

Interaction of Crosslinked Ethylene–Propylene–Diene Terpolymer Blends with Chlorinated Organic Penetrants

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ABSTRACT: The sorption and diffusion of halogenated hydrocarbon penetrants through different ethylene–propylene–diene terpolymer (EPDM) blends, such as EPDM/natural rubber, EPDM/bromobutyl rubber, and EPDM/styrene butadiene rubber (50/50 w/w), were studied. The diffusion coefficient of halogenated penetrants fell in the range $1.5\text{--}14.52 \times 10^{-7} \text{ cm}^2/\text{s}$ in the temperature range of 25–60°C. Transport data were affected by the nature of the interacting solvent molecule rather than its size and also by the structural variations of the EPDM blends. 1,2-Dichloroethane showed a lower mass uptake compared to other penetrants. The temperature dependence of the transport coefficient was used to estimate the activation parameters, such as the activation energy of diffusion (E_D) and the

activation energy of permeation (E_p) from Arrhenius plots. The activation parameters for E_D of aliphatic chlorinated organic penetrants was in the range 7.27–15.58 kJ/mol. These values fell in the expected range for rubbery polymers, well above their glass-transition temperature. Also, the thermodynamic parameters, such as enthalpy and entropy, were calculated and fell in the range 2–15 kJ/mol and 3–54 J/mol/K, respectively. Both first- and second-order transport kinetics models were used to investigate the transport kinetics, and first-order kinetics were followed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1366–1375, 2003

Key words: diffusion; thermodynamics; kinetics (polym.)

INTRODUCTION

The application of polymer membranes as barrier devices has created great interest in molecular transport through polymers. The use of polymers as barrier layers and as materials for cable coating, food packaging, electronic circuits,¹ and so on has been studied extensively. Polymer–solvent interactions have been reviewed by many researchers.^{2–7} Recently, Haragopad and Aminabhavi investigated the transport of organic penetrants through polymer membranes and found that swelling depends on the chemical structures.^{8–10} Barrer and Skirrow¹¹ followed the effect of crosslinking density on diffusion. The effect of penetrant size on diffusion has been studied by different researchers, and it has been found that equilibrium sorption of the sorbents decreases with increasing penetrant molecular size. Aminabhavi and Phayde¹² examined the molecular transport properties of santoprene thermoplastic elastomers in the presence of aliphatic hydrocarbons. According to them, for all liquids, equilibrium uptake was influenced by penetrant

size and shape, polymer morphology, and temperature.

Increasing social concern over the problem of hazardous waste disposal has promoted the study of such fundamental processes as the sorption, desorption, permeation, and diffusion of hazardous chemicals into polymeric barriers. Low-molecular-weight organic halocarbons released in waste land fills are known to contaminate ground water, soil, and air, posing an immediate threat to human health and hygiene.¹³ The use of polymer membranes as liners (in secure land fills) and storage tanks for hazardous liquids is increasing.¹⁴ In the application of such membranes as barrier materials, it is important to understand their interaction with organic liquids, which is of great environmental concern. It is also important to study the characteristics of membrane materials in the presence of hazardous liquids before they are used in the field.

Thomas and colleagues investigated the pervaporation of acetone-chlorinated hydrocarbon mixtures¹⁵ and *n*-alkanes¹⁶ through natural rubber (NR)/ethylene propylene rubber (EPR) and styrene butadiene rubber (SBR)/NR.¹⁷ Aminabhavi et al.^{8–10} reported for elastomers. A survey of literature revealed that ethylene–propylene–diene terpolymer (EPDM) blends have not been studied thoroughly.

EPDM and halo butyls have low permeability due to the compact structure of the polymer molecules in the EPDM and the mutual interference of the methyl

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TABLE I
Some Physical Properties of the Chlorinated Organic Penetrants at 25°C

Penetrant	Molecular weight	Boiling point (°C)	Molecular volume (cm ³ /mol)	Density (g/cc)	Viscosity (cP)	δ (cal cm ³) ^{1/2}	Dipole moment (D)
Dichloromethane	84.93	42	64.5	1.32 ^b	0.393 ^a	9.70	1.36
Trichloromethane	119.38	61	80.7	1.48 ^b	0.542 ^b	9.20	1.02
Tetrachloromethane	153.82	77	97.1	1.59 ^b	0.845 ^a	7.28	0.00
1,2-Dichloroethane	98.96	84	79.4	1.25 ^b	0.730 ^a	9.90	—
Tetrachloroethylene	165.83	121	102.7	1.50 ^b	0.798 ^a	9.3	0.00

^a At 30°C.

^b At 20°C.

groups of isobutene in halobutyls, which hinder molecular movement. They have better chemical and weathering resistance compared to NR and SBR. These elastomers find application in several areas. In all these applications, it is likely that these elastomers come in contact with organic solvents (liquids or vapours) that may affect the performance of the materials. Therefore, the performance of these elastomers should be matched for a particular problem to achieve optimum performance. For this purpose, a polymer blend can offer a convenient tool. The aim of polymer blending is to create a new series of polymeric membranes that combines the properties of the two homopolymers. The physical and mechanical properties and the permeation properties of the blend can be influenced by changing the blend components.

In our previous studies, we investigated the transport characteristics of NR blends in *n*-alkanes,¹⁸ aldehydes and ketones,¹⁹ and aromatic²⁰ hydrocarbon penetrants.

