Predictive Model for Polyurethane Blowing Agent Emissions into a House.

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ABSTRACT

As homes have become more energy efficient, they become more "air tight". With this trend in the building industry, the concern about emissions from building contents and building materials has increased. The intent of this paper is to present an outline of a mathematical model which can be used to estimate the concentration of blowing agent emitted from foam insulation which is present in a house. The basic assumption of the model is that the blowing agent emission process is a diffusion process. The sensitivity of the calculated concentration to the model input parameters is also discussed.

INTRODUCTION

As homes have become more energy efficient, they become more "air tight". A previous work published by Shankland [1] proposes a model that can be used to estimate the concentration of blowing agents emitted from foam insulation in a house. The information which is vital for estimating the concentration of the blowing agent is the diffusion rate of the blowing agent through the polymer and the number of air exchanged per hour in the house.

This paper will cover the experimental and predictive methods that can be used to obtain the diffusion coefficient of a blowing agent in a polymer. Once the diffusion rate has been obtained the method outlined by Shankland [1] will be used to calculate the blowing agent concentration in a house at various air exchange rates.

DIFFUSION COEFFICIENT

Diffusion coefficients of a blowing agent can be measured by means of a micro balance. A polyurethane film which had a thickness of 0.0035 in. was used in this study. The polyurethane film was placed in the microbalance which was controlled at a temperature of 30°C. The blowing agent was then introduced into the vapor space around the polyurethane film. The weight gain was recorded as the blowing agent diffused into the polyurethane film. The diffusion coefficient was then calculated as outlined by Balik[2].

Figures 1 and 2 show the mass increase of the polyurethane film as either HFC-245fa or HBA-2 diffused into the film. The diffusion constant for HFC-245fa in polyurethane was determined to be $1.35 \cdot 10^{-9}$ $cm^2 \cdot s^{-1}$ at 30°C. The diffusion constant for HBA-2 in a polyurethane film has been determined to be $1.30 \cdot 10^{-9}$ $cm^2 \cdot s^{-1}$ at 30°C. The diffusion rate of HFC-245fa is slightly higher than that of HBA-2 in a poly urethane film.

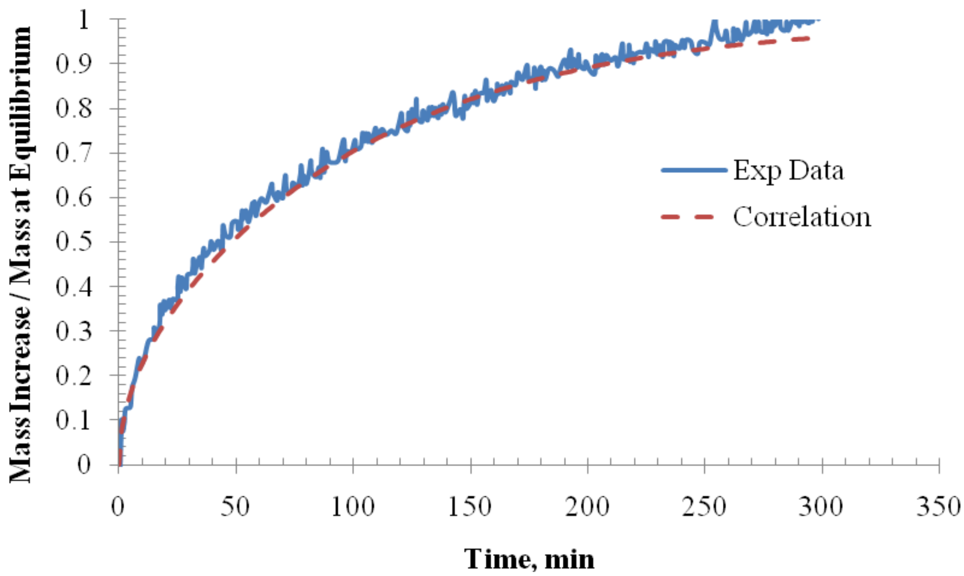

Figure 1. *Mass Increase from HFC-245fa Diffusing into a Polyurethane Film at 30°C*

