PERMEABILITY OF NANOPOROUS PEI
Andrei Nicolae and Vipin Kumar
Department of Mechanical Engineering, University of Washington, Seattle, WA

Abstract

Novel open-cell foams were created using the solid-state foaming process in polyetherimide (PEI). The cell size is in the 50 – 150 nm range. The structures’ fluid permeability, gas diffusivity, and tortuosity were determined by applying classical models to experimental data. This new class of materials is expected to have a variety of applications such as nanofilters for dialysis/aerosols, slow release of volatile substances in medical or agricultural fields, and others.

Introduction

This work is concerning polymer nanofoams, a thermoplastic material processed to have an interconnected porous structure with nanometer sized channels. These materials have applications in fluid filtration, medical devices, insulators, catalysts, and templates [1-3]. While many techniques exist to create such structures, the material discussed here is made by the solid-state foaming process [4-7]. This is a simple technique in which CO2 blowing agent is dissolved into the polymer in the solid state, and then heated to the glass transition to initiate cell nucleation and expand the polymer. Polyetherimide (PEI) expanded by this process has been shown to have an interconnected porous structure with channels on the order of 50-100 nm [8-10]. Dye permeation tests confirm that the nanostructure will allow fluids to flow through. However, no work has been done to quantitatively characterize this material and obtain its permeability. Krause et. al has performed basic experiments where nitrogen and helium gas was flowed through the cross-section of a PEI membrane, but no material property was derived from these experimental results [8]. In this work, a material property known as permeability is computed by experimental data in conjunction with a fluid flow model. Additionally, the diffusivity of gasses through the nanostructure is also computed and correlated to the permeability. Finally, the relationships between a processing parameter (foaming temperature) and porosity, permeability, and diffusivity are established.

The Solid Skin

One unavoidable artifact of the solid-state foaming process is the production of a solid (non-porous) skin that encloses the boundary of the polymer sample. Since no flow can occur through this region, the skin must be removed to expose the nanoporous core. Previous attempts to remove the skin layer showed that, during the removal process, the underlying porous structure was plastically deformed and the pores were thus shut [10]. Recently, a new technique was found wherein the skin was not wholly removed but rather machined/pierced in certain regions to expose the core only in those locations, leaving the remainder of the skin for structural support. This highly successful idea has now allowed repeatable PEI nanofoam samples to be produced for fluid flow experiments. Unlike Krause’s experiments where freeze-fractured samples were mounted such that flow occurred through the cross-section, the skin-machined samples presented in this work allow flow through the thickness. This is representative of a real application of the material such as for filtration where large areas are required.

Permeability

The macroscopic fluid velocity in an isotropic nanoporous material is antiparallel to the pressure gradient and scaled by $k/\mu$ where $\mu$ is the dynamic viscosity of the fluid and $k$ is known as the permeability (with dimensions of length$^2$) [1-3].

![Figure 1. Porous structure of PEI saturated at 5.0 MPa and foamed at 180C.](image)
If the flow is 1D, the permeability can be measured by applying a pressure difference at the boundary points and measuring the flow rate \( Q \). ASTM D6539-13 describes a method of doing so, which works for samples that are cylindrical with uniform boundaries. The permeability of a sample of cross-sectional area \( A \) and thickness \( h \) is given by [4]

\[
k = \frac{\mu Q h}{A \Delta p}
\]

However, when machining the skin of a PEI nanofoam the flow field is not 1D, therefore equation (2) cannot be used. To find the correct relationship for permeability, the fluid equations were solved numerically and a code was written to give an appropriate correction factor for the parameter \( A \) in equation (2) – this work is not presented here, however it has been experimentally verified and will be used throughout this study.

**Experimental**

The material used in this study came as 0.50 mm extruded sheets made from Ultem™ 1000 PEI resin. Samples were die cut into 1” disks and saturated with 99.9% purity CO2 for 48 hours. Immediately after removal from the CO2 environment, the samples were heated between flat aluminum plates with 20 N clamping force for 30 seconds at temperatures of 170, 180, 190, and 200 Celsius. This process was previously explored in detail by Miller et. al. [5] and used as a guide for sample preparation. For foaming temperatures below 170 C, the samples showed very little expansion so these temperatures were not investigated due to difficulty of machining the skin and performing the flow experiments. Samples foamed above 200 C were excessively warped and/or blistered, making them unsuitable for investigation. This phenomenon was observed and described by Miller [6] and Aher [7].

