Sorption/Desorption Studies on Polypropylene Geomembrane in the Presence of Hazardous Organic Liquids

T. M. AMINABHAVI, H. G. NAIK

Department of Chemistry, Karnatak University, Dharwad -580 003, India

Received 1 April 1998; accepted 31 August 1998

ABSTRACT: Experimental results of sorption/desorption obtained from a gravimetric method are presented for a polypropylene geomembrane with various organic liquids at 25, 50, and 70°C. The sorption data have been fitted to an Arrhenius relationship to obtain the heat of sorption. The sorption/desorption data have been analyzed using an empirical equation. The swelling of the PP geomembrane has also been studied for the chosen liquids. Experimental results and the derived quantities have been discussed to study the chemical resistivity of the geomembrane. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1291–1298, 1999

Key words: geomembrane; sorption; desorption; swelling

INTRODUCTION

Polymeric geomembranes are nonporous materials that are generally impermeable to aggressive organic liquids.^{1–6} They find applications as liners in the hazardous waste chemical ponds to protect the fertile soil from contamination. Therefore, a study of the resistivity of a geomembrane to organic chemicals is important in its selection as a successful barrier material under severe service conditions. Polypropylene (PP) has been used as a liner material in sludge ponds because it is known to provide good chemical resistivity in addition to retaining its mechanical properties. In an effort to study the suitability of PP geomembrane to 14 organic chemicals that are frequently found in landfill and impoundment sites, we have measured its sorption uptake values at 25, 50, and 70°C. Desorption and swelling experiments

Contract grant sponsor: Department of Science and Technology, New Delhi; contract grant number: SP/S1/H-26/96(PRU). Journal of Applied Polymer Science, Vol. 72, 1291–1298 (1999) have also been performed at 25°C. From a temperature dependence of sorption, the heat of sorption values have been computed from the Arrhenius equation. Such a database on PP-solvent systems would be useful to the liner manufacturers, vendors, purchasers, and reviewers of permit applications to select the most chemically resistant geomembrane for a given waste site.

EXPERIMENTAL

Materials

The chemicals chosen for the study are: benzene, toluene, *p*-xylene, trimethylbenzene, methoxybenzene, chlorobenzene, 1-chloronaphthalene, dichloromethane (methylene chloride), 1,2-dichloroethane, acetone, methyl ethyl ketone, methyl *iso*butyl ketone, cyclohexanone, and butyraldehyde (all were of analytical reagent-grade samples supplied from s.d. Fine Chemicals, Mumbai, India). However, 1-chloronaphthalene and butyraldehyde were supplied from Fluka, Germany. Some important properties of these liquids are given in

Correspondence to: T. M. Aminabhavi.

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/101291-08

Liquids	Chemical Formula	V_S cm ³ /mol	μ (D)	$\overset{\delta}{(\mathrm{Jcm}^{-3})^{1/2}}$
Democra	C II	20.4	0.00	0.17
Benzene		89.4 100 0	0.00	9.17
Toluene	$C_6H_5CH_3$	106.9	0.31	8.91
<i>p</i> -Xylene	$C_6H_4(CH_3)_2$	123.9	0.02	8.77
Trimethylbenzene	$C_{6}H_{3}(CH_{3})_{3}$	139.6	0.00	8.80
Methoxybenzene	$C_6H_5OCH_3$	109.3	1.25	9.50
Chlorobenzene	C_6H_5Cl	102.2	1.62	9.68
1-Chloronaphthalene	$C_{10}H_7Cl$	137.7	1.33	а
Dichloromethane	CH_2Cl_2	64.5	1.14	9.88
1,2-Dichloroethane	$C_2 H_4 Cl_2$	79.4	1.83	9.78
Acetone	CH ₃ COCH ₃	74.0	2.69	10.00
Methyl ethyl ketone	CH ₃ CH ₂ COCH ₃	90.2	2.76	9.30
Methyl <i>iso</i> -butyl ketone	(CH ₃) ₂ CHCH ₂ COCH ₃	125.8	a	а
Cyclohexanone	$C_5H_{10}CO$	104.7	3.80	9.90
Butyraldehyde	$CH_3(CH_2)_2CHO$	89.6	а	0.43

Table I	Some Physical Properties of Liquid Penetrants: Me	olar Volume (V), I	Dipole Moment (µ), ar	ıd
Solubilit	y Parameter (δ)			

^a Data not available.

