Diffusion of Organic Solvents into Polyurethane Network from Swelling Measurements

INTRODUCTION

The ability of polymeric materials to imbibe solvents and thus swell has long been a subject of several investigations.[1] Limited swelling of polymer in a solvent could be used to estimate the extent of crosslinking, molecular conformation, coil dimension, and thermodynamic flexibility among other factors.[2] This paper focuses on the limited swelling of polyurethane film in some selected solvents. Polyurethanes are among the most versatile of all polymer systems, being widely used as flexible and rigid foams, elastomers, coatings, adhesive films, and thermoplastics.[3] They usually comprise a di- or polyisocyanate, a long chain hydroxy-terminated polyol (a polyester or polyether), and a chain extender, usually a short chain glycol or diamine.

Solvent sorption and diffusion in polyurethane elastomers have been studied earlier in our laboratories[4] and elsewhere.[5-7] In severe application conditions the dimensional stability of polyurethane is an important property. Although polyurethane is known to be resistant to water and some organic solvents, a number of other solvents are known to induce the dimensional changes in it. Such changes have been rigorously treated earlier by using the hygroelastic behavior of polymers in the presence of solvents.[8] In this note, we present a new way of computing diffusion coefficient of solvent–polyurethane systems based on the volume expansivity of the polymer in the presence of a solvent due to limited swelling.

EXPERIMENTAL

Polyurethane (PU) used was obtained from PSI, Austin, Texas in sheets of 0.245 cm thickness. The base polymer is a Vibrathane B600 (Uniroyal) which was obtained from the reaction of polypropylene oxide and toluene diisocyanate. The prepolymer was cured with 4,4'-methylenebis(o-chloroaniline), i.e., MOCA, to give the desired PU. Thus, the two-phase morphology of PU consists of polyether diol as the soft segment and the aromatic diisocyanate acting as the hard segment.

Some representative engineering properties of PU are: tensile strength, 387 kg/sq cm (5500 psi); maximum percent elongation, 430; modulus for 300% elongation, 155 kg/sq cm (2200 psi); tear strength, 5 kg/sq cm (70 psi) all determined by ASTM D-470. The specific gravity is 1.101 and its T_g as found from DSC is $-43.27°C$. The solvents given in Table I are of reagent grade and double distilled before use.

The diffusion experiments at 25°C were performed by placing the circularly cut PU samples of diameter 1.9 cm, in respective liquids maintained at constant temperature taken in closed bottles. At periodic intervals the dimensional changes, i.e., increase in thickness and diameter of the samples were measured by means of a micrometer screw gauge and vernier caliperse, respectively. The precision in both of these measurements was around ±0.001 cm and in each case an average of duplicate runs were taken into account.

THEORY

In order to compute solvent diffusivity D, in the PU matrix, the diffusion equation based on Ficks formalism has been used.[9] Thus, the percent weight gain relative to the initial polymer weight $Q(t)$, of the PU sample is simply given as

$$Q(t) = \left(\frac{M_t}{W_0}\right) = \left(\frac{4}{h} \cdot \frac{M_\infty}{W_0}\right)\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \qquad (1)$$

where M_t is the weight of the liquid taken up at time t, compared to the initial weight of the dry membrane, M_∞ is the weight gain at equilibrium, h is the dry sample thickness, and D is the diffusion coefficient; the values of D calculated in this manner have been routinely used in the polymer literature.[10-12]

An alternative derivation is also possible for the disc-shaped geometry of the PU sample used in this research. In this approach, we will assume that increase in volume of the membrane at any given instant of time is proportional to the weight of the liquid taken up to that time so that

$M_t \propto$ (volume of membrane at time t

$\qquad -$ initial volume of membrane) $\quad (2)$

$$M_t = k\pi[r_t^2 h_t - r_0^2 h_0] \qquad (3)$$

$$M_\infty = k\pi[r_\infty^2 h_\infty - r_0^2 h_0] \qquad (4)$$

Table I   Sorption and Diffusion Results for Polyurethane–Solvent Systems at 25°C