The solid skin was pierced on both faces simultaneously by arrays of hexagonally packed needles. Figure (2) shows one part of the device.

To correctly calculate the total area pierced by the needles, their average diameter, and spacing, an image processing code was written to compute the information from photographs of the samples. The samples were photographed using a lens containing a scale bar, with back illumination by a lightbox. The information given by the image processing code was entered directly into the flow simulation code mentioned previously, and an “effective area” was computed which then accurately used in equation (2). The thickness of the core was digitally measured by fracturing the sample and photographing the cross-section.

**Permeability Results**

The results are summarized in table (1) and plotted in figure (4). Included is also the relative density \( \Phi \) which is defined as the foam density divided by the density of PEI.
Table 1. Permeability results from experiments.

<table>
<thead>
<tr>
<th>Foam temp.</th>
<th>Relative density</th>
<th>Mean permeability [m²]</th>
<th>St.dev [m²]</th>
<th>Mean St.dev</th>
<th>St.dev / mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>170 C</td>
<td>0.675</td>
<td>1.79 E-16</td>
<td>3.13 E-17</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>180 C</td>
<td>0.634</td>
<td>3.25 E-16</td>
<td>7.73 E-17</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>190 C</td>
<td>0.571</td>
<td>7.38 E-16</td>
<td>8.13 E-17</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>200 C</td>
<td>0.526</td>
<td>1.66 E-15</td>
<td>3.88 E-16</td>
<td>0.23</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4. Plot of permeability vs. foaming temperature. The error bars are +/- 1 standard deviation. The curve fit is a polynomial of degree 2.

The equation for the curve fit gives permeability $k$ and a function of temperature $T$.

$$k(T) = 10^{-14} (1.94 \cdot 10^{-4} T^2 - 0.0669 T + 5.78) \quad (3)$$

With units of meters squared and Celsius for $k$ and $T$ respectively. The residual sum of squares is $R^2 = 0.9998$ indicating very good agreement between data and model.

**Vapor Diffusion through the Nanostructure**

A different kind of flow test was conducted, wherein there was no bulk fluid pressure gradient but rather a concentration gradient of different gas species. Three pure substances, water, isopropyl alcohol, and acetone, were placed into an aluminum canister atop which a PEI nanofoam sample was placed to seal off the enclosure from the ambient environment. This was done by the use of a rubber O-ring and a screw-on lid to apply the sealing force. Tests were performed using an unfoamed PEI sample and confirmed that there were no leaks. Figure (5) shows a diagram illustrating the principle of the experiment as well as the physical setup.

Since the liquid rests at the bottom of the canister, only the vapor can interact with the nanofoam. The gas present is a mixture of air and the substance in the vapor state. Since the total pressure is 1 atmosphere which is well above the vapor pressure of the substances at the temperature at which the experiments were performed (room temperature), the system can be considered as a mixture of ideal gasses [8, 9]. Therefore, the partial pressure of the substance in the gas mix is simply its saturation temperature at 1 atmosphere.

**Diffusion Model**

Since there is no pressure difference across the sample in the bulk fluid, the substance exits the canister through the nanofoam at the molecular level by diffusion. The thermodynamic driving force is rather a concentration gradient. Fick’s law of diffusion models the diffusion flux $J$ as proportional to the concentration gradient:

$$J = -D_p \frac{\partial C}{\partial x}, \quad |J| = -D_p \frac{\partial C}{\partial x} \quad (4)$$

To compute $J$, the canisters were weighted periodically using a digital lab scale with accuracy of 10 µg. Since the vapor pressure is a function of temperature only and the sole driving force, the escape rate was constant regardless of the amount of liquid present in the canister. This evaporation rate $f$ [g/sec] was divided by the effective area $A_{eff}$ of exposed core, the same value as computed for the permeability calculations. The concentration is assumed zero on the face exposed to ambient air. Therefore, the diffusion coefficient is given by

$$D_p = \frac{f h RT}{M A_{eff} p_v} \quad (5)$$

where $R$ is the universal gas constant, $M$ the molar mass of the substance, and $p_v$ its vapor pressure at ambient temperature. Table 2 shows the diffusion coefficient computed for each substance with samples at each
foaming temperature. The same sample was used for all 3 substances to eliminate compounded uncertainty.

