NOTE

Diffusion Behavior of Sulfur Mustard and Its Oxygen Analog in Poly(ethylene terephthalate) Films

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INTRODUCTION

Sulfur mustard (SM, thiobis-1′1′ dichloroethane) is a bifunctional alkylating agent that can quickly penetrate animal skin due to its lipophilic properties.[1–3] It produces blisters in human skin which are very painful and slow to heal.[1,2] SM is also known to possess the unique property of breaking through a variety of synthetic polymeric materials with relative ease.[4–8] As a result it is the candidate agent against which protective materials are tested. Efforts have been made to find a suitable barrier which can prevent human exposure to sulfur mustard.[9]

Previous studies on the protection afforded by material against SM deal with formulation of newer compounds and methodologies adopted to assess the products.[4–8] It is well established that in a paracrystalline polymer the crystalline microstructure plays an important role in determining the diffusion properties of the polymer.[10,11] The diffusion of penetrant in semicrystalline polymers occurs almost exclusively through the amorphous phase. It is also known that heat setting of paracrystalline polymer leads to modification of amorphous as well as crystalline structure which, in turn, influences the properties of a polymer, including transport behavior.[12,13] Polyester is a material having good mechanical strength and chemical resistance; as a result it is a good candidate for protective and packaging material.

The present work was initiated to find the protective properties of poly(ethylene terephthalate)(PET) against SM and its oxygen analog, as well as to evaluate the effect of heat setting on the diffusion behavior of the films. A spot-disc (SD)[4,5,14] test method was employed to study the breakthrough times (BTT) of SM against PET films. Due to the biological hazard associated with handling SM, an oxygen analog of SM (OA) was used as a challenge chemical to measure diffusion coefficients by the weight-gain method.[4–6,15] Methylamine etching as well as scanning electron microscopic techniques were employed to interpret the results.

EXPERIMENTAL

Two commercially available PET films of two different thicknesses, namely, 25 and 50 μm (manufactured by M/S Garware Polyester, Mumbai, India), termed as sample A and sample B, respectively, were taken for the study. Both films were of the same base material, as revealed by pyrolytic gas chromatography as well as X-ray diffraction analysis.[4] Qualitatively, the orientation of both films appeared similar as revealed by the X-ray study.

(SM, $C_4H_8Cl_2S$), 98% pure by gas−liquid chromatography (GLC), synthesized in the Chemistry Division

of the Defence R&D Establishment, was utilized for the study. SM is an oily liquid with a density of 1.27 g/mL^3 at 25°C. It freezes at 14.4°C and has a boiling point of 215°C.

The OA of SM, $C_4H_8Cl_2O$, was utilized for the experiment as received from M/S E Merck, Darmstadt, Germany. It has a boiling point of 62°C and density of 1.22 g/mL^3 at 25°C.

While handling these chemicals, hand gloves and eye guards were used. The experiments were conducted in a ventilated room.

Heat Setting

Samples A and B were introduced into an oven at 165°C and kept at that temperature for 5 min. The samples were then allowed to cool rapidly in air (slack-quenched, SQ). Another set of samples was heat-set at 200°C for 5 min and quenched. These heat-set samples were tested for their resistance against SM and an OA.
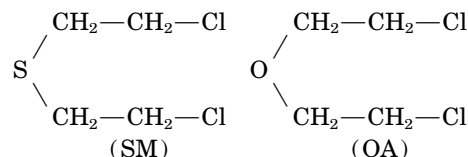
BTT Test

The permeation resistance of the PET films (both control and heat-set) against sulfur mustard was evaluated by the SD method.[14] A test specimen of 5-cm diameter was sealed with wax on a Congo Red paper spotted with SD (2,4-dichlorophenyl benzoyl chloride) reagent. SM (118 μl was placed over a filter paper (1 cm^2) lying over the test specimen in the center. The specimen was enclosed in a glass Petri dish (4.7-cm diameter), which was sealed with wax. This ensured that the edge effect due to the cutting of the specimen did not influence the diffusion of SM. The whole assembly was placed in a chamber at a constant temperature of 37 $\pm$ 0.5°C. The underside of the detector paper was observed for the appearance of blue spots using a 45-degree mirror located under the glass plate. Penetration of SM into the test specimen gives rise to blue spots caused by hydrogen chloride resulting from the reaction between SD reagent and SM. The interval between the time SM was placed on the test specimen and the first appearance of blue coloration was taken as the BTT. An average of five readings was considered as the BTT of the sample. From the BTT values, the corresponding diffusion coefficients were computed using the following equation:

$$t = L^2/\pi^2 D \qquad (1)$$

where t is the BTT of the specimen, L is the thickness of the specimen, and D is the diffusion coefficient.

