

Permeation and Diffusion of Environmental Pollutants through Flexible Polymers

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Synopsis

Permeation and diffusion characteristics of high density polyethylene (HDPE), elasticized polyolefin, and polychloroprene membranes have been determined for various organic pollutants at 22 and 50°C. A standard ASTM permeation cell method was used to measure the permeation rate while an immersion/weight gain method was used to obtain the diffusion coefficient. Thickness-dependent permeation rates were determined for HDPE membranes. An equimolar mixture of various permeants was also used to see the possibility of synergistic effects by combination of permeants. The experimental results are discussed in relation to the suitability of HDPE membranes in severe environments.

INTRODUCTION

Over the past years, the practical significance of permeation and diffusion characteristics of polymers has taken on a greater importance due to their applications as protective materials.¹ Although high density polyethylene (HDPE) has been frequently used as chemical barrier clothing, retention tank liners, and seals for undersea electronic devices, data in the literature on its permeability and diffusivity to various common organic pollutants are scanty. In view of this, a study was undertaken to investigate the diffusion and permeation of eight organic permeants at 22 and 50°C in three different thickness HDPE samples. Solubility and diffusivity of the permeants were computed from an immersion/weight gain method.²⁻⁴ A standard ASTM permeation cell was used^{5,6} to obtain the permeation data.

For comparison, elasticized polyolefin and polychloroprene (neoprene) were also tested, since their chemical resistivities have been reported in the trade literature to be similar to those of HDPE. Unlike HDPE, both elasticized polyolefin and polychloroprene underwent severe physical changes such as swelling, dissolution, disintegration, etc. Results of both permeation cell experiments and immersion/weight gain assays are discussed for HDPE membranes.

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EXPERIMENTAL

Materials

HDPE (Schlegel Corp.), elasticized polyolefin (Gundle), and polychloroprene (Carlisle Corp.) were tested with the eight permeants: 1,1,2-trichloroethane, 1,2-dichloroethane, methylene chloride, styrene, benzene, toluene, naphthalene, and 2-methylnaphthalene. These represent typical organic pollutants in landfill applications and exhibit a wide range of boiling points, vapor pressures, and solubilities in water. Six of the permeants are liquids while the last two are solids at room temperature (22°C). Three different HDPE membrane thicknesses (30, 60, and 100 mil) were used.

Measurement of Permeation Parameters

Immersion/Weight Gain Method

Membranes of 100-mil HDPE, 40-mil polyolefin, and 46-mil polychloroprene (each of 2 in. diameter) were immersed in the liquid permeants or solutions of (31%) and 2-methylnaphthalene (50%) in dimethylformamide (DMF). To study the possibility of synergistic effects by combination of permeants, an equimolar mixture was prepared (total volume 1597 mL) containing each of the permeants given in Table IV; this mixture was then used as a permeant. Each membrane was tested in triplicate at room temperature (22°C) and 50°C, the latter representing the working temperature of the membranes when used as liners.

Samples were placed in a desiccator over anhydrous silica gel before use for 24 h, and dry weights of the membranes were recorded before soaking in the permeants. The weights were recorded at various time intervals. When membranes were removed from the permeants, they were carefully blotted to remove the surface liquid before weighing. The mass of liquid uptake per mass of sample was determined as a function of time (t). Percent weight gains (M_t) were then plotted versus the square root of time.³ Solubilities of permeants in the polymers were calculated at equilibrium (i.e., when no further weight gains were observed). Diffusion coefficients D were calculated as³

$$D = \frac{\pi}{t} \left(\frac{LM_t}{4M_m} \right)^2 = \pi \left(\frac{l\theta}{4M_m} \right)^2 \quad (1)$$

where l is material thickness (cm), $\Theta (= M_t/t^{1/2})$ is slope of the plot of M_t versus $t^{1/2}$, and M_m is maximum percent weight gain (at equilibrium). Solubilities were calculated from M_m by correcting for density of polymers (density of HDPE = 0.94 g/cm³).