In this study, we attempted to examine the sorption and diffusion behavior of EPDM blends such as EPDM/NR, EPDM/bromobutyl rubber (BIIR), and EPDM/SBR (50/50 w/w) with chlorinated hydrocarbon penetrants such as dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, and tetrachloroethylene at 25, 40, and 60°C.

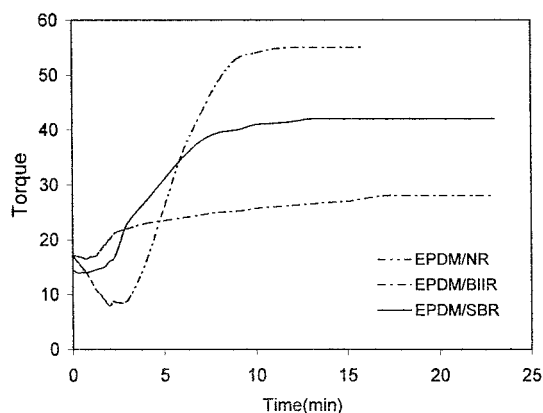


Figure 1 Curing characteristics of all EPDM blends (rheographs).

From the sorption data, the Arrhenius activation energy for diffusion (E_D) and the activation energy for permeation (E_P) were determined. From the temperature dependence of the sorption constant, the entropy of sorption (ΔS) and the enthalpy of sorption (ΔH) were also determined. Both first- and second-order transport kinetic models were used to determine rate constants for sorption studies.

EXPERIMENTAL

Materials

Elastomers such as EPDM, NR, SBR, and BIIR were obtained from M/s Vikrant Tyres Ltd. (Mysore, India) as gift samples. Analytical reagent grade solvents, namely, dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, and tetrachloroethylene (Sd. Fine Chemicals, Mumbai, India), were distilled before use. Some physicochemical properties of the penetrants are listed in Table I.

Methods

A 5 × 13-in. laboratory two-roll mill was used to mix the EPDM rubber blends. The cure characteristics of all EPDM blends were studied, and the rheographs are shown in Figure 1. The compounded EPDM

TABLE II
Recipe of EPDM Blends and Vulcanization Parameters

Ingredient	Composition (phr)		
	I	II	III
EPDM	50	50	50
NR	50	—	—
SBR	—	50	—
BIIR	—	—	50
ZnO	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0
Mercaptobenzothiozole (MBT)	0.5	0.5	0.5
Tetramethylthiuramdisulfide (TMT)	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5
Curing temperature (°C)	150	150	150
Curing time (min)	3.57	10.00	20.00

TABLE III
Physico-mechanical Properties of the EPDM Blends

	Blend		
	EPDM/NR	EPDM/BIIR	EPDM/SBR
Density (g/cc)	0.933	0.943	0.935
Tensile strength at break (N/mm ²)	1.49	1.75	1.06
Elongation at break (%)	250	806	190
Modulus at 100% elongation (N/mm ²)	9.06×10^{-3}	6.20×10^{-3}	10.28×10^{-3}
Surface hardness (shore A)	50	41	51

blends were cured at 150°C into sheets of dimensions $14 \times 12 \times 0.2$ cm³ in a hydraulic press under a pressure of 200 kg/cm². Curing times for the different blends are shown in Table II along with the compositions of the blends.

Tensile behavior and surface hardness of all blends were measured as per ASTM D 638 with a model 4302 Hounsfield universal testing machine (England) and ASTM D 785, respectively. Density was measured according to ASTM D 792 by the water displacement method. All of these tests were performed at room temperature, and for each test, at least six measurements were done; the average values are reported.

Sorption experiment

The vulcanized EPDM blend sheets were cut circularly (1.76 cm diameter) with a sharp edged steel die. The thicknesses of the specimens were in the range 0.2–0.26 cm. The specimens were dried in a desiccator in a controlled-humidity atmosphere for 2 days before the sorption experiments.

Sorption and diffusion of chlorinated hydrocarbons were studied with an immersion weight-gain method at temperatures of 25, 40, and 60°C. Dry weights of the cut samples were taken before immersion into airtight metal-capped test bottles containing the liquid. The samples were immersed in airtight glass bottles containing the solvents. After immersion into the respective liquids, the bottles were placed in a thermostatically controlled oven ($\pm 0.5^\circ\text{C}$). At an interval of 2 h, the specimen was taken out and wiped off with tissue paper and weighed immediately with an electronic balance that measured to an accuracy of ± 0.0001 g. The samples were reimmersed in the test bottles to permit continuation of the sorption until the saturation with excess liquid was established.

RESULTS AND DISCUSSION

Physicomechanical properties such as density, tensile strength, percentage elongation at break, tensile modulus at 100% elongation, and surface hardness of all EPDM blends before exposure to penetrants are given in Table III. A higher tensile strength (1.75 N/mm²) and percentage elongation at break (806%) were ob-

served for EPDM/BIIR systems compared to other blends. This may have been due to the higher compatibility of EPDM rubber with low unsaturated polymers such as halobutyls than the high unsaturated polymers such as NR and SBR. Stress versus strain plots for all EPDM blends are given in Figure 2. Mechanical properties such as tensile strength and percentage elongation of all blends after 80 h of exposure (equilibrium) in different penetrants are also tabulated in Table IV. Figures 3 and 4 show the variation of stress-strain curves after 80 h of exposure in different penetrants. As shown in the figures, both the curves followed the same trend. However, there was a marginal reduction in tensile behavior for all EPDM blends after exposure. This may have been due to the leaching of extra network materials and the weakening of secondary forces between polymer networks during a cycle of sorption-desorption.²¹

Sorption data were interpreted in terms of mass increase in concentration per 100 g of the EPDM blends versus the square root of time ($t^{1/2}$). Some typical sorption plots are shown in Figures 5–7. Figure 5 represents the sorption behavior of all EPDM blends in tetrachloroethylene. As shown in Figure 5, the EPDM/BIIR blend showed higher mass uptake compared to EPDM/NR and EPDM/SBR. This may be attributed to the presence of the halogen atom in BIIR, which showed more interaction toward chlorinated hydrocarbons.

