

Gas Permeation Resistance of a Perfluoroalkoxy-Tetrafluoroethylene Copolymer

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ABSTRACT: The permeation resistance of perfluoroalkoxy (PFA), a polytetrafluoroethylene (PTFE) copolymer, to various gases was explored. The diffusion and permeability coefficients for hydrogen, oxygen, nitrogen, and air were measured with extruded films using standard manometric techniques. For thicker films, transport properties were independent of film thickness. For the thinnest films, the diffusivity and permeability coefficients were slightly higher

because of reduced crystallinity. The solubility of these apolar permeants in PFA was quite low and behaved ideally. Therefore, the permeation characteristics of air could be calculated from those of nitrogen and oxygen. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2122–2125, 2006

Key words: diffusion; fluoropolymers; polytetrafluoroethylene (PTFE)

INTRODUCTION

Possessing a unique combination of toughness, purity, and chemical resistance had enabled PTFE copolymers to be employed by the microelectronics industry in fluid handling systems for many years.^{1,2} The properties that make these materials attractive for microelectronics applications also suit them well for the balance-of-plant (BOP) fluid handling components that direct flow of fuel, oxidants, reaction byproducts, and coolants through fuel cell stacks. As in microelectronic components,^{3,4} impurities can degrade or destroy fuel cells.^{5,6} For example, metal ions can bind with the exchange sites on perfluorosulfonate membranes, causing deterioration of fuel cell performance.⁵ Potentially harmful contamination could come from fuels, oxidants, or materials used in the construction of the cell stack itself, as well as from materials used in ancillary subsystems, such as BOP fluid handling components.

Although a great deal is known about the purity, mechanical and thermal properties of PTFE and its copolymers, less is known about their permeation characteristics. Therefore, this article explores the permeation resistance of perfluoroalkoxy (PFA), a melt-processible fluoropolymer, to hydrogen, oxygen, nitrogen, and air. The influence of gas pressure and specimen thickness was investigated for each gas.

EXPERIMENTAL

Materials and methods

PFA specimens⁷ with a thickness ranging between 0.051 and 0.76 mm were cut from extruded films (Teflon[®] LP Series, DuPont, USA). Melt temperature (T_m) and melt enthalpy (ΔH) were determined using differential scanning calorimetry (Perkin Elmer DSC7). Samples ranging in mass from 4 to 7 mg were cut from the PFA sheet, heated from 30°C to 350°C, cooled from 350°C to 30°C, and then heated again from 30°C to 350°C at a rate of 10°C/min. The resulting DSC scans were analyzed with the DSC7 software. DSC scans in triplicate were performed for each material. The crystalline fraction (x_c) was calculated as⁸

$$x_c = \Delta H / H_f, \quad (1)$$

where ΔH is the melting enthalpy and H_f is the melting enthalpy of the polymer in a 100% crystalline state.

The permeant gases used were hydrogen, oxygen, nitrogen and air (Industrial Grade, Toll Co., Minneapolis, MN). The gas permeation apparatus consisted of a sample holder inside 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. Data acquisition and control were performed remotely with a personal computer.

Permeation was measured according to standard manometric procedures⁹ as described below. A circu-

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TABLE I
Thermal Properties of PFA Films as a Function
of Thickness (B)

B (mm)	T_m (°C)	ΔH (J/g)	x_c
0.051	310 ± 1	15.6 ± 2.3	0.23 ± 0.04
0.13	311 ± 2	16.1 ± 1.2	0.24 ± 0.02
0.25	310 ± 1	20.5 ± 1.5	0.31 ± 0.02
0.51	311 ± 1	20.2 ± 0.0	0.30 ± 0.01
0.76	311 ± 1	20.0 ± 0.9	0.30 ± 0.01

lar PFA specimen with a diameter of 4.6 cm and an effective area (A) of 13.7 cm² was placed in the gas permeation apparatus. The apparatus was pumped down to approximately 20 mTorr and held at that pressure 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 was charged with the permeant gas. After pressure and temperature were allowed to equilibrate for a few minutes, the test was started. The downstream pressure rise (Δp_1) was recorded with the passage of time. (Temperature and upstream pressure, Δp , also were monitored over the duration of the experiment to assure they were constant.) All measurements were made at 25°C.

