

Permeation of Oxygen Through Polyurethane-Polyepoxide Interpenetrating Polymer Networks

SHOW-AN CHEN and HUI-LIN JU, *Industrial Chemistry Department, National Tsing Hua University, Hsinchu, Taiwan, China*

Synopsis

Oxygen permeation studies on polyurethane (PU)/polyepoxide (EP) interpenetrating polymer networks show that the increased crosslinking density owing to additional permanent chain entanglement (resulting from interpenetration) can decrease the coefficients of permeation, diffusion, and oxygen solubility. At 20% PU, at which the crosslinking density is maximum, these coefficients retain minimum values, while the tensile strength retains a maximum value.

INTRODUCTION

Interpenetrating polymer networks (IPNs) have been investigated extensively for their unusual physical properties, especially for their enhancement in tensile strength.^{1,2} This enhancement was attributed to the increased crosslinking density owing to permanent physical chain entanglement. However, studies on the effects of this increased crosslinking density on gas diffusional properties are scarce. Frisch et al.³ have measured water vapor permeability coefficient for polyurethane/polyepoxide IPNs and found no occurrence of maxima or minima in the composition plot. However, the diffusion mechanisms of gas and vapor in polymer were found to be different.⁴ The latter involves a vapor sorption, which can increase chain mobility, and therefore the diffusion rate, and vary the diffusion mechanism. In this work we chose oxygen as diffusate and studied how the increased crosslinking density affects the gas diffusion behavior. The IPNs studied were polyurethane/polyepoxide systems.

EXPERIMENTAL

Materials

The materials used and their description are listed in Table I. The polyols were dried at 100°C for more than 5 hr under a vacuum of about 0.1 mm Hg for removing the moisture. All other materials were used without further purification. Bromphenol blue indicator solution was prepared by dissolving 0.1 g of this indicator in 1.5 ml 1.0*N* NaOH aqueous solution and then diluting with distilled water to 1000 ml.⁶ Di-*n*-butylamine (DBA) solution, 2*N*, was prepared by diluting 338 ml DBA with toluene to 1 liter.⁶

TABLE I
Materials

Designation	Description	Source
TDI	tolylene diisocyanate (80/20 mixture of 2,4 and 2,6 isomers); reagent grade	Wako Chem. Co.
N-5018	polyester of adipic acid, ethylene glycol, and diethylene glycol; MW = 2000	Polyurethane Co.
BD	1,4-butanediol; reagent grade	Wako Chem. Co.
TMP	trimethylolpropane; reagent grade	Toyo Synthesis Co.
Epon 828	bisphenol A-epichlorohydrin resin; MW = 380; OH content = 0.06 g/100 g resin	Shell Chem. Co.
DMP-30	2,4,6-tris(dimethylamino-methylphenol)	Rohm and Hass Co.
Cellosolve acetate	reagent grade	Toyo Synthesis Co.
Di- <i>n</i> -butylamine	reagent grade	Wako Chem. Co.
Bromphenol blue indicator	extra pure	Wako Chem. Co.

PREPARATION OF NETWORKS⁵

Polyurethanes

Polyurethane (PU) prepolymer was prepared at 80°C under nitrogen atmosphere in a stirred-glass reaction kettle with reflux condenser. The procedure was to charge 20 g of tolylene diisocyanate (TDI) in the kettle, wait until 80°C was reached, then add an appropriate amount of the polyester polyol, N-5018, slowly (NCO/OH mole ratio 2/1) in order that one of the two hydroxyl group in each polyol molecule could react with one molecule TDI. The reaction was allowed to proceed until the theoretical isocyanate content was reached (about 6 hr) as determined by the di-*n*-butylamine method.⁶

The prepolymer was diluted to 50% by weight with cellosolve acetate, and then an equivalent weight of a mixture of 1,4-butanediol (BD) and trimethylolpropane (TMP) (mole ratio 3/1) was added as chain extender and curing agent. The solutions with and without 0.5% 2,4,6-tris(dimethylaminomethylphenol) (DMP-30) were then cast on an aluminum sheet coated with a thin layer of silicone releasing agent and cured at 135°C for 5 hr in a dry atmosphere to obtain PU film 0.02 cm thick. The gel time was about 25 min.

