Studies on Sorption Behavior of Sulfur Mustard and Oxygen Analog of Sulfur Mustard in Nitrile and Natural Rubber Blends

L. V. R. MURTHY, S. BANERJEE, BEER SINGH, R. S. CHAUHAN

Defence Research and Development Establishment, Jhansi Road, Gwalior-474002, India

ABSTRACT: The breakthrough time of sulfur mustard (SM) against blends of natural and nitrile rubbers was determined using the spot disc test (SDT) method. The breakthrough time of SM is closely related to the elongation properties of the blended rubbers. Blends containing higher proportions of nitrile rubber show better protective properties as revealed by higher breakthrough times. The diffusion of the oxygen analog of sulfur mustard (OA) across these blends follows an anomalous behavior in that, initially, they follow a Fickian behavior and later assume a non-Fickian mode. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 731–738, 1997

INTRODUCTION

Sulfur mustard (SM), thiobis-1-1′-dichloroethane, is a well-known blistering agent which has been used as a chemical warfare agent a number of times.[1,2] Among the various chemical warfare agents, SM is endowed with a unique property of breaking through varieties of materials.[3,4] Its penetration across the biological protective barrierlike skin is very fast.[1] As a result, it is a candidate agent against which protective materials are to be tested. Efforts have been made to find a suitable man-made protective barrier to protect human skin against SM exposure.

Previous studies concerning the diffusion of SM through various rubber materials deal with the measurement of diffusion across butyl, nitrile, and natural rubber sheets using FTIR and weight-gain methods for assessing the protective nature of rubber sheets.[4] The present study deals with the diffusion behavior of sulfur mustard across the blends of nitrile and natural rubber.

Many practical benefits can be obtained by blending polymer. Polymer blends can provide materials with improved properties like better chemical and environmental resistance and superior mechanical and diffusion properties. Attempts were made here, perhaps for the first time, to study the diffusion behavior of a challenge chemical and its dependence on the physical properties of the blends. Efforts were made to study the homogeneity of blends using a scanning electron microscope as well as to correlate the surface morphology with the diffusion data as the performance of polymer blends depends to an extent on their morphology.

EXPERIMENTAL

Materials

Nitrile rubber-JSR 230 and Ramix-grade natural rubber were used for the preparation of sheets. Black HAF-N330 (Philips Carbon, India), zinc oxide GR (SD India), marcaptobenzothiozole (MBTS, Bayer, Germany), stearic acid (Sta, Wilson, India), and sulfur laboratory reagent (LR) grade (Qualigens, India), and napthanic oil were added as ingredients for the preparation of the sheets. Nitrile and natural rubber blends of differ-

---

Table I   Formulations of Rubber Blends

Formulation	NBR (g)	NR (g)	Black (g)	Oil (mL)	ZnO (g)	Sta (g)	MBTS (g)
F_1	10	90	40	10	5	2	1
F_2	30	70	40	10	5	2	1
F_3	50	50	40	10	5	2	1
F_4	70	30	40	10	5	2	1
F_5	90	10	40	10	5	2	1

NBR, nitrile rubber; NR, natural rubber; Black, HAF-N330 (HAF, high abrasion furnace black); Sta, stearic acid; MBTS, mercaptobenzothiozole.

ent proportions were molded using a hydraulic press. The mixing of rubbers was done using a laboratory mixing mill. The composition of different formulations are given in Table I. The optimum curing time for the different formulations at 160°C was determined using a Monsanto R-100 rheometer.

Sulfur mustard (SM, $C_4H_8Cl_2S$, 98% pure by 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. SM freezes at 14.4°C and has a boiling point of 215°C.

The oxygen analog of SM (OA, $C_4H_8Cl_2O$) was utilized for the experiment as received from E. Merck, Germany. It has a boiling point of 62°C and a density of 1.22 g/mL^3 at 25°C. While handling these chemicals, hand gloves and eye guards are to be used. The experiments should be conducted in a ventilated room.

Methods

Spot Disc Test (Breakthrough Time, BTT Test)

The permeation resistance of polymeric films can be evaluated by the spot disc (SD) method.[4] The test is conducted by placing a specified quantity (118 μL on circular-shaped specimen of 5-cm diameter) of liquid SM on the top surface of the test material which rests on a Congo red indicator paper dotted with an SD reagent (2,4-dichlorophenyl benzoyl chloride). The experiment was conducted at 37 ± 1°C. The time required for SM to pass through the test material and affect the color change in the indicator paper is the mustard resistance of the material. An average of five readings was considered as the BTT of the sample and the results along with standard deviation values are given in Table II.