Diffusion coefficients (which were independent of permeant concentration) were used with solubilities S to compute the amount of permeant which could pass from a solution of concentration C_2 through the membrane in time t . The

following relationship was used⁷:

$$\frac{Q_t}{lc_2} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-Dn^2\pi^2 \frac{t}{l^2}\right) \quad (2)$$

Here, Q_t represents the diffusivity value which when multiplied by the solubility gives the total amount of permeant passing through a given area of membrane (e.g., 1 sq. c) in time t and C_2 is the concentration of permeant. As t approaches ∞ (i.e., steady state or equilibrium), eq. (2) reduces to

$$Q_t = \frac{Dc_2}{l} \left(t - \frac{l^2}{6D} \right) \quad (3)$$

A FORTRAN program was written to calculate permeation rates from eq. (3).

Permeation Cell Experiments

Permeation of the eight permeants from an equimolar mixture (1.25M each) through HDPE membranes was also measured by using the Standard ASTM F739-81 permeation cell assembly shown in Figure 1. All tubing, stoppers, and surfaces other than the HDPE were glass, stainless steel, or Teflon. Filtered

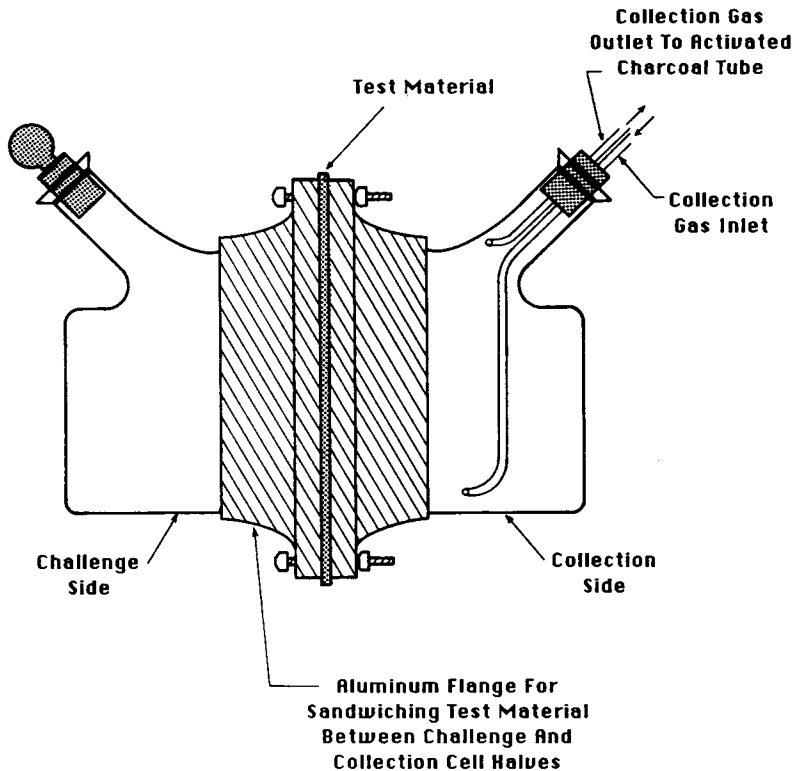


Fig. 1. Permeation test cell.

air was pumped into the challenge side of the cell to continually sweep permeants into the exit tube which was connected to an activated charcoal tube trap (SKC, Inc., Catalog No. 226-09). The sweeping rate was maintained at 55–65 mL/min. At various time intervals the charcoal tubes containing adsorbed permeants were replaced. The charcoal was eluted with carbon disulfide, and the chemicals were quantified by gas chromatography (GC). A bonded phase glass capillary column (BPI, 0.5 mm \times 50 m, Scientific Glass Engineering) and 1/8 in. \times 20 ft stainless steel column with 10% FFAP on Chromosorb were used for GC analyses.

RESULTS AND DISCUSSION

Results of the immersion/weight gain method are presented in Tables I and II. Elasticized polyolefin disintegrated in most of the permeants at 50°C, while polychloroprene underwent swelling and discoloration. Since Fickian diffusion does not apply to polymers that undergo physical/chemical changes, these polymers were not evaluated further. Two typical plots (22 and 50°C) of percent weight gain versus the square root time ($h^{1/2}$) for HDPE are shown in Figures 2 and 3. The plots are consistent with the typical Fickian diffusion in that there is a linear portion followed by a plateau of maximum weight gain. The similarities in the plots (Figs. 2 and 3) suggest that there was no thermal degradation of the membrane at 50°C. Unlike the HDPE membrane, the 40 mil thickness elasticized polyolefin membrane immersed in 1,2-dichloroethane experienced a continuous decrease in liquid uptake from 65 to 168 h; a similar tendency was observed for naphthalene solution from 41 to 168 h (see Table I). In all cases, M_t was higher at higher temperature.