Analysis

Gases permeate homogeneous materials by first dissolving and then diffusing.¹⁰ The downstream pressure rise (Δp_1) of a permeant can be converted to an equivalent volume of gas (V) at standard temperature and pressure (STP),

$$V = (\Delta p_1 / \Delta p_o)(T_o / T)V_s, \quad (2)$$

where T is the measurement temperature, V_s is the volume of the downstream side of the permeation apparatus, T_o is the standard temperature (= 273 K), and Δp_o is the standard pressure (= 1 atm or 76 cm Hg). The volume (V) of gas that permeates a film with time (t) under steady-state conditions depends on the permeability coefficient (P), as well as on film thickness (B), film area (A), and the applied upstream pressure (Δp),^{10,11}

$$V = P \cdot A \cdot \Delta p \cdot t / B. \quad (3)$$

The time required for a permeant to break through a film (t_b) depends on the film thickness (B) and the diffusion coefficient of the material,

$$t_b = B^2 / 6D. \quad (4)$$

Solubility coefficients were calculated for permeability and diffusion coefficients as

$$S = P / D. \quad (5)$$

RESULTS AND DISCUSSION

Table I shows the thermal properties of the PFA films. The peak melt temperature was the same for all films, $T_m = 310^\circ\text{C}$. In contrast, melt enthalpy and crystalline fraction varied slightly with film thickness. The melt enthalpy of the thinnest film was $\Delta H = 16$ J/g, whereas for the thicker films, it was $\Delta H = 20$ J/g, in agreement with the reported range of values for PFA.¹² The surfaces of molded semicrystalline polymers usually are covered with a thin, amorphous "skin."¹³ For the thinnest specimens, it appeared that the amorphous skin represented a significant portion of the PFA film, leading to a measurable reduction in overall crystallinity. The corresponding crystalline weight fractions (x_c) of the various PFA films, which were calculated from eq. (1) using a ΔH_f of 67 J/g,⁸ varied between 23% and 30%.

Figure 1 shows the downstream pressure (Δp_1) with the passage of time for oxygen permeating a 0.51-mm PFA film under an applied upstream pressure of $\Delta p = 2.1$ atm. Initially, Δp_1 remained constant. After about 30 min, oxygen broke through, and Δp_1 began to increase with time, reaching a steady state after several hours. Other measurements behaved similarly, but breakthrough times and Δp_1 increase rates depended on sample thickness and gas.

The downstream pressures (Δp_1) from Figure 1 were converted to gas volumes at STP [eq. (2)] and then plotted as $V B A^{-1} \Delta p^{-1}$ versus t according to eq. (3), shown in Figure 2 (dots represent experimental data and the solid line represents linear regression from

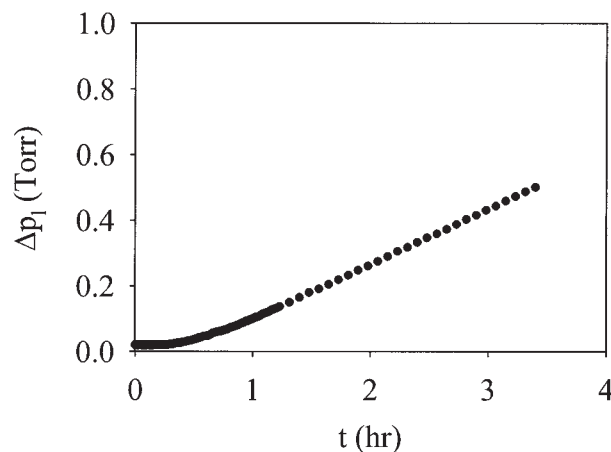


Figure 1 Downstream pressure (Δp_1) versus time (t) of oxygen gas permeating a 0.51-mm PFA film under an applied upstream pressure of $\Delta p = 2.1$ atm.