Mechanical Properties

Dumbbell-shaped specimens having a test length of 45 and 5 mm width were prepared from the sheets. SM, 5 μL, was applied uniformly on the middle portions of the dumbbell-shaped specimens. Sufficient time (36 h) was allowed for SM diffusion into the specimen before tensile testing. The stress–strain data of all the samples were recorded using a Good brand Testometric Micro 350 tensile tester with a crosshead speed of 400 mm/min. Ten specimens each of control as well as SM-exposed samples were tested.

Diffusion Measurements

Due to the biological hazard associated with handling of SM, an oxygen analog of SM (OA) was used as a challenge chemical to measure the diffusion coefficients. All the polymer sheets (F_1, F_2, F_3, F_4, F_5) were cut into circular pieces (diameter 2 cm) by a steel die. The thickness of each rubber sheet was 1.6 mm, measured at several points using a micrometer with an accuracy of ±0.01 mm. The pieces were dried in a vacuum oven at 80°C to remove surface-absorbed moisture. The specimens were cooled in a dessicator. The pieces were then immersed in OA in test bottles, after recording their initial weight. The sample weights were taken at different time intervals after removing extraneously held OA by padding them with a filter paper each time. The experiment was conducted at 30°C. All the weights were recorded by employing a Mettler analytical balance having a sensitivity of 10^{-5} g. Complete sorption data are provided in Table III and the results were plotted as uptake Q_t (mol %) of OA versus $t^{1/2}$.

Chemical Etching

Specimens of rubber blends as well as pure natural and nitrile rubber were etched at room temper-

Table II   Physical and Chemical Properties of Rubber Blends

	Control		SM Exposed			Diffusion Coefficients	
Sample	Strength (MPa)	Percent Elongation (MPa)	Strength (MPa)	Percent Elongation (MPa)	SM BTT (min)	D(OA) (cm^2/s)	D(SM) (cm^2/s)
F_1	10.6	531	10.1	360	207	6.3×10^{-6}	2.09×10^{-7}
F_2	11.3	466	10.9	331	323	4.7×10^{-6}	1.34×10^{-7}
F_3	11.9	415	10.6	321	345	3.9×10^{-6}	1.25×10^{-7}
F_4	12.2	303	9.2	252	685	3.8×10^{-6}	6.3×10^{-8}
F_5	13.7	290	9.9	256	830	3.6×10^{-6}	5.2×10^{-8}

ature in 2% KMnO$_4$ solution for 18 h, washed with running water, air-dried, and observed under a scanning electron microscope.

Scanning Electron Microscopy

The blends of rubber were studied under a JEOL scanning electron microscope JSM 840 at 5 kV. The specimens were coated with a thin layer of gold in a JFC-1100 sputter coating unit before observation.

RESULTS AND DISCUSSION

Table I gives the blend composition as well as details of various ingredients used for the preparation of rubber sheets. Except the blend propor-

Table III   Sorption Behavior of Polymer Blends

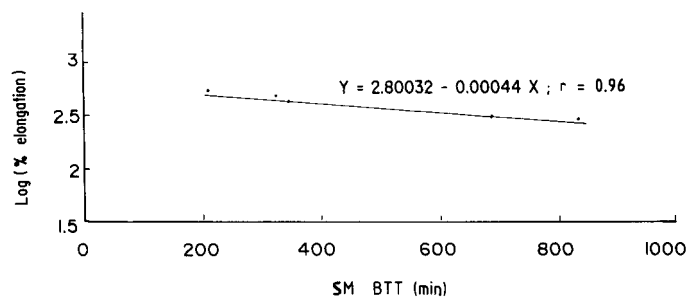| t (min)	$\sqrt{t}$	F_1 Q_t	F_2 Q_t	F_3 Q_t	F_4 Q_t	F_5 Q_t
1	1	0.05	0.10	0.12	0.16	0.20
2	1.4	0.11	0.18	0.19	0.26	0.35
4	2.0	0.17	0.24	0.28	0.34	0.50
5	2.2	0.22	0.28	0.31	0.39	0.66
10	3.2	0.24	0.32	0.45	0.54	0.84
15	3.9	0.25	0.34	0.48	0.56	0.92
30	5.5	0.26	0.36	0.50	0.61	1.00
120	10.9	0.28	0.42	0.55	0.69	1.12
240	15.5	0.30	0.44	0.57	0.73	1.27
360	18.9	0.31	0.45	0.59	0.75	1.28
480	21.9	0.33	0.46	0.60	0.76	1.30
660	25.7	0.34	0.47	0.61	0.78	1.32
900	30.0	0.35	0.48	0.61	0.80	1.34
1020	31.9	0.36	0.49	0.62	0.81	1.35
1140	33.7	0.36	0.49	0.62	0.81	1.35
1200	34.6	0.36	0.49	0.62	0.81	1.35