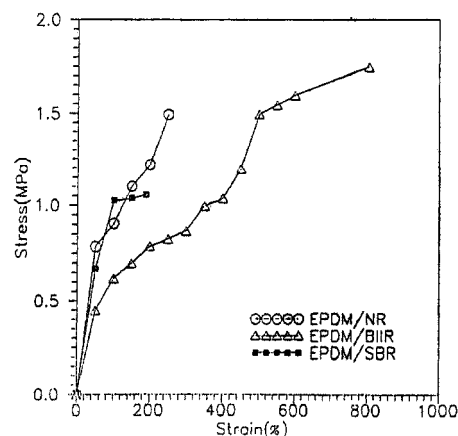


Figure 2 Stress versus strain curves for all EPDM blends.

TABLE IV
Mechanical Properties of EPDM Blends after Exposure to Penetrants for 80 h
(Equilibrium) at Room Temperature

Penetrant	Property					
	EPDM/NR		EPDM/BIIR		EPDM/SBR	
	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
Unexposed	1.49	250	1.75	806	1.06	190
Dichloromethane	1.29	278	1.50	563	0.73	166
Trichloromethane	1.09	181	1.17	478	1.70	146
Tetrachloromethane	1.32	203	1.71	641	1.29	97
1,2-Dichloroethane	1.24	197	1.20	534	0.94	150
Tetrachloroethylene	1.04	141	1.34	568	1.52	141

The nature of the probe molecules on the liquid transport through EPDM blends is shown in Figure 6. Higher maximum mass uptake (S ; which was obtained from the plateau region of the sorption plots) values were observed in carbon tetrachloride and tetrachloroethylene penetrants (6–14 g/g) compared to other systems (2–10 g/g). This was due to the difference in the polarity of the probe molecules. The non-polar EPDM blends had more affinity toward CCl_4 and tetrachloroethylene molecules; both penetrants had dipole moment values of zero. The liquid sorption decreased with increases in the polarity of penetrant in the case of EPDM/SBR and EPDM/NR (except EPDM/BIIR), which followed the trend with an increase in the polarity as $\text{CCl}_2=\text{CCl}_2 > \text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > (\text{CH}_2)_2\text{Cl}_2$. In most cases, EPDM/BIIR showed the reverse order. During the initial sorption stages, up to 50% of the completion of the sorption, penetrant uptake increased linearly with $t^{1/2}$ values. At later stages of the sorption experiments, due to saturation equilibrium, the sorption curves for all of the penetrants and at all temperatures attained plateau regions.

The effect of temperature on the sorption characteristics were studied at 25, 40, and 60°C, except for

dichloromethane because of its low boiling point. The sorption increased with temperature for all of the blends; this is illustrated in Figure 7. This effect followed the conventional theory that at higher temperatures, an increase in free volume occurs due to the increased movement of the chain segments of the elastomers.^{8–10}

One of the factors that affected the transport characteristics was the solubility parameter (δ) of the probe molecule. The difference in δ of the matrix and that of the probe molecule was less, which influenced the transport of that molecule through the membrane. The effect of δ on equilibrium mass uptake (M_∞) is shown in the Figure 8. As δ increased from 8.6 to 9.9 (cal/cm³)^{1/2}, M_∞ decreased from 657 to 126%.

The mechanism of transport in the system under investigation was determined with the following equation^{22,23}:

$$\log M_t/M_\infty = \log K + n \log t \quad (1)$$

where M_t and M_∞ are the mass uptake in the sorption at time t and at equilibrium, respectively. K is a constant that depends on the structural characteristics of

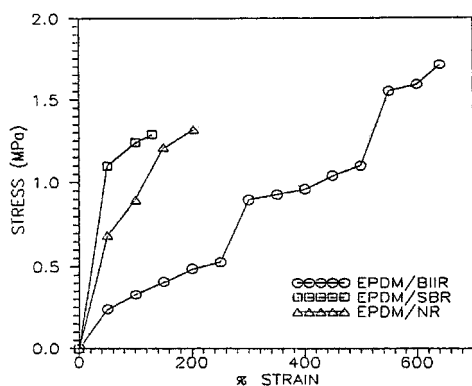


Figure 3 Stress versus strain curves for all EPDM blends after exposure in dichloromethane for 80 h.

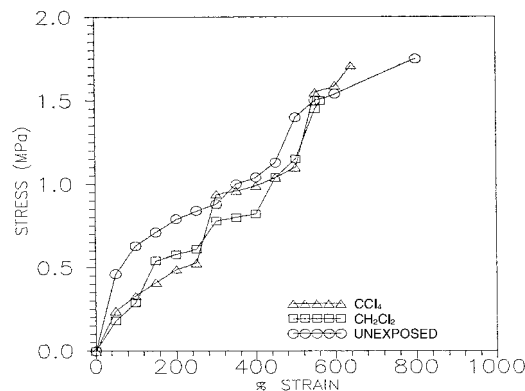


Figure 4 Stress versus strain curves for all EPDM blends before and after exposure in dichloromethane and carbon tetrachloride penetrants.

