Sorption of Sulfur Mustard and Its Oxygen Analog in Black and Nonblack-Filled Butyl Rubber Membranes

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ABSTRACT: Butyl rubber (IIR) membranes containing a 0–50% volume fraction of carbon black (GPF N660) or nonblack fillers (talc/precipitated $CaCO_3$/fullers earth) were prepared by solution casting and evaluated for permeation resistance to the vesicant, bis(2-chloroethyl)sulfide, or sulfur mustard (SM) and its oxygen analog (OA), bis(2-chloroethyl)ether. The diffusivity of the chemicals was determined from the breakthrough time (BTT), obtained using the spot disc test and a gravimetric method. The permeation parameters, calculated from the sorption data, were used to determine an optimum filler content for maximum protection against SM. To investigate the effect of carbon loading on the permeation properties of IIR, the permeation of SM and OA in carbon-loaded black membranes was compared with nonblack membranes and interpreted in terms of the dispersion of carbon in the membranes. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 503–511, 1998

Key words: butyl rubber; permeation; sulfur mustard; membrane; protection; fillers

INTRODUCTION

Butyl rubber is well known for its permeation resistance to most chemicals, including chemical warfare agents[1,2] such as bis(2-chloroethyl)sulfide, better known as sulfur mustard (SM). SM is a vesicant and causes blistering on body cells even on short-term exposure[3] and it also penetrates most materials. It is therefore the most suitable challenge chemical for permeation studies. However, the handling of SM poses practical difficulties. So, wherever a larger quantity of the chemical was required, an oxygen analog (OA) of SM, that is, bis(2-chloroethyl)ether, was chosen. OA is less toxic with no perceptible blistering ef-

fect, while being structurally similar to SM in molecular dimensions.[4]

Protection against SM in the event of chemical contamination or chemical warfare is generally afforded by carbon-filled butyl vulcanizates, in the form of a protective ensemble such as respirators, gloves, and overshoes. To maximize the protective potential of these devices, it is necessary to optimize the carbon content in the formulation. With an aim to arrive at an optimum carbon loading, we investigated the sorption behavior of SM and the OA in carbon black (GPF N660)-filled IIR membranes with the volume fraction of black varying from 5 to 50%. The protection afforded by the black membranes against SM was also evaluated from the SM sorption data and was compared with nonblack membranes with inorganic fillers [such as talc, precipitated (ppt) calcium carbonate, and fullers earth] and unfilled IIR. The sorp-

Table I   Characteristics of Fillers Used in IIR Membranes

Sample No.	Filler	Supplier	Particle Size (microns)[a]	Surface Area (m^2/g)
1	Carbon black (GPF N660)	Philips Carbon, India	0.05	38
2	$CaCO_3$ (precipitated)	Qualigens, India	10	5
3	Talc $(3MgO \cdot 4SiO_2 \cdot H_2O)$	Fluka, Switzerland	< 10 (325 mesh)	4
4	Fullers earth (clay)	Rubo-Chem, Bombay, India	20	42

[a] As mentioned in product catalog.

tion data was also fitted into empirical relations to determine the permeation parameters.

EXPERIMENTAL

Materials

The materials used in this study were detailed in an earlier article.[1] SM and the OA were distilled prior to use (GC purity > 99%); other chemicals were used as received. The average surface area (BET, single point) of black and nonblack fillers determined using a nitrogen absorption[4] technique in a Quantasorb (Model QSJR 2) are given in Table I.

Preparation and Characterization of Membranes

The IIR membranes were made by casting from 10% w/v solutions of the rubber in toluene as re-

ported earlier.[1,5] The recipe and curing conditions used are given in Table II. Fillers were incorporated into IIR during the mixing stage with continuous stirring. Concentration of the filler was varied from 0 to 35 phr (volume fraction 0–50%). The thickness of the cured membranes was maintained at 0.3 ± 0.05 mm. The membranes were characterized by their density, mechanical properties, surface morphology, and SM breakthrough time (BTT). The density was determined by the ratio of mass to volume (area × thickness) of the membranes. Thickness was measured using a micrometer screw guage (accuracy ±0.001 cm) and mass was recorded on Sartorius balance (accuracy 1×10^{-5} g).