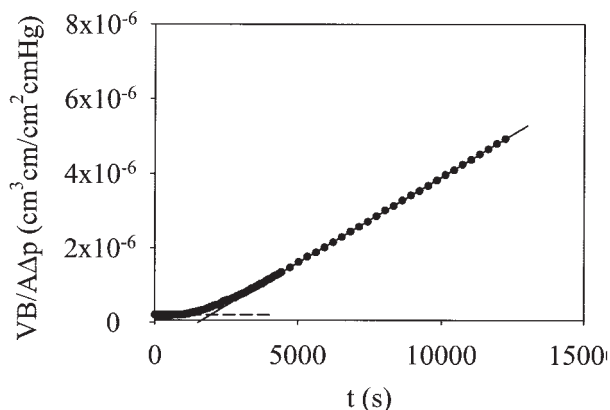


Figure 2 Plot of $V B \Delta p^{-1}$ versus time (t) of oxygen permeating a 0.51-mm PFA film under an applied upstream pressure of $\Delta p = 2.1$ atm.

longer times). The slope of the line in Figure 2 equals the permeability coefficient (P), which for this film had a value of $P = 4.6 \times 10^{-10} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} (\text{cm Hg})^{-1}$. Breakthrough time (t_b) was estimated from the intersection of two lines—the first was defined by the permeability coefficient and the second was a zero slope line passing through the initial Δp_1 at $t = 0$ s. For the data in Figure 2, t_b was 1960 s (about 33 min), corresponding to a diffusion coefficient of $D = 22 \times 10^{-8} \text{ cm}^2/\text{s}$.

Figure 3 shows downstream pressure (Δp_1) versus time for oxygen permeating a 0.13-mm PFA film at various upstream pressures (Δp). As this film was relatively thin, permeation quickly reached steady state. Because Δp_1 increased proportionally to Δp , the three Δp values showed the same permeability coefficient, $P = (5.4 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} (\text{cm Hg})^{-1}$. The average breakthrough time from this thinner film was only $t_b = (114 \pm 6)$ s, corresponding to $D = (24 \pm 1) \times 10^{-8} \text{ cm}^2/\text{s}$.

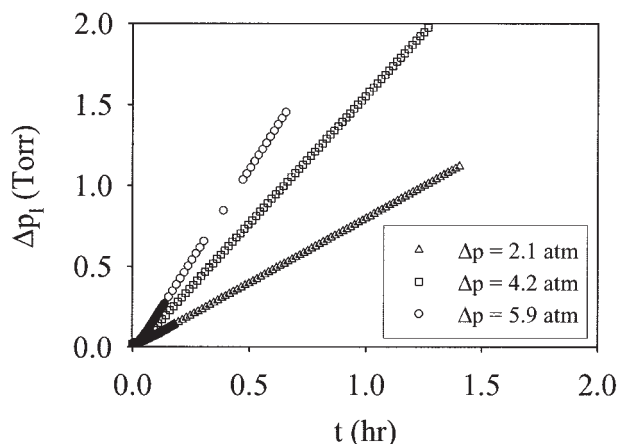


Figure 3 Downstream pressure (Δp_1) versus time (t) of oxygen gas permeating a 0.13-mm PFA film at various upstream pressures (Δp).

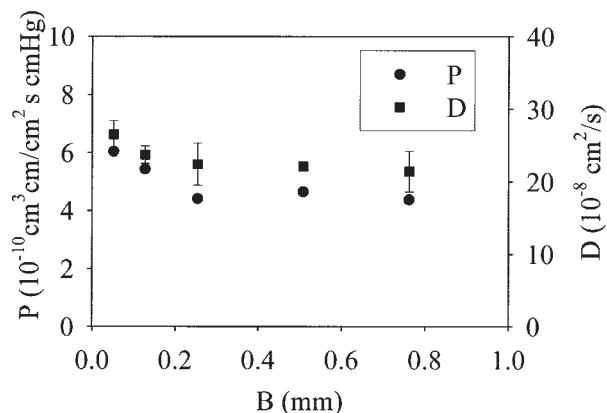


Figure 4 Permeability coefficients (P) and diffusion coefficients (D) of oxygen through PFA films of various thicknesses (B).