At 22°C (Fig. 2), equilibrium was reached rapidly (\sim 36 h) for methylene chloride; with 1,2-dichloroethane and 1,1,2-trichloroethane it took 144 and 256 h, respectively. Absorption behavior of styrene, toluene, and benzene appear to be almost identical as these attained equilibrium around 36–44 h (data not shown to avoid overcrowding). Thus, it appears that the substituted benzene derivatives behave closely similar to the parent benzene molecule. Surprisingly, for either naphthalene or 2-methyl naphthalene, no equilibrium was attained at 22°C within the course of the experiment and hence diffusion coefficients could not be evaluated. At 50°C, both naphthalene and 2-methylnaphthalene reached equilibrium around 36 and 100 h, respectively. However, other permeants namely, 1,1,2-trichloroethane, 1,2-dichloroethane, styrene, benzene, and toluene took about 16–20 h to reach equilibrium (see Fig. 3). Table III presents diffusion coefficients as calculated from the slopes of initial linear portions of the curves. As anticipated, both diffusivity and solubility values increased with an increase in temperature (at 50°C).

Typical data for the transport of permeants through 30 and 100 mil HDPE at 22 and 50°C, respectively, are shown in Figures 4 and 5. At 22°C, no permeation was observed for 100 mil HDPE during the 1-week experiment. Generally, the onset of steady state permeation was rapid. From the slopes of the straightlines permeation rates were calculated which are listed in Table IV. For 60 mil HDPE at 22°C a high permeation rate was observed for methylene chloride and low values were seen for 1,1,2-trichloroethane, 1,2-dichloroethane, styrene, benzene, and toluene; however, intermediate val-

TABLE I
Average Percent Weight Gain for Three Different Membranes at 22°C

Permeant	Hours									
	3	6	24	41	65	96	168	216	264	384
1,1,2-Trichloroethane	a			2.35	3.05	3.65	5.15	6.00	6.70	7.30
	b	68.10	91.65	91.60	96.82	98.81	98.12	99.05		
	c			174.45	182.83	185.57	187.21	189.30		
1,2-Dichloroethane	a			2.65	3.44	4.10	5.15	5.30	5.40	5.40
	b	46.05	48.08	49.09	48.05	51.05	50.05	49.08		
	c			115.39	114.74	120.83	120.83	120.83		
Methylene chloride	a	1.70	2.60	6.00	8.22	8.90	8.86			
	b	89.00	94.05	99.05	90.08	102.05	104.00	104.00		
	c			122.03	153.09	157.31	159.38			
Styrene	a	1.00	1.60	3.60	5.40	7.00	7.50	7.70	7.70	7.70
	b	75.00	75.50	76.00	80.04	80.05	80.05			
	c			116.91	118.98	121.29	121.74	122.20	123.10	124.10
Benzene	a	1.20	1.92	4.54	6.50	7.72	8.00			
	b			75.05	77.56	84.06	77.85			
	c			96.34	102.84	106.42	104.99			
Toluene	a	1.35	2.14	5.00	7.45	8.52	8.60			
	b	85.05	87.00	91.00	91.00	95.08	95.08	94.69		
	c			101.18	105.99	108.33	109.33	108.00	110.30	111.20
Naphthalene	a			0.21	0.26	0.31	0.40	0.45	0.51	0.62
	b	3.65	5.20	6.30	6.60	6.75	6.60			
	c			32.20	29.05	28.77	27.89			
2-Methyl naphthalene	a			0.36	0.47	0.56	0.73	0.83	0.93	1.13
	b	6.10	8.90	10.30	10.70	10.80	10.70	10.85		
	c			49.69	33.68	46.32	45.81			
DMF	a			0.08	0.12	0.12	0.15	0.17	0.21	0.24
	b	1.80	2.60	3.30	3.30	3.30	3.30			
	c			18.93	16.84	16.00	15.24			
Mixture	a	0.84	1.26	2.83	4.24	5.80	6.80	8.05	8.15	8.15
	b	83.04	84.05	85.09	86.05	88.69	90.00	89.00		
	c			138.80	143.74	147.72	149.11	148.44	150.19	107.28

^a Data for 100 mil HDPE membrane.