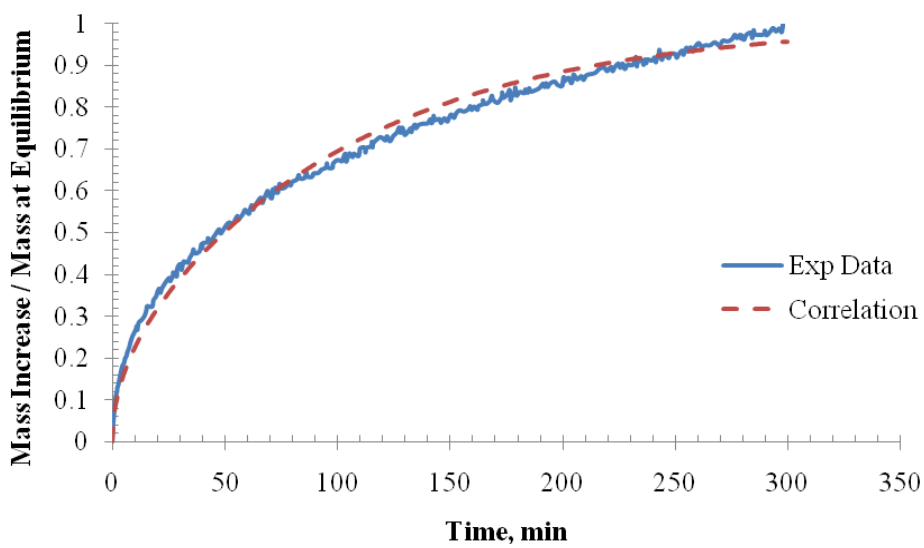

Figure 2. *Mass Increase from HBA-2 Diffusing into a Polyurethane Film at 30°C*

CALCULATION USING MOLECULAR STRUCTURE

Diffusion coefficients can be difficult and time consuming to measure experimentally. In some cases it is beneficial to have an idea of the diffusion rate without experimental measurements. The diffusion coefficient can be calculated using molecular dynamics. In this study the polyurethane matrix is constructed of various chain length polyurethane molecules. The interaction forces in the matrix allow for the polymer to form a regular lattice structure as shown in Figure 3. Once the polyurethane matrix has been formed blowing agent molecules are introduced at one end. The blowing agent is then allowed to diffuse through the polymer matrix over a period of time. The rate at which the blowing agent moves through the polymer allows for the calculation of the diffusion coefficient. Figure 3 shows the diffusion of HCFC-141b and HFC-245fa through the polymer. While this model is purely predictive, it generally will only allow for relative values of diffusion coefficients. This means that if a value for HFC-245fa has been measured then it is possible to tell if the new molecule will diffuse faster or slower than HFC-245fa. This method was used to calculate the diffusion constants for HCFC-141b, HFC-245fa and HBA-2. The results all relative to HFC-245fa are shown in Table 1. When compared to the experimental values, the calculated diffusion coefficients show the correct trend but the magnitude is slightly off. This still will serve as a good comparative tool in determining if a molecule will tend to diffuse out faster or slower than an existing blowing agent.