Table I. The PP geomembranes used were fabricated at NSC plant, Galesburg, IL, in sheets of dimensions $28 \times 22 \times 0.110$ cm, and were supplied by Mr. John Siebken. Some representative properties of PP geomembrane are listed in Table II.

Methods

The mass uptake experiments were performed at 25, 50, and 70°C in an electronic incubator (WTB Binder, Germany), maintained at the desired

temperature within an accuracy of $\pm 0.5^{\circ}$ C. The circularly cut disc-shaped sheet geomembrane samples (dia ≈ 2.00 cm) were conditioned to dryness in a vacuum oven at 25°C for 48 h before experimentation. These samples were then exposed to about 15–20 mL of the liquids kept inside screw-tight test bottles maintained previously at the desired temperature. The test bottles were placed inside the incubator that was calibrated with a quartz thermometer for precise temperature control. After placing the samples, the mass

Table II	Some Typ	ical Properties	s of the PP	Geomembrane
----------	----------	-----------------	-------------	-------------

Property	Method	Units	Polypropylene
Thickness	ASTM D 751, NSF mod.	mm	1.085
Density	ASTM D 1505	g/cm ³	0.91
Carbon black content	ASTM D 1603	%	2.3
Tensile Properties	ASTM D 638		
Stress at yield		MPa	_
Stress at break		MPa	18.8
Strain at yield	1.3" gage length (NSF)	%	_
Strain at break	2.0" gage or extensometer	%	_
Modulus of elasticity	ASTM D 638	MPa	
100% secant modulus		MPa	10.8
Dimensional stability	ASTM D 1204, NSF mod.	%	0.4
Tear resistance	ASTM D 1004	N/cm	692
Puncture resistance	ASTM D 4833	N/cm	2058
Water absorption	ASTM D 570 at 23°C	%	_
Water vapor transmission	ASTM E 96	g/day m ²	_

		S (mass %)		K (in g/g (mol) ⁿ)			^{<i>i</i>})
		Sorption		Desorption		Sorption		Desorption
Liquids	25°C	50°C	70°C	25°C	25°C	50°C	70°C	25°C
Benzene	157.2	294.9	464.7	62.9	5.64	6.05	6.55	11.07
Toluene	213.1	337.7	489.0	70.5	5.96	6.13	5.83	4.06
<i>p</i> -Xylene	230.3	339.6	478.6	72.2	5.08	5.95	6.64	1.14
Trimethylbenzene	215.7	319.4	428.1	71.2	4.13	4.67	5.28	0.29
Methoxybenzene	34.1	64.5	108.7	25.5	4.38	5.68	9.17	4.00
Chlorobenzene	256.3	405.2	556.6	74.3	4.06	5.59	6.36	1.06
1-Chloronaphthalene	86.6	155.5	235.3	47.1	2.22	2.88	3.03	0.24
Dichloromethane	118.7	а	а	55.2	7.01	а	а	11.03
1,2-Dichloroethane	33.6	66.0	121.0	24.7	5.12	6.86	10.15	5.49
Acetone	34.1	а	а	4.1	3.20	а	а	1.12
Methyl ethyl ketone	9.7	18.4	25.9	8.9	3.36	5.73	11.61	3.12
Methyl <i>iso</i> -butyl ketone	22.6	45.1	72.6	18.0	3.13	4.57	7.13	4.63
Cyclohexanone	21.4	49.6	84.1	16.7	2.70	3.20	4.01	3.01
Butyraldehyde	18.5	31.9	36.3	14.2	3.93	4.85	7.57	3.22

