CT Associates, Inc.
7121 Shady Oak Road, Eden Prairie, MN 55344-3516
Telephone: [redacted] Fax: [redacted]
Website: http://www.ctassociatesinc.com

Hydrochloric Acid Gas Permeation through Various Polymeric Materials

Submitted to:
Reto Schoeb
Levitronix

Submitted by:
Mark Litchy
CT Associates, Inc.

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Objective:

The magnets in Levitronix's pump impellers are susceptible to attack by concentrated acids. To protect them from attack, the magnets are encapsulated with a perfluoroalkoxy (PFA) coating. However, permeation of an acid gas through the coating may cause premature failure. The lower the rate of the acid gas permeation through the polymeric material, the longer the expected life of the impeller.

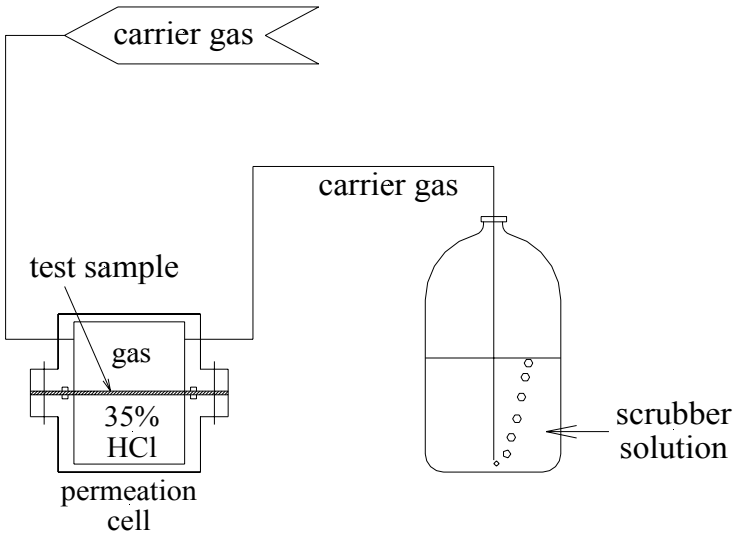
The objective of this project was to measure the permeation rate of concentrated hydrochloric acid (HCl) through several polymeric materials. The materials selected were polypropylene (PP), polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), ethylene chlorotrifluoroethlyene (ECTFE), Daikin AP-211SH PFA, Dupont PFA 440HP, Dupont PFA 940HP, and polyethylene (PE) 1000. This test work will aid in determining appropriate alternative magnet encapsulation materials.

Experimental:

Permeation measurements were made using the test system shown in Figure 1. In this system, the material to be tested was placed in a permeation cell. Each cell was placed in a temperature-controlled enclosure. Each cell contained two chambers with a test sample between them. The bottom chamber was filled with 15 ml of 35% HCl. The upper chamber was continuously purged with air that swept any acid gas that permeated through the test sample into a scrubber.

The amount of HCl permeating through the test sample was determined by measuring the concentration of chloride ions in the scrubber over time. Concentration was measured using a specific ion electrode. Tests were conducted at temperatures of 30°C, 42°C, and 55°C. The thickness of each test sample was 1.5 mm. Background chloride concentrations were measured prior to adding HCl to the cells. Two negative controls were included in the tests. All materials were tested in triplicate. However, results are only presented for two of the ECTFE samples and one of the PVDF samples at 30°C, as will be discussed later. Tests were conducted in two rounds. The initial round included eight test cells (2 control samples, 2 PP samples, 2 PVDF samples, 1 PTFE sample, and 1 ECTFE sample). After the first round was complete, four additional materials were added to the test matrix (Daikin PFA, PFA 440HP, PFA 940HP, and PE 1000). As a result, 12 additional tests cells were added to the test. Thus, in round two, there were a total of 20 test cells (2 control samples, 1 PP sample, 1 PVDF sample, 2 PTFE samples, 2 ECTFE samples, and 3 samples of Daikin PFA, PFA 440 HP, PFA 940 HP, and PE 1000).

