# NOTE

# Diffusion of CFC 11 and Hydrofluorocarbons in Polyurethane

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Received 17 September 1997; accepted 6 January 1998

Key words: diffusion; permeability; blowing agents; polymer foam

## **INTRODUCTION**

Since Rowland and Molina first warned that the chlorine from chlorofluorocarbons (CFCs) could destroy ozone in the stratosphere, there has been extensive scientific and political controversy over the fate of these chemicals.<sup>1</sup> Recent observations of ozone depletion over the Arctic supported the hypothesis that the ozone loss is owing to photochemical process.<sup>2</sup> Because CFCs are so stable, they can reach the ozone layer before being destroyed by a natural process. As a result, in 1987, the nations of the world agreed in Montreal to implement regulatory controls by calling for a 50% cutback in yearly CFC production by the end of the century. The protocol was strengthened in 1992 in Copenhagen to cease CFC production after 1995 in developed countries. Therefore, hydrofluorocarbons (HCFCs) were developed to replace CFCs after the Montreal protocol, and can be used until 2030. Although HCFCs still contain chlorine, they are more environmentally benign than CFCs, owing to the presence of carbon-hydrogen bonds that can be easily broken before reaching the ozone layer.

CFC 11 has been widely used in insulation foams because it is an easily handled liquid molecule that persists in the foam to maintain the foam's thermal

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resistance. However, the complete ban on CFC 11 necessitates the search for alternative blowing agents, which will produce foams having properties comparable to those made with CFC 11. During aging, the thermal resistance of insulating polymer foams decreases because of the counter-diffusion of the blowing agent and air. Consequently, information concerning loss of blowing agents from foams is a very important criterion in the selection of blowing agents. Models of blowing agent loss from insulating foams show that this aging phenomena is a complex function of the blowing agent's diffusivity and solubility.<sup>3,4</sup> In this study, the solubilities of CFC 11 and three HCFCs in polyurethane are measured at room temperature at various blowing agent pressures. The purpose of this work is to evaluate the suitability of HCFCs as blowing agents for rigid polyurethane insulating foams.

## DATA ANALYSIS

#### **Diffusion Coefficient**

If the diffusion coefficient is independent of concentration, the one-dimensional diffusion process is generally described by the following expression:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{1}$$

where C is the penetrant concentration and D is the mutual diffusion coefficient. The solution of eq. (1) with

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Journal of Applied Polymer Science, Vol. 70, 2069–2073 (1998) © 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/102069-05

appropriate initial and boundary conditions, for a film of thickness 2l(-l to l) exposed to an infinite reservoir of penetrants, is given by<sup>5</sup>:

$$\frac{C-C_0}{C_1-C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \times \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{4l^2}\right] \cos\left[\frac{(2n+1)\pi x}{2l}\right] \quad (2)$$

In sorption experiments, the sorbed mass is obtained by integrating eq. (2) over the film thickness. At short times, if  $M_t$  denotes the total amount of penetrant that has diffused into the polymer sample at time t, and  $M_{\infty}$  the corresponding quantity at equilibrium, the following equation can be derived<sup>3</sup>:

$$\frac{M_t}{M_{\infty}} = \frac{2}{\sqrt{\pi}} \left(\frac{Dt}{l^2}\right)^{1/2} \tag{3}$$

Consequently, by plotting  $\sqrt{t}$  vs.  $M_t/M_{\infty}$ , the diffusion coefficient can be determined from the initial slope of this relationship.

#### **Solubility Coefficient**

The solubility coefficient can be defined by Henry's  $law^3$ :

$$S\left(\frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}}\right) = \frac{n_{\text{sol}}}{V_{\text{pol}} P_{\text{sol}}}$$
(4)

where  $n_{\rm sol}$  is the number of moles that have been absorbed in the polymer,  $P_{\rm sol}$  is the pressure of the penetrant at equilibrium, and  $V_{\rm pol}$  is the volume of the polymer sample. In the literature, the solubility coefficient is often reported in  $[{\rm m}_{\rm STP}^3/{\rm m}^3$ -atm], where the subscript  $_{\rm STP}$  means standard temperature and pressure (273.15 K and 1 atm). To report data using this unit, a product of gas constant, R, and  $T_o$  (273.15 K) needs to be multiplied to the right side of eq. (4).