Sorption Experiment

Due to the biological hazard associated with handling SM, an OA was used as a challenge chemical to measure diffusion coefficients by the weight-gain method.[4–6,16,17] The chemical structure of SM and OA are given below:

$$S \begin{cases} CH_2\text{—}CH_2\text{—}Cl \\ CH_2\text{—}CH_2\text{—}Cl \end{cases} (SM) \qquad O \begin{cases} CH_2\text{—}CH_2\text{—}Cl \\ CH_2\text{—}CH_2\text{—}Cl \end{cases} (OA)$$

Both control and heat-set samples of films A and B were cut into circular pieces (5-cm diameter) by a steel die. The pieces were then immersed in OA in test bottles, after recording their initial weight. The liquid-to-specimen ratio was kept very high. The sample weights were taken at different time intervals (t) after removing extraneously held OA by padding them with a filter paper each time. The experiment was conducted at 30°C. The weights were recorded employing a Mettler analytical balance having a sensitivity of 10^{-5} g. The results were plotted as mol % uptake of OA versus $t^{1/2}$ where t is the time in minutes.

Diffusion coefficients (D) for OA were calculated from the slope of the initial linear portions of the sorption curves using the following equation[4–6,16,17]:

$$D = \pi(h\theta/4M_\infty)^2 \qquad (2)$$

where D is the diffusion coefficient, θ is the initial slope of sorption curve, h is the thickness of the rubber film, and M is the maximum mol equilibrium uptake of the solvent by 100 g of the polymer sample.

Amine Etching

It is known that methylamine etching can bring out subtle structural differences which are not discernable by X-ray or mechanical behavior. The films (both control and heat-set) were subjected to controlled chemical etching[18–20] in 40% methylamine aqueous solution in sealed bottles for 2 h at 20°C without agitation. Details of the procedure are presented elsewhere.[21]

Scanning Electron Microscopy

Surface morphological studies of the samples subjected to methylamine etching were made with a JEOL JSM-840 scanning electron microscope at 5 kV. The samples were coated with a thin layer of gold using a JFC-1100 sputter-coating unit prior to examination.

Table I   BTT and Diffusion Coefficients of PET Films

Sample	Thickness (um)	SM BTT (h)	Increase in BTT (%)	Diffusion Coefficient cm²/s	
				D (SM)	D (OA)
A Control (untreated)	25	40	—	0.439×10^{-11}	1.2×10^{-9}
A Heat-set (165°C)	25	114	185	0.154×10^{-11}	0.072×10^{-9}
A Heat-set (200°C)	25	92	130	0.191×10^{-11}	—
B Control (untreated)	50	24	—	2.929×10^{-11}	4.5×10^{-9}
B Heat-set (165°C)	50	96	300	0.732×10^{-11}	0.12×10^{-9}
B Heat-set (200°C)	51	84	250	0.876×10^{-11}	—

RESULTS AND DISCUSSION

Table I presents the data on breakthrough time as well as diffusion coefficients of SM for the two films. Sample A (25 μ) showed a breakthrough time of 40 h. The film heat-set at 165°C registered a value of 114 h, an increase of 185% from the control without any change in the gross physical properties, such as thickness and stiffness. The physicomechanical properties of control films have been described in earlier reports.[18,20] The sample heat-set at 200°C however showed an average BTT of 92 h. The heat-setting at 200°C lowered the BTT value by 19.3% compared with the film heat-set at 165°C. The overall improvement attained by heat-setting at 200°C was, however, 130% from the control.

Improvement in the breakthrough time of SM as a result of heat-setting for sample B (50 μ) showed a similar trend. The enhancement in the breakthrough time was 300% for the 165°C heat-set film from the control, whereas for the 200°C heat-set film the improvement was only 250%. However, there was a marginal increase in the thickness of the film at 200°C and it became a little stiffer (qualitatively).

