Water Vapor Diffusion in Polymer Networks

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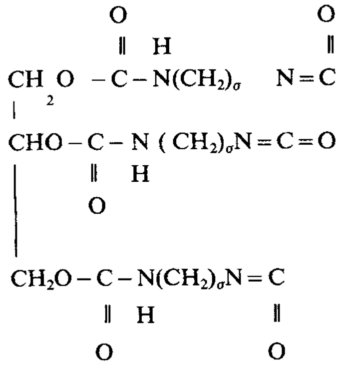
Polymeric materials are used and stored in a wide range of humidity conditions. Therefore, much research has been carried out (Dement'ev, 1989; Pranjoto, 1991; Jou, 1992) on the diffusion and sorption patterns of water vapor in polymers, the state of sorbed water, and the chemical and physical properties of polymers. Network formation from the reaction of a multifunctional isocyanate prepolymer with moisture is an established technology for coatings. In this method, isocyanate groups of the prepolymer will interact with water to become amines. Amines will then interact with isocyanates, so there is a competition for isocyanates between water and amines. When water enters into the polymer networks, it will plasticize the polymer and react with unreacted isocyanates. To avoid ambiguity, diffusion studies were carried out on well-cured polymer networks.

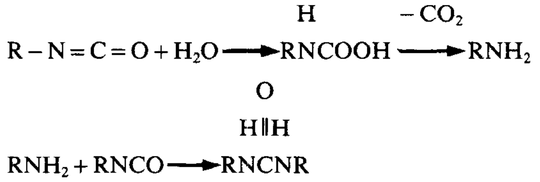
Experimental Studies

Materials

The prepolymer used in this experiment is Desmodur N-100 purchased from Mobay Corporation. The prepolymer is a mixture of oligimers based on 1,6-hexamethylene diisocyanate. The major component of this prepolymer is a tri-isocyanate having the following chemical structure:



The isocyanate groups present in the prepolymer react with water vapor, leading to the formation of polymer networks. The two reactions involved are (Flory, 1953):



$$R-N=C=O+H_2O \longrightarrow R\overset{H}{N}COOH \xrightarrow{-CO_2} RNH_2$$

$$RNH_2+RNCO \longrightarrow R\overset{H}{N}\overset{O}{\overset{\|}{C}}\overset{H}{N}R$$

Film preparation

Films of Desmodur N-100 were drawn on glass plates with a draw-down knife. The glass plates were then placed in a closed chamber. The bottom of the chamber was filled with water to ensure that the prepolymer was cured under constant temperature and 100% relative humidity. Film thickness was measured by a micrometer. The micrometer was calibrated and zeroed in by applying equal pressure on both sides of the film. The accuracy of the micrometer was ±0.1 mil.

Reaction of the isocyanate groups

The film was dissolved in toluene overnight, so that the unreacted prepolymer would leach into the solvent. Excess di-*n*-butylamine was added to react with the unreacted prepolymer. Then, titration was achieved using HCl solution. The converted groups were defined as the difference between the initial and unreacted isocyanate groups. The extent of reaction (x) was calculated as the ratio of converted groups to initial isocyanate groups.

Glass transition temperature determination

The glass transition temperatures (T_g) of the films were measured with a Perkin-Elmer DSC-7 instrument. The sample pans were sealed, but water could still come out. The heating rate used in each experiment was 20°C/min. The midpoint of the jump in the specific heat of a second thermal scan was taken as T_g. The sample weight was about 10–15 mg.

Vapor diffusion experiments

The amount of water vapor absorbed by a moisture-cured polymer was measured by a CAHN 2000 microbalance. The sensitivity of the measurement was ±1 μg. The temperature

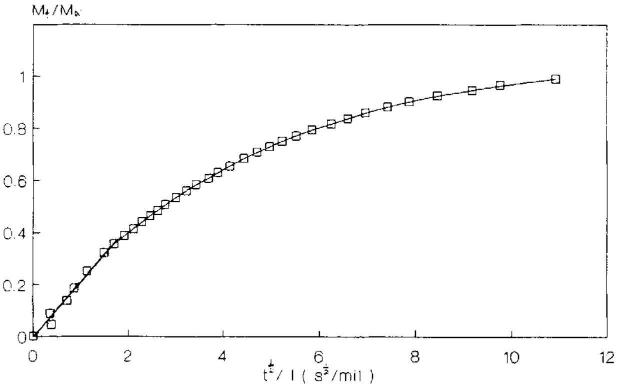


Figure 1. Typical sorption curve taken from desorption at 40°C.