Evaluation of Permeation Resistance

The membranes were dried in a vacuum oven for 24 h at 100°C to remove surface-absorbed mois-

Table II   Recipe for Elastomer Membranes

| Ingredients	Description[a]	phr (per hundred parts of rubber)
Butyl rubber (IIR)	Polysar 301, d 0.92, MW 3×10^5	100.0
Zinc oxide	d 5.61	3.0
Stearic acid	mp 340 K	2.0
Filler	As given in Table I	Varied as desired
Tetramethylthiuram disulfide (TMTD)	mp 429 K	1.0
Mercaptobenzothiazole sulfide (MBTS)	mp 450 K	0.5
Sulfur	Insoluble, mp 373 K	1.5

MW: molecular weight; d: density; mp: melting point.

[a] Cast from toluene. Solvent evaporated at 318 K for 30 h, cured in an air oven for 5 h at 353 K, and postcured for 20 min at 413 K.
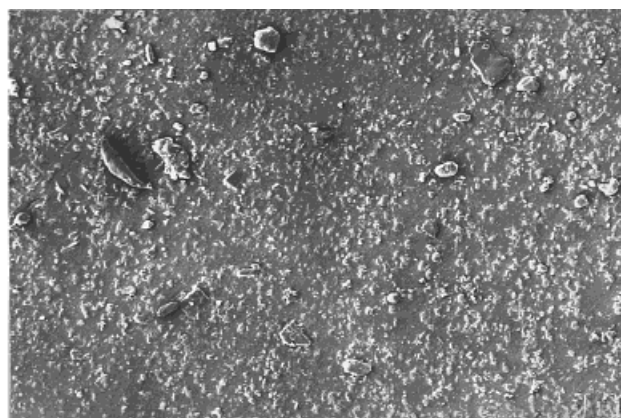
Table III   SM BTT in Nonblack and Black-filled IIR Membranes (by SD Test)

		BTT at 298 K (in min)			
Sample No.	phr of Filler	Talc	CaCO$_3$	Clay	Carbon
1	5	520	610	530	680
2	10	655	855	825	900
3	15	790	880	815	1500
4	20	580	650	600	2280
5	25	—	515	—	1200
6	30	475	—	510	1080
7	35	—	470	—	480

SM BTT of unfilled cured IIR membrane (at 298 K) = 450 min.
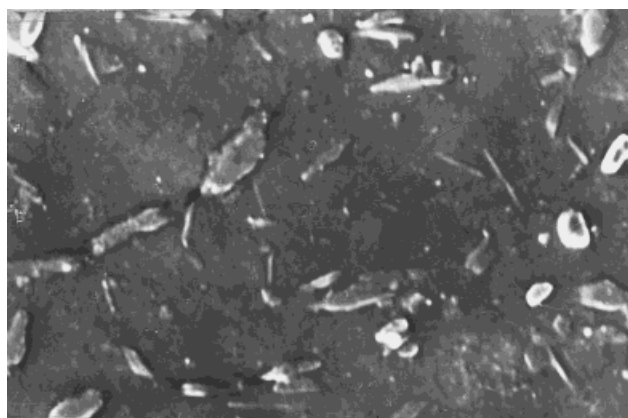
(a)

(b)

(c)

Figure 1   SEM of nonblack filler-loaded (20 phr) butyl rubber membranes (magnification ×750): (a) fullers earth; (b) talc; (c) CaCO$_3$.

