Gas Permeation Resistance of Fluoropolymers

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Abstract
With a unique combination of toughness, purity, and chemical resistance, fluoropolymers are excellent candidates for balance of plant components. This paper explores the permeation resistance of PFA (a melt processable fluoropolymer) to hydrogen and oxygen. The influence of specimen thickness and gas pressure has been investigated for each gas.

Materials and Methods
Perfluoroalkoxy (PFA) specimens (1) were cut from extruded films (DuPont Teflon® LP Series) with thickness ranging between 0.002 inch and 0.030 inch (0.051 mm to 0.76 mm). Permeant gases were hydrogen and oxygen (Industrial Grade, Toll Co., Minneapolis, MN). The gas permeation apparatus consisted of a sample holder inside of a temperature-controlled chamber, a series of valves, an upstream ballast tank, a pressure transducer (300 psi Heise PM Digital Indicator) for the upstream gas, and a downstream solid-state manometer (10 Torr MKS Baratron Type 627B). The apparatus was constructed from stainless steel. Connections were made by welding or with VCR flanges to prevent leaks. Acquisition of temperature and pressures as well as control were done remotely with a personal computer.

Permeation measurements were made according to standard manometric procedures (2) as described below. A circular PFA specimen with a diameter of 4.6 cm and an effective area (A) of 13.7 cm^2 was placed in the gas permeation apparatus. The apparatus was pumped down to approximately 20 mTorr and held overnight to remove volatile constituents from the apparatus as well as from the PFA specimen. The next day, the apparatus was leak tested. If the leak rate was sufficiently low, then the upstream side of the apparatus with charged with hydrogen or oxygen. After pressure and temperatures were allowed to equilibrate for a few minutes, the test was started. The downstream pressure rise ($-\Delta p_l$) was recorded with the passage of time. (Temperature and upstream pressure (Δp) also were monitored over the duration of the experiment to assure their constancy.) All measurements made at 25°C.

Analysis
Gases permeate through homogeneous materials by first dissolving and then diffusing (3). The downstream pressure rise ($-\Delta p_l$) of the permeant can be converted to an equivalent volume of gas (V) at standard temperature and pressure (STP),

$$V = (\Delta p_l / \Delta p_o)(T_o/T)V_s, \quad (1)$$

where T is the temperature at which the measurement was made, V_s is the volume of the downstream side of the permeation apparatus, T_o is standard temperature (= 273K) and Δp_o is standard pressure (= 1 atm or 76 cmHg). The volume (V) of gas that permeates through a film with time (t) under steady state conditions depends on the permeability coefficient (P), as well as film thickness (B), film area (A), and the applied upstream pressure (Δp) (3,4),

$$V = P \cdot A \cdot \Delta p \cdot t / B. \quad (2)$$

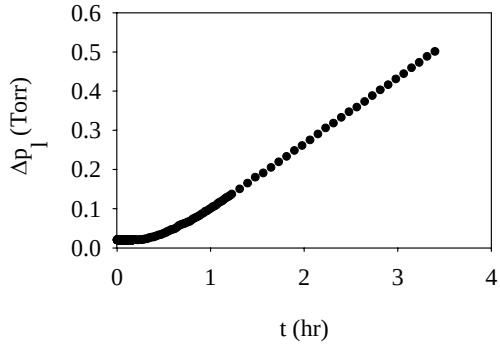

Figure 1. Downstream pressure (Δp_l) *versus* time (t) of oxygen gas permeating through a 0.020 inch (0.51 mm) PFA film under an applied upstream pressure of $\Delta p = 2.1$ atm.

Results and Discussion

Figure 1 shows the downstream pressure (Δp_l) with the passage of time for oxygen permeating through a 0.020 inch (0.51 mm) PFA film under an applied upstream pressure of $\Delta p = 2.1$ atm. Initially, Δp_l remained constant. After about 30 min, oxygen broke through and Δp_l began to rise with time, reaching steady state after several hours. Other measurements behaved similarly, but break through times and Δp_l rise rates depended on sample thickness and the gas.

The downstream pressures (Δp_l) from Figure 1 were converted to gas volumes at STP [equation (1)] and then plotted in Figure 2 as $V \cdot B/A \cdot \Delta p$ *versus* t according to equation (2). The points are experimental data and the solid line represents linear regression from longer times. The slope of the line in Figure 2 is equal to the permeability coefficient (P), which for this film, has a value of $P = 4.6 \times 10^{-10}$ $cm^3 \cdot cm/cm^2 \cdot s \cdot cmHg$.