#### **Permeation Coefficient**

If a steady state has been reached, and if Henry's law is valid, the permeation coefficient can be expressed as follows:

$$P = S \cdot D \tag{5}$$

In the literature, the permeation coefficient is usually reported in  $[cm_{STP}^3/cm$ -s-cm Hg].



Figure 1 Schematic diagram of desorption apparatus.

#### **EXPERIMENTAL**

Previous studies<sup>4</sup> have indicated that the diffusion coefficients for CFC 11 and other hydrocarbons in polyurethane at room temperature are very low. For example, a polyurethane sample 0.02 cm thick would take over 300 years to reach equilibrium if both sides of the sample were exposed to CFC 11. The duration time of such an experiment would be excessive even if a thin film of polyurethane foam thick enough to be representative of the bulk foam was utilized. Because direct measurement of blowing agent loss from rigid polyurethane foams is inhibited by the length of the experiments, an alternative approach was utilized to determine the diffusivity and solubility of blowing agents in very thin samples of pure polyurethane. The available models of foam aging were then used to evaluate the alternative blowing agents. In this study, a microtome was used to produce very thin polyurethane samples so that experiments could be conducted over a reasonable period of time. A simple desorption experimental technique was developed which permitted measurements of the diffusivity and solubility of blowing agents in the thin polyurethane samples at ambient conditions. Compared to conventional gravimetric sorption experiments, the technique introduced in this study has several advantages because it is simple, inexpensive, and several experiments can be conducted simultaneously.

A schematic diagram of the apparatus used in this investigation is presented in Figure 1. It consists of a glass reservoir formed by joining an upper and lower halves by a clamp and an O-ring seal. By a series of valves, this reservoir can be connected to a vacuum pump, a pressure transducer, and a source of the blowing agent. This apparatus can be considered to consist of two parts—the reservoir and the auxiliary apparatus—which can be used to serve several reservoirs. Before the experiment is initiated, the reservoirs are opened and a sample of the polyurethane is introduced. In a typical experiment, the polyurethane sample consists of approximately 0.2 g of thin uniform slices of polyurethane contained in an aluminum screen bucket.

	Formula	Molecular wt.	Boiling Point (°C)	Solubility Parameter (cal/cm <sup>3</sup> ) <sup>1/2</sup>	van der Waals Volume (m²/kmol)
CFC 11	$CCl_3F$	137.38	24	7.617	$4.605 imes10^{-2}$
HCFC 141b	$CH_3CCl_2F$	116.96	32	7.812	$4.748 imes10^{-2}$
HCFC 142b	$CH_3CClF_2$	100.5	-9	7.592	$4.12 imes10^{-2}$
HCFC 22	$CHClF_2$	86.48	-41	8.497	$3.102 imes10^{-2}$

#### Table I Properties of Blowing Agents<sup>8</sup>

The following experimental procedures are then followed:

- 1. The reservoir containing the aluminum bucket and the polyurethane samples is evacuated and kept under vacuum for several days to remove materials that may have been absorbed by the polyurethane such as water and air.
- 2. The blowing agent vapor is introduced into the reservoir until the desired pressure is attained.
- 3. The reservoir is removed from the auxiliary filling apparatus and held in a constant temperature room for 2–3 weeks to permit equilibrium to be established between the blowing agent absorbed in the polyurethane and the blowing agent vapor.
- 4. After equilibrium is attained, the reservoir is reconnected to auxiliary apparatus.
- 5. Auxiliary apparatus is evacuated and the valve on top of the reservoir is opened so that the pressure of the blowing agent can be determined with a pressure transducer.
- 6. The desorption experiment is initiated by evacuating the blowing agent in the reservoir and quickly replacing the blowing agent vapor with dry air so that the reservoir can be taken apart.
- 7. The bucket containing the polyurethane samples is quickly transferred to a conventional toploading microbalance, which is housed in a box that is continuously purged with dry air. The weight of the bucket is measured over time.