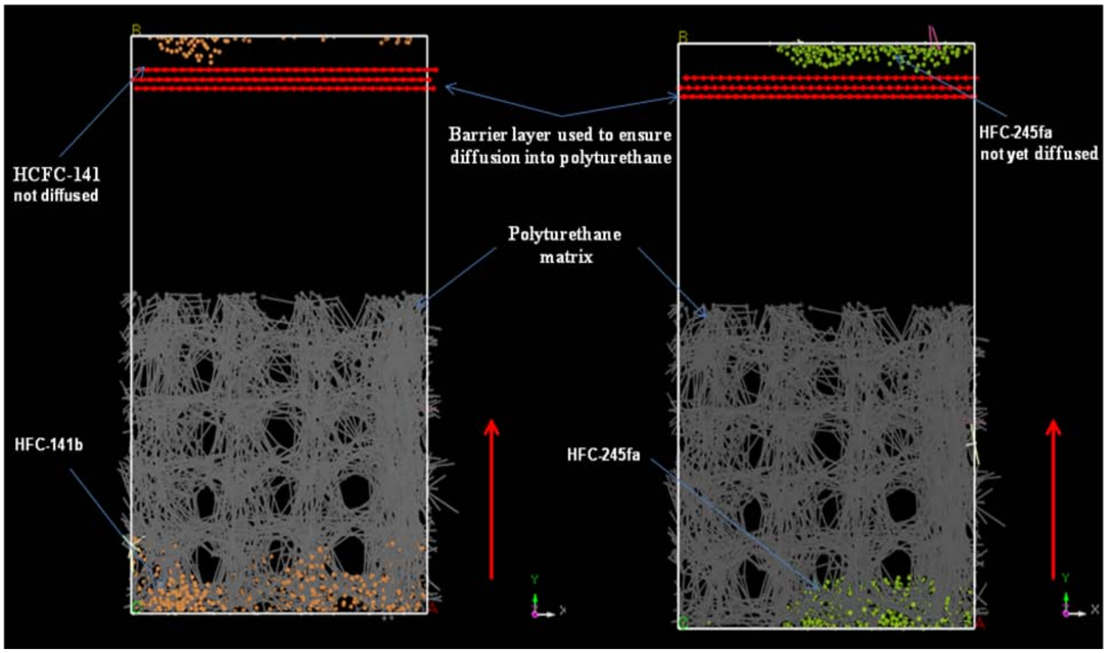

Figure 3. *Molecular Dynamic View of Diffusion*

Table 1. Diffusion Coefficient Calculated by Molecular Dynamics		
Blowing Agent	Diffusion Coefficient Relative to HFC-245fa	Experimental Diffusion Coefficient Relative to HFC-245fa
HCFC-141b	2.25 ± 0.82	4.87
HFC-245fa	1.00 ± 0.80	1.00
HBA-2	0.90 ± 0.4	0.96

ESTIMATION OF BLOWING AGENT IN A HOME

A model home of identical dimensions as those proposed by Shankland[1] was used in this work. In this case the model home is insulated using spray foam which fills the cavity of the walls. The foam is exposed from the front and is sealed to the studs and outside wall. The assumption has been made that the blowing agent does not diffuse through the studs or the outside wall. It is also assumed that 100% of the blowing agent that diffuses through the front face of the spray foam enters the house. Eq. 1 and 2 are used to estimate how much of the blowing agent will diffuse into the home over a period of time. Eq. 2 is the one dimensional diffusion through a surface neglecting the edge effects. In order to calculate the percentage of a wall that is exposed to foam the area covered by studs must be removed. It is assumed that studs cover ~14% of the wall area.

$$\varepsilon_F = \frac{16D \cdot c_0}{l_z} \frac{W_a \cdot \alpha}{4} \tag{1}$$

$$C = \frac{\varepsilon_F}{V} \sum_{n=0}^{\infty} \frac{\exp\left[\frac{-(2n-1)^2 \pi^2 D \cdot t}{4 \cdot l_z^2}\right] - \exp(-\nu \cdot t)}{\nu - \left[\frac{(2n+1)^2 \pi^2 D}{4 \cdot l_z^2}\right]} \tag{2}$$

The estimation was run using the parameters which are given in Table 2. The worst case or most air tight condition for the test is considered to be 0.35 air exchanges per hour (ach) the average case is 0.60 ach. Figures 4 and 5 show the results for both the worst case and average case air exchange rates for both HFC-245fa and HBA-2. Since the diffusion coefficients for both HFC-245fa and HBA-2 are very similar the concentrations versus time are also very similar. The instantaneous concentration of either HFC-245fa or HBA-2 never exceeds 4.0 ppmv in the home after insulation and the average concentration for anytime greater than 1 day is well below 2.0 ppmv.

Table 2. Input Parameters

House Size	Symbol	House
		1600 sq. ft
Foam Thickness	l_z	4 in.
Doors		2 X 2 m^2
Windows		12 x 1 m^2
House Volume	V	362.4 m^2
Wall Area	W_a	102.9 m^2
Percentage of the Wall covered by Foam	α	86%
Air Exchange Rate	ν	
Worst Case		0.35 ach
Average Case		0.60 ach
Temperature		30°C
Diffusion Coefficient	D	
HFC-245fa		$1.35 \cdot 10^{-9}$ $cm^2 \cdot s^{-1}$
HBA-2		$1.30 \cdot 10^{-9}$ $cm^2 \cdot s^{-1}$