The diffusion coefficients (D) determined from the BTT of SM using eq. (1)[22] revealed that after the heat-setting the coefficient of diffusion decreased. Study of diffusion of penetrant molecules in a semicrystalline polymer offers some scope for investigating both the molecular nature of the noncrystalline region and the overall morphology of the polymer.[13]

Figure 1 shows the sorption curve of the OA of SM for the two PET films before and after heat-setting at 165°C. Since the calculated diffusion coefficients for SM indicate a similar trend for 200°C heat-set films, the sorption curves of OA only for 165°C heat-set films are given. The diffusion coefficient determined from the slope of the initial linear portion of sorption curves indicates that slack-quenching at 165°C improves the resistance to OA penetration. The sorption of the chemical becomes less as compared with the control. However, the uptake of the challenge chemical was initially faster in the case of heat-set samples as compared with the corresponding controls. The steady state was also attained in a shorter duration for heat-set samples.

The step-behavior of sorption could be explained in terms of a "skin" structure found on the surface of thermoplastic polymers.[12] The crystallites of "skin" structure sorb much less and do not permit transport of the penetrant molecules. It is known that the penetrant molecules can be transported by the tortuous amorphous layers which are anchored in the crystal lattice. The initial portion of the curve perhaps represents the resistance of the "skin" structure toward the penetrant molecules. Later, the transport is facilitated by the amorphous layer, when the uptake of OA becomes large, and then a steady state is achieved. Thus the sorption curves indicate the inhomogeneity of response to the penetrant molecules, which appeared to be structure-dependent. For the heat-set films which become compact and uniform after the treatment, their diffusion coefficients reduced.

To confirm whether the sorption mechanism follows the Fickian mode, the sorption data of the penetrant–polymer system have been fitted to the following relation[6,16,17]:

$$\ln(M_t/M_\infty) = \ln K + n \ln t$$

where M_t and M_∞ represent the mol % uptake at time t and at equilibrium time. K is a constant characteristic of the polymer–solvent system. The values of n address the type of transport mechanism. A value of $n \leq 0.5$ represents the Fickian mechanism and $n > 0.5$ indicates non-Fickian transport. From a least-squares analysis of the $\ln(M_t/M_\infty)$ data versus $\ln t$, the values of n have been obtained for both control and heat-set samples. The values of n are 0.72 and 0.59 for control samples A and B, respectively, whereas for the heat-set samples the values reduced to $n = 0.5$ for both films. This indicates that the diffusion behavior of OA against samples A and B is not Fickian in the case of the control samples, whereas the mode of transport becomes Fickian-like in the case of the heat-set samples. However, during sorption experiments significant swelling anomalies were not observed in either PET sample. Thus, the diffusion coefficients calculated can be regarded as concentration-independent.[17]
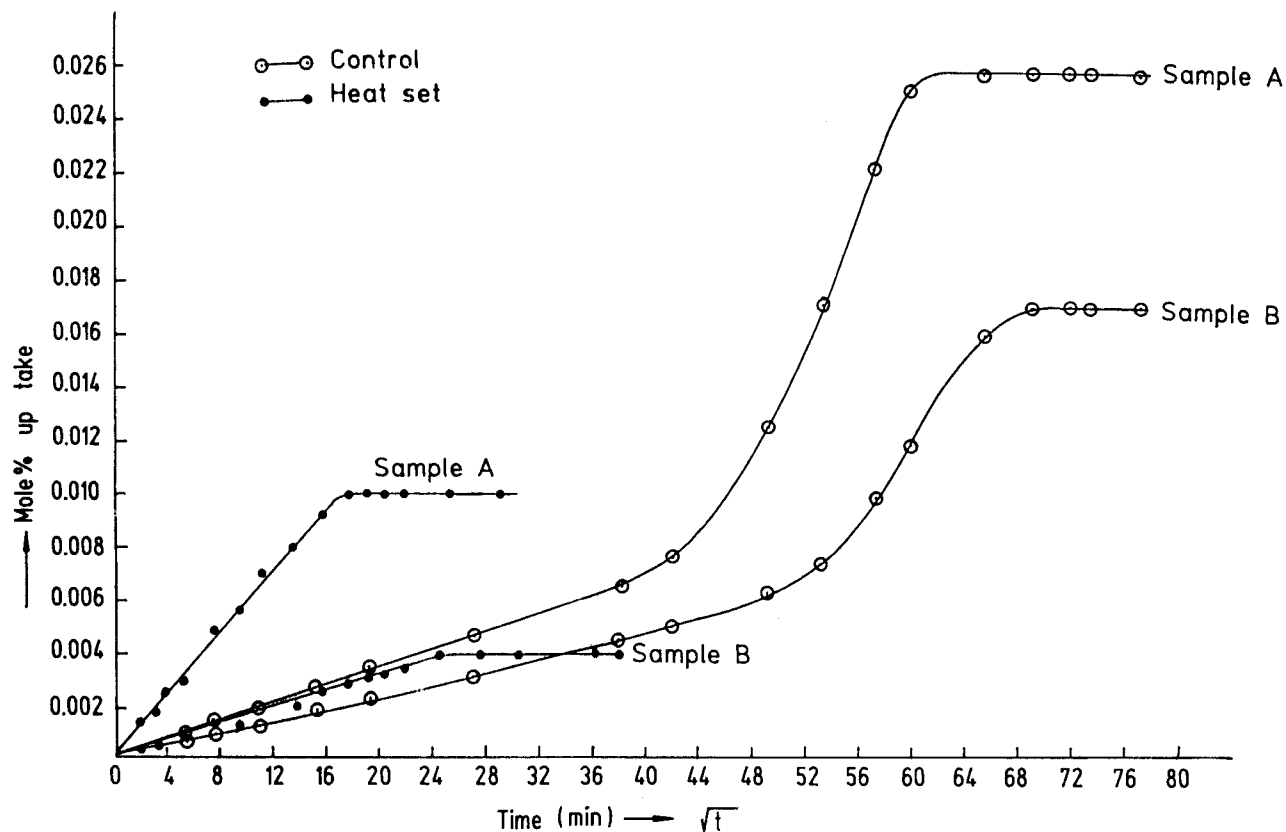
Figure 1 Sorption behavior of oxygen analog of sulfur mustard in PET films.