Polyepoxides (EP)

Epon 828 (bisphenol A epichlorohydrin resin) was diluted to 50% by weight with cellosolve acetate; then 2% by weight DMP-30 was added. Films were prepared as above. The gel time was about 1 hr.

Interpenetrating Polymer Networks (IPNs)

Epoxy resin solutions with DMP-30 were first heated at 135°C for 30 min and then mixed with PU solutions to yield 20/80, 25/75, 50/50, and 75/25 by weight of PU/EP solutions. The solutions were then cast into films as described above.

Measurements

Tensile Elongation

The tensile elongations at break were measured using a Dillon Universal Testing Machine at room temperature and a cross-head speed of 2 in./min. Specimens were 0.125-in.-wide dumbbells. Results reported were the average of six specimens.

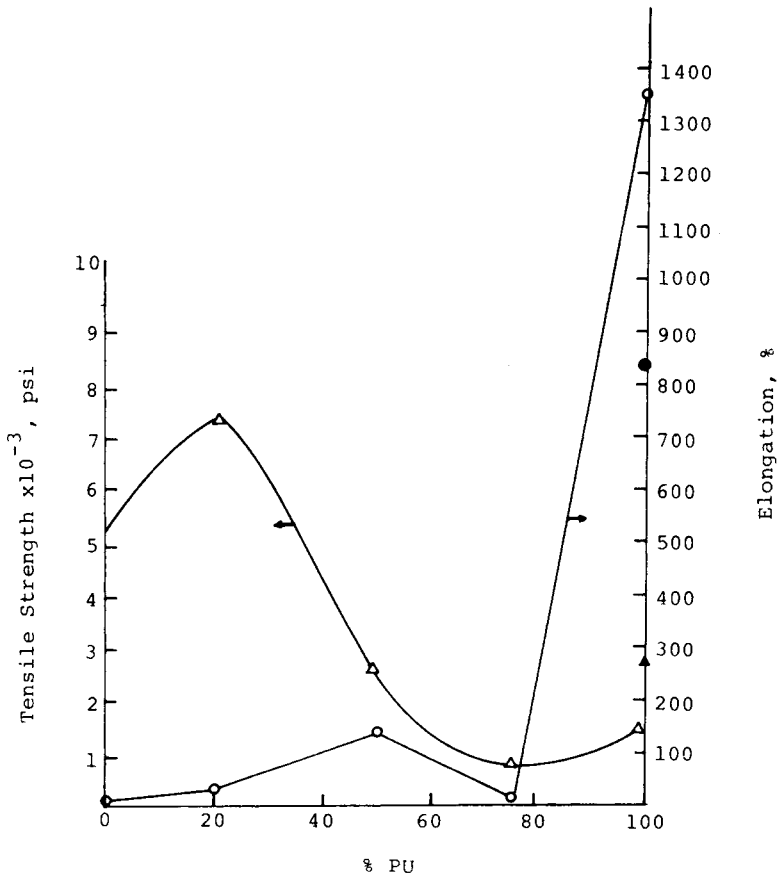


Fig. 1. Tensile elongation vs. polyurethane concentration; (●) and (▲) designate tensile strength and % elongation, respectively, of PU cured in the presence of DMP-30.

