

# Sorption/desorption behaviour of polyurethane foam

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## ABSTRACT

Polyurethane foam (PUF) is widely used in indoor consumer products. Despite the strong interactions with volatile organic compounds (VOCs), the effect of PUF on indoor concentrations of VOCs has not been examined. This study determines the behaviour of PUF as a potential sink for or source of VOCs in indoor air. Eight aromatic VOCs ranging in molecular weight from naphthalene to benzene were studied. Rapid determination of the polymer/air partition coefficient ( $K$ ) and polymer-phase diffusion coefficient ( $D$ ) was achieved using a dynamic microbalance. Sorption of VOCs by PUF is fully reversible.

## INDEX TERMS

Diffusion; Indoor air; Microbalance; Sorption, VOC

## INTRODUCTION

Worldwide production of polyurethane foam (PUF) has been estimated at more than 6 million tons per year (Braun *et al.*, 1985), of which over half is typically used indoors. The high sorption capacity of PUF for various organic compounds was recognized several decades ago. For example, PUF was found to be effective in high volume gas sampling of various polycyclic aromatic hydrocarbons (PAH) and organochlorines (Burdick and Bidleman, 1981; Pankow, 1989). Indoor PUF can serve as both a sink for and source of VOCs. After the manufacturing process is complete, PUF materials typically contain residual quantities of VOCs that may be released into air. Sorption and desorption of VOCs can take place in sequential fashion. When the indoor VOC concentrations are high, PUF will sorb VOCs from the air, thus acting as a sink. As the VOC concentrations in the indoor air decrease, the direction of the mass transfer driving force may be reversed resulting in desorption of VOCs. Such cyclic VOC sink/source effects can significantly alter dynamic indoor air concentration profiles (Zhao *et al.*, 2002).

The primary motivation for this study is to characterize the source/sink behaviour of PUF for an array of eight common indoor VOCs using a simple and rapid procedure that couples dynamic microbalance measurements with a physically based diffusion model (Cox *et al.*, 2001).

## METHODS

A flexible polyether-type PUF was purchased from Airtex (Cokato, MN). The bulk density was 0.022 g/cm<sup>3</sup> at 21°C and the bulk porosity was 97.6%. This commercial product is widely used in pillows, beds, sofa pads and cushions in homes and offices. Before use, the PUF samples were washed using *n*-hexane, air-dried, and then baked at 105°C for 6 h. The oven-dried PUF samples were sealed in aluminium foil and stored for use. Figure 1 provides a photomicrograph showing the PUF structure. The vertical line in the centre of the image is a piece of wire with a diameter of 76 µm.

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**Figure 1** Photomicrograph of PUF at a magnification of 60 $\times$ .

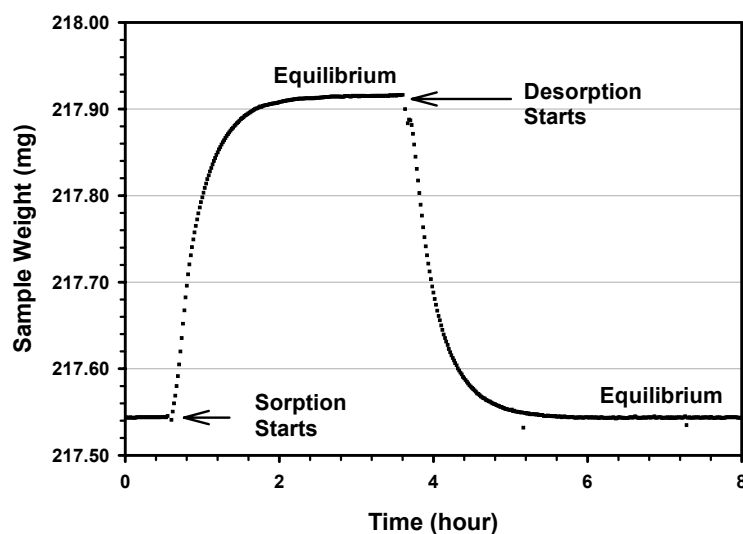
A dynamic gravimetric method was used in sorption and desorption tests. A high-resolution (0.1–0.5  $\mu\text{g}$ ) dynamic microbalance (Cahn D200-02) equipped with a computer-based data-acquisition system was employed to measure and record the change in PUF specimen weight during the equilibrium and kinetic tests. The temperature in the microbalance enclosure was kept at  $21 \pm 1^\circ\text{C}$  during the experiments. A detailed description of the microbalance system is provided elsewhere (Cox *et al.*, 2001).

For VOC sorption tests, known gas-phase concentrations of each VOC were generated by combining a stream of clean air (Medical Air USP, UN1002, Air Products) and a constant emission rate diffusion cell (Dynacalibrator Model 190, VICI Metronics, Inc., CA). The relative humidity of the clean air was 16 ppmv. A mass flow controller (Tylan FC-280S) was used to control the influent air flow-rate. The microbalance recorded the weight gain of the PUF as VOC-laden influent air was introduced into the sample chamber. Following sorption equilibrium, desorption was initiated by turning off the VOC source and passing only clean air into the sample chamber. As desorption proceeded, the transient weight loss was recorded until the desorption process was complete.

