Barrier Properties of Surface Sulfonated HDPE Films

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SYNOPSIS

Films of high-density polyethylene (HDPE) have been sulfonated by solid–gas phase reaction using gaseous sulfur trioxide (SO_3) of different concentrations in nitrogen. The effect of concentration of SO_3 in an $SO_3 + N_2$ gas mixture and time of sulfonation on solvent and gas barrier properties of sulfonated HDPE films was studied by determining toluene and oxygen permeability of HDPE films sulfonated with different concentrations of SO_3 for different times. The color developed in sulfonated HDPE films during sulfonation could be bleached by aqueous sodium hypochloride solution. The effect of sodium hypochloride solution treatment on oxygen permeability of sulfonated HDPE films was also studied.

INTRODUCTION

Polyethylene, due to its low price, easy processibility, good physical properties, and chemical inertness, has acquired considerable importance in the packaging industry. The present trend in the packaging industry is to replace metal containers by plastic. Although PE is the preferred material, it has high permeability for oxygen and solvents and as such cannot be used as a container material for hydrocarbon solvents or materials containing hydrocarbon solvents. Surface modification of PE by sulfonation or fluorination improves solvent barrier properties of PE considerably. Such surface sulfonated HDPE containers are used as fuel tanks in automobile industries.

Many patents and publications[1-5] describe the process of sulfonation of HDPE containers to improve solvent barrier properties from the industrial point of view and solvent barrier properties of surface sulfonated HDPE is determined using bottles. However, little information is available regarding solvent and gas barrier properties of surface sulfonated HDPE films.[6-13]

Surface sulfonation of HDPE films by gaseous sulfur trioxide is invariably accompanied by undesirable color formation, deepening with the extent of sulfonation. The color can be bleached to some extent by treatment with bleaching agents, such as sodium hypochloride and $KBr + KBrO_3$ solutions. However, the effect of such treatment on gas and solvent permeability properties is not known.

This article describes sulfonation of HDPE films using gaseous sulfur trioxide in N_2 and the effect of the extent of sulfonation and bleaching of sulfonated film with sodium hypochloride or $KBr + KBrO_3$ solution on their oxygen permeability.

EXPERIMENTAL

Materials

HDPE films (MFI 190/5–1.0 g/10 min, density 0.945, thickness 100 μm) were supplied by M/S Polyolefin Industries (PIL), Bombay. Oleum was 20% LR grade (S.D. Chemicals, Bombay), $KBr + KBrO_3$ (0.5*M*).

Surface Sulfonation of HDPE Films

HDPE films were sulfonated on one side by passing an $SO_3 + N_2$ gas mixture of desired SO_3 content over the film in a glass apparatus for different times at room temperature (27°C).

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Generation of $SO_3 + N_2$ Mixture

An $SO_3 + N_2$ mixture of the desired SO_3 concentration was generated in a specially designed glass assembly. Nitrogen and oleum of a known flow rate were allowed to pass through a U tube containing ceramic beads. The U tube assembly was heated electrically up to 160°C. The concentration of SO_3 in the gas mixture was determined by titrating, with standard 0.1N alkali, the sulfuric acid generated by dissolving a known volume of the $SO_3 + N_2$ mixture at 27°C in distilled water.

Sulfonation of HDPE Films

HDPE films of size 8″ diameter were sulfonated on one side in a specially designed glass apparatus by passing an $SO_3 + N_2$ mixture of known SO_3 content for the desired time over the film, which was mounted on a glass plate and placed in the glass apparatus flushed with dry nitrogen. The $SO_3 + N_2$ mixture was passed over the film continuously at the rate of 200 mL/min for the desired time at 27°C. The apparatus was flushed with N_2 to remove SO_3 gas, and the film was removed from the apparatus, washed with water, placed in 5% NH_4OH solution for 1 min, washed again several times with distilled water, and air dried at room temperature.

Determination of Solvent Permeability of Sulfonated HDPE Films

Solvent permeability of the films was determined using a specially fabricated aluminium cell. The cell is a small hollow cylinder of 2″ diameter and 1″ depth with a screw cap system. The screw cap has a circular hole of 2″ diameter at the center, where HDPE film can be fixed airtight using a Neoprene rubber O-ring. The cap mounted with film was then fixed to the solvent-filled cell with a tight screw. The system was made airtight. Initially the cell was weighed on a digital balance to the accuracy of ±10 mg and placed in a chamber at 27°C upside down so that solvent in the cell rested on the film. The cell was weighed after desired time intervals, and loss in solvent was determined.

Characterization of Sulfonated Films

Solvent permeability was determined using the formula

$$\% \text{ wt loss} = (1 - W_1/W_0) \times 100$$

where W_0 = original weight of the solvent, and W_1 = weight of solvent after permeation.

Determination of Oxygen Permeability

Oxygen permeability of HDPE films was determined per the ASTM D1434 standard on a CSI-built gas permeability cell at 10 ± 0.5 psi O_2 pressure at 30 ± 0.1°C.