t, dipping time; Q, uptake (mol %).

tions, all other parameters were kept constant. Table II presents the data on mechanical properties, the diffusion coefficient for OA, and the SM breakthrough time measurements on blends of nitrile and natural rubbers. The data indicate that the breaking load of the blend systematically increases with increase in the nitrile content. However, the percent elongation at break decreases with an increasing proportion of nitrile rubber in the blend. The nitrile rubber : natural rubber (NBR : NR) (10 : 90) blend F_1 had a strength of 10.6 MPa and an elongation at break 531%, whereas the NBR : NR (90 : 10) blend had a strength of 13.7 MPa and elongation at break of 290%. Figure 1 presents the data on SM breakthrough time and percent elongation of the rubber samples. These two parameters have a very high degree of association ($r = .96$), indicating the dependence of SM breakthrough time on percent elongation at break of the rubber specimens.

Exposure to SM deteriorates the tensile as well as elongation properties. The reduction in elongation is higher in the case of higher natural rubber content. It is interesting to note that the reduction in percentage elongation at break after exposure to SM is consistent with the increasing ratio of nitrile rubber in the blend. It appears that exposure to SM makes these rubbers behave like a brittle material compared to the unexposed samples. This is in conformation with the observed behavior of SM as an antiplasticizer in PET films where the elongation of exposed films showed considerable reduction.[5,6] It is assumed that SM may be restricting the mobility of chains by functioning as an antiplasticizing agent and altering the mechanical behavior of the specimen. Antiplasticization has been observed in many polymer−diluent systems. Based on previous studies, it is inferred that antiplasticization results from one or more of the following: (1) a decrease in free vol-

Figure 1 Curve showing correlation between SM BTT and percent elongation of blends.

ume upon the addition of the diluent, as the diluent fill the excess volume of the polymer, and (2) polymer–diluent interaction, which creates steric hindrance and decreases the segmental mobility of the polymer.[7,8]

The molecular transport of liquids into rubbery polymers is a complex phenomenon which depends on the properties of the polymer as well as of the liquid.[9,10] Understanding the transport properties of small molecules in the polymer membrane is crucial in evaluating the barrier properties of polymer membranes. The BTT measurement on these rubber blends against SM shows that the blends which had higher proportions of nitrile rubber show greater BTT. The blends containing higher proportions of nitrile rubber (70% or more) are suitable as protective barriers as they offer more than 10 h of resistance against SM; the safe limit for a protective device as per the TNO test method is 8 h.[11,12] Whereas the higher percentage of natural rubber in the blend lowers the resistance to SM diffusion as indicated by lower BTT values, the TNO Gc method was devised as a confidence building laboratory test. The method is as follows: The protective film was positioned on a horizontally oriented glass cell. The specimen was fixed with a glass ring of 3–5 mm height and rubber bands. The exposed surface area of the sample was 1.5 cm^2. There was a flow of air parallel to the surface of the specimen at 0.5 M/s. SM, 1 μL, was placed on the surface. A flow of air (6 L/h) underneath the specimen transport the penetrated SM vapors to a bubbler. The vapor was trapped in an organic solvent (diethylsuccinate/diethylphthalate). A solution of SM thus obtained was analyzed by the GLC technique.[12]