## RESULTS AND DISCUSSION

### Sorption Equilibrium and Partition Coefficient

To determine sorption capacities of PUF for various VOCs, tests were conducted using the dynamic microbalance. Figure 2 shows the sorption and subsequent desorption profile for styrene. The influent VOC concentration of styrene was  $0.13 \text{ g/m}^3$ . Similar profiles were also obtained for water vapour and seven other VOCs (naphthalene, 1,2,4-trimethylbenzene, *p*-xylene, ethylbenzene, chlorobenzene, toluene and benzene). Comparing the sorption and desorption data in Figure 2 reveals that sorption of styrene is reversible. Sorption or desorption equilibrium was reached within  $\sim 3 \text{ h}$  for styrene. The equilibrium VOC uptake is calculated from the weight gain of the PUF specimen.



**Figure 2** Transient weight gain/loss of PUF sample during sorption/desorption of styrene.

By repeating the sorption equilibrium tests using a range of VOC concentrations in the influent air, sorption isotherms for each VOC and water vapour were established. Figure 3 shows sorption isotherms for styrene and toluene. Over the concentration range tested, both isotherms are linear, suggesting that sorption of VOCs to PUF is characterized by a partitioning or solid-phase dissolution process. When compared with uptake of water vapour (data not shown), the sorption capacities for VOCs are orders of magnitude higher. For each VOC, the sorption equilibrium is described using the polymer–air partition coefficient,

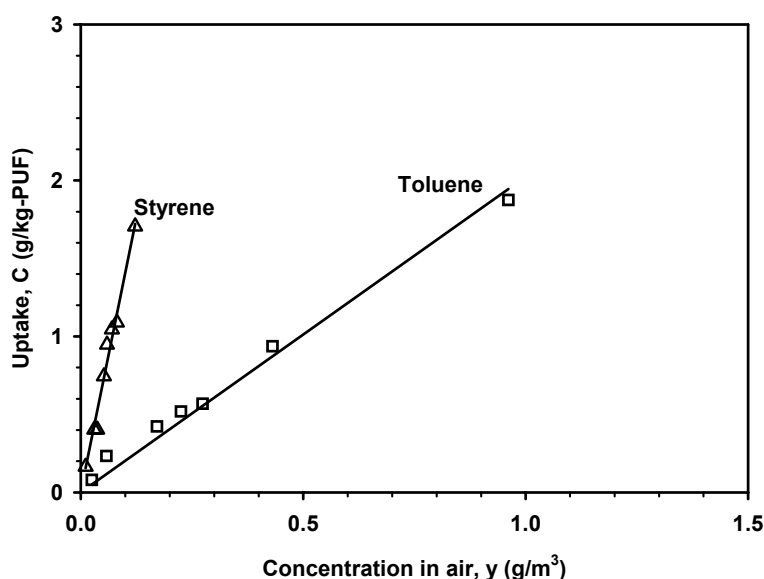
$$K = \frac{C_i}{y_i} \quad (1)$$

where  $C_i$  is the concentration of species  $i$  in the polymer-phase (g VOC/m<sup>3</sup> polymer), and  $y_i$  is the corresponding concentration of species  $i$  in the gas-phase (g VOC/m<sup>3</sup> air).

From the dynamic microbalance test data (Figure 2), the equilibrium uptake of VOC by the PUF specimen can be derived from the difference between the initial and equilibrium weight for each known concentration of VOC in the influent air. Thus, the partition coefficient  $K$  for each species can be determined. Table 1 summarizes the measured  $K$  values for the VOCs in this study. The  $K$  value for water vapour is 0.039, which is significantly smaller than for the VOCs.

### Diffusion Coefficient

The PUF specimen used in the sorption/desorption experiments was cylindrical in shape, approximately 8 cm long and 1.25 cm in diameter. A photomicrograph (Figure 1) shows that the PUF material is composed of a matrix of interlinked polymer strands (microcylinders) with a mean diameter of about 76 μm. The foam is 97.6% air and the air-filled macropores between the polymeric microcylinders range in size from 0.3 to 0.8 mm. Conceptually, sorption of VOCs takes place via the following three sequential steps: (1) mass transfer of the VOC from the sample chamber through the air-filled macropores to a microcylinder, (2) sorption or partitioning of the VOC to the exterior surface of the microcylinder, and (3) diffusion of VOCs into the interior of the polymer microcylinder.



