

Characterizing Membrane Sorption and Diffusion with Flux Lateral Force Microscopy

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ABSTRACT

Bulk permeability measurements provide an incomplete descriptor of permeability when considering heterogeneous or anisotropic membranes. Localized measurements of flux allow for independent assessment of constituent contributions to total permeability. Analogous to a puck on an air hockey table, permeate flow in membranes contributes to a local reduction in surface friction. By positioning a lateral force microscope (LFM) onto a custom membrane stage, in a technique coined Flux-LFM, local variations in friction force and hence permeability can be measured directly at the surface, with nanoscale resolution. Here two membranes, a high permeability alumina Anodisc® and a reverse selective poly(trimethylsilyl propyne) (PTMSP) membrane, are investigated.

Keywords: Flux-LFM, AFM, poly(trimethylsilyl propyne)

1 INTRODUCTION

The design of advanced gas separation membranes often focuses on the interplay between gas permeability, given by

$$P_n = S_n D_n$$

and selectivity, given by

$$\alpha = \frac{P_A}{P_B}$$

where P_n , S_n , and D_n are the permeability, solubility coefficient, and diffusion coefficient of species n respectively and α is the selectivity between two gas species. Ideally, permeability and selectivity are maximized, resulting in faster more cost effective separations. Often though, permeability or selectivity are gained at the expense of one another, as larger diffusing pathways tend to have lower selectivity. [1]

Many new membrane systems have sought to exploit heterogeneous or anisotropic features to enhance permeability-selectivity tradeoff. For microscale heterogeneous media, such as polymer blends or composites, the performance of the discrete phases can be evaluated on the basis of the neat material contributions. However, as size domains are increasingly pushed towards

the sub-100 nm length scale, assumptions of bulk-like behavior for separate domains are no longer valid.

It is becoming increasingly well understood that polymers undergoing nanoscale confinement have enhanced relaxation, mechanical, and transport properties compared to their bulk counterparts. [2-7] In thin polymer films, the glass transition has been shown to advance or retard depending on the specific interactions between the polymer and substrate. Analogous observations have been made for polymer nanocomposites where particle-particle distances are comparable to thin film thicknesses. [7]

While multiple techniques have been developed to study relaxation and mechanical properties in confined systems, direct, local measurement of functional properties such as permeability has been more limited. To address this need, Wei and Overney have recently introduced Flux-Lateral Force Microscopy (Flux-LFM) as a local surface sensitive permeability measurement technique.[8] Using the left-right photo diode signal from a scanning force microscope (SFM), it is possible to measure local variations in friction on a surface. Using a custom fabricated SFM stage / membrane chamber, it was shown that as gas permeates through the membrane, a reduction in surface friction is observed.

Here, we compare the Flux-LFM response of an inorganic anodisc membrane to that of a reverse selective poly(trimethylsilyl propyne) (PTMSP) membrane. The anodisc is unique in its exceptionally high permeability in light of a relatively small 100 nm pore size. This high permeability is attributed to the highly parallel continuous pore structure shown in Figure 1.

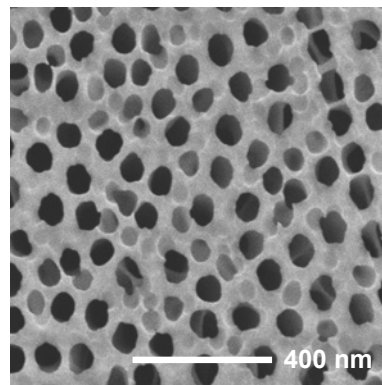


Figure 1: SEM image of 100 nm Anodisc

PTMSP is chosen because it exhibits the highest permeability of any known polymer. PTMSP is also of interest for future local surface permeability studies given that it shows a dramatic interfacial enhancement effect in the presence of silica nanoparticles.

2 EXPERIMENTAL

2.1 Sample Preparation

100 nm diameter pore anodiscs were obtained from Whatman Co. and mounted with epoxy on to a 25.4mm aluminum disc with a 3 mm hole.

PTMSP was obtained from Gelest Inc and dissolved into toluene, producing a 2% polymer solution. The polymer solution was cast on to a glass substrate and dried under vacuum at room temperature for 7 days. Subsequently, the film was removed from the substrate by scoring the edges and immersing the film in water, floating the detached film to the surface. An epoxy covered 25.4mm aluminum disc with 3mm hole was positioned beneath film, and brought to the surface, fixing the film to the substrate. The sample was dried for 3 more days under vacuum at room temperature prior to testing. All measurements were performed in a nitrogen atmosphere with relative humidity less than 5%.