Table III Sorption and Desorption Results (S in mass %) and Parameter $K [g/g (mol)^n]$ of eq. (5) with Organic Liquids + PP Geomembrane

^a Data not obtained.

determinations were done at suitably selected time intervals by removing the samples and after wiping from the surface adhered solvent drops using a filter paper. These were then placed on a top-loading digital Mettler balance (Model AE 240, Switzerland, sensitive to (0.01 mg) to measure the mass uptake. The total time spent by the geomembrane outside the solvent container was kept within 20–30 s to minimize possible error. When the samples attained sorption equilibrium, i.e., until no mass gain occurred—which did not change significantly over a further period of 1 or 2 days—the equilibrium sorption value M_{∞} (i.e., maximum mass uptake) was considered as sorption coefficient, S expressed in g/g units.

$$M_t = \left(\frac{W_t - W_0}{W_0}\right) \times 100 \tag{1}$$

where W_0 is the initial weight of the sample, and W_t is its weight at time *t*, for the immersion period. These data are presented in Table III. The desorption expressed in mass % units was calculated as:

$$M_t = \left(\frac{W_t^d - W_0^d}{W_0^d}\right) \times 100 \tag{2}$$

Here, W_t^d refers to mass of the desorbed geomembrane at time, t and W_0^d is the mass of the polymer after complete desorption, i.e., original mass of the geomembrane.

RESULTS AND DISCUSSION

Equilibrium mass uptake values, i.e., the dynamic sorption plots of the PP geomembrane with the aromatic liquids (benzene, toluene, p-xylene, trimethylbenzene, chlorobenzene, methoxybenzene, and 1-chloronaphthalene), at 25, 50, and 70°C, as well as desorption results at 25°C, are presented in Figure 1. It is observed that at 25°C, uptake values of toluene, trimethvlbenzene, chlorobenzene, and p-xylene are higher than benzene. The uptake of methoxybenzene is the lowest, and is independent of time over longer times, whereas for 1-chloronaphthalene, the uptake increases with time. Sorption of methoxybenzene is lower than 1-chloronaphthalene, and for both these liquids, sorption values are nearly three times smaller than all the other monocyclic aromatics.

At 50°C, the sorption curves for methoxybenzene and 1-chloronaphthalene vary identically to those observed at 25°C. On the other hand, pen-



Figure 1 Sorption curves, i.e., mass % uptake (M_t) vs. square root of time $(t^{1/2})$ for PP geomembrane with (\bigcirc) benzene, (\triangle) toluene, (\Box) *p*-xylene, (\bullet) trimethylbenzene, (\blacktriangle) chlorobenzene, (\blacksquare) 1-chloronaphthalene, and (\blacktriangledown) methoxybenzene at (a) 25°C, (b) 50°C, (c) 70°C, and (d) desorption curves at 25°C.

etrants like toluene and p-xylene show almost identical sorption curves; hence, their dependencies are shown by a single curve. Benzene shows lower values of sorption than all the other substituted benzenes; chlorobenzene has the highest uptake value at 50°C. At 70°C, for all the liquids except methoxybenzene and 1-chloronaphthalene, the sorption curves show slight decreasing trends after reaching equilibrium, suggesting a leaching out phenomenon at a higher temperature. For 1-chloronaphthalene, at all temperatures the sorption curves are sigmoidal, suggesting deviations from the Fickian mode. This is because 1-chloronaphthalene is a bigger molecule (molar volume = $137.9 \text{ cm}^3/\text{mol}$), and hence, it migrates slower. The desorption of PP-penetrant systems shown in Figure 1 are indicative of the fact that low sorbing liquids show lower values of desorption and desorb much slower than the high sorbing liquids and vice versa. However, no deg-



Figure 2 Sorption curves, i.e., mass % uptake (M_t) vs. square root of time $(t^{1/2})$ for PP geomembrane with (\bigcirc) dichloromethane, (\triangle) 1,2-dichloroethane, (\square) methylethyl ketone, (\bullet) methyl *iso*-butyl ketone, (\blacktriangle) cyclohexanone, (\blacksquare) butyraldehyde, and (\triangledown) acetone at (a) 25°C, (b) 50°C, (c) 70°C, and (d) desorption curves at 25°C.

radation of the geomembrane occurred with any of the liquids studied.

