Effect of Sulfur Mustard on Microhardness of Poly(ethylene terephthalate) Films

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SYNOPSIS

The effect of sulfur mustard (SM), a well-known chemical warfare agent on the microhardness of two poly(ethylene terephthalate) (PET) films was investigated at different loads. SM induces hardness in PET films, perhaps due to an antiplasticizing effect. Heat treatment of the films enhanced their microhardness. The heat-set films show a further increase in their microhardness after exposure to SM. These results were supported by physicochemical techniques like plasma and amine etching, which revealed complex etching phenomena giving rise to a structure-specific pattern. The film having a higher weight loss due to plasma and amine etching showed lower microhardness. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Sulfur mustard (SM) 1,1'-thiobis(2-chloroethane) is a bifunctional alkylating agent which has been used as a chemical warfare agent a number of times.[1] While there is an extensive literature on its reactivity to biomolecules,[2,3] as far as we are aware, data concerning the effect of SM on microhardness of poly(ethylene terephthalate) (PET) are still not available. Microhardness is one of the important mechanical parameters which can offer direct information to changes in the morphology and microstructure of thermoplastic.[4,5] In the present article, the effect of SM on the microhardness of PET is presented. These results are substantiated by plasma as well as chemical etching techniques which are sensitive to the microstructure of polymers.

EXPERIMENTAL

Commercially available PET films of two thicknesses, 25 and 50 μ, termed samples A and B, respectively, were taken for the study. These were subjected to X-ray diffraction as well as to pyrolytic GC analysis to determine their characteristic structure pattern. Both films conform to the same base material.

Samples were heat-set at 230°C and then rapidly brought to room temperature (quenched) after heat setting for 5 min in an air oven under slack as well as tension conditions.

Plasma Etching

Polyester films were kept in a discharge tube. A radio-frequency (rf) oscillator was used as the source to provide a glow discharge with a power output of about 100 W. Activated species of the air produced in the glow discharge were allowed to impinge on the sample for 10 min. The air pressure was maintained at 1 Torr.

Amine Etching

Control as well as plasma-etched films were subjected to chemical etching in a 40% aqueous methylamine solution in sealed bottles to prevent the loss of gaseous methylamine. The sample-to-liquid ratio was kept high. Experiments were run without agitation. The etching was carried out at 27°C for 1 h.

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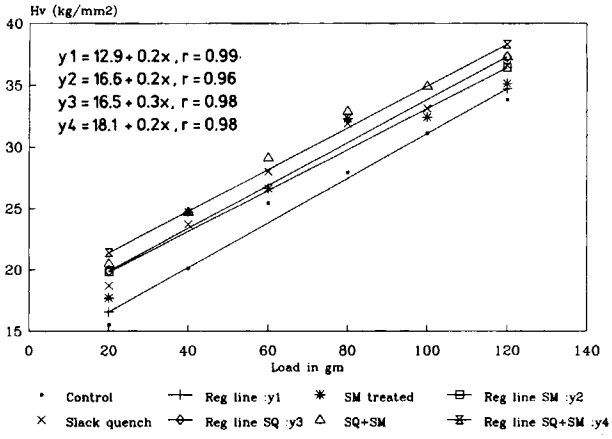

Figure 1 Load–hardness plot for sample A for control as well as SM-treated films before and after slack quenching.

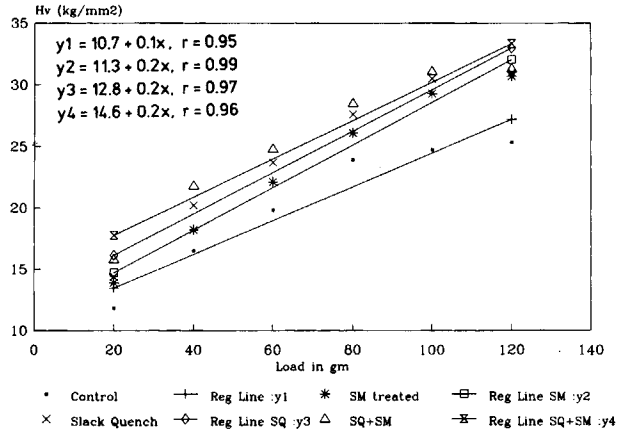

Figure 2 Load–hardness plot for sample B for control as well as SM-treated films before and after slack quenching.