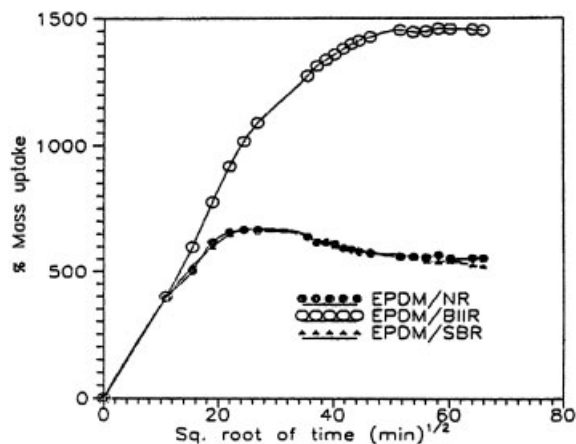


Figure 5 Percentage mass uptake versus $t^{1/2}$ for all EPDM blends in tetrachloroethylene.

the polymer in addition to its interaction with the solvent. The magnitude of n denotes the transport mode. For the normal Fickian mode of transport (usually described as case I), where the rate of polymer chain relaxation is higher compared to the diffusion rate of the penetrant, the value of n is 0.5. When n is 1, the transport phenomenon is said to be case II (relaxation controlled), where chain relaxation is slower than liquid diffusion. If the value of n is between 0.5 and 1, the mode of transport is said to be anomalous. Some plots of $\ln M_t/M_\infty$ versus $\ln t$ for different halogenated penetrants are displayed in Figure 9. The estimated values of the constants n and K are tabulated in Table V and are accurate to ± 0.01 and ± 0.005 units, respectively.

For all the systems, the values of n were between 0.44 and 0.54, which suggests that the observed diffusion mechanism could be classified as a Fickian mode of transport.⁸⁻¹⁰ The results of n did not show any systematic trend on the temperature. This was also supported by the initial linear plots of percent mass

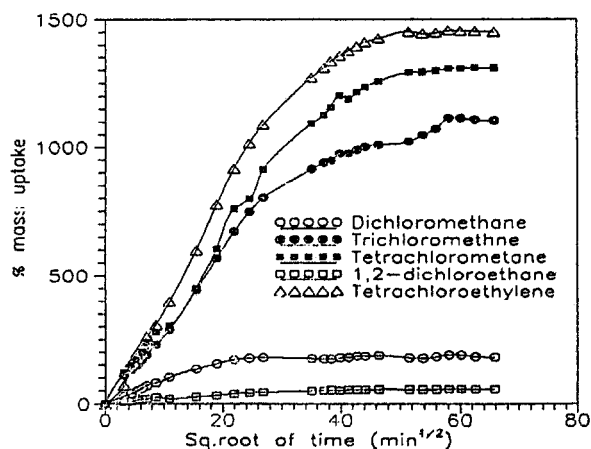


Figure 6 Percentage mass uptake versus $t^{1/2}$ for EPDM/BIIR blends in all chlorinated organic penetrants.

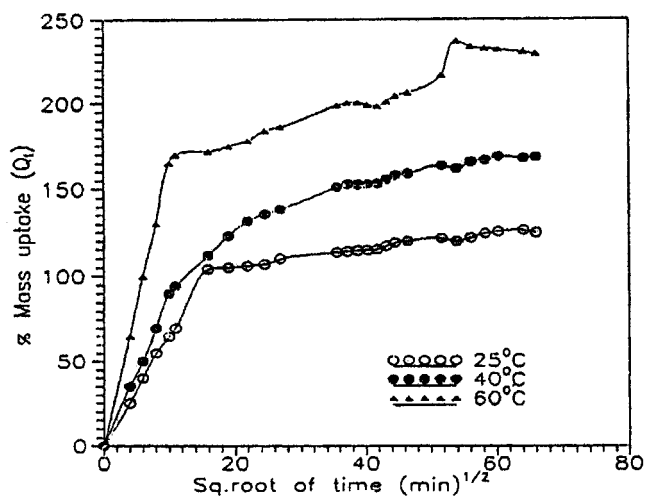


Figure 7 Percentage mass uptake versus $t^{1/2}$ for EPDM/NR blends in 1,2-dichloroethane at different temperatures.

uptake Q_t versus $t^{1/2}$, shown in Figures 5-7. However, K depends on the polymer-solvent interaction and the temperature. The values of K also exhibited a trend similar to the sorption; that is, these results in general varied according to the sequence EPDM/BIIR < EPDM/NR < EPDM/SBR. As shown in Table V, the values of K increased with increases in temperature.²⁴

The diffusion coefficient (D) of the polymer-solvent system is important in many areas of science and technology. Values of D were calculated from the initial linear sorption plots of Q_t versus $t^{1/2}$ for the different systems under investigation with the following equation^{23,25}:

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

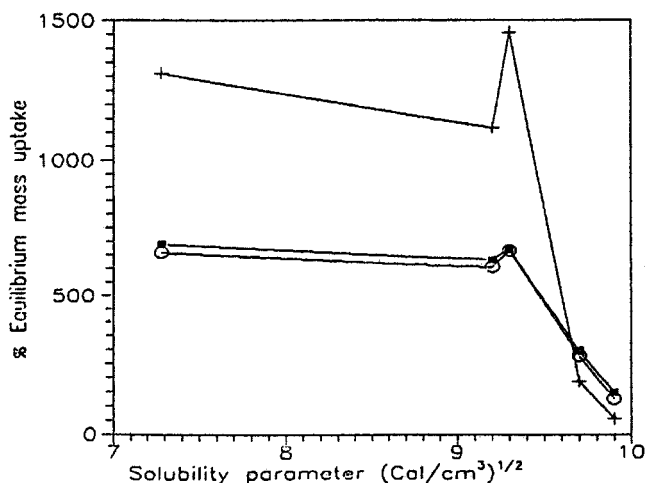


Figure 8 δ versus M_∞ for all EPDM blends at room temperature.