In order to explain the observed changes, the films were subjected to methylamine etching. Because methylamine etching is selective to discriminate between the crystalline and amorphous regions, it etches the amorphous portion along with highly stressed regions preferentially.[19] Figure 2 shows the surface of control as well as heat-set films. The surface of film A after controlled methylamine etching did not show any etch pattern [Fig. 2(a)]. Similarly, heat-set films of sample A did not reveal any surface relief after amine etching [Fig. 2(b,c)]. Sample B, however, showed etched lines which were parallel to the film drawing direction [Fig. 2(d)], indicating that sample B is more susceptible to methylamine etching. This lends support to the assumption that sample B is relatively amorphous and stressed compared with sample A.[15] This will lead to lower BTT values compared with sample A. The heat-set films, however, were devoid of any etch patterns [Fig. 2(e, f)]. It is well established that when semicrystalline-oriented films are exposed to temperatures in excess of their glass transition temperatures, the built-in stress and strain introduced during their fabrication process are relieved. At 165°C only the diffusion process of amorphous segments predominates, where the local

constraints on the amorphous chains are removed. Consequently, the noncrystalline segments will gain enough mobility from the supplied thermal energy and rearrange themselves. Because of surface tension and the compactness of the structure, the diffusion process may proceed outward, i.e., to the surface. Simultaneously, ordering of chains in the amorphous phase at the periphery may occur, leading to a "hole-filling process" which makes the structure homogenous.[23,24] The resultant structureless surface after methylamine etching also indicates a stress-free surface. Thus, for a sample heat-set at 165°C, the molecules of SM may not find easily accessible regions on the surface, giving rise to larger BTT. This leads to overall low absorption of the challenge chemical (OA) as well.