In Figure 2, the mass % uptake as well as desorption data of the nonaromatic liquids viz., dichloromethane, 1,2-dichloroethane, methyl ethyl ketone, methyl *iso*-butyl ketone, cyclohexanone, acetone, and butyraldehyde are presented. At 25°C, dichloromethane shows higher sorption, while for methyl ethyl ketone, the lowest sorption is observed. With 1,2-dichloroethane and acetone, the sorption curves are almost identical and hence, a common curve is displayed for both penetrants. The equilibrium sorption values for methyl *iso*-butyl ketone, butyraldehyde, and cyclohexanone are almost the same, but only the initial sorption curves are very different. At 50°C, the % uptake curve for 1,2-dichloroethane is higher than all the other penetrants, but for methyl ethyl ketone, sorption is lowest. Other liquids exhibit intermediate sorption tendencies. The mass % uptake curves at 70°C also vary almost in the same manner as those of the sorp-



Figure 3 Arrhenius plots of $\ln S$ vs. 1/T for the PP geomembrane with (a) aromatic liquids and (b) other liquids with the same symbols as in Figures 1 and 2.

tion curves at 50°C except for 1,2-dichloroethane, for which no data at 70°C were obtained due to its lower boiling temperature. The desorption curves included in Figure 2 at 25°C indicate a rapid desorption for dichloromethane than 1,2-dichloroethane. The low sorbing penetrants like acetone, cyclohexanone, methyl ethyl ketone, methyl *iso*butyl ketone, and butyraldehyde also exhibit lower desorption rates and vice versa.

The equilibrium mass % uptake values presented in Table III show that for all the aliphatic liquids, the uptake values are generally much smaller than those observed for aromatic liquids at all the temperatures. In general, sorption increases with increasing temperature, suggesting increased segmental movements of the PP chain segments and thereby accommodating more solvent molecules at higher temperatures. This prompted us to estimate the heat of sorption, ΔH_S by fitting the ln S values with 1/T, as displayed in Figure 3. The values of ΔH_S have been computed from the relation.

$$\ln S = \ln S_0 - \frac{\Delta H_S}{RT} \tag{3}$$

The estimated values of ΔH_S are given in Table IV. The values of ΔH_S are positive for all penetrants, and these decrease systematically from benzene to trimethylbenzene, suggesting an increased driving force during their molecular transport. Furthermore, it also suggests that the

heat of condensation is positive and greater in magnitude than the heat of mixing, according to the relation: $\Delta H_{\rm mix} = \Delta H_S + \Delta H_v$. The term ΔH_S depends on heat of vaporization of the liquid, ΔH_v , so that: $\Delta H_S = H_{\rm cond} + \Delta H_{\rm mix}$. The $\Delta H_{\rm mix}$ is, therefore, a function of the interaction parameter, χ , which can be calculated as:⁷

$$\chi = \beta + \frac{V_S}{RT} \left(\delta_S - \delta_P\right)^2 \tag{4}$$

Table IV Heat of Sorption (ΔH_S in kJ/mol), Interaction Parameter, χ , and Swelling Index, α (cm³/g) of PP Geomembrane + Penetrants