Due to the hazardous nature of SM, an oxygen analog of SM (OA) was used as a model compound

for the sorption experiments. The chemical structure of these two compounds was previously described.[4] The diffusion coefficient of OA as determined by the weight-gain method revealed that as the percentage of nitrile rubber increases the resistance to diffusion increases systematically and the diffusion coefficient decreases. Figure 2 shows the sorption curves for five rubber samples having different blend proportions of nitrile and natural rubber. Diffusion coefficients (D) for OA were calculated from the slope of the initial linear portions of the sorption curves using the following equation[9]:

$$D = \prod [h\theta/4M_\infty]^2 \qquad (1)$$

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

The diffusion coefficients of SM were computed using the following equation[13]:

$$t = l^2/\prod{}^2 D \qquad (2)$$

where t is the breakthrough time; l, the thickness of the sample; and D, the diffusion coefficient. These data are given in Table II. Comparison of the diffusion coefficients of SM and OA indicate that OA diffuses faster than does SM through the studied blends. This may be due to the smaller molecular size of OA compared to SM.[4] Both these coefficients follow a similar pattern. This indicates that OA can be used for a rapid and safer evaluation of the rubber samples for their suitability in NBC use.
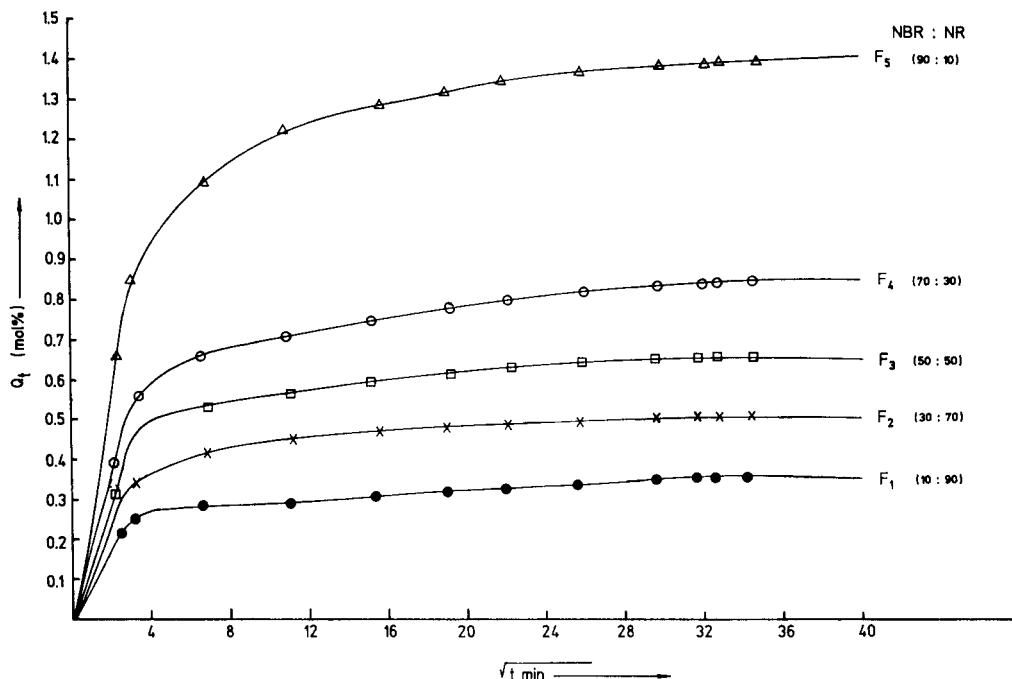
From Figure 2, it can be observed that the up-

Figure 2 OA sorption curves of the rubber blends.