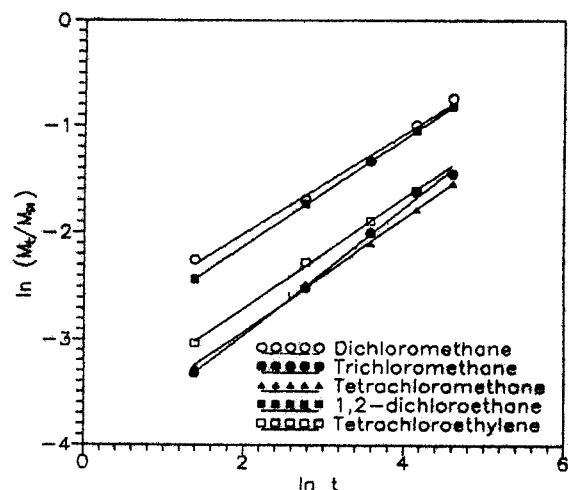


Figure 9 $\ln M_t/M_\infty$ versus $\ln t$ for EPDM/BIIR blends in all penetrants.

where h is the thickness of the polymer membrane, θ is the slope of the initial linear portion of the sorption curve, and M_∞ is the equilibrium mass uptake. The calculated values of D for all EPDM blend-penetrant systems are given in Table VI. The variation of D s depended on the nature of the penetrant molecules and also the structural characteristics of the elastomers. As shown in Table VI, D s for all blend-penetrant systems increased with increasing temperature. The D values were in the range 1.5×10^{-7} to 14.32×10^{-7} cm^2/s from 25 to 60°C. For the EPDM/BIIR blend, D decreased from 5.61×10^{-7} to 1.5×10^{-7} cm^2/s , with a decrease in polarity of the penetrant, and the following trend was observed: dichloromethane > trichloromethane > tetrachloromethane. This may have been due to the higher compatibility of polar polymers with polar penetrants and, hence, faster diffusion with respect to polar penetrants. For EPDM blends, the trend of D values were as follows: EPDM/BIIR < EPDM/NR \cong EPDM/SBR. However,

D did not vary with the molecular volume of the penetrants.

The permeability coefficient (P) is calculated from the simple equation

$$P = DS \quad (3)$$

The calculated P values are also tabulated in Table VI. As shown in Table VI, permeability increased with increasing temperature because the molecular relaxation or movement increased with increasing temperature, which in turn, increased the free molecular volume.^{19,20} Hence, permeation increased with temperature, and also, the permeability showed systematic relation on the polarity of the probe molecule.

P values for tetrachloromethane and tetrachloroethylene were more comparable to other penetrants due to the nonpolar nature of the probe molecule. This may have been due to the nonpolar nature of the selected rubbers, such as NR, EPDM, and SBR, through which nonpolar penetrants could easily penetrate. For nonpolar penetrants the permeability values ranged from 19×10^{-7} to 72×10^{-7} cm^2/s , whereas those of polar penetrants such as dichloromethane, trichloromethane, and 1,2-dichloroethane were in the range of 5×10^{-7} to 50×10^{-7} cm^2/s . The permeability increased with decreasing polarity of the probe molecule.

Activation parameters

E_D and E_P were calculated from the Arrhenius relation

$$X = X_0 \exp(E_a/RT) \quad (4)$$

where, X_0 is the preexponential factor, R is the molar gas constant, T is the absolute temperature, and X is the coefficient (i.e., D for diffusion and P for the permeation process). Arrhenius plots for diffusion and permeation processes for all of the EPDM blends in

TABLE V
 n and K Values of EPDM Blends at Different Temperatures

Blend	Temperature (°C)	Dichloromethane		Trichloromethane		Tetrachloromethane		1,2-Dichloroethane		Tetrachloroethylene	
		n	$K \times 10^2$	n	$K \times 10^2$	n	$K \times 10^2$	n	$K \times 10^2$	n	$K \times 10^2$
EPDM/NR	25	0.50	5.641	0.46	4.978	0.50	4.978	0.50	4.735	0.44	6.392
	40	0.50	6.890	0.50	6.720	0.50	6.081	0.46	5.784	0.50	6.720
	60	—	—	0.50	6.720	0.46	7.615	0.52	6.392	0.50	7.808
EPDM/BIIR	25	0.50	4.855	0.53	1.657	0.54	1.831	0.50	4.504	0.50	2.472
	40	0.50	3.688	0.50	3.421	0.50	3.174	0.58	2.534	0.51	2.801
	60	—	—	0.50	4.396	0.50	3.877	0.53	4.285	0.50	4.285
EPDM/SBR	25	0.50	6.234	0.50	5.366	0.50	4.076	0.50	4.504	0.50	5.785
	40	0.50	8.629	0.47	7.615	0.45	6.234	0.44	6.720	0.45	6.081
	60	—	—	0.48	7.427	0.47	7.808	0.50	8.005	0.50	6.890

Units: K ; g/g (min)^n .