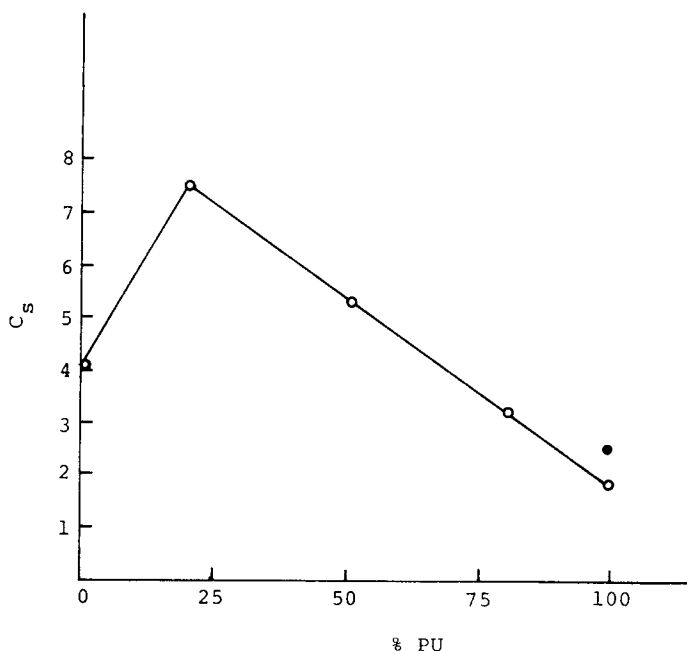


Fig. 2. Crosslinking density parameter (C_s) vs. polyurethane concentration: (●) designate C_s of PU cured in the presence of DMP-30.

Crosslinking Density

Crosslinking densities of the films were measured using the swelling method⁷ and characterized by the parameter C_s expressed as volume of the film in ml before swelling per gram of solvent swelled:

$$C_s = w_0/\rho(w_2 - w_1)$$

where ρ is the density of unswelled sample and w_0 , w_2 , and w_1 are, respectively, the weights of the film before immersing in toluene, after immersing in toluene until swelling equilibrium is reached, and after evacuating the swelling solvent at 60°C until constant weight is reached.

Dynamic Mechanical Properties

Dynamic mechanical properties at various temperatures were measured using a Dynamic Rheovibron DDV-II from the Toyo Measuring Instrument Co. Measurements were made at a frequency of 110 Hz, heating rate of 1°C/min, and temperature interval of 2–3°C. The temperature of which $\tan \delta$ gives a maximum value was regarded as the phase transition temperature.

Oxygen Permeations

Oxygen permeations through the films were measured using an Aminco-Goodrich No. 766-F gas permeability apparatus at 40 and 50°C and a pressure drop of 5 atm. Oxygen permeation coefficient P was calculated using