Scanning Electron Microscopy

All scanning electron microscope observations were made with a JEOL-JSM 840. Samples were coated with a thin layer of gold produced by ion sputtering in an ion sputter JFC-1100.

SM Treatment

SM, 2 μL (98% pure by GLC, synthesized in our establishment), was applied at five different places uniformly on the surface of 1 sq cm of each film. The samples were allowed to dry at ambient temperature for 36 h.

Microhardness

Microhardness measurements were performed with a Carl-Zeiss Vicker's microhardness tester MPH-10. The microhardness values in kg/mm^2 were derived from the residual projected impression using the equation $H = Kp/d^2$, where d is the mean diagonal length of the indentation; p, the applied force in kg; and K, a geometrical factor equal to 1.854. A total of 20 readings were taken at each load. The loads of 20, 40, 60, 80, 100, and 120 g were employed. A loading cycle of 10 s was used.

Statistical Analysis

The average values of microhardness were plotted against corresponding loads. The regression lines were computed using the least-square method. The Student "t" test was also conducted to determine the level of significance between the values. The values at each load are statistically different at the 1% level. Though the regression lines appear to merge at certain loads, the hardness values are different statistically. The degree of association between load and microhardness for each set of experiments is very high, ranging from 0.95 to 0.99. These values are given in Figures 1–3.

RESULTS AND DISCUSSION

Figure 1 shows load vs. hardness plots for sample A for the control as well as slack-quenched films which were subsequently exposed to SM. It indicates that SM-exposed films, both the control as well as quenched, show increased hardness compared to the unexposed films. The hardness induced by SM in the control film is almost equal to the hardening produced by slack quenching. However, at higher

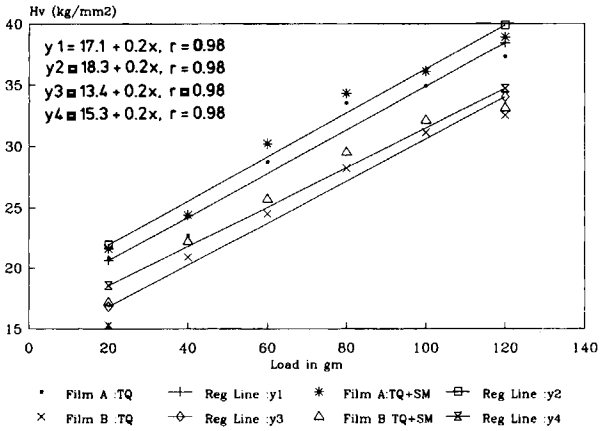

Figure 3 Load–hardness plot for tension-quenched (samples A and B) films before and after SM treatment.

loads, the slack-quenched samples register higher hardness values.

Figure 2 depicts the changes in microhardness of sample B films as a result of SM exposure for control as well as after slack quenching. The hardness of the slack-quenched films is further enhanced after SM interaction.

Figure 3 shows the microhardness plot for tension-quenched films (A and B) before and after SM exposure. The regression lines reveal an increase in microhardness after SM exposure. Sample A (both tension-quenched and subsequent SM-treated) registers higher mirohardness as compared to sample B.