take of the chemical increases with increasing nitrile content in the blends. It is known that permeability of a liquid through a polymer is a complex function of chain flexibility, intermolecular interaction, phase and aggregation state of polymer blends, packing density, and extent of crosslinking. Natural rubber, by way of its chain configuration, has a high amorphous structure, chain flexibility, and comparatively weak interchain interaction. All these factors are conducive to high permeability. It is well known that the introduction of substituents like $-Cl$, $-OH$, $-C_6H_5$, and $-C{\equiv}N$ into the main chain enhance the interchain interaction[14] and, hence, reduce the chain mobility. Nitrile rubber has a linear compact structure with a denser macromolecular packing. The substituents like $-C{\equiv}N$ in the main chain lower the free activation energy of the diffusion, reduce chain mobility, and, in turn, show lower permeability. To confirm whether the sorption mechanism follows the Fickian mode or not, the sorption data of the penetrant–polymer system were fitted to the following relation[9,15]:
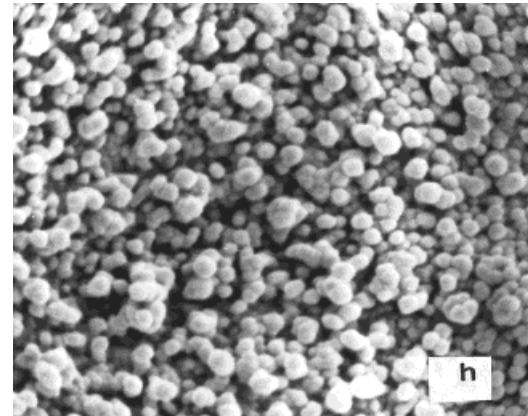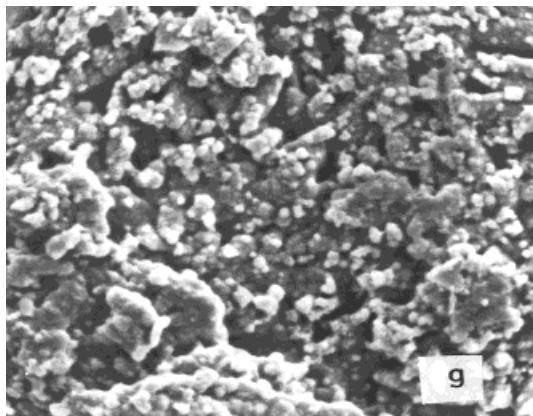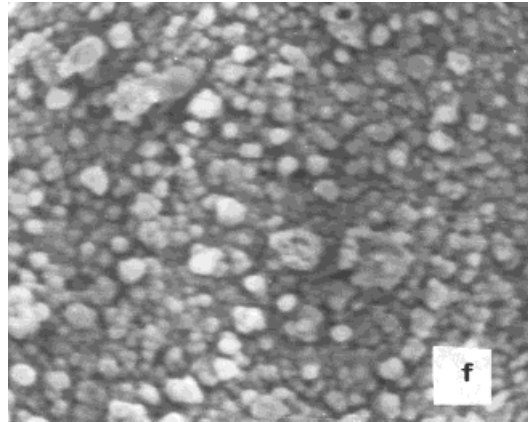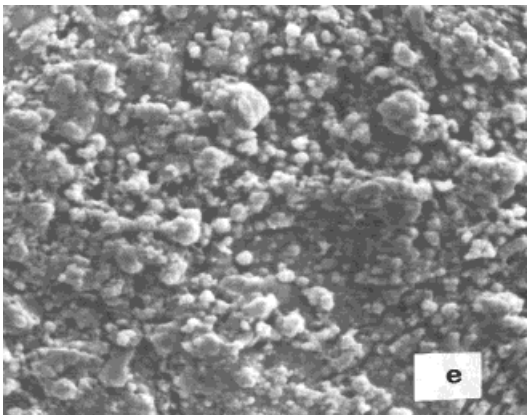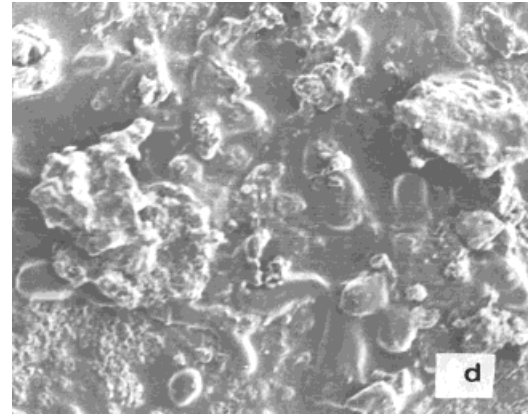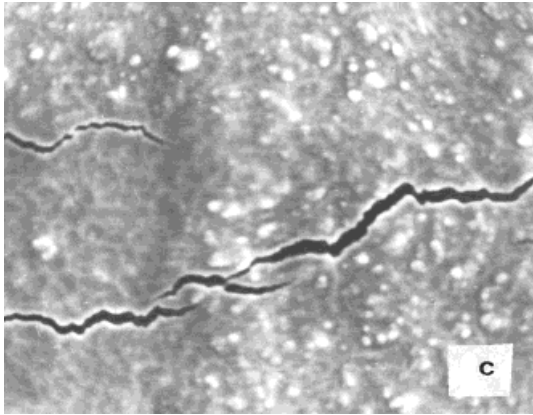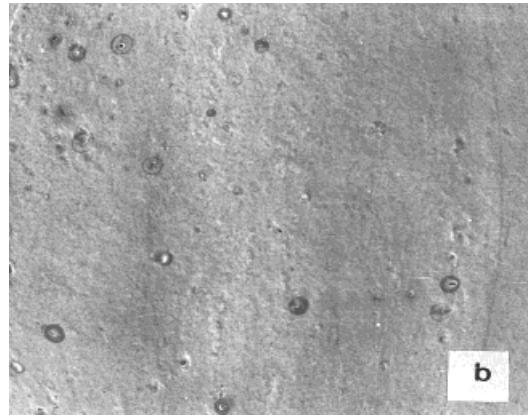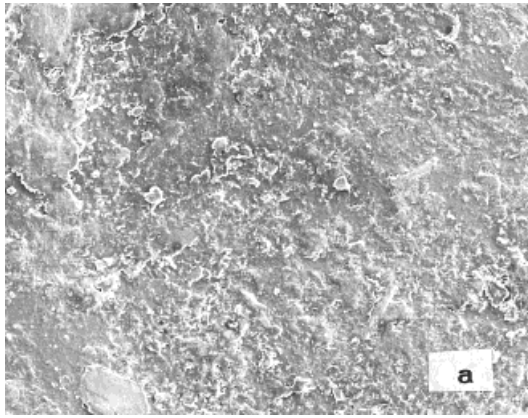
$$\ln(M_t/M_\infty) = \ln K + n \ln t \qquad (3)$$