Solvent	S (mol %)	$D \times 10^7$ (cm²/s) from[a] L_t^c	L_r^c	$\bar{D} \times 10^7$ (cm²/s)[b]	$D \times 10^7$ (cm²/s), Eq. (6)	n, Eq. (8)
Benzene	0.909	2.67	6.83	4.75	2.70	0.58
Toluene	0.653	1.83	3.48	2.66	2.09	0.50
p-Xylene	0.468	1.69	0.91	1.31	1.21	0.74
Mesitylene	0.334	0.98	0.88	0.93	0.52	0.50
Chlorobenzene	0.938	2.31	6.98	4.65	4.47	0.67
Bromobenzene	0.939	1.74	3.33	2.53	2.78	0.53
Nitrobenzene	0.864	0.80	1.15	0.98	0.65	0.60
o-Dichlorobenzene	0.894	1.30	1.23	1.27	1.03	0.50
Anisole	0.742	1.53	4.46	3.00	2.37	0.62

[a] Calculated from a relation similar to Eq. 6.
[b] Average of D's from L_t and L_r data.
[c] L_t and L_r represent the % increase in thickness and radius respectively.

where the k's in eqs. (3) and (4) are proportionality constants; r_0, r_t and h_0, h_t are radius and thickness of PU samples at time $t = 0$ and at longer time t, respectively. The quantities r_∞ and h_∞ represent the equilibrium values, i.e., $t = t_\infty$. Substituting for M_t and M_∞ into eq. (1), we get

$$[r_t^2 h_t - r_0^2 h_0] = \left[\frac{4(r_\infty^2 h_\infty - r_0^2 h_0)}{h}\right]\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \quad (5)$$

The left-hand side of eq. (5), i.e., $(r_t^2 h_t - r_0^2 h_0)$ is nothing

but the change in volume ΔV_t, during swelling. The term $(r_\infty^2 h_\infty - r_0^2 h_0)$ is thus equal to maximum change in volume ΔV_∞. From a least-squares analysis of the linear portion (at 50% equilibrium) of the plot of ΔV_t versus $t^{1/2}$ (see Figs. 1 and 2), the slope G can be computed, from which values of D are deduced:

$$D = \pi\left(\frac{Gh}{4\Delta V_\infty}\right)^2 \quad (6)$$

According to the theory of hygroelasticity,[8] the dimensional changes, i.e., changes in thickness Δh and radius
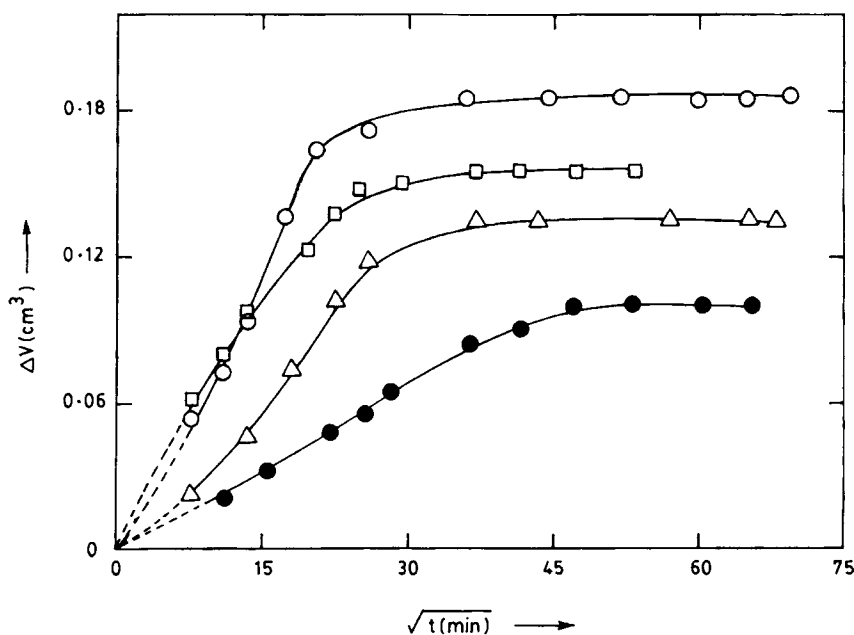