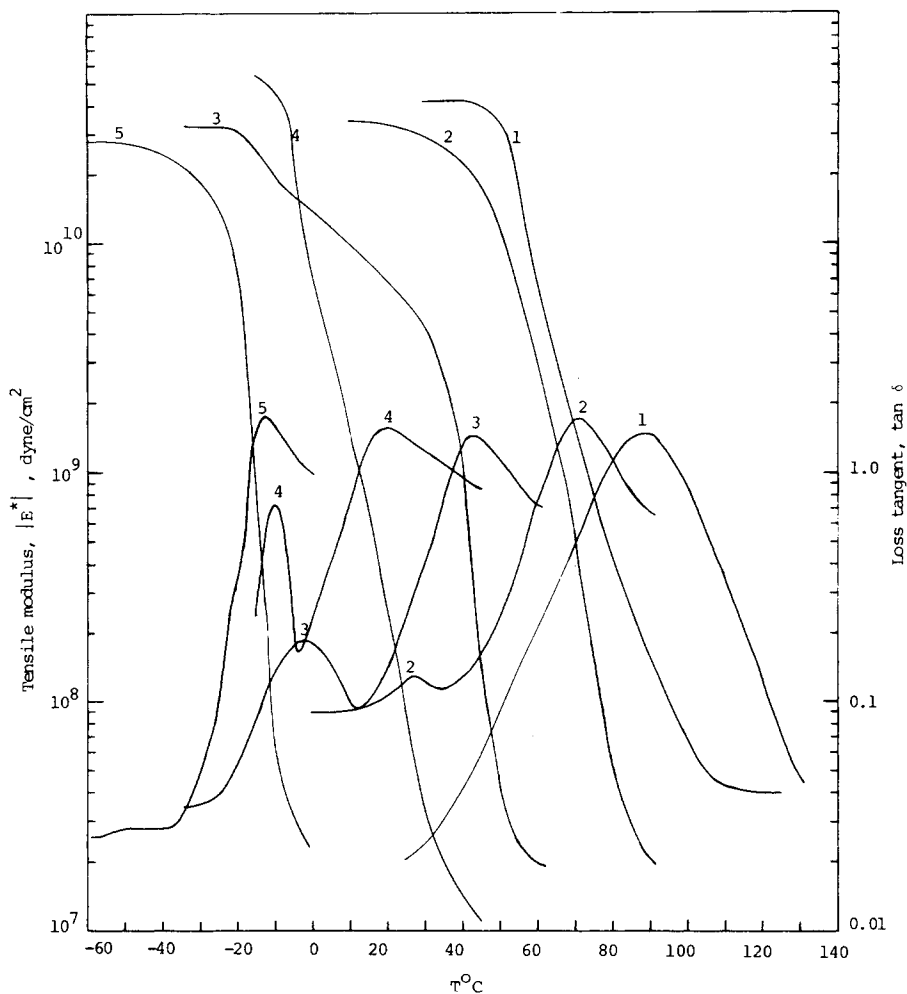


Fig. 3. Dynamic mechanical properties vs. temperature of the IPNs. % PU: (1) 0; (2) 20; (3) 50; (4) 75; (5) 100.

$$P = V_r l / A \Delta P$$

where V_r is the volume of gas permeated (based on 23°C and 1 atm) per sec at steady state, l is the film thickness in cm, A is the film cross-sectional area for gas permeation, and ΔP is pressure drop. The diffusion coefficient D was calculated from data of total permeation Q_t versus time using Barrer's time lag method⁴:

$$D = l^2 / 6\lambda$$

where λ is the time at which the extrapolated linear portion of the Q_t curve (steady-state portion) intersects the time axis. The solubility coefficient S of oxygen in the film was then calculated using the relation⁴

$$P = DS$$

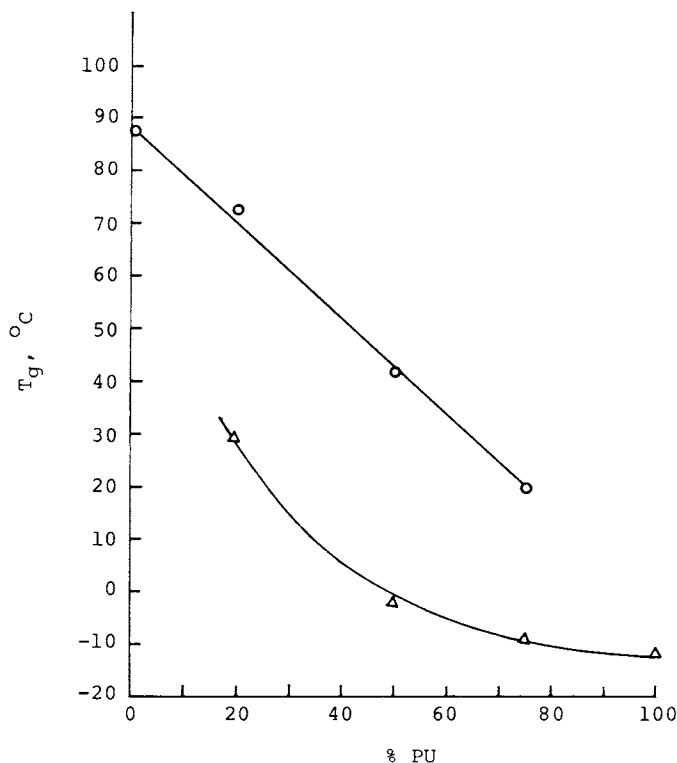


Fig. 4. Phase transition temperature vs. polyurethane concentration: (O) EP-riched phase; (Δ) PU-riched phase.