where M_t and M_∞ represent the uptake (mol %) at time t and at equilibrium time. K is a constant characteristic of the polymer–solvent system. The

values of n indicate 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-square analysis of the $\ln(M_t/M_\infty)$ data vs. $\ln t$, the values of k and n were obtained. The values of n ranged from 0.47 to 0.73 (n values for $F_1 = 0.73$, $F_2 = 0.54$, $F_3 = 0.50$, $F_4 = 0.47$, $F_5 = 0.55$), which indicate that the diffusion behavior of OA across the polymer blends may be Fickian or anomalous depending on the polymer composition.[16] However, any systemic dependence of n on temperature was not observed, and during sorption experiments, no significant swelling was observed with any of the polymer blends. Thus, the diffusion coefficients calculated from eq. (1) can be regarded to be concentration independent.[9]

The diffusion characteristic of polymer blends may also depend on their surface morphology to some extent, particularly in incompatible ones. Therefore, surface examination of these polymer blends was undertaken after etching, which brings out subtle structural differences in materials. Figure 3 shows the surface morphology of F_1 and F_5 before and after SM exposure as well as $KMnO_4$ etching.

Figure 3(a,b) presents the surface of blends F_1 and F_5, respectively. Both the micrographs show a relatively smooth surface with no distinct topo-

logical features. Figure 3(c,d) shows the surface of SM-exposed F_1 and F_5 samples. SM induces surface cracks in the blend having a higher proportion of natural rubber (F_1), perhaps due to differential swelling and contraction behavior. After $KMnO_4$ etching, the surface of F_1 revealed [Fig. 3(e)] two types of globular structures. Bigger globules with large numbers and the other with smaller-sized globules which were less in number were observed. Figure 3(f) depicts the morphology of F_5 after etching, showing a uniform and almost monophasic appearance. The heavier globules were very fewer in number.

To identify the two types of globules, the surface morphology of pure natural and nitrile films were also examined after $KMnO_4$ etching. The natural rubber surface showed only larger globules or aggregates of globules of varying size [Fig. 3(g)]. Figure 3(h) shows the surface of nitrile rubber after etching. It shows well-arranged embedded globules with a monophasic appearance.

From the foregoing, it appears that natural rubber has a tendency to form larger aggregates whereas nitrile rubber globules may conform to smaller aggregates or globules. Considering the properties of nitrile and natural rubber which differ in their structural conformation and other properties, during blending, coalescene at the microscopic level cannot be ruled out. Studies on the effect of concentration and compatibilization and coalescence in polymer blends have shown that coalescence of dispersed components during mixing is governed by the interfacial mobility. Elastic recoil of varying magnitude is expected to cause polymeric drops to separate. The difference in globular size of nitrile and natural rubber at different concentrations could be attributed to the effect of coalescence. As mentioned earlier, the size of the globules may influence their diffusion behavior along with other macromolecular characteristics of individual polymers.