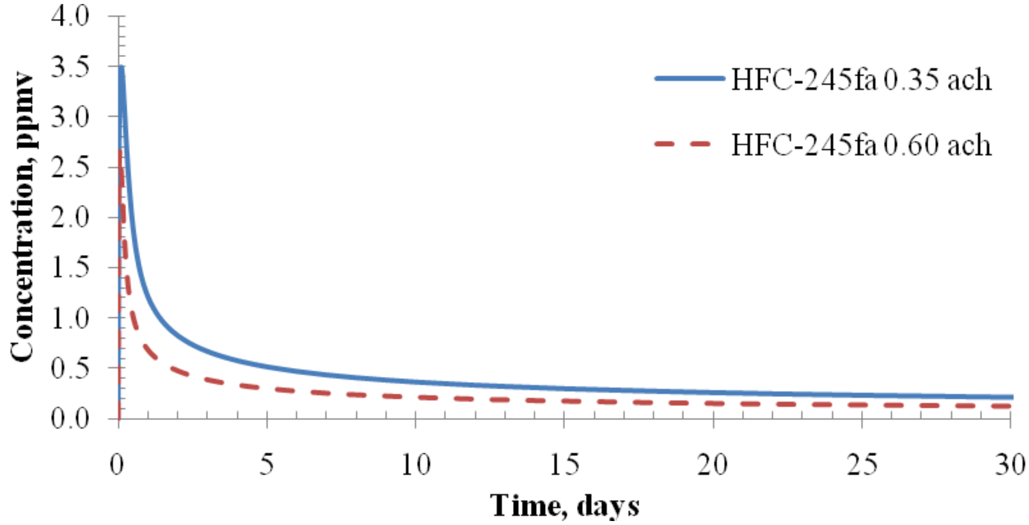

Figure 4. *Concentration of HFC-245fa inside the home after insulation.*

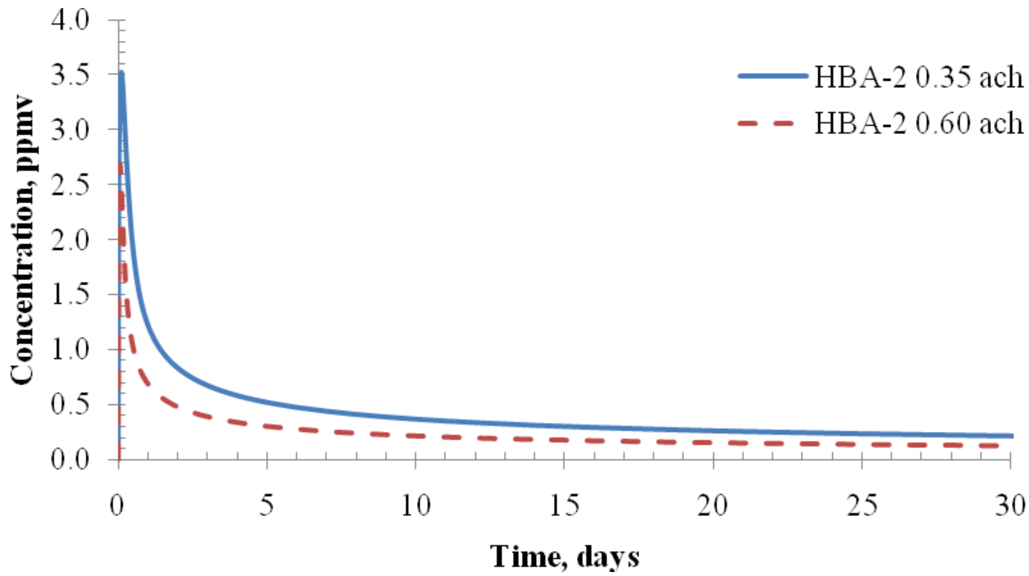

Figure 5. *Concentration of HBA-2 inside the home after insulation.*

A previous experimental study from Bogdan et. al[3] investigated the potential exposure to HFC-245fa when applying spray foam in several different areas of a home. The application was done in areas of high and low air change rates. The samples collected in the full seal 1st and 2nd floor areas are of particular interest in this case. The ambient temperature was 30-31°C (86-88°F) which is a good match for the experimentally determined diffusion coefficients. Figure 6 shows that low air exchange rate data from Figure 4 along with the experimentally determined concentrations in a house. The trends are very similar and the instantaneous values of the HFC-245fa concentration are reproduced remarkably well.