TABLE VI
D, S, and P Values of EPDM Blends at Different Temperatures

Blend	Temperature (°C)	Dichloromethane		Trichloromethane		Tetrachloroethane		1,2-Dichloroethane		Tetrachloroethylene						
		D × 10 ⁷	S	P × 10 ⁷	D × 10 ⁷	S	P × 10 ⁷	D × 10 ⁷	S	P × 10 ⁷	D × 10 ⁷	S	P × 10 ⁷			
EPDM/NR	25	6.08	2.79	16.86	3.73	6.07	22.69	4.27	6.57	28.11	4.25	1.26	5.38	6.70	6.67	44.74
	40	11.43	2.59	29.71	8.32	5.90	49.16	6.37	6.61	42.17	4.64	1.68	7.84	7.14	6.15	44.0
	60	—	—	—	9.27	4.97	46.19	9.55	5.80	55.98	9.77	2.37	23.17	11.08	5.66	62.73
EPDM/BIIR	25	5.61	1.89	10.66	2.19	11.17	24.56	1.5	13.12	19.69	3.09	0.56	1.76	2.22	14.59	32.43
	40	6.34	2.56	16.29	3.92	10.54	41.36	2.53	13.10	33.26	3.59	0.90	3.25	2.90	14.40	41.80
	60	—	—	—	6.73	8.70	58.65	2.68	13.47	36.24	11.84	1.31	15.66	4.49	14.24	64.00
EPDM/SBR	25	5.56	2.98	16.61	6.25	6.34	39.69	4.12	6.89	28.44	3.63	1.50	5.44	4.88	6.73	32.92
	40	10.69	2.84	30.37	10.58	6.21	65.65	2.42	6.50	40.60	5.46	1.55	8.50	6.21	6.55	40.71
	60	—	—	—	11.76	5.58	65.73	11.00	6.06	66.80	14.32	2.03	29.41	11.48	6.35	72.9

Units: P and D; cm²/s and S; g/g;

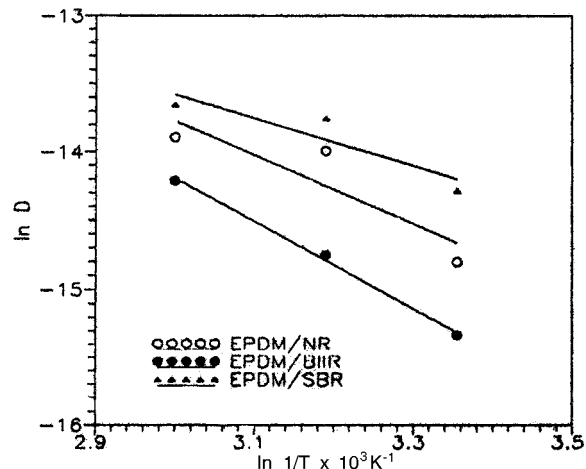


Figure 10 Arrhenius plots of EPDM blends for diffusion in trichloromethane.

trichloromethane and 1,2-dichloroethane are shown in Figures 10 and 11, respectively. As shown in Table VII, there was no systematic variation in E_D and E_P values, but higher E_D and E_P values were observed for the EPDM/BIIR blend compared to other blends due to a higher degree of cohesive energy density in the polymer chain. E_D and E_P values were in the range 7.27–15.58 and 7.56–49.88 kJ/mol, respectively. These values were within the expected range for rubbery polymers, well above their glass-transition temperatures.^{26,27}

Similarly, the temperature-dependent equilibrium sorption constant (K_s) values could be fitted to the vant Hoff's relation²⁸ to estimate ΔH and ΔS of the sorption process:

$$\log K_s = [(\Delta S/2.303R) - (\Delta H/2.303R)(1/T)] \quad (5)$$

ΔH and ΔS were calculated from the slope and intercepts, respectively, by the vant Hoff's plot. vant Hoff's

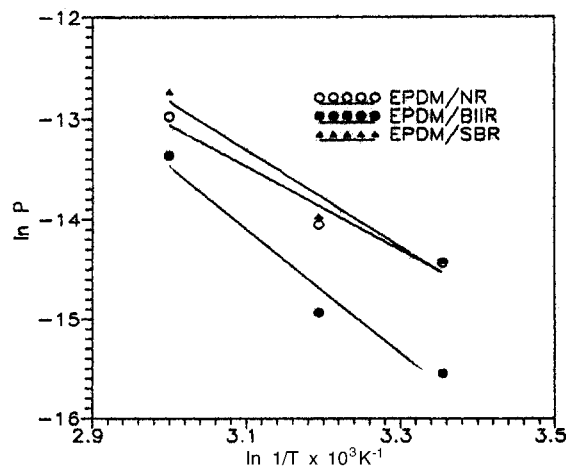


Figure 11 Arrhenius plots of EPDM blend for permeation in 1,2-dichloroethane.