Table IV Interrelation Between Carbon Loading, Density, SM Diffusivity, and Mechanical Properties of IIR Membranes

Carbon (phr)	Content (% Volume Fraction)	Thickness[a] of Membranes (mm)	Density (g/cc) of Membranes	SM Diffusivity[b] $D \times 10^{13}$ (m^2/s) at 298 K	Hardness[c] (Shore A)	Stress at Break[c] (kg/cm^2)	Strain at Break (%)	Young's Modulus[c] (kg/cm^2)
0	0	0.34	0.794	4.342	55.3	11.93	121	7.89
5	8.8	0.35	0.797	3.045	54.7	15.99	151	8.82
10	16.9	0.36	0.799	2.434	51.0	16.68	163	10.64
15	24.5	0.38	0.897	1.627	56.3	19.42	237	18.82
20	31.5	0.41	1.103	1.246	55.9	21.28	696	16.02
25	38.0	0.40	1.128	2.253	57.6	24.23	388	9.55
30	44.0	0.39	1.029	2.381	47.0	24.09	349	10.58
35	50.0	0.37	0.920	4.821	46.5	23.37	192	11.90

[a] Average of 10 readings at 10 different points.
[b] Calculated using eq. (1).
[c] Average of five readings.

ture and then evaluated for permeation resistance to SM and the OA using the diffusivity and sorption data obtained from the spot disc breakthrough time (SD BTT) test and the gravimetric method. SD BTT is a standard method[1,2,5–7] involving the oxidation of thioethers with active halogen.[8] BTT is the time taken for the appearance of a blue color on the detector paper (Congored paper dotted with a 2,4-dichlorophenylbenzoylchloroimide solution) from the initial application of SM spots on the specimen membrane. An average of five readings was reported as the SM BTT; minimum and maximum readings varied ±15% from the average. For a given thickness of the sample and a given temperature, the higher the BTT value (in minutes), the lower the diffusivity of the chemical. The diffusion coefficient (D) was calculated using the relation

$$D = x^2/\Pi^2 t \tag{1}$$

where x is thickness of the membrane and t is the breakthrough time.[9,10]

For the determination of sorption profiles, black and nonblack IIR membranes were exposed to SM and the OA in a closed chamber at 298 K for 2 weeks. During this period, the membranes were weighed periodically to estimate the concentration of the chemicals sorbed. Mole percent sorption was plotted as function of square root of time to represent the nature of sorption. The data were fitted into an empirical relation[1,2,5,11]

$$\frac{Q_t}{Q_m} = Kt^n \tag{2}$$

where Q_t is the amount of SM or the OA sorbed; Q_m, the equilibrium quantity sorbed; K, a constant characteristic of the polymer–solvent interaction; and n, the transport coefficient which describes the nature of the sorption ($n \leq 0.5$ implies Fickian diffusion; $n > 0.5$ implies non-Fickian diffusion).[11–13] K and n were obtained from the intercept of the plot of log Q_t/Q_m versus log t (for $Q_t/Q_m \leq 0.6$).