Pressure changed from 4.8 to 3.4 cm·Hg.

of the sorption chamber was controlled to ±0.2°C. Successive sorption methods were applied to study the solubility and diffusivity of water vapor in polymer networks. The diffusion coefficient D was calculated from the initial slope of the sorption or desorption curve, that is, the plot of M_t/M_∞ against $t^{1/2}/\ell$, where M_∞ is the equilibrium sorption (or desorption), M_t is the amount sorbed at time t, and ℓ is the film thickness. A typical curve for the Fickian diffusion is shown in Figure 1. The standard equation,

$$D=\frac{\pi}{16}\left[\frac{d(M_t/M_\infty)}{d(t^{1/2}/\ell)}\right]^2, \tag{1}$$

was used for the calculation (Crank, 1973; Crank and Park, 1981).

Results and Discussion

Reaction kinetics

The extent of reaction between water vapor and the isocyanate groups is shown in Figure 2 and well represented by Eq. 2 with a correlation coefficient of 0.99:

$$x=100[1-\exp(-kt)] \tag{2}$$

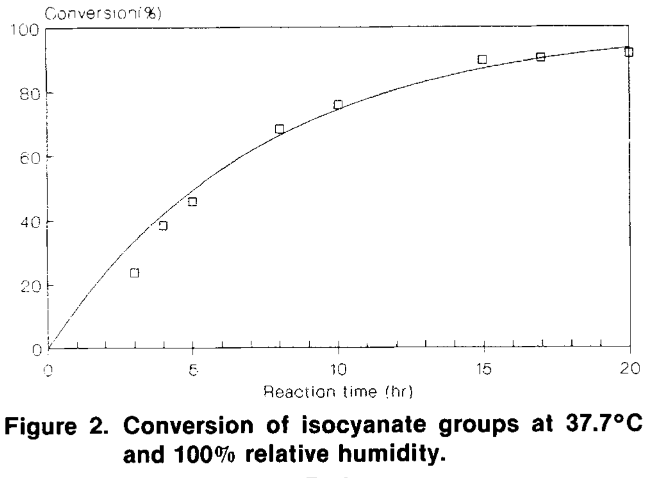


Figure 2. Conversion of isocyanate groups at 37.7°C and 100% relative humidity.

□, data points; ——, Eq. 2.

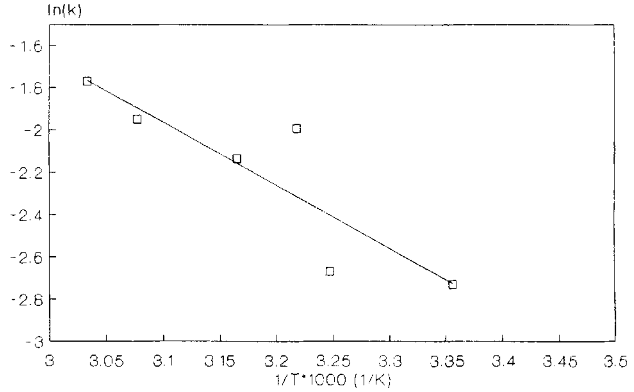


Figure 3. Relationship between reaction constant and temperature.

□, data points; ——, regression line.

where x is the percentage conversion of the isocyanate moiety, t is the reaction time (h), and k is a constant. The form of Eq. 2 is typical of a first-order irreversible reaction with a rate constant k (Levenspiel, 1972). The value of k at 37.7°C is 0.136 h^{-1}. A plot of ln k vs. $1/T$ (Figure 3) is approximately linear and can be represented by Eq. 3:

$$\ln k=7.26-2977/T \tag{3}$$

From the slope of the plot, the activation energy of the reaction is calculated to be 5.9 kcal/mol.

Glass transition temperature

Because additional reaction of the residual isocyanate groups with water vapor may occur during the sorption experiments, at least in the films for which the curing reaction is incomplete, the glass transition temperatures after sorption experiments have also been measured. These values are listed in Table 1, in which T_i and T_f represent the beginning and end of the glass transition region. It is known that when a polymer absorbs water, T_g of the polymer decreases due to the plasticization effect of water. The effect of water on T_g was minimized because the second thermal scan of DSC was taken as T_g. Therefore, in each case, T_g increased, and the transition range became narrower after the sorption experiment due to additional reactions between water vapor and the residual isocyanate groups. From the sorption data which will be described later, at a relative pressure of 0.9, 100-g polymer networks absorbed about 6 g of water; therefore, the extent of swelling is not great.