CONCLUSION

The diffusivities of the rubber blends were found to increase linearly with the increase in percent elongation at break. BTT has a very high correlation ($r = .96$) with the elongation properties of blended rubbers. The reduction in elongation can be attributed to the antiplasticizing behavior of SM. Both SM and its oxygen analog (OA) tend to modify the surface of rubber blends on exposure. The effect is more pronounced in the blends having a higher content of natural rubber which induces cracks of varying size. SM appears to be more potent than is the OA in deteriorating the surface. The $KMnO_4$ etching is able to bring subtle differences to the polymer blends.

REFERENCES

1. B. Papirmeister, A. J. Feister, S. I. Robinson, and R. D. Ford, *Medical Defense Against Mustard Gas. Experimental Models of Sulfur Mustard Injury,* LRC Press, Boca Raton, FL, 1991, pp. 299–347.
2. R. S. Chauhan, L. V. R. Murthy, and R. C. Malhotra, *Bull. Environ. Contam. Toxicol.,* **51,** 374 (1993).

Figure 3 (a) Scanning electron micrograph showing surface of blend F_1. Relatively rough surface. (Magnification 1000×.) (b) Scanning electron micrograph showing surface of blend F_5. Smooth surface. (Magnification 1000×.) (c) Scanning electron micrograph showing surface of SM-exposed F_1. SM-induced granularity and surface cracks seen. (Magnification 1000×.) (d) Scanning electron micrograph showing surface of SM-exposed sample F_5. Aggregates of particles on surface. No visible cracks. (Magnification 1000×.) (e) Scanning electron micrograph of $KMnO_4$-etched sample F_1. Aggregated globules are in a large number. (Magnification 10,000×.) (f) Scanning electron micrograph of $KMnO_4$-etched blend F_5. Monophasic dispersion of globules. (Magnification 10,000×.) (g) Scanning electron micrograph of $KMnO_4$-etched natural rubber film. Larger globules or aggregates of globules of varying size. (Magnification 10,000×.) (h) Scanning electron micrograph of $KMnO_4$-etched nitrile rubber film. Well-arranged globules of uniform size. (Magnification 10,000×.)

3. H. P. Hjermstad, *J. Appl. Polym. Sci.,* **24,** 1885 (1979).

4. S. Banerjee, R. P. Semwal, and S. Agarwal, *J. Appl. Polym. Sci.,* **57,** 1483 (1995).

5. L. V. R. Murthy, A. C. Pandey, A. K. Srivastva, and R. S. Chauhan, *J. Appl. Polym. Sci.,* **60,** 147 (1996).

6. R. S. Chauhan, L. V. R. Murthy, S. Banerjee, and N. Singh, *Polym. Int.,* **42,** 251 (1997).

7. W. J. Jackson, Jr. and I. R. Caldwell, *J. Appl. Polym. Sci.,* **11,** 211 (1967).

8. S. L. Anderson, E. A. Grulke, P. T. Delassus, P. B. Smith, C. W. Kocher, and B. G. Landes, *Macromolecules,* **28,** 2944 (1995).

9. S. B. Harogoppad and T. M. Aminabhavi, *J. Appl. Polym. Sci.,* **42,** 2329 (1991).

10. M. Saleen, A. F. A. Asfour, and D. Dee Kee, *J. Appl. Polym. Sci.,* **37,** 617 (1989).

11. Tests on NBC clothing, Prins Maurits Laboratory TNO, The Netherlands.

12. B. Singh, S. M. Baronia, R. Nath, M. V. S. Suryanarayana, and N. B. S. N. Rao, *Res. Ind.,* **39,** 165 (1994).

13. A. E. Chalykh, in *Experimental Methods of Polymer Physics,* A. Ya. Malkin, Ed., Mir, Moscow, 1983, Chap. 25.

14. A. Tager, *Physical Chemistry of Polymers,* 2nd ed., Mir, Moscow, 1978, Chap. 21.

15. D. Kim, J. M. Caruthers, and N. A. Peppas, *Macromolecules,* **26,** 1841 (1993).

16. N. M. Franson and N. A. Peppas, *J. Appl. Polym. Sci.,* **28,** 1299 (1983).