TABLE VII
Activation Parameters, ΔH , and ΔS Values in Different Chlorinated Organic Penetrants

Blend	Parameter	Trichloromethane	Tetrachloromethane	1,2-Dichloroethane	Tetrachloroethylene
EPDM/NR	E_D	12.28	9.50	9.35	7.55
	E_P	15.31	16.90	31.97	7.56
	ΔH	9.50	3.74	11.37	5.19
	$-\Delta S$	54.04	38.24	-2.99	44.06
EPDM/BIIR	E_D	13.12	7.27	15.28	7.96
	E_P	20.79	13.85	49.88	14.96
	ΔH	4.75	4.35	13.85	3.15
	$-\Delta S$	37.82	34.91	-5.81	30.34
EPDM/SBR	E_D	7.29	12.03	15.58	8.16
	E_P	12.47	19.00	40.22	19.56
	ΔH	3.63	2.93	7.12	3.11
	$-\Delta S$	36.16	35.33	9.97	39.07

Units: E_D and E_P , kJ/mol, ΔH , kJ/mol, and ΔS , J/mol/K.

plots for all EPDM blends in trichloromethane are given in Figure 12. The thermodynamic parameters measured with these plots are tabulated in Table VII. The average estimated error in ΔH was about ± 4 J/mol; for ΔS , it was about ± 1 J/mol/K. As shown in Table VII, ΔS values were negative for all of the blends except those with 1,2-dichloroethylene, which suggests that the structure of the solvent molecules was retained, even in the sorbed state. The ΔS values were in the range 2–15 J/mol/K. However, ΔH values for all the liquids were positive, which suggests that the sorption was an endothermic process and that it was dominated by Henry's law mode; that is, the sorption proceeded through the creation of new sites or pores in the polymer. The ΔH values were between 3 and 54 kJ/mol.

Sorption kinetics

During diffusion and sorption of liquid through polymer membranes, a structural rearrangement takes place in the polymer matrix, and this induces kinetic

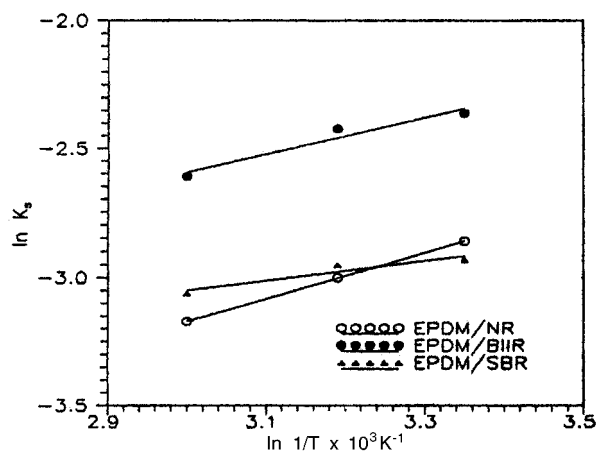


Figure 12 van't Hoff's plots for all EPDM blends in trichloromethane.

behavior. Transport kinetics mainly depends on the segmental mobility and availability of the free volume within the polymer matrix. We calculated the first-order rate constant (k_1) with the equation

$$dC/dt = k_1(C_\infty/C_t) \quad (6)$$

which on integration gives

$$k_1 t = 2.303 \log[C_\infty/(C_\infty - C_t)] \quad (7)$$

where k_1 is the first-order rate constant (min^{-1}) and C_t and C_∞ represent the concentrations at time t and at equilibrium, respectively. A plot of $\log(C_\infty - C_t)$ versus time t for EPDM/BIIR blends in tetrachloroethylene at different temperatures is shown in Figure 13. The slope of the graph gives the values of k_1 , which are given in Table VIII. This constant was in the range $1.91\text{--}16.95 \times 10^3/\text{min}^{-1}$. The rate constant decreased from 4.81 to $1.61 \times 10^3 \text{ min}^{-1}$ with decreasing polarity

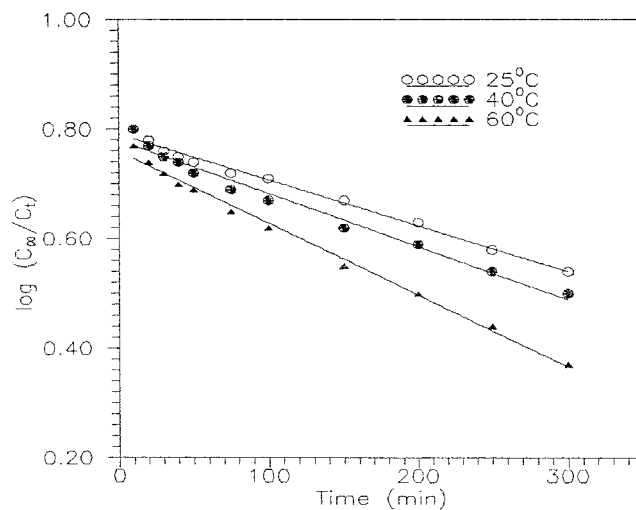


Figure 13 First-order kinetics of EPDM/BIIR in tetrachloroethylene.

TABLE VIII
 $k_1 \times 10^{-3}$ of EPDM Blends at Different Temperatures

Blend	Temperature (°C)	Penetrant				
		Dichloromethane	Trichloromethane	Tetrachloromethane	1,2-Dichloroethane	Tetrachloroethylene
EPDM/NR	25	3.5	8.77	5.86	2.44	6.97
	40	8.18	10.66	8.01	0.96	9.21
	60	—	11.21	13.16	9.20	16.95
EPDM/BIIR	25	4.81	2.04	1.61	5.75	1.91
	40	4.14	2.69	2.06	3.19	2.03
	60	—	2.00	2.48	5.31	2.51
EPDM/SBR	25	5.75	5.95	4.31	1.43	5.54
	40	9.87	9.21	5.45	4.26	6.66
	60	—	10.01	6.16	8.80	9.42

(dipole moment = 1.36–0.00 units) of the penetrant for the EPDM/BIIR blend system. The kinetic rate constant is a measure of the speed with which the solvent molecules migrate within the polymer matrix.

k_1 values followed a regular increasing trend, from 6.97 to 16.95 $\times 10^3 \text{ min}^{-1}$, with increasing temperature, from 25 to 60°C, except for some systems. The increase in k_1 values indicated an increase in the rate of diffusion with temperature.