Table 1. Glass Transition Temperatures Before and After Sorption Experiments

Reaction T (°C)	Reaction Time (h)	Before Sorption			After Sorption		
		T_g (°C)	T_i	T_f	T_g (°C)	T_i	T_f
35	20	107	96	116	111	105	115
42.8	18	103	98	110	107	101	112
43	18	106	99	112	111	105	117
60	18	108	103	113	111	107	115
60	18	104	99	109	111	108	114

* Heating rate = 20°C/min

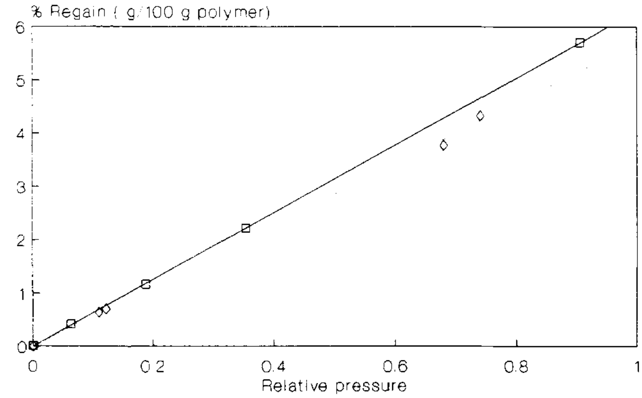


Figure 4. Equilibrium desorption isotherm.
□, 42.5°C; ◇, 57°C.

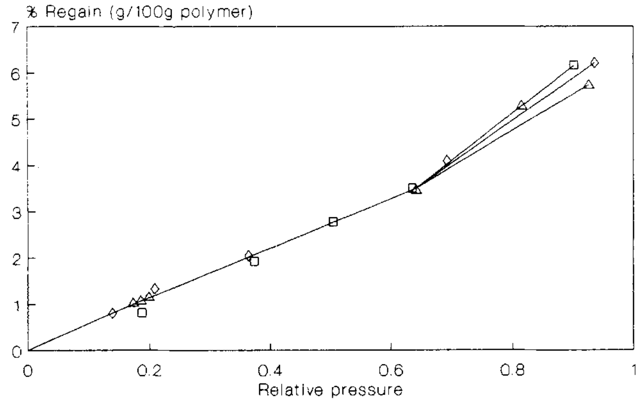


Figure 5. Equilibrium sorption isotherm.
□, 41.5°C; ◇, 49.8°C; △, 56.8°C.

Diffusion of water vapor in polymer networks

To eliminate the effect of incomplete reaction, a film cured at 60°C for 18 h with an initial conversion of 95% was exposed to several sorption-desorption cycles.

After several sorption-desorption cycles, the film was subjected to successive sorption and desorption experiments. The equilibrium desorption data collected at 42.5°C and 57°C are shown in Figure 4. Relative pressure is the ratio of operating pressure to saturated pressure. Saturated pressure can be calculated from the steam table. The enthalpy of desorption calculated using Clapeyron equation was −1.40 kcal/mol. The magnitude of the enthalpy is typical of water sorption in polar polymers. The sorption curves in Figure 5 lie slightly below the desorption curves when the relative pressure is less than 0.6; the difference is about 3% at 42.5°C. There is no significant difference in the amounts absorbed at three temperatures: that is, the temperature coefficient is near zero. Although the discrepancy between sorption and desorption results is outside the range of experimental error, we have not attempted to resolve the difference. When the relative pressure is higher than 0.6 (regain larger than 3%), the sorption curves deviate from linearity due to clustering of water molecules, and the amount of water sorbed at lower temperatures is higher. This is consistent with the negative enthalpy value found in desorption experiments.

If the diffusion coefficient depends on concentration, $D = D_o^* f(C)$, the average diffusion coefficient, $\bar{D}$, obtained from the experiments is related to $f(C)$ by Eq. 4 (Crank and Park, 1981):

$$\bar{D} = D_o \int_{C_i}^{C_f} f(C)\,dC/(C_f - C_i) \qquad (4)$$

Desorption results at three different temperatures are listed in Table 2. The concentration dependence of D can be approximated by an empirical equation:

$$f(C) = \exp(\alpha C) \qquad (5)$$

The D_o values determined at three different temperatures, 41.5, 49.8 and 56.8°C, are 1.11, 2.26 and 4.40×10^{-9} cm$^2 \cdot$s^{-1}, respectively, and the corresponding α values are 0.68, 0.63, and 0.59. Thus, D_o increases with temperature as one would expect, but α decreases with increasing temperature. Linear dependence of ln D_o and α on $1/T$ can be expressed as:

$$\ln D_o = 8.81 - 9{,}260.4/T$$

and

Table 2. Desorption Experiments at Three Different Temperatures

	Pressure Range (cm·Hg)		Rel. Pres.	C (μg)	Regain (%)	$\bar{D}$ (10^{-9} cm^2/s)	
	P_2	P_1				Exp.	Cal.
a	5.41	3.81	0.902	1,244	6.245	47.8	48.4
	3.81	2.87	0.636	942	4.729	—	
	2.87	2.06	0.477	766	3.845	—	
	2.06	0.00	0.345	634	3.183	3.93	3.95
b	8.48	5.87	0.936	1,202	6.034	55.12	58.20
	5.87	3.81	0.641	813	4.081	21.74	21.03
	3.81	1.75	0.416	584	2.932	—	
	1.75	0.00	0.191	390	1.958	4.41	4.46
c	10.80	7.95	0.840	826	4.147	37.69	38.55
	7.95	6.35	0.617	630	3.163	24.97	23.57
	6.35	3.87	0.494	499	2.505	—	
	3.87	0.00	0.312	326	1.637	7.37	7.41

C = desorbed water weight; film cured at 60°C for 18 h; operating temperature, (a) 41.5°C, (b) 49.8°C, and (c) 56.8°C.

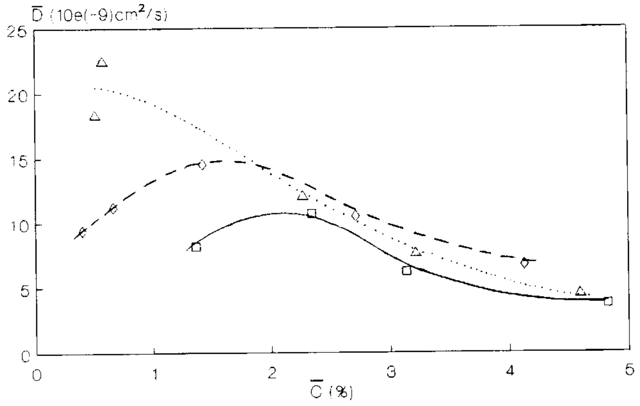


Figure 6. Concentration dependence of *D* from successive sorption.
□, 41.5°C; ◇, 49.8°C; △, 56.8°C.

$$\alpha = -1.23 + 600.6/T$$

The temperature coefficient of D_0 corresponds to an apparent activation energy of 18.4 kcal/mol. This high activation energy compared to the values for other polymers is most likely due to the restricted segmental mobility in the cross-linked structure.

Unlike the D values determined from successive desorption experiments, the diffusion coefficients obtained from successive sorption experiments change with concentration in a more complex manner. At relative pressures below 0.6, the diffusion coefficient increases with water concentration, but a further increase in relative pressure causes a marked drop in D (Figure 6). The decrease in D is again most likely due to water clustering.

Conclusion

We came to the following three conclusions:

1. The reaction between N-100 prepolymer and water vapor obeyed the first-order irreversible kinetics.
2. The glass transition temperatures of polymer networks were between 104°C and 108°C. The T_g values increased after the sorption experiments due to the reaction between water vapor and the residual isocyanate groups.
3. An exponential dependence of D on concentration was found to fit the $\overline{D}$ values calculated from successive desorption experiments. The value of D_o increases at higher temperatures, while the magnitude of α decreases. However, the diffusion coefficients determined by the successive sorption method have a more complex concentration dependence.

Acknowledgment

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Literature Cited

Crank, J., *Mathematics of Diffusion*, Oxford Univ. Press, London (1973).

Crank, J., and G. S. Park, *Diffusion in Polymers*, 4th ed., Academic Press, London (1981).

Dement'ev, A. G., T. K. Khlystalova, and I. I. Mikheyeva, "Diffusion and Sorption of Water Vapor in Polyurethane Foam," *Polym. Sci. U.S.S.R.*, **31**, 2291 (1989).

Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, New York (1953).

Jou, J., and P. Huang, "Compatability Effect on Moisture Diffusion in Polyimide Blends," *Polym.*, **33**, 1218 (1992).

Levenspiel, O., *Chemical Reaction Engineering*, 2nd ed., Wiley, New York (1972).

Pranjoto, H., and D. D. Denton, "Gravimetric Measurements of Steady-State Moisture Uptake in Spin-Coated Polyimide Films," *J. of Appl. Polym. Sci.*, **42**, 75 (1991).

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