Although some blowing agent is lost from the polyurethane samples before the first weight measurements are made, the linear relationship at early times between the amount of material absorbed as a function of the square root of time can be used to extrapolate the weight measurements back to time zero to determine the total amount of blowing agent in the polyurethane foam. This procedure was checked with duplicate experiments utilizing polyurethane samples of different thicknesses. The solubility of a blowing agent in the polyurethane is related to the mass of blowing agent in the samples before the desorption experiment was initiated. The mutual binary diffusion coefficient for the blowing agent–polyurethane system is determined by the weight change during the early stages of the sorption process. The polyurethane samples were provided by Elf Atochem North America, Inc., in the form of a rod approximately 1/4" in diameter. Uniform slices of polyurethane were cut from the rod using a microtome. Scanning Electron Microscope measurements indicate that resulting samples are fairly uniform in thickness and range from 6.4 to 7.4  $\mu$ m. Similarly, the blowing agents were also provided by Elf Atochem North America, Inc., and the properties of these blowing agents are presented in Table I.

#### **RESULTS AND DISCUSSION**

The experimental results for the blowing agent-polyurethane systems are presented in Table II. In this table, P is the pressure of the blowing agent in the reservoir when equilibrium is attained between the polymer and the vapor phase. The activity of this system is determined by the ratio of the blowing agent pressure to the vapor pressure of the pure blowing agent at the experimental temperature of 24°C, which was maintained in the constant temperature room during all the experiments. Table II also gives the measured solubility of the blowing agent in the polymer,  $S_{\rm pol}$ , as well as the diffusivity and resulting permeability of the blowing agent in the polyurethane.

Models of blowing agent transport in rigid insulating foams indicate that an effective diffusion coefficient,  $D_{\text{eff}}$ , for the transport of the blowing agent through the foam can be estimated from the solubility and diffusivity of the blowing agent in the polymer phase of the foam.<sup>4</sup> Such models indicate that the ratio of  $D_{\text{eff}}$  for two blowing agents can be determined by the following expression:

$$\frac{D_{\text{eff},1}}{D_{\text{eff},2}} = \frac{D_{\text{pol},1}S_{\text{pol},1}}{D_{\text{pol},2}S_{\text{pol},2}} \times \frac{f_g + (1 - f_g)S_{\text{pol},2}RT}{f_g + (1 - F_g)S_{\text{pol},1}RT}$$
(6)

where  $f_g$  is the void volume fraction of the foam. Because the value of  $f_g$  is very close to 1.0 for most foams, the second term of the right side of eq. (6) is generally

Blowing Agent	P (psi)	Activity	wt %	$\frac{S_{\rm pol}RT_o}{({\rm cm}_{\rm STP}^3/{\rm cm}^3\text{-}{\rm atm})}$	$\begin{array}{c} D_{\rm pol} \times 10^{12} \\ (\rm cm^2\!/\!s) \end{array}$	$P_{ m pol}  imes 10^{12}$ (cm $^3_{ m STP}$ /cm-s-cmHg)
CFC 11	12.8	0.860	12.1	29.93	10.6	4.17
	9.6	0.645	9.9	31.85	8.3	3.47
	9.4	0.631	10.7	35.58	8.5	3.99
	6.4	0.430	5.8	26.79	2.9	1.03
	3.0	0.201	4.1	39.40	0.9	0.49
HCFC 141b	8.6	0.780	11.5	49.25	15.9	10.30
	6.2	0.562	8.9	51.56	10.1	6.85
	3.1	0.281	4.0	44.38	2.0	1.17
HCFC 142b	13.5	0.302	3.4	9.95	4.3	0.56
	7.3	0.163	2.5	13.44	1.9	0.34
HCFC 22	13.9	0.095	3.1	10.30	35.2	4.77
	11.4	0.078	2.6	10.34	20.0	2.73