Table 1. Diffusion coefficient computed from evaporation tests. The units are in mm²/s.

<table>
<thead>
<tr>
<th>Foaming Temp</th>
<th>Water</th>
<th>Isopropyl</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>170°C</td>
<td>0.285</td>
<td>0.234</td>
<td>0.320</td>
</tr>
<tr>
<td>180°C</td>
<td>0.303</td>
<td>0.270</td>
<td>0.349</td>
</tr>
<tr>
<td>190°C</td>
<td>0.391</td>
<td>0.399</td>
<td>0.362</td>
</tr>
<tr>
<td>200°C</td>
<td>0.582</td>
<td>0.520</td>
<td>0.643</td>
</tr>
</tbody>
</table>

A plot of the results in table (2) shows that the diffusion coefficient is similar to all three substances moving through the nanostructure, and has a quadratic relationship to foaming temperature as does the permeability.

The function that fits the data in figure (6) is

$$D_p(T) = 0.0005 T^2 - 0.1472 T + 13.047$$

with residual sum of squares for this fit is 0.9954, again indicating strong agreement between data and model.

The diffusion coefficient $D_p$ through porous media is modeled by [11]

$$D_p = c\phi D_0/\tau$$

where $\tau > 1$ is the tortuosity, $\phi$ is the porosity, $D_0$ is the diffusion coefficient in the fluid occupying the pores, and $c$ is a constrictivity factor which can be approximated as 1 since the pore sizes are above 1 nm [12].

Since the diffusion coefficient through air $D_0$ of water, isopropyl alcohol, and acetone differs but is on the same order of magnitude, the diffusion coefficient through the porous medium $D_p$ also differs, a fact shown by the data.

The ratio $D_p/D_0$ is called the diffusivity and by equation (9) is dependent on the porous structure only. This fact can be used to find the tortuosity of the material as defined in the above equation. For water vapor through excess air, the diffusion coefficient at 293.15 K is $D_0 = 2.42 \cdot 10^{-5} \text{ m}^2/\text{s}$ [13, 14]. Table 3 shows the diffusivity and tortuosity of the PEI nanoporous samples in this study.

Table 2. Structure properties of PEI nanofoams as computed from diffusion data.

<table>
<thead>
<tr>
<th>Foaming Temp</th>
<th>$D_p/D_0$</th>
<th>Porosity $\phi$</th>
<th>Tortuosity $\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>170°C</td>
<td>0.0118</td>
<td>0.469</td>
<td>39.8</td>
</tr>
<tr>
<td>180°C</td>
<td>0.0125</td>
<td>0.501</td>
<td>40.1</td>
</tr>
<tr>
<td>190°C</td>
<td>0.0162</td>
<td>0.550</td>
<td>34.0</td>
</tr>
<tr>
<td>200°C</td>
<td>0.0240</td>
<td>0.586</td>
<td>24.4</td>
</tr>
</tbody>
</table>

Figure (7) compares the diffusivity of nanoporous PEI with literature values of various materials [11, 15, 16].

Conclusions
The permeability, diffusivity, and tortuosity are properties of porous materials which were unknown for nanoporous polyetherimide created with the solid-state foaming process. In this work, all three of these properties were experimentally quantified for PEI samples saturated with CO2 at 5.0 MPa and foamed at 170, 180, 190, and 200 Celsius. A quadratic dependence of both permeability and diffusivity on foaming temperature was found and correlated to the linear dependence of porosity on temperature. Both permeability and diffusivity are comparable to that of sandstone, showing that mass transport through the structure is slow due to the small pore sizes of the nanofoam.

References