Figure 1   Volume change versus square root of time for polyurethane with benzene (○), toluene (□), p-xylene (△), and mesitylene (●) at 25°C.
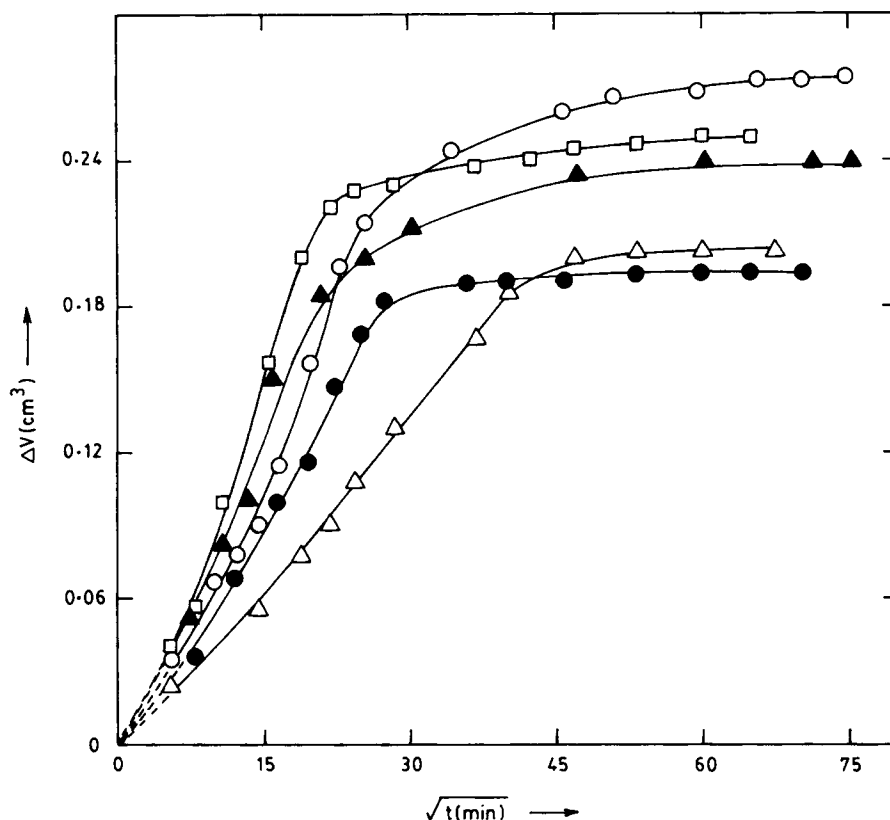
Figure 2 Volume change versus square root of time for polyurethane with o-dichlorobenzene (○), chlorobenzene (□), nitrobenzene (△), anisole (●), and bromobenzene (▲) at 25°C.

Δr, of the polymer samples can be similarly calculated by using the general equation

$$D = \pi\left(\frac{Gh}{4\Delta X_\infty}\right)^2 \qquad (7)$$

where ΔX_∞ may be either Δh_∞ or Δr_∞. Since the average values of diffusivity $\bar{D}$, as calculated from eq. (7) independently for values of Δh_∞ and Δr_∞, take into account (as a rough approximation) the isotropic swelling, then it should be identical to D values calculated from eq. (6), based on volume considerations. Various results are presented in Table I. In the linear expansion of eq. (7) $(\Delta X/X_0)^2$ is neglected relative to $(\Delta X/X_0)$.

RESULTS AND DISCUSSION

The maximum mole percent solvent sorption S in PU membranes decreases all the way from benzene to mesitylene. Similarly, there is a decreasing trend for L_t, L_r, and diffusion coefficients in case of benzene, toluene, p-xylene, and mesitylene.[4] Chlorobenzene and bromobenzene exhibit almost identical sorption behavior, but the diffusion coefficients of bromobenzene are smaller than

chlorobenzene. Diffusive trends of nitrobenzene and o-dichlorobenzene are almost identical. However, anisole exhibits S and D values which are intermediatary to benzene and toluene. It is heartening to note that there is good agreement between the average diffusivities ($\bar{D}$) and those calculated from eq. (6).