^b Data for 40 mil elasticized polyolefin membrane.

^c Data for 46 mil polychloroprene membrane (swelling of membrane and discoloration were observed for all permeants).

TABLE II
Average Percent Weight Gain for Three Different Membranes at 50°C

Permeant	Hours									
	3	6	24	48	72	144	192	240	360	
1,1,2-Trichloroethane ^d	a		8.73	10.83	11.20	11.30	11.30	11.10		
1,2-Dichloroethane ^d	c		195.00	204.00	206.00	210.50	215.50	216.91		220.00
Styrene ^d	a	2.40	7.22	8.00	8.00	8.00				
	c	3.92	124.00	130.08	138.00	141.00	139.04	141.03		144.09
Benzene ^d	a	5.15	10.74	10.94	10.90	10.90				
	c	7.90	125.00	127.00	125.00	126.00				
Toluene ^d	a	5.14	11.96	12.00	12.05	12.05				
	c	8.22	103.08	109.03	110.00	110.08				
Naphthalene	a		12.31	12.43	12.42	12.50				
	c	12.50	107.00	109.00	110.00	115.00	118.02	121.00	121.00	1.90
	a		0.85	1.20	1.31	1.70	1.80	1.81		
	b		12.72	12.74						
	c	12.60	31.05	31.00	33.00	33.00				
2-Methyl naphthalene	a		1.40	1.90	2.32	3.00	3.10	3.10		3.10
	b	18.90	19.40	19.41						
	c		35.02	36.04	38.00	37.00				
DMF	a		0.24	0.34	0.42	0.50	0.56	0.53		
	b	4.06	4.60	4.49	5.10	5.20				
	c		18.25	18.26	20.00	19.20				
Mixture ^d	a	3.40	10.80	11.70	11.70	11.70				
	c		146.00	155.00	156.00	157.00				

^{a, b, c}The same meaning as in Table I.

^dFor these permeants the 40 mil elasticized polyolefin membrane disinterated at 50°C.

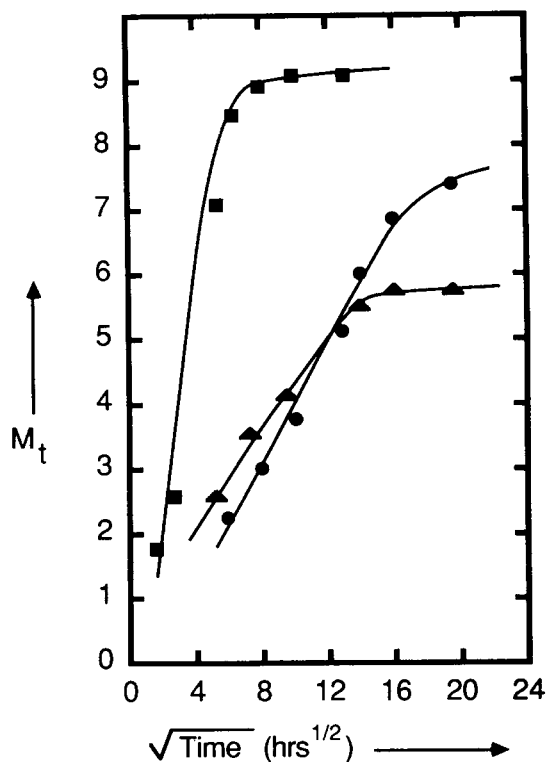


Fig. 2. Percent weight gain vs. $\text{time}^{1/2}$ for HDPE at 22°C: (●) 1,1,2-trichloroethane; (▲) 1,2-dichloroethane; (■) methylene chloride.