Schott²⁹ explained the use of second-order kinetics for swelling experiments. The equation used to evaluate the second-order swelling is

$$dC/dt = k_2(C_\infty - C_t)^2 \quad (8)$$

where k_2 is the second-order rate constant. The integrated form of the equation is

$$k_2 t = [1/(C_\infty - C_t) - (1/C_\infty)] \quad (9)$$

The typical second-order kinetic plot for the EPDM/SBR blend in tetrachloroethylene at different temperatures is given in Figure 14. The slope of the plots

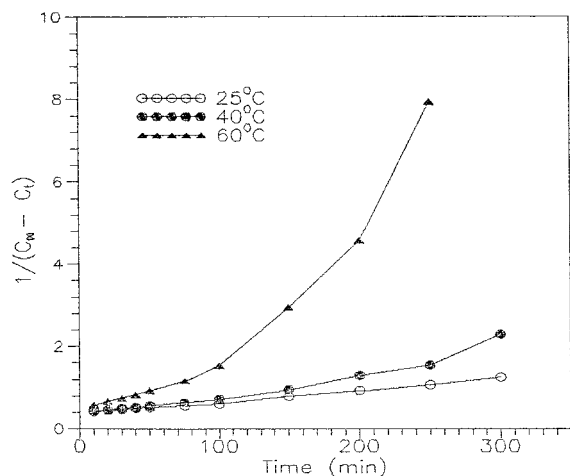


Figure 14 Second-order kinetics of EPDM/SBR blends in tetrachloroethylene.

gives the values of k_2 , which are compiled in Table IX. The k_2 values were in the range 0.83–40 $\times 10^3 \text{ min}^{-1}$ and did not follow any systematic trend. However, the plot was slightly curved in the middle. Because a straight line was obtained for the first-order kinetics, first-order kinetics seems to be more appropriate than second-order kinetics for the transport of chlorinated penetrants through EPDM blends.

Molar mass between the physical entanglements

The molar mass (M_c) between physical entanglements in EPDM blends was calculated with the classical theory of Flory and Rehner.³⁰ These results are also included in Table X. In most of the blends, M_c increased with increasing size of the penetrants, and these values varied between 355 and 1086.

CONCLUSIONS

Rubber goods with lesser diffusivity are needed in applications involving gaskets, oil seals, and liners to prevent the loss of oil, vapors, steam, and so on. In the absence of actual field experience on the long-term performance of elastomeric membranes, there exists a need for the use of simple laboratory methods to predict their service life. Hence, in this study, we tried to identify the effect of halogenated penetrants on the properties (performance) of EPDM blends.

The transport of aliphatic chlorinated hydrocarbons through structurally different EPDM blends was studied by sorption gravimetric analysis. The results of these studies on polymer–solvent interactions will be important in the successful application of these materials in sorption experiments and barrier packaging. The Fickian model was used to estimate D and transport data. Factors such as solvent type and the nature of the elastomeric blend seemed to exert tremendous influence on the transport characteristics. D values for EPDM/BIIR blends varied in the sequence dichloromethane > trichloromethane > tetrachloromethane. The D values for these penetrants ranged from 1.5

TABLE IX
 $k_2 \times 10^{-3}$ (min⁻¹) for EPDM Blends with Different Penetrants

Blend	Temperature (°C)	Penetrant				
		Dichloromethane	Trichloromethane	Tetrachloromethane	1,2-Dichloroethane	Tetrachloroethylene
EPDM/NR	25	6.66	7.5	10.00	12.5	4.00
	40	15.00	15.00	18.75	9.37	10.00
	60	—	25.00	40.00	37.5	6.66
EPDM/BIIR	25	9.61	1.15	0.75	35.00	0.83
	40	5.76	1.66	1.07	14.28	0.68
	60	—	0.93	0.93	11.53	1.07
EPDM/SBR	25	11.11	4.16	3.33	8.33	5.00
	40	20.00	6.25	5.00	7.14	5.00
	60	—	9.37	7.14	10.00	6.81

TABLE X
 M_c Between Crosslinks for EPDM Blends in Chlorinated Organic Penetrants

Blend	Dichloromethane	Trichloromethane	Tetrachloromethane	1,2-Dichloroethane	Tetrachloroethylene
EPDM/NR	353	668	864	454	944
EPDM/BIIR	355	743	943	753	1086
EPDM/SBR	611	935	850	545	948

$\times 10^{-7}$ to 14.32×10^{-7} cm²/s in the temperature range 25–60°C. With EPDM/BIIR blends, D decreased with decreasing polarity of the probe molecules. The temperature activated the diffusion process, which was supported by the higher D values. At higher temperatures, equilibrium penetrant uptake was high due to the increase in the polymer free volume. Arrhenius parameters such as n and K were estimated for the transport process. Values of n were between 0.44 and 0.54, which suggests that the observed diffusion mechanisms showed a Fickian mode of transport. E_D 's of EPDM blend-penetrant systems were in the range 7.27–15.58 kJ/mol. vant Hoff's equation was used to obtain ΔS and ΔH of sorption. Gibb's free energy for the sorption process was positive.

Transport kinetics were studied in terms of the first- and second-order kinetics model. However, first-order kinetics seemed to be more appropriate for the systems studied. The polymer network structure was analyzed by the estimation of the molecular mass between the crosslinks.

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