Liquids	$\begin{array}{c} \Delta H_S \\ (\text{kJ/mol}) \end{array}$	χ	α (cm ³ /g)
Benzene	20.5 ± 0.2	0.36	1.80
Toluene - V-lor o	15.6 ± 0.7 12.7 ± 0.0	0.34	2.45
<i>p-</i> Aylene Trimethylbenzene	13.7 ± 0.9 12.9 ± 0.3	$0.34 \\ 0.34$	2.63 2.43
Methoxybenzene	21.8 ± 1.0	0.48	0.34
Chlorobenzene	14.5 ± 0.2	0.44	2.30
1-Chloronaphthalene	18.9 ± 0.1	а	0.69
Dichloromethane	а	0.47	0.89
1,2-Dichloroethane	24.0 ± 1.7	0.48	0.26
Acetone	а	0.53	0.05
Methyl ethyl ketone	18.8 ± 1.4	0.38	0.12
Methyl <i>iso</i> -butyl ketone	22.1 ± 0.1	а	0.03
Cyclohexanone	26.0 ± 0.8	0.57	0.23
Butyraldehyde	13.1 ± 3.2	0.34	0.17

^a Data not obtained.

where δ_s and δ_p are, respectively, the solubility parameters of solvent, and polymer, β is lattice constant whose value is generally taken as 0.34, V_S is the molar volume of the liquid, and *RT* has the conventional meaning.

To calculate χ , a prior knowledge of the solubility parameter of the polymer, δ_p is needed. The procedure suggested by Gee⁸ has been used to compute δ_p . A plot of the swelling parameter α = $[(M_a - M_b)/M_b \rho_s]$ vs. δ_s (where M_a and M_b are, respectively, mass of the geomembrane after and before liquid sorption; ρ_S is density of the solvent) was constructed, and δ_p was obtained from the maximum value of α , which was observed at a δ_s value of 9.17 $(J/cm^3)^{1/2}$ for the PP geomembrane. Using these values in eq. (4), the values of χ were calculated, and these values are also included in Table IV along with the results of α . The values of χ ranged between 0.34 to 0.57, which is expected of the rubbery polymer-solvent systems. These values are generally higher for the aromatic liquids than the nonaromatics. A similar observation also holds good for the values of α presented in Table IV.

Fractional mass % uptake results, before the attainment of 50-55% equilibrium have been fitted to the empirical relationship:^{9, 10}

$$\frac{M_t}{M_{\infty}} = Kt^n \tag{5}$$

where, M_t and M_{∞} have the same meanings as before. The values of K represent the extent of interactions between the penetrants and the geomembrane. The values of K and n have been obtained by the method of least squares, but only the results of K are presented in Table III. The values of K show a systematic increase with increasing temperature. The values of n for the present systems range between 0.50 and 0.55, suggesting the Fickian transport.^{11–17}

The dimensional response of the network PP geomembrane has been studied from a calculation of the change in volume of the geomembrane due to swelling. To measure this, we have used the experimental results of changes in thickness and diameter of the geomembrane. These measurements were done using the micrometer screw gauge and vernier calipers, respectively, within an accuracy of ± 0.001 cm. Swelling results of the PP geomembrane expressed as maximum % increase in thickness, Δh_{∞} and diameter, Δd_{∞} along with ΔV_{∞} are also presented in Table V. In gen-

Table V Percent Maximum Increase in Thickness (Δh_{∞} in cm), Diameter (Δd_{∞} in cm), and Volume ($\Delta V_{\infty}/V_0$) of PP Geomembrane

Liquids	Δh_{∞}	$\Delta {d}_{\infty}$	ΔV_{∞}
Benzene	113.1	13.75	1.76
Toluene	140.7	19.48	2.44
<i>p</i> -Xylene	145.1	21.05	2.59
Trimethylbenzene	134.6	19.60	2.36
Methoxybenzene	24.6	2.87	0.32
Chlorobenzene	129.7	17.06	2.15
1-Chloronaphthalene	41.1	4.76	0.55
Dichloromethane	66.4	6.62	0.89
1,2-Dichloroethane	21.2	2.88	0.28
Methyl ethyl ketone	8.7	1.25	0.11
Methyl <i>iso</i> -butyl ketone	16.1	2.12	0.21
Cyclohexanone	12.1	1.62	0.16

eral, high swelling of the PP geomembrane is observed for the aromatic liquids when compared to nonaromatic liquids. The swelling plots, i.e., $\Delta V_t/V_0 \text{ vs. } t^{1/2}$, are presented in Figure 4 at 25°C. It is observed that for *p*-xylene, ΔV_m is higher than toluene, which in turn, is higher than trimethylbenzene and chlorobenzene. The swelling curve for benzene is lower than all the other substituted benzenes. For methoxybenzene and 1-chloronaphthalene, swelling is lower than all the other liquids. Among the low sorbing aliphatic liquids, dichloromethane shows nearly three times higher swelling than the other aliphatic liquids.