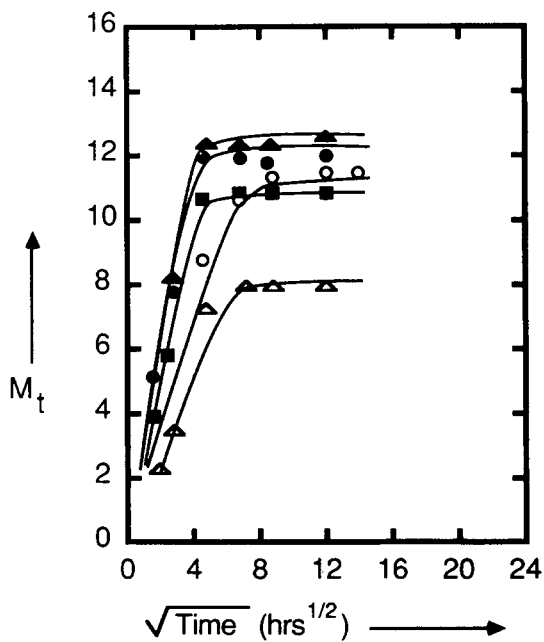


Fig. 3. Percent weight gain vs. $\text{time}^{1/2}$ for HDPE at 50°C: (○) 1,1,2-trichloroethane; (Δ) 1,2-dichloroethane; (■) styrene; (●) benzene; (▲) toluene.

TABLE III
Diffusion Coefficients and Related Parameters for
Various Permeants in HDPE Membranes

Permeant	Temp (°C)	θ	M_m (%)	$D \times 10^4$ (cm^2/h)
1,1,2- Trichloroethane	22	0.47	7.30	0.51
	50	1.78	11.3	3.00
1,2- Dichloroethane	22	0.44	5.40	0.81
	50	1.47	8.00	4.10
Methylene chloride	22	1.47	8.90	3.20
Styrene	22	0.94	7.70	1.80
	50	2.41	10.9	6.00
Benzene	22	0.87	8.00	1.50
	50	3.89	12.00	13.00
Toluene	22	1.25	8.60	2.60
	50	4.30	12.50	15.00
Naphthalene	50	0.13	1.30	1.20
2-Methyl naphthalene	50	0.20	2.60	0.73

ues were obtained for several permeants with varying thicknesses of the membrane at both 22 and 50°C. Permeation rates were higher at higher temperatures and were dependent on membrane thickness. For instance, lower rates were observed for 100 mil samples at 50°C than for 60 or 30 mil samples. The 100 mil thickness HDPE membranes were generally impermeable to any of the permeants at room temperature. Recent data of Okor and Anderson⁸ for sodium chloride permeant also showed that a decrease in permeation rate is associated with an increase in film thickness; the films used by these

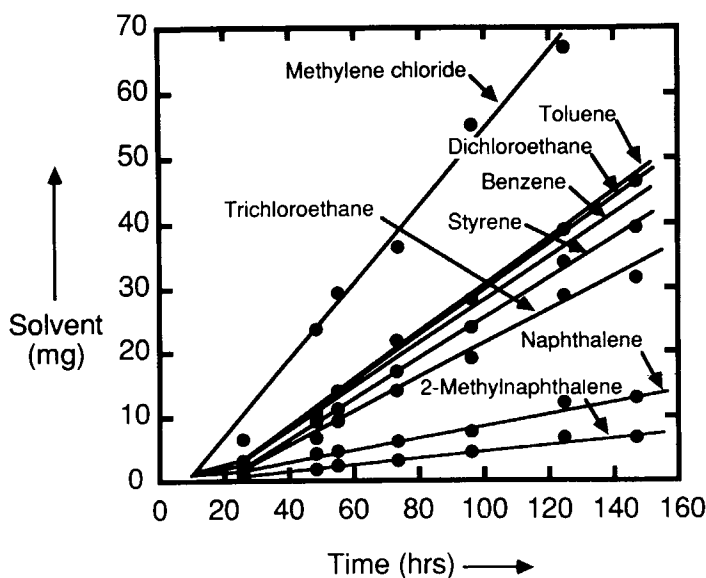


Fig. 4. Transport of permeants through 30 mil HDPE at 22°C.