The sorption coefficient (S) was determined by the weight gain method, by computing the number of moles of the chemical sorbed per unit volume (area × thickness) of the membrane at atmospheric pressure. The product of D and S yielded the permeability coefficient ($P = D \times S$).
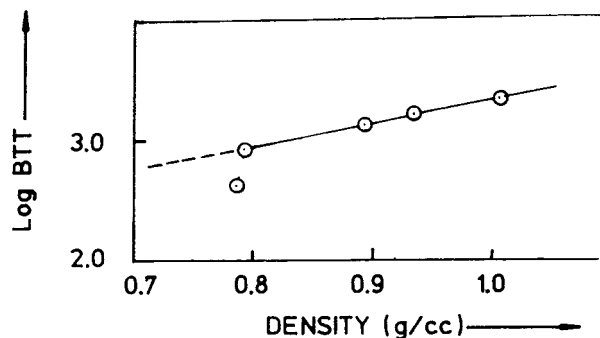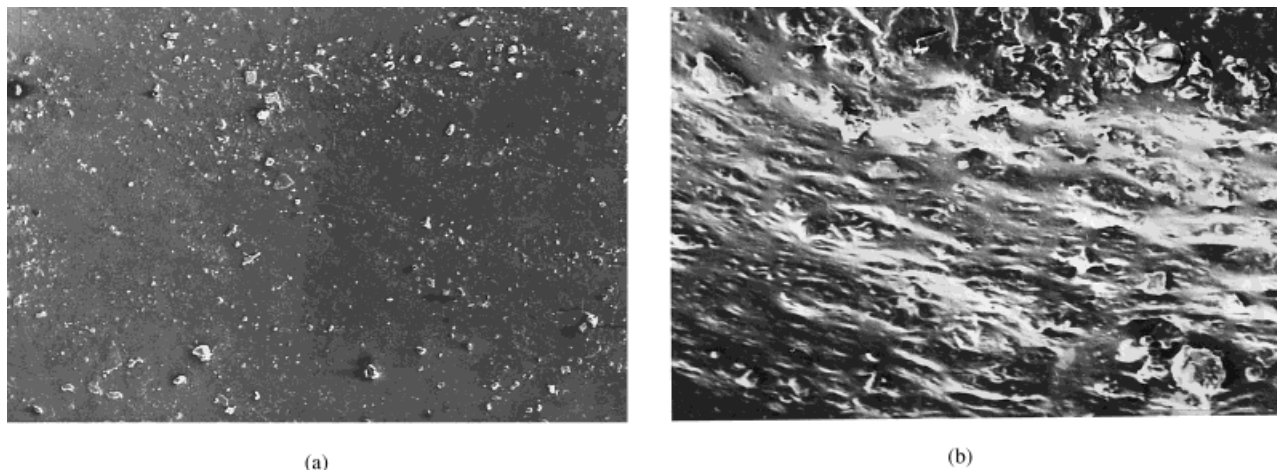

Figure 2 Relation between density and BTT.

Figure 3 SEM of carbon-loaded butyl rubber membranes (magnification ×750): (a) 15 phr carbon (below optima); (b) 30 phr carbon (above optima).

Evaluation of Mechanical Properties and Surface Morphology

The stress, strain at break (%), and modulus of dumbbell-shaped membrane specimens were determined using a Testometric Micro 350 Goodbrand Jeffrey Tensile testing machine in accordance with ASTM D412. The hardness (Shore A) was measured using a durometer according to ASTM D 2240, with an accuracy of ±1°. The surface morphology of the membranes was determined from scanning electron micrographs obtained using a JEOL JSM 840 electron microscope at 5 kV and 6×10^{-10} amperes. The nonstained membranes were coated with gold using an ion sputter (JFC-1100).

RESULTS AND DISCUSSION

From Table III, it is observed that SM has a longer BTT in carbon black-filled IIR membranes as compared to nonblack inorganic filler-loaded membranes, the trend in SM BTT being carbon $> CaCO_3 >$ fullers earth $>$ talc. Since the membranes were cast in an organic solvent (toluene), it is likely that the inorganic fillers have a nonuniform dispersion and agglomeration in the elastomer membrane. This was also manifest in the scanning electron micrographs of the filled membranes [Fig. 1(a–c)].

Butyl rubber membranes were processed using furnace carbon black (GPF N 660) in preference to channel blacks due to two reasons: First, the

Table V Sorption Data for SM Vapors (at 298 K) in Nonblack and Black IIR Membranes Obtained Using Gravimetric Method

Sample No.	$\sqrt{\text{Time}}$ (min)	Change in Weight $(\Delta W)^a$ in mg			$Q_t \times 10^3$		
		C-0	C-10	C-20	C-0	C-10	C-20
1	10.95	1.98	3.41	—	1.32	2.19	—
2	13.60	9.45	4.69	0.1	6.27	3.02	0.07
3	15.49	12.07	6.69	1.83	8.01	4.44	1.25
4	17.32	14.36	9.88	2.33	9.54	6.36	1.59
5	18.97	16.65	13.28	3.19	11.06	8.55	2.19
6	37.14	27.14	21.89	8.91	18.03	14.10	6.11
7	100.99	33.50	22.22	11.72	22.25	14.76	8.04