Table II Results for Polyurethane/Blowing Agent Systems at Room Temperature

close to 1.0. Therefore, as a first approximation, the ratio of the effective diffusivities for two blowing agents is equivalent to the ratio of the two permeabilities. Based on this analysis, Table II indicates that HCFC 142b and HCFC 22 would be good candidates as substitutes for CFC 11. However, in current foam production technology, liquid blowing agents are preferred.<sup>6</sup> In this case, only HCFC 141b would be an appropriate blowing agent as a replacement for CFC 11 in polyure-thane foams in spite of its somewhat higher permeability. Consistent with this study, Jarfelt<sup>7</sup> reported higher effective diffusion coefficients for HCFC 141b compared to CFC 11 based on experimental measurements using polyurethane foams directly.

Table I indicates that there are strong similarities between CFC 11, HCFC 141b, and HCFC 142b, both in terms of solubility parameter and van der Waal's volume. Thermodynamic theories for polymer-solvent systems would indicate that species with similar solubility parameters would have equivalent solubilities in a given polymer when the solubility in terms of weight fraction or volume fraction is considered at given solvent activity. The experimental results for all the blowing agents in terms of weight percent blowing agent in the polyurethane as a function of blowing agent activity are presented in Figure 2. In this figure, the solid line is provided solely for a visual aid. The solid symbols in Figure 2 correspond to the solubility data for CFC 11, HCFC 141b, and HCFC 142b. The open symbols refer to HCFC 22. This figure clearly indicates that the solubilities of all these blowing agents at given activity are quite similar. The major deviation is for HCFC 22, which would be anticipated by the higher solubility parameter of this blowing agent.

Table II indicates that there is an apparent large variation in the mutual binary diffusion coefficients for the various blowing agents in polyurethane. However, it is well known that the diffusion coefficients of solvents in polymer exhibit a very strong dependency on the solvent concentration.<sup>9</sup> Typically, solvents will swell polymers and increase their mobility and, consequently, their diffusivity in the polymer. Another guide for diffusion of solvents in polymers is the molecular size of the solvent. Table I indicates that this criteria would suggest that HCFC 22 would diffuse quicker than the other three blowing agents because of its smaller van der Waal's volume.

Figure 3 presents a correlation of the mutual binary diffusion coefficients of all the blowing agents in the polyurethane as a function of the weight percent blowing agent in the polymer. As in Figure 2, the open symbols in this figure refer to HCFC 22, while the solid symbols refer to the other three blowing agents. Again, the line in this figure is presented as a visual aid. This approximate correlation indicates that the mutual binary diffusion coefficients are indeed increasing func-



**Figure 2** Solubility data for blowing agent–polyurethane systems at 24°C. The results are expressed as wt % blowing agent in the polymer as a function of the activity of the blowing agent. The solid symbols refer to CFC 11, HCFC 141b, and HCFC 142b. The open symbols refer to HCFC 22.



**Figure 3** Diffusivity data for blowing agent-polyurethane systems at 24°C. The mutual binary diffusion coefficients are presented as a function of the wt % blowing agent in the polymer. The solid symbols refer to CFC 11, HCFC 141b, and HCFC 142b. The open symbols refer to HCFC 22.

tions of the solubility of the blowing agents in the polyurethane foam. Figure 3 also clearly shows that the HCFC 22 has a significantly higher diffusion coefficient in polyurethane as anticipated.

Figures 2 and 3, in conjunction with Table I, indicate that these correlations can be used as a guide in considering other alternative blowing agents in polyurethane. Of course, other properties of blowing agents in addition to solubility and diffusivity are important in this application such as the thermal conductivity of the blowing agent vapor in the foam and the interaction of the blowing agent with ozone.

Seong-Uk Hong gratefully acknowledges the postdoctoral fellowship from Elf Aquitaine, Inc.

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