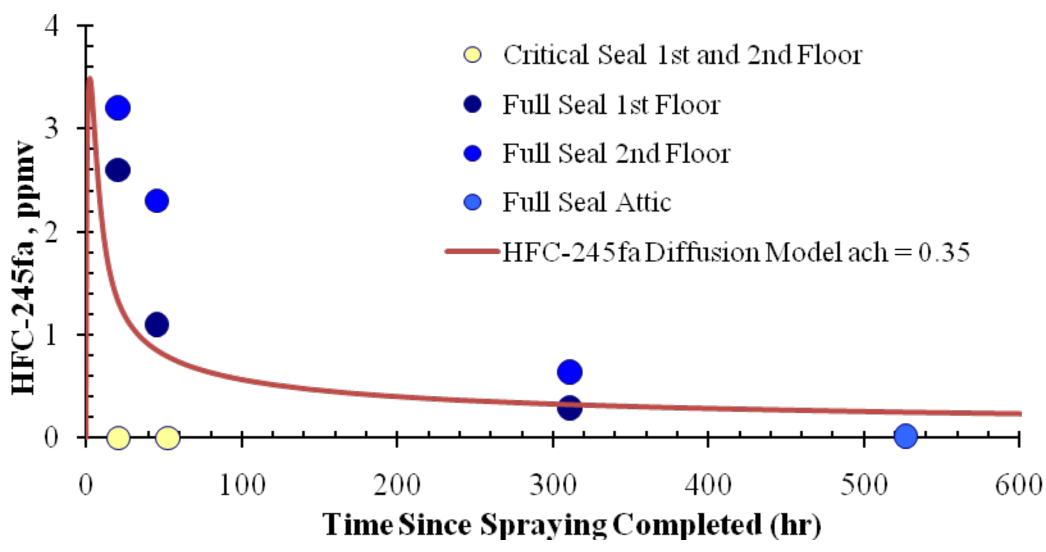

Figure 6. *Comparison of HFC-245fa diffusion model to data from a home.*

SUMMARY

The diffusion coefficients of HFC-245fa and HBA-2 in a polyurethane film have been experimentally determined and predicted using molecular dynamics. The diffusion coefficients were then used to model the release of HFC-245fa or HBA-2 into a home that had been insulated using spray foam. Table 3 shows the average concentration in a home over 7 time intervals. Since the diffusion coefficients of the two blowing agents are similar the average concentrations are also very

similar. In all cases the average blowing agent concentration in the home is < 2 ppmv. As the foam ages the blowing agent concentration quickly drops to well below 0.1 ppmv over the lifetime of the home.

Table 3. Average concentration in the home over a period of time.

Condition	Exposure Interval	Average Concentration, ppmv	Condition	Exposure Interval	Average Concentration, ppmv
	HFC - 245fa			HBA-2	
0.35 ach	0 - 2 days	1.538	0.35 ach	0 - 2 days	1.550
	2 - 7 days	0.568		2 - 7 days	0.573
	7 - 60 days	0.223		7 - 60 days	0.225
	60 days - 1 year	0.088		60 days - 1 year	0.088
	1-5 year	0.038		1-5 year	0.039
	5-10 years	0.023		5-10 years	0.023
	10-20 years	0.014		10-20 years	0.014
0.60 ach	0 - 2 days	0.909	0.60 ach	0 - 2 days	0.916
	2 - 7 days	0.329		2 - 7 days	0.332
	7 - 60 days	0.130		7 - 60 days	0.131
	60 days - 1 year	0.051		60 days - 1 year	0.052
	1-5 year	0.022		1-5 year	0.023
	5-10 years	0.013		5-10 years	0.013
	10-20 years	0.008		10-20 years	0.008

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2. Balik, C. M.; On the Extraction of Diffusion Coefficients from Gravimetric Data for Sorption of Small Molecules by Polymer thin Films; *Macromolecules*; 1996, 29, 3025-3029

3. Bogdan, M.; Blair, K.; Jennison, E.; Monitoring of HFC-245fa Exposure in Spray Foam Applications; *CPI polyurethanes 2010 Technical Conference Proceedings*; 2010

BIOGRAPHIES

Ryan Hulse

Ryan Hulse is a Sr. Technical manager in the Fluorine Products division of Specialty Materials at Honeywell. In this role Ryan has responsibility for the modeling and simulation, physical properties, and solvent programs within Fluorine Products. A key goal in this role is to identify and qualify early adopters of newly developed low global warming potential solvents. During his time at Honeywell Ryan has been responsible for physical property measurements needed for new product design and process support. Ryan has been involved in a variety of projects including new refrigerant development, low global warming potential blowing agents, process design, fumigants, and electrolytes for super-capacitors. This work has resulted in 3 US patents, 10+ pending patent applications and several technical papers. He continues to evaluate competitive offerings and looks to determine value-added opportunities for Honeywell. Ryan holds a bachelor of science and Ph.D. in Chemical Engineering from Brigham Young University.

Mary Bogdan

Mary Bogdan is a Sr. Principal Scientist for Honeywell working at the Fluorine Products Buffalo Research facility. She has earned a bachelor’s degree in Chemistry/Biochemistry and an MBA from Canisius College. Since joining Honeywell in 1989, Mary has held numerous positions in research and development. She currently supports the fluorine products blowing agent business leading application research projects and providing blowing agent technical service to the global spray foam industry. She is a Six Sigma Black belt. She has over 20 US patents and has numerous published technical articles on the development and use of fluorocarbons as foam blowing agents. She is currently a member of the SPFA Board of Directors.

Nancy Iwamoto

Nancy Iwamoto, has a Ph.D. in Organic Chemistry from the University of Washington, with industrial experience in a variety of material areas including optical storage media, propellants, adhesives, dielectrics, and polymer films. She has over 20 years of experience in applied molecular modeling, and is currently the manager of Molecular Modeling in Honeywell Specialty Materials.