Determination of Contact Angle

Contact angle of virgin and sulfonated HDPE films was measured on a Rame Hart contact angle goniometer using triple distilled water (only the sessile drop contact angle was determined). Films were conditioned in a constant humidity chamber before determining contact angles.

RESULTS AND DISCUSSION

The extent of sulfonation of HDPE films by an $SO_3 + N_2$ gas mixture depends on the time and SO_3 concentration in the gas mixture at constant temperature. To understand the effect of these parameters on sulfonation, HDPE films were sulfonated for 5, 10, and 15 min using 3.5, 5.5, 7.5, and 10% concentrations of SO_3 in an $SO_3 + N_2$ gas mixture. Contact angle is the measure of hydrophobic or hydrophilic characteristics of surfaces. Contact angle of water with a surface decreases as the surface becomes hydrophilic. HDPE is highly hydrophobic and shows a contact angle of 93° for water, which decreases considerably on sulfonation due to introduction of hydrophilic SO_3H groups. Table I gives contact angles of water with HDPE films sulfonated with 3.3, 5.5, 7.5, and 10 vol % SO_3 in the gas mixture for 5, 10, and 15 min. Contact angle decreases as time, or concentration of SO_3 in the gas mixture, is increased, indicating that the extent of sulfonation depends on both.

Toluene permeability of virgin and sulfonated HDPE films was determined at 27°C after 24 h. Mean values of three separately tested films under similar conditions are tabulated in Table I. Virgin HDPE film shows toluene permeability of 2.1 ± 0.1 % wt loss per 24 h, which reduces to 0.13 % wt loss on sulfonation for 15 min with a gas mixture of 5.5 vol % of SO_3 in N_2. A lower concentration of SO_3 gas (3.3 vol %) does not have a significant effect on toluene permeability even after 15 min exposure. Considerable degradation of the surface is observed on sulfonation with a gas mixture of higher SO_3

Table I Characteristics of Sulfonated HDPE Films

Conc. of SO_3, vol % in N_2	Sulfonation Period (min)	Toluene % wt loss/24 h	Contact Angle, $\theta°$	Oxygen Permeability $[(cm^3\ cm)/(cm^2\ s\ cmHg) \times 10^{10}]$
Virgin HDPE	—	2.1	93	2.45
3.3	5	1.35	70	2.30
	10	1.30	58	1.70
	15	0.80	46	1.60
5.5	5	1.20	58	1.80
	10	0.50	40	1.70
	15	0.13	34	0.80
7.5	5	0.32	58	1.50
	10	0.20	32	1.30
10	5	1.15	32	1.70
	10	0.20	20	—
	15	0.21	20	0.20

concentration. HDPE films sulfonated with 10 vol % of SO_3 gas mixture darken considerably even after 5 min of exposure. Sometimes toluene permeability of such films increases due to degradation of the surface.

Table I gives oxygen permeability of HDPE films sulfonated with 3.3, 5.5, 7.5, and 10 vol % SO_3 for 5, 10, and 15 min. Surface sulfonation also improves the oxygen barrier properties of HDPE films (Table I). Virgin HDPE film shows oxygen permeability of 2.45, which is reduced to 0.8 on sulfonation for 15 min with 5.5 vol % SO_3 in an N_2 gas mixture. Oxygen permeability decreases as time and concentration of SO_3 in the gas mixture is increased. However, it is more sensitive to an increase of sulfonation time than the concentration of SO_3 in the gas mixture.

Surface sulfonation of the film is accompanied by color formation, and color deepens as time or concentration of SO_3 in the gas mixture is increased. In fact, at higher concentrations of SO_3, the film becomes very dark within a few minutes. This color can be bleached to some extent by treating sulfonated film with sodium hypochloride or KBr + $KBrO_3$ solution. Table II describes oxygen permeability of sulfonated HDPE films after treatment with 2% NaOCl solution and 0.5*M* KBr + $KBrO_3$ solution for different times. These results show that the oxygen permeability of sulfonated HDPE films is not altered much by treatment with NaOCl or KBr + $KBrO_3$ solutions, although these treatments bleach the dark color of the films to a considerable extent after treatment for 2 to 3 min.

CONCLUSIONS

1. Sulfonation is sensitive to the concentration of SO_3 and time of sulfonation.
2. Sulfonation improves the oxygen and solvent barrier properties.
3. As the extent of sulfonation increases, a dark

Table II Effect of Oxidizing Agent on Oxygen Permeability of Sulfonated HDPE Films (100 μm) (Sulfonated with 7.3 vol % of SO_3 for 5 min)

	Permeability Coefficient $[(cm^3\ cm)/(cm^2\ s\ cmHg) \times 10^{10}]$		
Film No.	Before Treatment	Time of Treatment (min)	After Treatment with NaOCl Solution
I	1.10	2	1.14
II	1.00	5	1.00
III	0.98	15	0.90
			After treatment with KBr + $KBrO_3$
IV	1.07	1	0.99
V	1.05	2	0.97
VI	1.26	3	1.39

brown color develops on the surface of the HDPE films.

4. The undesired color of the sulfonated films can be bleached using an oxidizing agent without affecting their barrier properties.

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