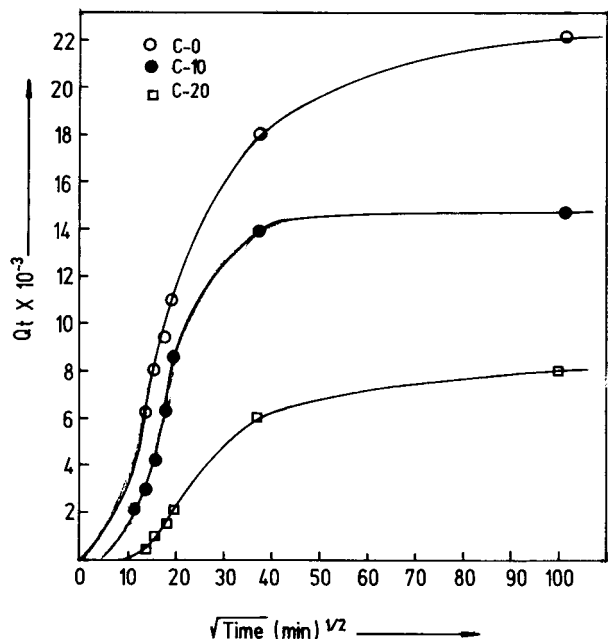[a] Initial weight of C0 = 0.946649 g, C10 = 0.97596 g, C20 = 0.90161 g.

Figure 4 SM vapor sorption in butyl unfilled and carbon-loaded membranes (at 298 K).

organic low polarity butyl rubber prefers the less polar furnace blacks to the more polar, more highly oxygenated channel blacks. Second, the absorption by channel blacks is much less than by furnace blacks.[14]

Optimization of Carbon Loading

The furnace black content in butyl rubber membranes was optimized in terms of the diffusivity of SM, determined using the SD BTT method. The BTT of SM in IIR membranes increased with carbon black, showing a maximum at 20 phr of the filler, but decreased considerably with further increase in the filler content (Table III). At the max-

imum, the BTT value increased to five times the value with unfilled rubber. In other words, the SM diffusivity was lowered in carbon-loaded membranes, as reflected in the diffusion coefficients (Table IV).

It seems possible that densely packed structures are formed when rubber is bound on the carbon surface, reducing in the process the diffusivity through the matrix. The density of the carbon-loaded membranes and their SM BTT values followed nearly the same trend, indicating a direct correlation between the two. Density increased in carbon-filled membranes from 0.79 to 1.1 g/cc as the carbon was varied from 0 to 25 phr; correspondingly, there was an increase in the BTT from 450 to 1200 min. This was manifest in a plot of log BTT versus density (Fig. 2), which was found to be linear up to 20 phr of carbon in the membrane.

At a carbon concentration beyond 20 phr, discontinuity in the composite structure is likely, which may be due to filler agglomeration, nonuniform dispersion of the filler, as well as dilution of the matrix by the filler,[15] as reflected in the scanning electron micrographs (Fig. 3). Similar reasons may be assigned to the decrease in strain at break (%) of the membranes loaded with carbon beyond 20 phr.

Parameters for SM Sorption

The sorption data for SM vapors at 298 K in black (C10 and C20) and nonblack (C0) butyl rubber (IIR) membranes obtained using the gravimetric method is given in Table V. The sorption plots (Fig. 4) obtained from the above data are sigmoidal at lower times and level-off later, showing the equilibrium. The equilibrium in C10 and C20 is reached much faster that in nonblack rubber.

