may have taken place only in the surface of the polyethylene film because of the low diffusivity of both gases, as described before. Provided that polyethylene should react to the utmost extent [poly(di-substituted vinylidene)] at the above ratio of chlorine and sulfur content, polyethylene would have 39.8% chlorine and 22.8% sulfur. However, there is no relation between the depth of the photochlorosulfonated layer and the transmissible depth of light, because chlorine atoms act as radical carriers, just as in the Reed reaction⁷ of paraffins. This assumption is supported by the fact that the unirradiated back film in two layers can react. As to the chlorine content, photochlorosulfonated polyethylene has almost the same *chlorine* content of photochlorinated polyethylene film⁸ obtained under similar conditions, where the chlorine content of photochlorosulfonated polyethylene film was 14.0% compared with 14.5% of photochlorosulfonated polyethylene, for a reaction time of 3 hr.

Figure 2 shows the oxygen gas permeability constant at 20°C and contact angle for water of photochlorosulfonated polyethylene film against reaction time. It can be seen that the curve of permeation data rapidly decreased with increase in reaction time and

that the contact angle also decreased with reaction time, and that both were in saturation above 0.5 hr. These tendencies are well correlated with that of elemental analysis.

Oxygen permeability constant decreased to about $\frac{1}{2.5}$ (0.11×10^{-10} cc(S.T.P.)cm/cm²-sec-cm Hg) of that of polyethylene at a reaction time of 3 hr, being comparable to 0.105×10^{-10} cc(S.T.P.)cm/cm² sec-cm Hg, the value of nonplasticized poly(vinyl chloride). Photochlorinated polyethylene film⁸ has an oxygen permeability constant of 0.128×10^{-10} cc(S.T.P.)cm/cm²-sec-cm Hg under reaction conditions similar to those described above.

With respect to wettability, the contact angle decreased from 94° for polyethylene to 58° for the photochlorosulfonated polyethylene. The latter value is much lower than 68°, the value for poly(vinyl chloride). No change was observed in the contents of chlorine or sulfur, in oxygen permeation, and in contact angle if either light or mixed chlorine and sulfur dioxide gas was lacking.

The infrared spectra obtained for the photochlorosulfonated polyethylene film are given in Figure 3. The salient features of chlorosulfonated polyethylene are strong bands at 1160 and 1360 cm⁻¹ due to the vibrating —SO₂Cl, and a complicated broad range of 600–700 cm⁻¹, which is ascribed to —C—S—.⁹ In addition, the same bands that have been seen in photochlorinated polyethylene film⁸ are observed at 610 and 665 cm⁻¹, which are assigned to the secondary CCl stretching mode of —CH₂—CHCl—CH₂— and to the deformed configuration of carbon chain or —CHCl—CHCl— units, respectively.¹⁰ The 1270 cm⁻¹ band cannot be seen in photochlorosulfonated polyethylene. It can be concluded from the spectra data and elemental analysis data that polyethylene photochlorosulfonated to a full extent has side groups of —Cl and —SO₂Cl at a ratio of 0.58:1.

Apparently the introduction of such polar side chains as —Cl and —SO₂Cl causes an increase in the cohesive energy of polymer as well as in superficial affinity of base polymer and results in a decrease in the permeability to oxygen.

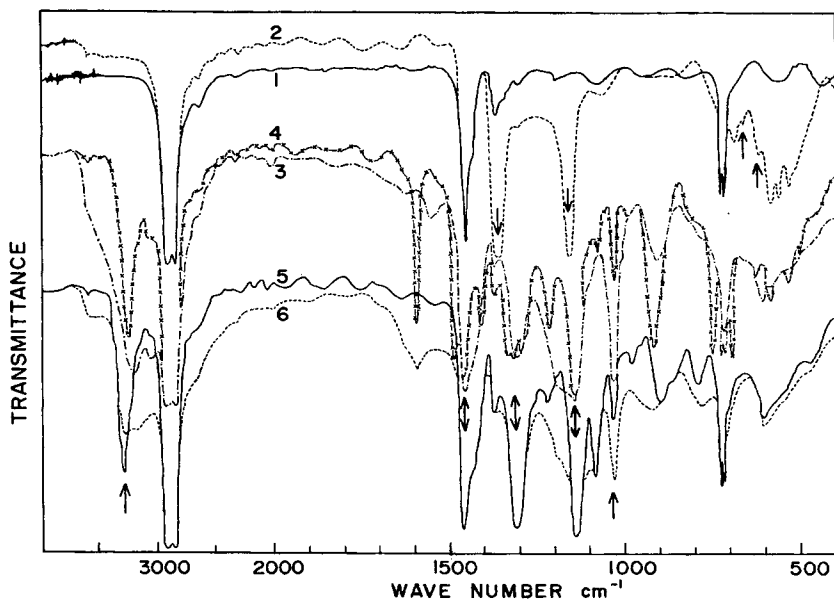


Fig. 3. Infrared spectra for photochlorosulfonated polyethylene samples treated with several amines: (1) control polyethylene film; (2) polyethylene film photochlorosulfonated for 1 hr at 20°C. Further reaction for 15 hr at 40°C with (3) 28% ammonia water; (4) aniline; (5) *n*-butylamine; (6) ethylenediamine hydrate (85%).

For further identification, the photochlorosulfonated polyethylene film for a reaction time of 1 hr was immersed for 15 hr at 40°C in such amines as 28% ammonia water, aniline, *n*-butylamine, and ethylenediamine hydrate (85%), and infrared spectra were obtained as presented in Figure 3. It is clear that the bands at 1360 cm^{-1} and 600–700 cm^{-1} all disappeared when the photochlorosulfonated polyethylene was reacted with these four amines, respectively, and that the band at 1160 cm^{-1} also vanished, except in the sample reacted with ammonia. The presence of this band is due to the characteristic absorption band of ammonia itself. Furthermore, in all cases new strong bands appeared at 3200–3300 cm^{-1} due to NH stretching absorption¹¹ and in other regions such as 1030, 1150, 1310, and 1460 cm^{-1} . Among them, the bands at 1150 cm^{-1} and 1310 cm^{-1} can be ascribed to the $-\text{SO}_2-$ grouping and the second sulfone band, respectively.¹¹

From these facts it can be concluded that polyethylene film reacts with chlorine and sulfur dioxide gas under ultraviolet light to produce a useful, superficially chlorosulfonated polyethylene film which has low oxygen gas permeability and high surface energy, as shown by the contact angle. In addition, the treated film can further react with several amines to give poly(ethylene sulfonamides).

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