**Figure 3** Experimental (symbols) sorption isotherms of styrene and toluene with PUF.

**Table 1** Properties of VOCs studied and measured values for  $D$  and  $K$

VOC	$K$	$D$ (m <sup>2</sup> /s)	$P_{\text{vap}}$ (Pa)	MW
Naphthalene	6400	$0.066 \times 10^{-13}$	23.6	128
1,2,4-Trimethylbenzene	440	$1.0 \times 10^{-13}$	304.0	120
Styrene	310	$1.9 \times 10^{-13}$	926.6	104
<i>p</i> -Xylene	130	$2.7 \times 10^{-13}$	1005	106
Ethylbenzene	110	$3.7 \times 10^{-13}$	1173	106
Chlorobenzene	140	$3.3 \times 10^{-13}$	1415	113
Toluene	58	$4.2 \times 10^{-13}$	3582	92
Benzene	19	$7.0 \times 10^{-13}$	11 790	78

Based on a diffusion coefficient in air of about  $10^{-5}$  m<sup>2</sup>/s, the characteristic time for transport by pore diffusion into the interior of the PUF sample (through a radial distance of about 0.65 cm) is roughly 2 s. Comparing this to the characteristic time for sorption equilibration (on the order of hours) shows that diffusion within the solid microcylinders is the rate-limiting step in the overall sorption process. The PUF can therefore be envisioned as a single infinitely long polymeric microcylinder. For this cylindrical geometry, the governing diffusion equation is (Crank, 1975):

$$\frac{\partial C}{\partial t} = \frac{1}{r} \cdot \frac{\partial}{\partial r} \left( rD \frac{\partial C}{\partial r} \right) \quad (2)$$

where  $D$  is the diffusion coefficient within the polymeric microcylinders. Under the experimental conditions, the following initial and boundary conditions apply:

$$C = 0 \quad \text{at } 0 < r < a \quad \text{and } t = 0 \quad (3)$$

$$C = Ky_0 \quad \text{at } r = a \quad \text{and } t \geq 0 \quad (4)$$

where  $y_0$  is the VOC concentration in the chamber air and  $a$  is the mean radius of the microcylinders. An analytical solution for Eqns (2)–(4) is given by Crank (1975):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a_2 \alpha_n^2} \exp(-D \alpha_n^2 t) \quad (5)$$

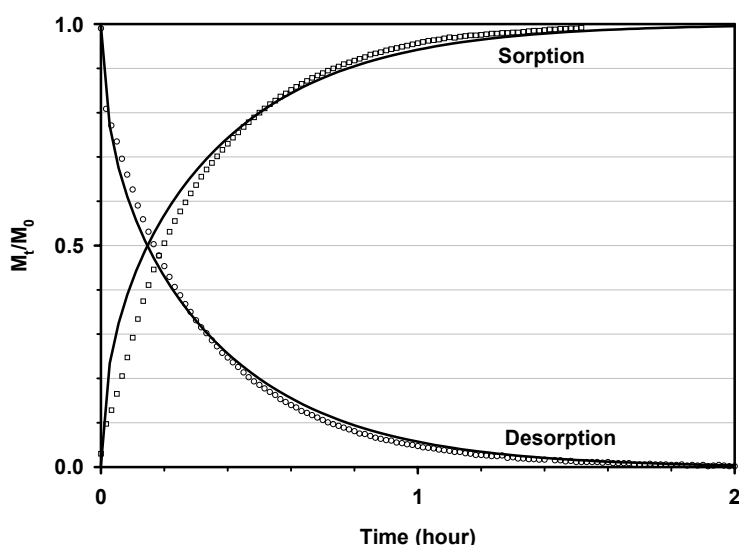
where  $M_t$  denotes the total mass of a VOC which has entered the cylinder in time  $t$ ,  $M_\infty$  the corresponding quantity after infinite time or when equilibrium is reached, and the  $\alpha_n$ s are the positive roots of

$$J_0(a \alpha_n) = 0 \quad (6)$$

where  $J_0$  is a Bessel function of the first kind of zero order. The diffusion coefficient during sorption or desorption for various VOCs was determined by fitting Eqn (5) to the transient experimental sorption or desorption data. The best fit was achieved by minimizing the mean squared error between model prediction and experimental data. Figure 4 demonstrates the determination of the diffusion coefficient for styrene in PUF using this method. The best fit to the kinetic data resulted in a  $D$  value of  $2.0 \times 10^{-13} \text{ m}^2/\text{s}$ . Figure 4 shows that the same  $D$  value can also be used to predict the corresponding desorption data, confirming the symmetrical nature of the sorption and desorption profiles. Diffusion coefficients for the other VOCs are summarized in Table 1. The  $D$  value for water vapour in PUF was determined to be  $6.0 \times 10^{-13} \text{ m}^2/\text{s}$ . The values for  $D$  are typical for diffusion in rubbery polymeric materials (Little and Hodgson, 1996).

## CONCLUSIONS

The dynamic microbalance test procedure coupled with appropriate diffusion models has been successfully used to characterize sorption and diffusion properties of slab-like diffusion-controlled materials such as vinyl flooring (Cox *et al.*, 2002). The polyurethane foam in this study represents a polymeric material with cylindrical geometry. Using the simple microbalance experimental approach, VOC sorption and desorption behaviour can be readily established.



**Figure 4** Determination of the diffusion coefficient for styrene in PUF.

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