The interaction of SM with PET films which resulted in increased hardness could be explained on the basis of the antiplasticizing behavior. It is well known that an antiplasticizer interacts with a glassy polymer in such a way that it reduces elongation and increases the elastic modulus.[6] Since the microhardness testing is a measure of plastic deformation caused by dislocation and slip movement, it can be inferred that SM helps in reducing the deformation as measured by microindentation. Structurally, the antiplastcizing molecules are physically absorbed at the interfaces of an amorphous structure that exists in polymer and influences their mechanical properties. In our recent study (to be published separately),[7] it was observed that the SM-exposed PET films showed a significant reduction in elongation compared to the unexposed specimens.

During slack quenching, a considerable amount of shrinkage and chain folding occurs and the amorphous content per crystallite decreases. This, in turn, leads to compactness of the structure, thereby increasing the surface hardness. Similarly, during tension quenching, realignment of the structural domain takes place, resulting in a more ordered crystalline structure. However, due to the smaller size of the SM molecules, they are able to penetrate the amorphous domain and influence the elastic and plastic deformation behavior.

These film samples were subjected to plasma as well as to amine etching in order to explain the observed difference in their microhardness. These techniques permit the progressive removal of less ordered or poorly crystalline material from exposed surfaces and reveal the underlying structure.[8] Table I shows the weight loss data for films which were subjected to plasma etching. The films were also etched subsequently by a methylamine solution. However, the weight loss due to the combined action of plasma and amine etching was not determined. It can be seen that sample A, which has a higher microhardness than that of sample B, is more resistant to plasma as well as to chemical etching.

Table I Effect of Plasma and Amine Etching on PET Films

	Average Weight Loss (%)	
Etching	Sample A	Sample B
Plasma	0.40	1.1
Chemical (amine)	0.15	0.53

Figure 4 shows the topological relief of the control as well as of the plasma-etched films of samples A and B. The smooth surfaces of the control films [Fig. 4(a) and (d)] are evident. The surface is devoid of any structural details. After exposing these films to the ion species, the surface becomes rough due to selective removal of material from the films. Figure 4(b) shows the surface topology of sample A after plasma treatment, having finer granular surfaces as compared to sample B [Fig. 4(e)] whose surface texture is rough and granular. Figure 4(c) and (f) present the surface of plasma-etched PET films which were subsequently subjected to amine etching. A mosaic-patterned surface became evident for sample B, which represents the combined action of physical and chemical etching. However, for sample A, the surface still remained granular.

During plasma treatment, initially, the loosely bound material is expected to be knocked out from the exposed surface. Once the process of removal of the material has started, it is a common experience that even a well-supported structure will collapse if the supporting (weaker) bonds are removed.[8] However, these structural changes on the surface were not visible by an electronmicroscope until these films were subsequently treated with methylamine. Many workers have reported that amine etching is selective enough to discriminate between the crystalline and amorphous parts.[9-11] The methylamine removed the less-ordered structure weakened by the plasma ions [Fig. 4(f)]. Accretion of small cavities formed by removal of material may thus lead to the formation of continuous larger cavaties [Fig. 4(f)], particularly in the absence of sharp boundaries between crystalline and amorphous zones present in the film.

CONCLUSION

The study shows that SM alters the microhardness of PET films. The extent of hardness induced by SM is more in sample A than in the other sample.