RESULTS AND DISCUSSION

Tensile Elongation Properties and Crosslinking Densities in the Polymer Blends

The tensile elongation properties of IPNs are shown in Figure 1. The tensile strength curve shows a maximum at 20% PU and a minimum at 75% PU. The % elongation increases slightly with increasing PU content, except at 75% PU. The crosslinking densities of IPNs in Figure 2 show that there is a maximum at 20% PU as in the case of tensile strength.

From these two property curves, we know that our polyblends are IPNs as those produced by Frisch et al.⁵ Thus, the maximum in tensile strength at 20% PU can be attributed to the increase in crosslinking density owing to permanent physical chain entanglement resulting from interpenetration,⁵ while the minimum in tensile strength at 75% polyurethane, is probably due to weakening of the polyurethane structure resulting from disruption of hydrogen bonding. The reasons why the increased crosslinking density was mainly due to permanent physical chain entanglement rather than to copolymerization were given in the work of Frisch et al.,⁵ who noted that this occurrence of maximum tensile strength cannot be caused by a rubber toughening effect owing to the presence of a rubber phase in the glassy matrix (the heterogeneity of the IPNs is discussed in the next section). The reason is that the toughening effect is usually characterized by a decrease in tensile stress and an increase in elongation and in the area below

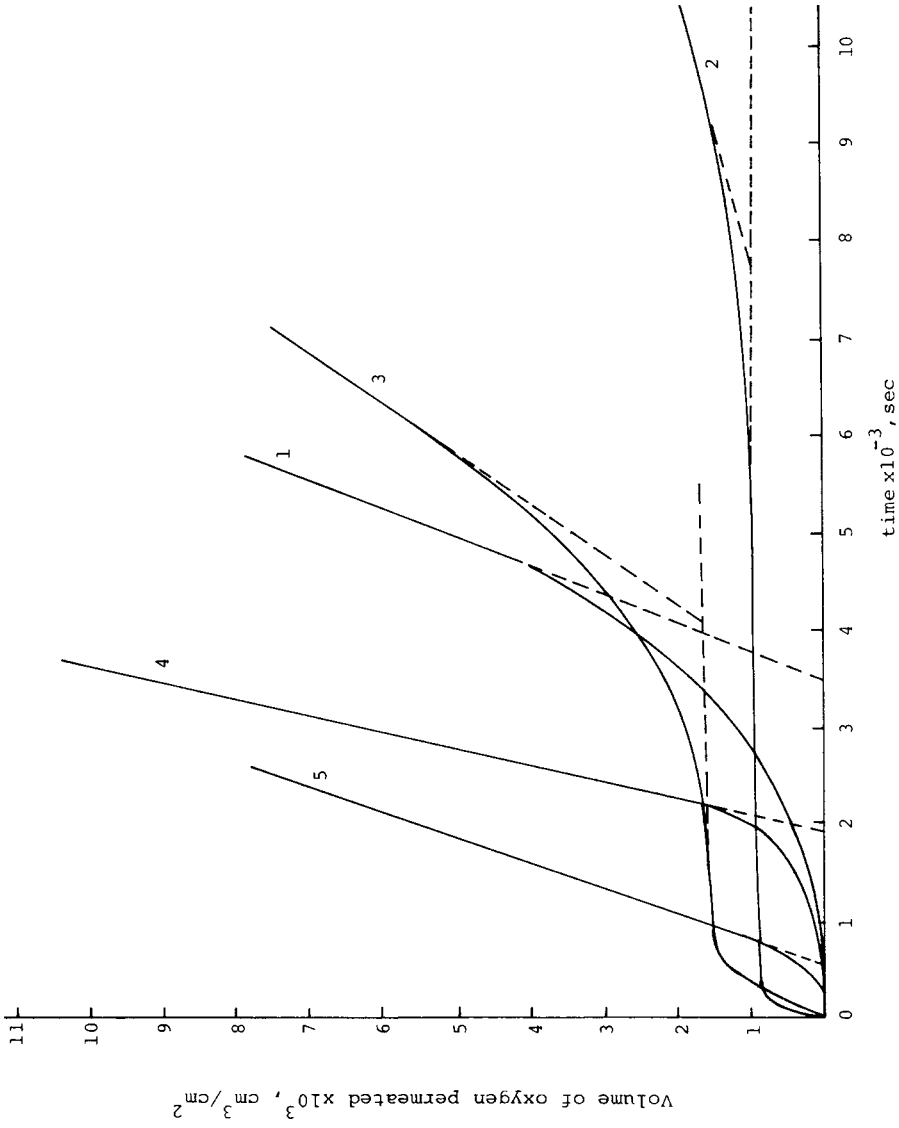


Fig. 5. Total volume of oxygen permeated per unit area vs. time at 40°C . % PU: (1) 0; (2) 20; (3) 50; (4) 75; (5) 100.

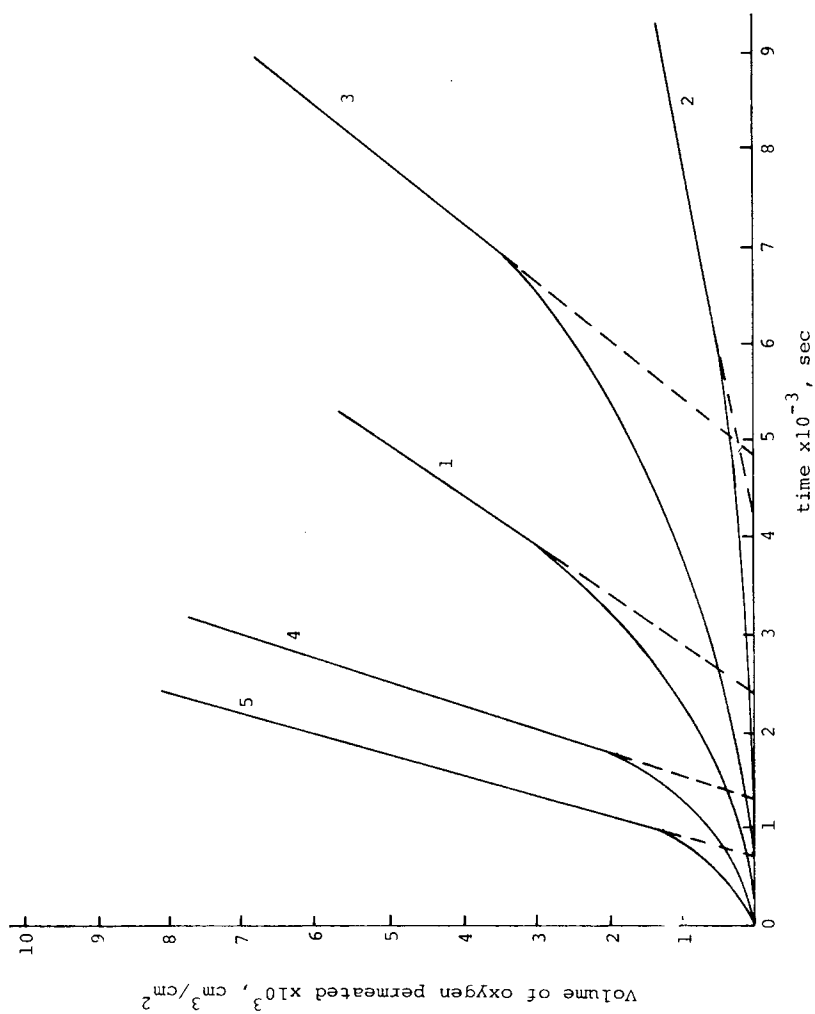


Fig. 6. Total volume of oxygen permeated per unit area vs. time at 50°C. % PU: (1) 0; (2) 20; (3) 50; (4) 75; (5) 100.