It is reported that in case of samples heat-set at 200°C for a short duration the crystallites of PET may not have enough time to rearrange themselves in a more ordered and regular structure, though the crystallization attained at 200°C is higher than that at 165°C.[23,24] As a result the crystallites would have a wider range of imperfections. Thus, in the temperature range between 185 and 200°C two processes occur (namely, crystallization and crystal perfection) which
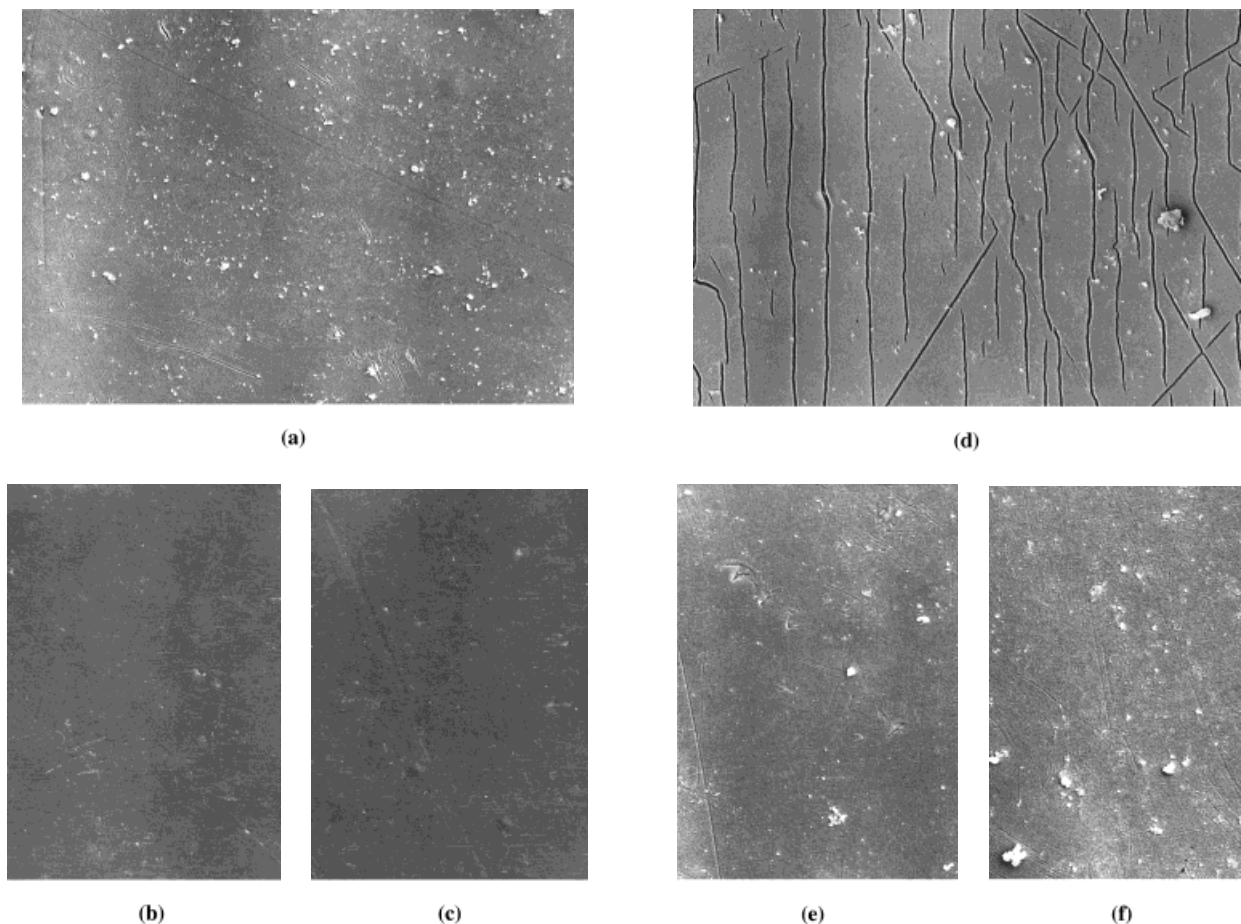
Figure 2 (a) Sample A (control) amine-treated; no etch pattern formed; magnification: 1,500×. (b) Sample A (165°C SQ), amine-treated; no etch pattern seen; 1,500×. (c) Simple A (200°C SQ), amine-treated; no visible etch pattern; 1,500×. (d) Sample B (control) amine-treated; narrow etch lines visible on the surface; 1,500×. (e) Sample B (165°C SQ) amine-treated; surface devoid of any etch pattern; 1,500×. (f) Sample B (200°C SQ) amine-treated; no etch pattern visible; 1,500×.

probably compete with each other. In these cases the rate of crystallization is very fast but the crystal perfection is poor. For such structures the movement of penetrant molecules may be faster. This may lead to faster penetration of the chemical and comparatively lower BTT than that at 165°C.

Under the controlled etching, the methylamine molecule may not be able to etch heat-set surfaces because of their overall higher crystalline structure.

The greater improvement, in general, for sample B after heat-setting could be attributed to the crystallization of the amorphous region to a greater extent and the compactness of the structure attained by shrinkage (increase in thickness at 200°C).

CONCLUSIONS

The heat-setting of PET films at the moderate temperature of 165°C improves its resistance to the diffusion of SM very significantly, without affecting such properties as stiffness and thickness. This simple method can be utilized to enhance the protection properties of packaging material. The transport properties of the oxygen analog of SM are also modified as a result of heat-setting of the films. Chemical etching was used to bring out smaller structural details caused by heat-setting.

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