2.2 Bulk Permeance

Given that the total surface gas flux is expected to be the dominant property in Flux-LFM, bulk permeance was calculated rather than thickness normalized bulk permeability. Bulk permeance was determined using a constant pressure, variable volume apparatus. Permeance is given by

$$P = (Q/A)/(p_2 - p_1),$$

where P is the permeance, Q is the volumetric flow rate, A is the membrane area, p_2 is the chamber pressure and p_1 is atmospheric pressure. Q was determined via a 10 ml bubble meter.

2.3 Flux-LFM

Flux-LFM measurements were made using a Topometrix Explorer SFM operating on a custom fabricated membrane chamber stage. The Flux-LFM setup is shown schematically in Figure 2. Pressurized gas is fed in to the membrane chamber and maintained at a fixed pressure. The SFM is brought into contact with the membrane and scanned in a 50 line $1\mu\text{m} \times 1\mu\text{m}$ region. The friction force is determined from the difference in lateral deflection between the forward and reverse scanning directions,

averaging over the 50 lines. Measurements were made at a range of pressures, while also varying the normal load on the cantilever, giving both friction force and friction coefficient information.

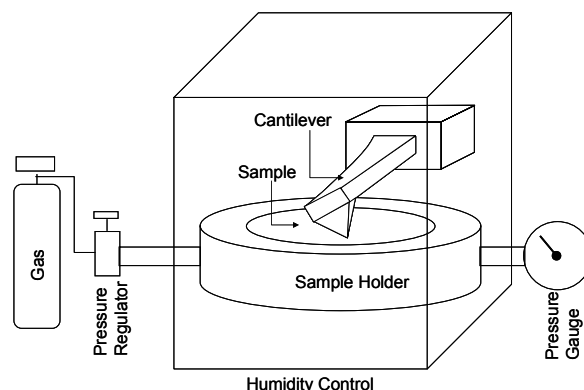


Figure 2: Schematic of F-LFM system

3 RESULTS AND DISCUSSION

The bulk permeance of the anodisc was found to be $10.5 \mu\text{m}/(\text{Pa s})$, $5.1 \mu\text{m}/(\text{Pa s})$ and $3.6 \mu\text{m}/(\text{Pa s})$ for helium, nitrogen and carbon dioxide, respectively. The bulk permeance of PTMSP was $0.014 \mu\text{m}/(\text{Pa s})$ and $0.028 \mu\text{m}/(\text{Pa s})$ for He and CO_2 respectively. It is observed that the anodisc is strongly size selective, favoring smaller permanent gases over larger sorbing gases. In contrast, PTMSP exhibits reverse selectivity, favoring the larger, but more soluble CO_2 to the smaller He.

Figure 3 shows a friction vs pressure relationship for the Flux-LFM measurement made on the anodisc with helium, at multiple loads. Friction force decreases in a systematic manner with increasing pressure, owing to the increased flux acting on the cantilever tip.

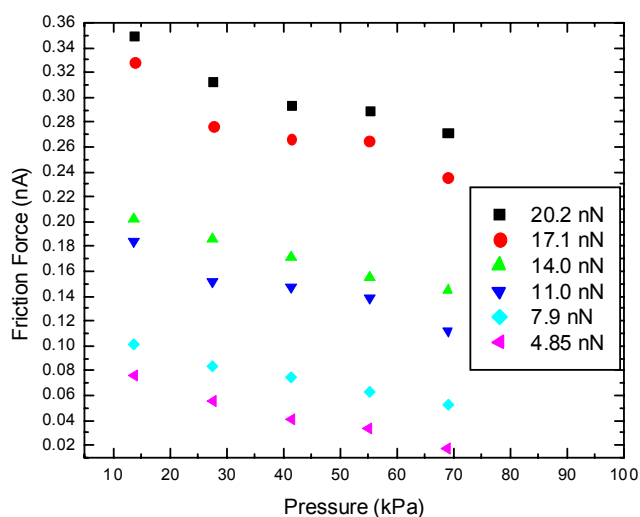


Figure 3: Flux-LFM response on anodisc with He permeate at multiple cantilever loads.

Figure 4 compares the friction force – pressure gradient from flux-LFM to the bulk permeance. It was observed that bulk permeance was linearly proportional to the friction – pressure gradient, suggesting the out flow of gas acts linearly on the cantilever tip.