Plots of increase in volume (ΔV) due to swelling versus square root of time as shown in Figure 1 for methyl-substituted benzenes show a decreasing tendency from benzene to mesitylene via toluene and p-xylene. Such plots for other liquids are given in Figure 2. Here, o-dichloro-, chloro-, and bromobenzene exhibit higher rates of volume increases in comparison to anisole and nitrobenzene.

In order to establish the type of transport mode for PU–solvent systems, attempts have been made to fit the swelling results to an empirical relation similar to the one used for weight gain experiments.[13] Thus,

$$\log\left(\frac{V_t}{V_\infty}\right) = \log k + n\log t \qquad (8)$$

The estimated values of n lie around $\frac{1}{2}$ for some penetrants shown in Table I, suggesting the existence of a Fickian-type transport mode. However, with some other solvents like benzene, p-xylene, chlorobenzene, nitrobenzene, and

anisole, the n values tend to exceed 0.55, suggesting that non-Fickian diffusion mechanism may be operative. Such mechanisms exist when the rate of diffusion and the polymer relaxation rates are comparable. Even the appearance of sigmoidal shapes of the curves of ΔV vs $t^{1/2}$ as given in Figures 1 and 2 are a further proof that diffusion may be non-Fickian. Such anomalies have also been observed earlier.[14]

One of the most recent attempts to explain the nature and mechanism of solvent imbided into a polymer network structure is that of Smith and Fisher,[15] who related solvent uptake to its diffusivity in the polymer structure. The effect of polymer porosity has also been reported by Poinescu and co-workers.[16] There has, however, not been a precise quantitative method of solvent uptake prediction and the effects of polymer stress relaxation rate on the mechanism of solvent uptake into a network of polymer membrane. More research in this area is still needed to warrant a deeper understanding as to how the rate constant of swelling and the viscoelastic properties of the polymer will greatly influence the swelling mechanism.

CONCLUSIONS

The mechanism of limited swelling of a phase-segregated crosslinked polyurethane network in some selected commonly used industrial solvents has been studied at 25°C. The equilibrium volume increase has been used to determine diffusion and sorption coefficients. The data obtained during the course of these investigations fits a mechanistic growth model that predicts solvent uptake. This method offers a suitable and alternative way of determining the structural strength and resistance of polymers in contact with common solvents.

References

1. T. M. Aminabhavi, U. S. Aithal, and S. S. Shukla, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **C28**(3 & 4), 421 (1988).

2. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.

3. U. S. Aithal, T. M. Aminabhavi, R. H. Balundgi, and S. S. Shukla, *J. Macromol. Sci. Revs. Macromol. Chem. Phys.*,**C30**(1), 43 (1990).

4. U. S. Aithal, Ph.D. thesis, Karnatak University, Dharwad, 1989.

5. N. S. Schneider, C. F. Mee, R. Goydan, and A. P. Angelopoulos, *J. Polym. Sci. Polym. Phys. Ed.*, **27**, 939 (1989).

6. W. Nierzwicki and Z. Majewska, *J. Appl. Polym. Sci.*, **24**, 1089 (1979).

7. G. W. C. Hung, *Microchem. J.*, **19**, 130 (1974).

8. D. Cohn and G. Marom, *Polymer*, **20**, 501 (1979).

9. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon, Oxford, 1975.

10. T. M. Aminabhavi and P. E. Cassidy, *Polym. Commun.*, **27**, 254 (1986).

11. T. M. Aminabhavi, R. W. Thomas, and P. E. Cassidy, *Polym. Eng. Sci.*, **24**, 1417 (1984).

12. U. S. Aithal, T. M. Aminabhavi, and P. E. Cassidy, *Polym. Prepr.*, **30**(1), 17 (1989).

13. H. L. Frisch, *Polym. Eng. Sci.*, **20**, 2 (1980).

14. G. Astarita and G. C. Sarti, *Polym. Eng. Sci.*, **18**, 388 (1978).

15. P. M. Smith and M. M. Fisher, *Polymer*, **25**, 84 (1984).

16. I. C. Poinescu, C. Beldie, and C. Vlad, *J. Appl. Polym. Sci.*, **29**, 23 (1984).

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