Figure 4 shows the permeability (P) and diffusion (D) coefficients of oxygen through PFA films of varying thickness (B). The thinnest films had a smaller fraction of crystallinity and consequently allowed faster permeation. For the thicker films ($B \geq 0.25$ mm), P and D were invariant, $P = (4.5 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} (\text{cm Hg})^{-1}$ and $D = (22 \pm 2) \times 10^{-8} \text{ cm}^2/\text{s}$.

The permeation characteristics of hydrogen, nitrogen, and air through PFA were similar to those of oxygen: permeation rates were proportional to the applied upstream pressure, and the thinnest films exhibited slightly higher permeability and larger diffusion coefficients than did the thicker films. Table II summarizes the mass transfer coefficients of the thicker PFA films. Similarities aside, hydrogen permeated faster than oxygen and nitrogen, primarily because of its smaller molecular size.¹⁴ The P values measured for nitrogen and oxygen agreed well with previously published results.¹⁵ (No information was given in Pauly¹⁵ regarding diffusion coefficients, grade of PFA, sample preparation, or test conditions.)

The solubility coefficients, also listed in Table II, were quite low. On a mass basis at standard temperature and pressure, the amount of gas dissolved in these PFA films would be quite small, from 1.8 $\mu\text{g/g}$

TABLE II
Permeability Coefficients (P), Diffusion Coefficients (D) and Solubility Coefficients (S) of the Various Gases through PFA Film ($B \geq 0.25$ mm) at 25°C

Permeant	P	D	S
	($10^{-10} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$)	($10^{-8} \text{ cm}^2/\text{s}$)	($10^{-3} \text{ cm}^3 / \text{cm}^3 \cdot \text{cmHg}$)
Hydrogen (H_2)	12.2 ± 0.3	230 ± 60	0.61 ± 0.30
Nitrogen (N_2)	1.5 ± 0.1	11 ± 1	1.4 ± 0.1
Oxygen (O_2)	4.5 ± 0.1	22 ± 2	2.1 ± 0.2
Air	2.1 ± 0.1	13 ± 1	1.6 ± 0.1

TABLE III
Permeability Coefficients (P), Diffusion Coefficients (D)
and Solubility Coefficients (S) of the Air through
PFA Film (B ≥ 0.25 mm) at 25°C

Permeant	P	D	S
	($10^{-10}\text{cm}^3 \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$)	($10^{-8}\text{cm}^2/\text{s}$)	($10^{-3}\text{cm}^3/\text{cm}^3 \cdot \text{cmHg}$)
Measured	2.1 ± 0.1	13 ± 1	1.6 ± 0.1
Calculated	2.2 ± 0.2	13 ± 3	1.5 ± 0.2

for hydrogen to $106 \mu\text{g/g}$ for oxygen. With such low concentrations, Henry's law should apply, and ideal behavior is expected. Moreover, the gases would not be expected to interact strongly with each other or with the polymer. Therefore, it would be expected that the permeation characteristics of mixtures could be estimated from mass transfer coefficients of the pure gases. Table III lists mass transfer coefficients calculated using the following equations,

$$P = x_n P_n + x_o P_o, \quad (6)$$

$$D = x_n D_n + x_o D_o, \quad (7)$$

and

$$S = x_n S_n + x_o S_o, \quad (8)$$

where P_n , D_n , and S_n are the mass-transfer coefficients for nitrogen; P_o , D_o , and S_o are the mass-transfer coefficients for oxygen; and x_n and x_o are the mole fractions of nitrogen and oxygen in air ($x_n = 0.79$ and $x_o = 0.21$). Calculated and measured values for air were in very good agreement.

CONCLUSIONS

Hydrogen, with its smaller molecular size, permeated faster through PFA than did oxygen and nitrogen. The

larger permeation rates for the thinnest films were a result of less crystallinity. Where films were more than 0.25 mm thick, permeability, diffusion, and solubility coefficients were independent of applied upstream pressure and thickness. These coefficients can be used to estimate the permeation of hydrogen, nitrogen, and oxygen (or mixtures of these gases) through PFA components of various shape, area, and thickness.

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