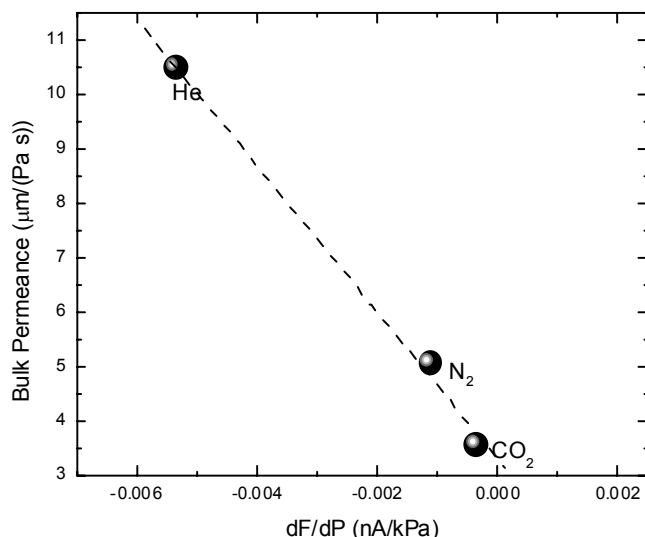


Figure 4: Relationship between bulk permeance and Flux-LFM response.

In contrast to the Anodisc, the drastically reduced permeance of the PTMSP film resulted in a decreased signal to noise ratio, and hence friction pressure gradients could not be measured within the standard variation in surface friction. However, by comparing the friction coefficient, given by

$$\mu = L / F$$

where F is the friction force and L is the load, it is still possible to gain flux information from the polymer membrane. Friction coefficient is a rheological parameter that describes the energy dissipative capacity of the surface. Hence, it is sensitive to mechanical property changes that arise as a result of gas sorption in the polymer. Figure 5 compares the friction coefficient vs pressure for various gases in both PTMSP and the Anodisc. CO_2 in PTMSP represents a gas-membrane combination where sorption is expected to contribute heavily to flux, whereas both He and CO_2 in the Anodisc are not expected to contribute significantly to rheological changes in the membrane. In the Anodisc, no general trend was observed in the friction coefficient in varying the pressure. The data does show high scatter though, attributed to the dramatic topography of the open pore structure. In contrast, CO_2 in PTMSP shows a positive correlation between friction coefficient and pressure, with little scatter in the data. This suggests that the sorbed gas increases the energy dissipative capacity

of the membrane, likely through a plasticization mechanism. The ability to detect internal sorption with a surface sensitive technique owes itself to the tools sensitivity to rheology both on, as well as near the membrane surface as a result of the normal force of the cantilever.

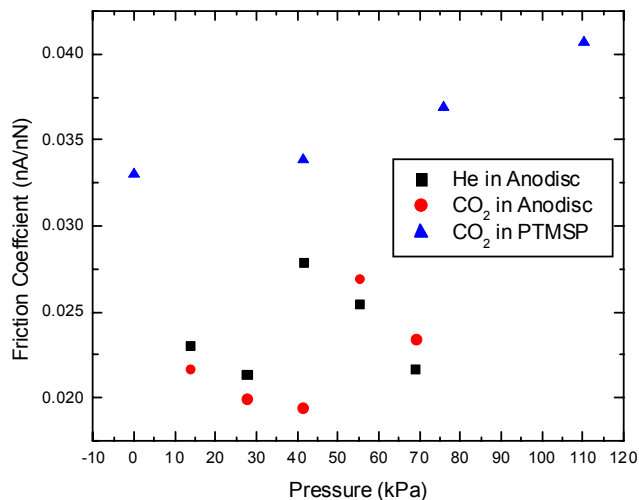


Figure 4: Friction coefficient vs pressure for CO_2 in PTMSP as well as He and CO_2 in the Anodisc.

4 CONCLUSION

In high permeance systems, such as the anodisc, Flux LFM has been shown as highly sensitive to surface gas flux. In dramatically lower permeance systems, such as relatively thick polymer membranes, it is not possible to resolve normal forces acting on the cantilever tip, however it is possible to resolve local rheological changes stemming from the sorption of the gas in the polymer. By moving to thinner polymer films, with higher permeance it may be possible to simultaneously resolve pure sorption near the surface, as well as total gas flux through the membrane. Regardless, the tool appears sensitive enough to various forms of gas flow to add utility for investigation of heterogeneous membrane materials.

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