Table VI   Parameters for SM Vapor Permeation in Nonblack (C0) and Black (C10, C20) IIR Membranes at 298 K

Sample No.	Parameter	Value		
		C0	C10	C20
1	Q_m (mol %)	22.25	14.76	8.04
2	K (g/g min^n)	0.186	0.079	0.045
3	n	0.76	1.39	1.50
4	$D \times 10^{13}$ (m^2/s)	4.34	2.43	1.256
5	$S \times 10^3$ (mol m^{-3} Pa^{-1})	3.59	2.51	2.02
6	$P \times 10^{16}$ (mol m^{-1} s^{-1} Pa^{-1})	15.58	6.09	2.53

Table VII   Few Important Properties of SM and OA

Sample No.	Property	SM	OA
1	Chemical name	Bis(2-chloroethyl)-sulfide	Bis(2-chloroethyl)-ether
2	Formula	$(CH_2CH_2Cl)_2$ S	$(CH_2CH_2Cl)_2O$
3	Molecular weight	159	143
4	Density (g/cc)	1.27	1.22
5	Molecular diameter (Å)	6.98	6.83
6	Cross-sectional area (m^2)	-38.33×10^{-20}	-36.70×10^{-20}
7	Vesicant action	Blister agent	Nonblister agent

Hence, further sorption is restricted in the former. The transport coefficient (n) is > 0.5, implying a non-Fickian transport. Also, the lower K for C10 and C20 (Table VI) indicates less solvent–substrate interaction in the black-loaded butyl formulation,[2] and as a result, the D of C10 and C20 is expected to be lower than that of C0. The sorption (S) and permeability coefficients (P) also follow the same trend.

OA as a Model Compound of SM

A few important properties of SM and the OA are collated in Table VII for comparison. It is observed that SM and the OA have a similar cross-sectional area and molecular diameter besides being structurally similar. The OA was also suggested as a simulant of SM, for adsorption studies on active carbon for the removal of toxic chemicals from contaminated water.[4]

SM versus OA Sorption in IIR Membranes

While the BTT of SM was determined using the SD method, the BTT of the OA could not be obtained by the same method due to the absence of the thio moiety in the OA; hence, a gravimetric method was used to obtain the sorption kinetics of the OA. The sorption profiles of the OA in unfilled butyl are plotted in Figure 5. The transport coefficient n is < 0.5, implying a Fickian diffusion. The diffusion coefficient (D) for the OA can therefore be obtained by Fick's second law. The most commonly used method of determining D is by using sorption kinetics under isobaric–isothermal conditions. If the sample has a plate of thickness h, then under the boundary conditions $0 < x < h$ and $0 < C < C_{equiv}$, Fick's second law can be solved as follows:

$$D = \prod (h\theta/4Q_m)^2 \qquad (3)$$

where θ is the slope of the rectilinear part of the sorption curve.

The D values obtained by using the above formula (Table VIII) indicate that the OA diffuses much faster than does SM in unfilled IIR. So, OA can be safely chosen instead of SM as a challenge chemical for determining the protection time of a given formulation. An additional advantage in using the OA is that the liquid permeation can
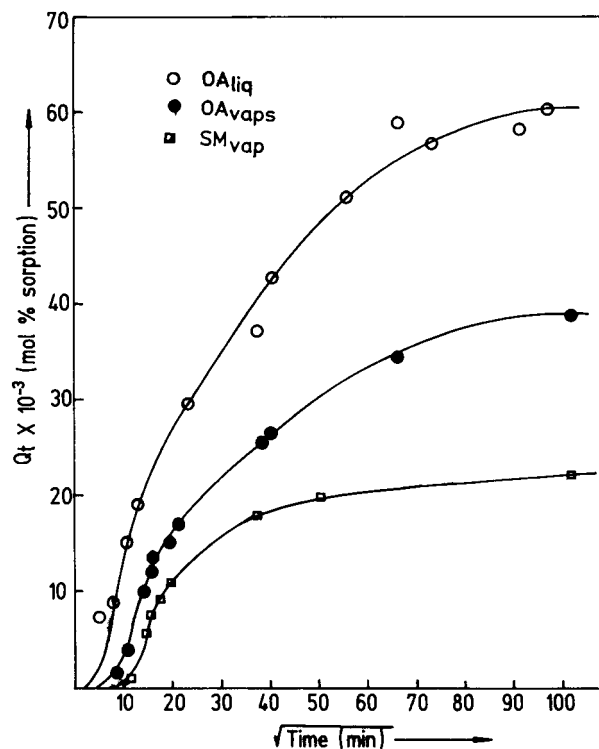
Figure 5 Sorption of OA (liquid versus vapor) and SM (vapor) in unfilled butyl at 298 K.