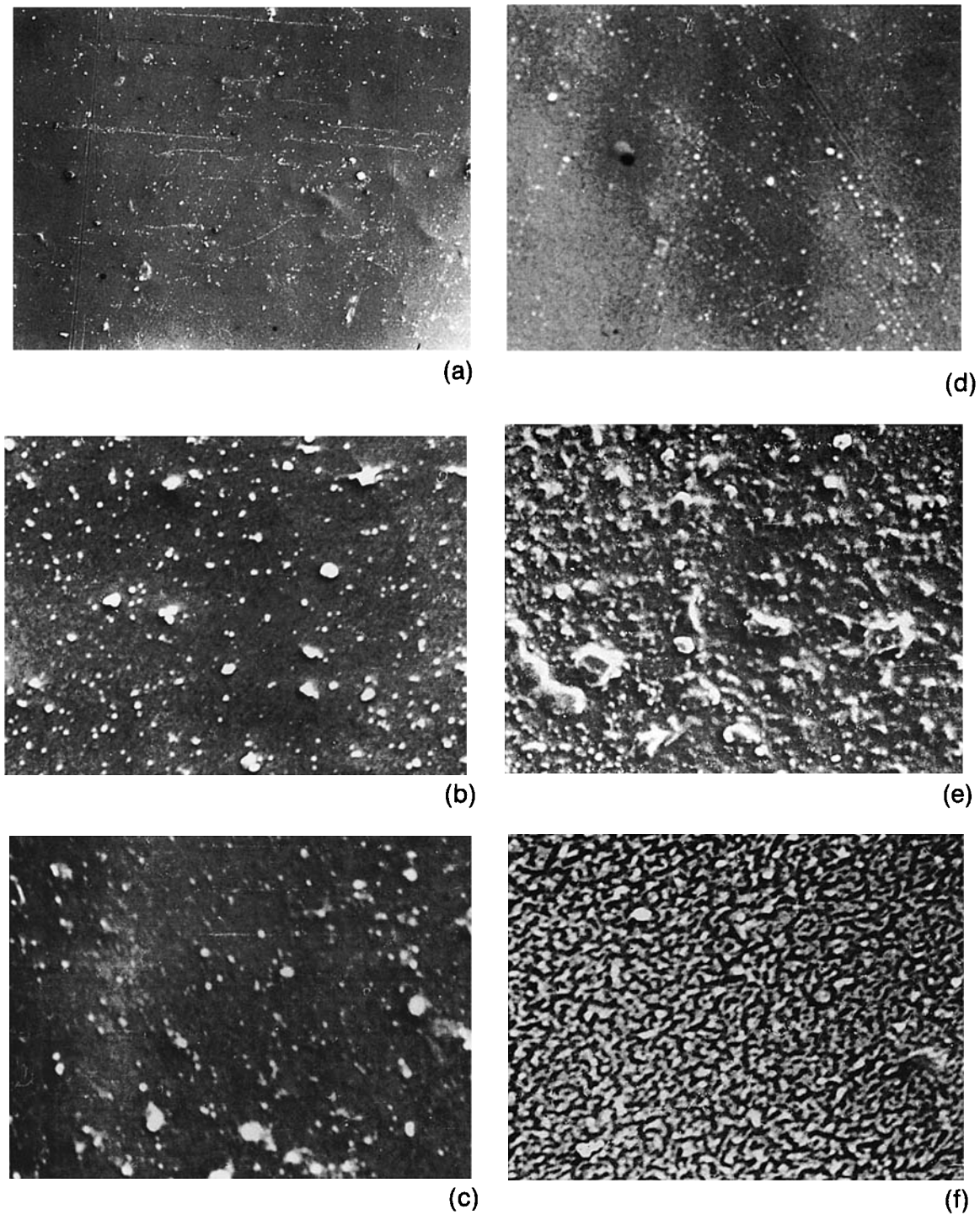

Figure 4 Topological relief of control and etched films: (a) smooth surface of unetched sample A (5500×); (b) surface of plasma-etched sample A showing fine granular deposits (5500×); (c) surface of plasma-etched sample A, subsequently treated by methylamine. Surface virtually resembles 4(b) (5500×); (d) smooth surface of unetched sample B (5500×); (e) surface of plasma-etched sample B. rough surface emerges due to removal and redeposition of etched material (5500×); (f) surface of plasma-etched sample B. Mosaic pattern formed due to combined action of plasma and amine etching (5500×).

Basically, sample A had a higher hardness than did sample B. However, the pattern of increased hardness after quenching treatment followed by SM exposure are similar in both cases though the magnitude is different. In less-ordered material (sample B), which registered a higher weight loss due to physical and chemical etching as well as showing a typical surface topology, had a lower microhardness compared to sample A.

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