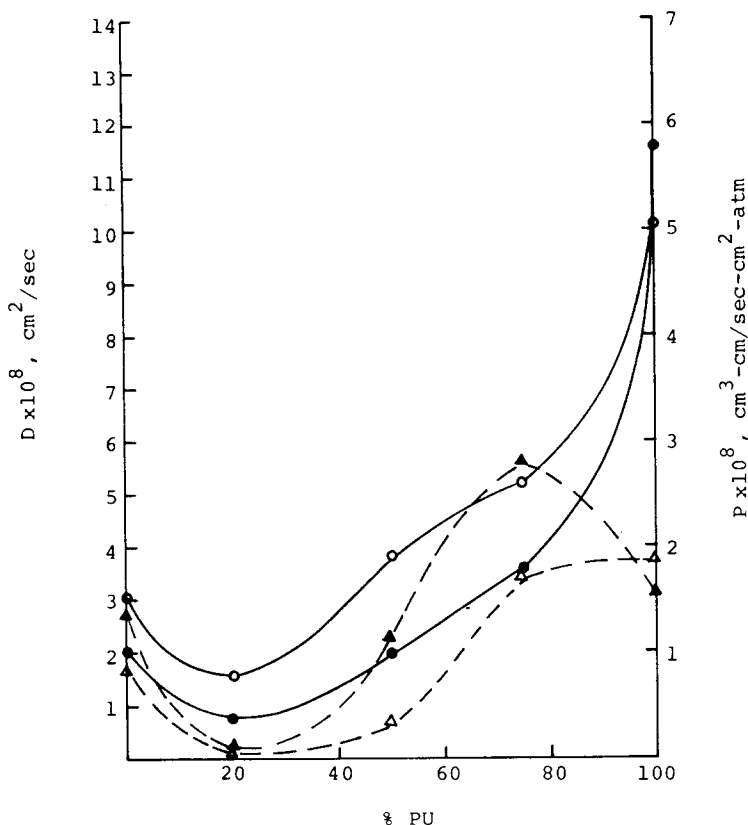


Fig. 7. Coefficients of diffusion and permeation vs. polyurethane concentration at 40 and 50°C: (●) D at 40°C; (○) D at 50°C; (▲) P at 40°C; (△) P at 50°C.

the tensile elongation curve. In our case, the elongation at the maximum tensile strength is very small, implying that at this composition the IPN is not the toughest one.

Dynamic Mechanical Properties

The dynamic mechanical properties (tensile modulus $|E^*|$ and loss tangent $\tan \delta$) versus temperatures are shown in Figure 3. $\tan \delta$ curves show that each IPN has two-phase transition temperatures as indicated by two maxima, one related to the PU-rich phase and the other to the EP-rich phase. These two transition temperatures in each IPN are different from those of the pure polymers; they shift toward each other as shown in Figure 4. The degree of shifting increases with increasing concentration. The amount of PU-rich phase in each blend is smaller than that of the PE-rich phase, even for IPNs containing 50 and 75% PU. The $\tan \delta$ curve of IPNs containing 20% PU shows a fairly small damping peak for PU-rich phase, indicating a better mixing than in the other two blends. This is also confirmed by the location of maximum crosslinking density at 20% PU in Figure 2.

From $|E^*|$ curves it can be seen that at room temperature, IPNs containing 20 and 50% PU are in the glassy state and the nearly glassy state, respectively.

Since PU at room temperature is in the rubbery state, it has a low $|E^*|$ value, about 10^7 dyn/cm². This would indicate that the phase structure in these two IPNs would be either of the continuous phase (EP-rich phase)/dispersed phase (PU-rich phase) type or of the interwoven phase network type. For IPNs containing 75% PU, the $|E^*|$ value is in rubbery state, about 10^8 dyn/cm², and the $\tan \delta$ peak for PU-rich phase is sharp, indicating that the continuous phase is the PU-rich phase and the dispersed phase is the EP-rich phase.

Oxygen Permeation

Oxygen permeation measurements were carried out for IPNs at 40 and 50°C, as shown in Figures 5 and 6. In Figure 5, oxygen permeations at 40°C through films of EP, PU, and IPNs containing 75% PU were found to follow Fick's law. But for films of IPNs containing 20 and 50% PU, permeations were two-stage as in the case of vapor sorption of sorption of polymer at its glass transition region. The permeation rates were very fast at the beginning, then decreased to zero for a period of time, and finally rose and reached steady-state values.