Table VIII Sorption Data for Permeation of SM and OA in Unfilled IIR at 298 K

		Permeant		
Sample No.	Permeation Parameter	SM_{vap}	OA_{vap}	OA_{liq}
1	BTT (min)	64.0	36.0	06.0
2	$Q_m \times 10^3$ (mol %)	22.0	39.0	60.0
3	K (g/g min^n)	0.186	0.018	0.035
4	n	0.76	0.285	0.342
5	$D \times 10^{13}$ (m^2/s)	4.34[a]	4.77[b]	8.59[b]
6	$S \times 10^3$ (mol m^{-3} Pa^{-1})	3.59	6.88	6.09
7	$P \times 10^{16}$ (mol m^{-1} s^{-1} Pa^{-1})	15.58	31.85	52.34

[a] Calculated using eq. (1).
[b] Calculated using eq. (3).

also be studied easily, unlike for SM which poses practical difficulties due to the risk in handling. Studies on the correlation between SM and the OA permeation are proposed for predicting the liquid permeation behavior of SM in the membranes.

Also, for the OA, the BTT for liquid permeation is lower than for vapor permeation. The converse is the case with diffusion coefficients, implying faster permeation of the chemical in the liquid state than in the vapor state. The OA liquid sorption was also investigated in carbon-loaded IIR membranes (C10, C20, and C30); the sorption kinetics are plotted in Figure 6. It is apparent from the plots that the Q_m of the OA is least in C20. However, no attempt was made to estimate the diffusion coefficients due to non-Fickian transport in filler-loaded membranes.

CONCLUSION

The permeation resistance of butyl rubber to SM and the OA is enhanced by the incorporation of carbon black into the formulation. The black IIR membranes have a higher protection potential than that of the nonblack inorganic filler-loaded IIR. The protection afforded by the elastomer membranes against hazardous chemicals can be assessed using the SD BTT test along with the gravimetric method for a detailed investigation of the sorption of the chemicals in the membranes. The OA can be used as a suitable model compound

of SM in the gravimetric method for permeation studies.
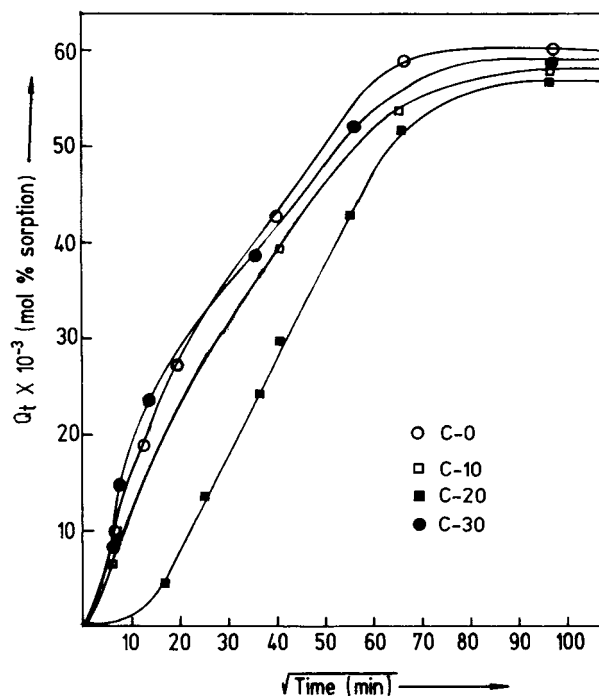
Figure 6 OA (liquid) sorption in unfilled and carbon-loaded butyl rubber membranes at 298 K.

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