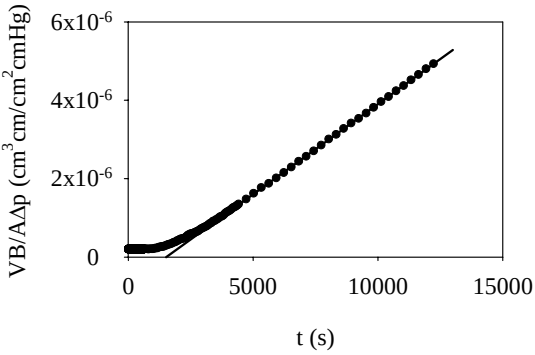

Figure 2. A plot of $V \cdot B/A \cdot \Delta p$ *versus* time (t) for oxygen permeating through a 0.020 inch (0.51 mm) PFA film under an applied upstream pressure of $\Delta p = 2.1$ atm.

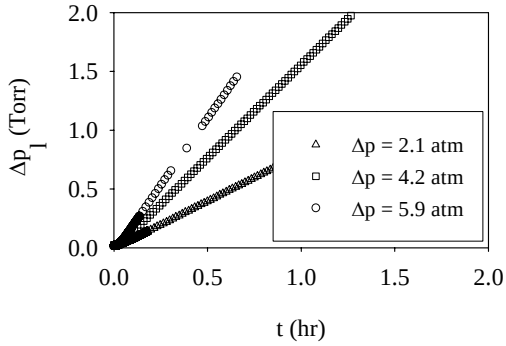

Figure 3. Downstream pressures (Δp_l) *versus* time (t) of a 0.005 inch (0.13 mm) PFA film for oxygen gas at various upstream pressures (Δp).

Figure 3 shows downstream pressures (Δp_l) *versus* time for oxygen permeating at various upstream pressures (Δp). As this film was relatively thin, permeation quickly reached steady state. Δp_l increased proportionally with Δp. Consequently, the three Δp values gave the same value of the permeability coefficient, $P = (5.4 \pm 0.1) \times 10^{-10}$ $cm^3 \cdot cm/cm^2 \cdot s \cdot cmHg$.

Permeability coefficients (P) of oxygen through PFA films of various thickness (B) are shown in Figure 4. The thinnest films had a smaller fraction of crystallinity and consequently allowed oxygen to permeate faster. For the thicker films (B ≥ 0.01 inch or 0.25 mm), P values were invariant, $P = (4.5 \pm 0.1) \times 10^{-10}$ $cm^3 \cdot cm/cm^2 \cdot s \cdot cmHg$.

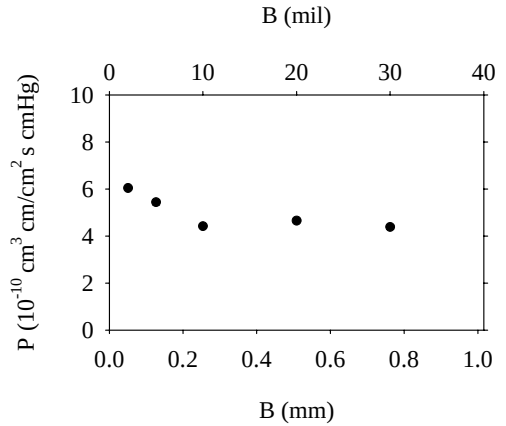

Figure 4. Permeability coefficients (P) of oxygen through PFA films of various thickness (B).

Table 1. Permeability coefficients (P) of hydrogen and oxygen through PFA film (B ≥ 0.01 inch or 0.25 mm) at 25°C.

Permeant	P (10^{-10}cm^3·cm/cm^2·s·cmHg)
Hydrogen (H_2)	12.2 ± 0.3
Oxygen (O_2)	4.5 ± 0.1

Permeability coefficients (P) of hydrogen and oxygen through thicker PFA films are summarized in Table 1. The permeation characteristics of hydrogen through PFA were similar to those of oxygen: permeation rates were proportional to the applied upstream pressure; the thinnest films allowed greater hydrogen permeation; films thicker than 0.010 inch (0.25 mm) showed a single P value. Similarities aside, hydrogen permeated faster than oxygen, primarily due to its smaller molecular size (5,6).

The permeability coefficients estimated here describe an intrinsic property of this PFA that can be used to estimate transfer of hydrogen or oxygen through components of different shape, area and thickness. Also, it should be noted that the permeability of PFA is comparable to other engineering thermoplastics (7).

Conclusions

Hydrogen, with its smaller molecular size, permeated faster through PFA than oxygen. The larger permeation rates for the thinnest films were due to less crystallinity. Permeability coefficients for both hydrogen and oxygen were independent of applied upstream pressure and thickness, where films were more than 0.010 inches (0.25 mm) thick. Subsequently, these permeability coefficients can be used to estimate steady-state transfer of hydrogen and oxygen gas through PFA components of various shape, area, and thickness.

Acknowledgments

We thank Entegris Fuel Cell for their support of this work and for allowing publication.

References

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