CONCLUSIONS

Geomembranes with high resistivity to organic liquids are used as liners for hazardous waste ponds. Their primary function is to prevent leachates and liquid components of the wastes from leaking, and thereby avoiding pollution of the ground water. In the absence of actual field data on long-term performance of geomembranes, we need to use the predictive tools based on the simulated testing of geomembranes.

The goal of the present study is to identify factors that limit the long-term performance of the geomembranes, and to develop test protocols to evaluate their performance. In this article, we have presented liquid mass % uptake (sorption) and desorption data of the PP geomembrane for 14 organic liquids at 25, 50, and 70°C to show its usability in such environments. From a tempera-



Figure 4 Percent increase in volume (ΔV_m) vs. square root of time $(t^{1/2})$ for the PP geomembrane with (A) aromatic liquids, and (B) aliphatic liquids at 25°C. Symbols are the same as given in Figures 1 and 2.

ture dependence of sorption, the heat of sorption values are calculated, and these are dependent on the nature of the penetrant liquids rather than the chemical structure of the base polymer. At any rate, the choice of a particular geomembrane will depend upon the chemistry of the hazardous chemical to be retained.

The authors thank the Department of Science and Technology, New Delhi (SP/S1/H-26/96(PRU)) for major financial support of this study. Gratitude is also extended to Mr. Jack Donaldson and Mr. John Siebken of the National Seal Company, Galesburg, IL, for a supply of PP geomembranes.

REFERENCES

- 1. Cooke, J.; Rebenfeld, L. Geotextiles Geomembr 1988, 7, 7.
- John, M. W. Geotextiles; Blakie & Sons, Ltd.: London, 1987.
- Koerner, R. Designing with Geosynthetics; Prentice Hall: Englewood Cliffs, NJ, 1990.
- Haxo, H. E., Jr.; Miedema, J. A.; Nelson, N. A. Elastomerics 1985, 117, 29.

- Stastna, J.; De Kee, D. Transport Properties in Polymers; Technomic Publishing Co.: Lancaster, PA, 1995.
- Ortego, J. D.; Aminabhavi, T. M.; Harlapur, S. F.; Balundgi, R. H. J Hazard Mater 1995, 42, 115.
- 7. Hildebrand, J. H.; Scott, R. L. The Solubility of Nonelectrolytes; Reinhold: New York, 1950, 3rd ed.
- 8. Gee, G. Trans Faraday Soc 1942, 38, 418.
- Franson, N. M.; Peppas, N. A. J Appl Polym Sci 1983, 28, 1299.
- Lucht, L. M.; Peppas, N. A. J Appl Polym Sci 1987, 33, 1557.
- Harogoppad, S. B.; Aminabhavi, T. M. Macromolecules 1991, 24, 2598.
- Aminabhavi, T. M.; Munnolli, R. S.; Ortego, J. D. Polym Int 1995, 36, 353.
- Aminabhavi, T. M.; Munnolli, R. S.; Ortego, J. D. Waste Manage 1995, 15, 69.
- Aminabhavi, T. M.; Harlapur, S. F.; Balundgi, R. H.; Ortego, J. D. J Appl Polym Sci 1996, 59, 1857.
- Aminabhavi, T. M.; Naik, H. G. J Hazard Mater 1998, 60, 175.
- Harogoppad, S. B.; Aminabhavi, T. M.; Balundgi, R. H. Polym Commun 1991, 32, 120.
- Harogoppad, S. B.; Aminabhavi, T. M. J Appl Polym Sci 1992, 46, 725.