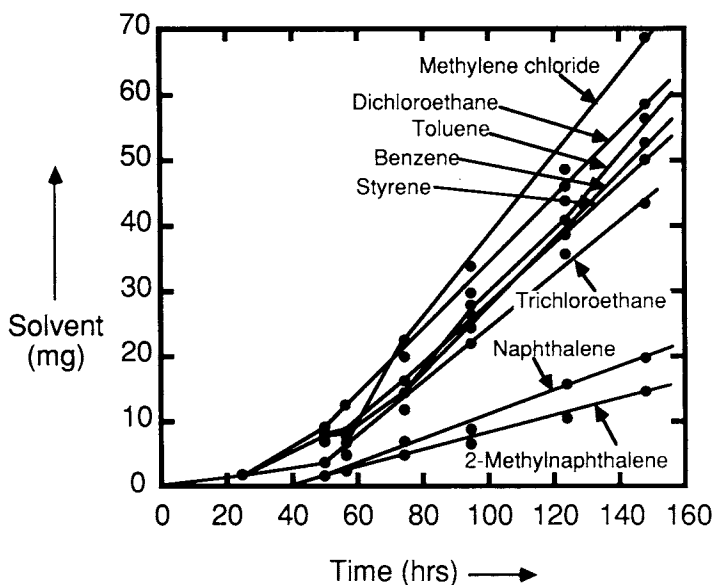


Fig. 5. Transport of permeants through 100 mil HDPE at 50°C.

TABLE IV
Permeation Rates of Various Permeants through HDPE Membranes

Permeant	Permeation Rate ($\text{g}/\text{cm}^2/\text{h}$) 10^5 at				
	22°C for		50°C for		
	30 mil	60 mil	30 mil	60 mil	100 mil
1,1,2-Trichloroethane (0.167 g/mL)	1.3	0.19	4.8	5.1	2.1
1,2-Dichloroethane (0.124 g/mL)	1.8	0.31	8.0	7.6	2.5
Methylene chloride (0.106 g/mL)	2.9	2.8	3.2	3.7	2.9
Styrene (0.130 g/mL)	1.5	0.15	5.5	5.3	2.3
Benzene (0.098 g/mL)	1.7	0.17	5.5	5.9	2.3
Toluene (0.098 g/mL)	1.8	0.16	5.6	5.7	2.5
Naphthalene (0.160)	0.40	0.04	2.4	2.2	1.0
2-Methyl naphthalene (0.178 g/mL)	0.27	—	1.5	1.30	0.77

workers were acrylate-methacrylate copolymers plasticized with glycerol triacetate or glycerol tributyrate.

CONCLUSIONS

Diffusion and permeation characteristics of HDPE membranes to several permeants has been studied to assess the potential applications of these membrane in a variety of situations. The study indicated no failure or

deterioration of the membranes justifying their continual use as protective barriers. HDPE appears to be a good liner membrane for applications in landfills and containment facilities because of its superior resistivity to chemical attack and biodegradation.⁵ At this stage, it is not known what exposure times at 50°C would be required before failure of the membrane would occur. Accelerated life testing experiments could possibly provide additional data in this area. Furthermore, it is to be noted that the immersion/weight gain method is a useful screening test for studying the transport of liquid in polymer membranes.

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References

1. P. E. Cassidy, T. M. Aminabhavi, and C. M. Thompson, *Rubber Chem. Technol.*, **56**, 594 (1983).
2. P. E. Cassidy, T. M. Aminabhavi, and J. C. Brunson, *Rubber Chem. Technol.*, **56**, 357 (1983).
3. T. M. Aminabhavi, R. W. Thomas, and P. E. Cassidy, *Polym. Eng. Sci.*, **24**, 1417 (1984).
4. B. D. Barr-Howell, N. A. Peppas, and T. G. Squires, *J. Appl. Polym. Sci.*, **31**, 39 (1986).
5. Refer to Manufacturer's specifications on resistance to soil burial, ASTM D3083.
6. EPA Test Methods for Evaluating Solid Waste (Physical/Chemical Methods) SW-846, 2nd ed., July 1982.
7. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, Oxford, 1975.
8. R. S. Okor and W. Anderson, *J. Appl. Polym. Sci.*, **31**, 291 (1986).

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