This two-stage phenomenon is probably due to the fact that as oxygen molecules diffuse to the surface of the film, the phase which has a transition temperature close to 40°C suddenly expands as a result of rapid initial absorption of oxygen.⁴ This expansion then extends the underlying layer of this phase which rapidly admits oxygen. The expansion further propagates through the film via this phase. During this period, the oxygen molecules also diffuse into the other phase, which is at the glassy state or rubbery state in our case. However, the rate is much slower. This gives a high initial permeation rate. As oxygen diffuses to the interfaces between these two phases, microcracks are probably created. As the number of microcracks increases, the rate of oxygen diffusing into the film and then penetrating into the glassy or rubbery phase becomes much faster than that through the phase in the transition state. This causes no visible permeation during this period. As oxygen passes through the glassy or rubbery phase, the rate rises and then reaches a steady state.

For IPNs containing 20% PU, the EP-rich phase at 40°C was in the glassy state and the PU-rich phase in the glass transition region. For IPN containing 50% PU, the EP-rich phase at this temperature was in the glass transition region, and the PU-rich phase was in the rubbery state. Since permeation through rubbery material is faster than through glassy material, permeation in the latter film reached a steady state faster than that in the former. For IPNs containing 75% PU, both phases were in the rubbery state and the diffusion was one stage.

The above explanation for the two-stage phenomenon is in favor of the aforementioned interwoven phase network structure for IPNs containing 20 and 50% PU. If they were of continuous/dispersed phase structure, then the IPNs containing 20% PU would not give a rapid initial permeation rate (but this is not the case).

For permeation at 50°C, as illustrated in Figure 6, the permeation curves show that the diffusion followed Fick's law and was one stage. For IPNs containing 50 and 75% PU, both phases in each IPN were in the rubbery state or nearly rubbery state; the permeation was of course one stage. For IPNs containing 20% PU, the EP phase was in the glassy state, while the PU phase was in the rubbery state, so the diffusion also followed Fick's law.

TABLE II
Coefficients of Diffusion (D), Permeation (P), and Solubility (S) at 40 and 50°C

PU %	$D \times 10^8, \text{cm}^2/\text{sec}$		$P \times 10^8, \text{cm}^3 \text{cm}/\text{sec cm}^2 \text{atm}$		S, atm^{-1}	
	40°C	50°C	40°C	50°C	40°C	50°C
0	2.07	3.02	1.38	0.853	0.665	0.282
20	0.79	1.55	0.117	0.059	0.148	0.038
50	2.04	3.82	1.17	0.345	0.576	0.090
75	3.56	5.21	2.82	1.76	0.790	0.338
100	11.6	10.1	1.59	1.89	0.137	0.187

The permeation coefficient P , the diffusion coefficient D , and the oxygen solubility coefficient S were calculated using the permeation data in Figures 5 and 6. The time lag method was used to calculate D . For cases where two-stage diffusion occurred, the time lags were determined by extrapolating the steady-state permeation curve to intersect with the horizontal line which is tangent to the horizontal portion of the permeation curve. This is reasonable, since the permeation rate was nearly zero at the beginning of the second stage. The period of time for the first stage could be considered as time required for the oxygen gas to arrive at the interfaces of the rubbery or glassy phase. P , D , and S of the IPNs versus composition are given in Figure 7 and Table II.

Figure 7 shows that at 20% PU, P , D , and S retain minimum values at 40 and 50°C. This can be attributed to the increased crosslinking density owing to permanent physical chain entanglement. At 75% PU, P at 40 and 50°C were retained maximum values. This can be attributed to the disruption of hydrogen bonding in PU, causing more room for dissolving the oxygen.

CONCLUSIONS

Interpenetrating polymer networks at a certain composition at which the increased crosslinking density owing to physical chain entanglement is maximum impart a minimum permeability coefficient, diffusion coefficient, and solubility coefficient of gas.

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