Figure 1. Test system schematic for measuring acid gas permeation



Results and discussion:

A background test was performed with eight test cells at a temperature of 55°C prior to filling the cells with hydrochloric acid. The rate of chloride collected over time was low (<0.02 μmoles/day) during the three-week test.

Figures 2-4 show permeation measurements for all eight materials at 30°C, 42°C, and 55°C, respectively. Results are presented for three samples of each material at each temperature. The graphs present total mass of acid collected in the scrubber over time. The graphs include linear regressions of the data after steady-state was achieved. The slope of each curve gives the permeation rate through the material in micromoles per day. Note that the non-steady-state results are not presented in Figures 2-4. Examples of the permeation rate measurements for each material at 30°C including non-steady-state results are presented in Appendix A.

In round one, the first temperature tested was 30°C. The PP and PTFE samples reached steady-state within two weeks. The PVDF and ECTFE samples, which had significantly lower permeation rates, also appeared to have achieved steady-state during this period, when in fact they had not. As a result, the test was concluded after 40 days at 30°C, but it took longer than 40 days for the HCl permeation rate through these materials to reach steady-state. The permeation rate is the product of the solubility of the gas in the polymer times the diffusion rate of the gas through the polymer. It turns out that both PVDF and ECTFE have very low HCl diffusivities. A low diffusivity means than it takes a long time to reach steady-state. Thus, the initial permeation rates were thought to be lower than they actually were since steady-state had not yet been achieved. After the tests at 42°C and 55°C were complete, the test results for the PVDF and ECTFE samples at 30°C appeared suspiciously low since they did not follow the curve established by the higher temperature results. As a result, the time spent measuring permeation rates at the 30°C temperature was increased during the second round test. During the second round tests, it was verified that the permeation rates measured at 30°C during round one for the PVDF and ECTFE materials were incorrect. In fact, it took more than 8 weeks to achieve steady-state at 30°C for the ECTFE and PVDF materials (see Appendix A). Hence, the permeation results for the ECTFE sample and PVDF samples at 30°C in round one are not included in this report.

Figure 2a. HCl permeation rate measurements at 30°C

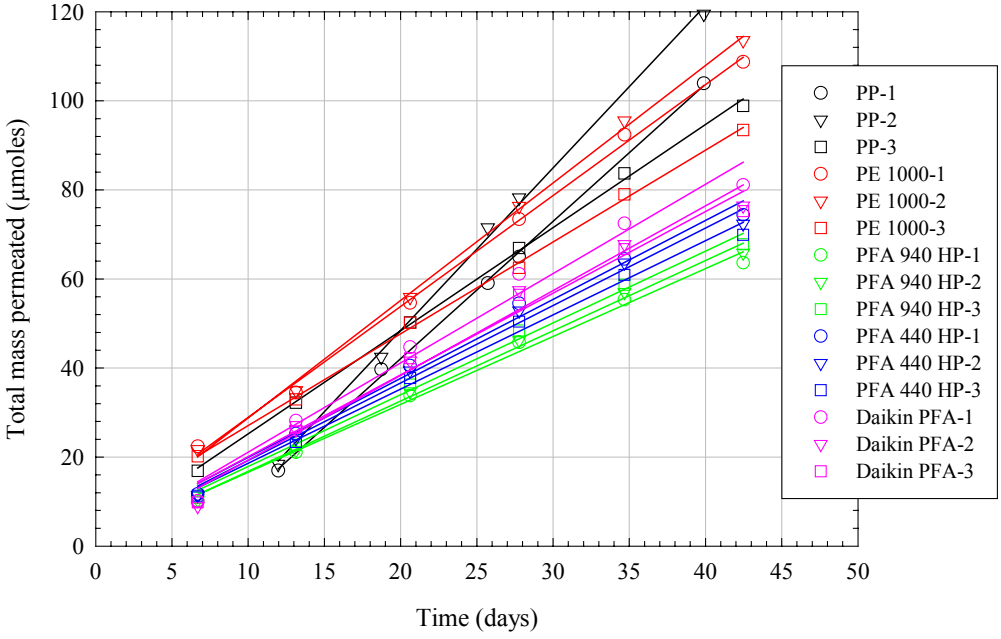
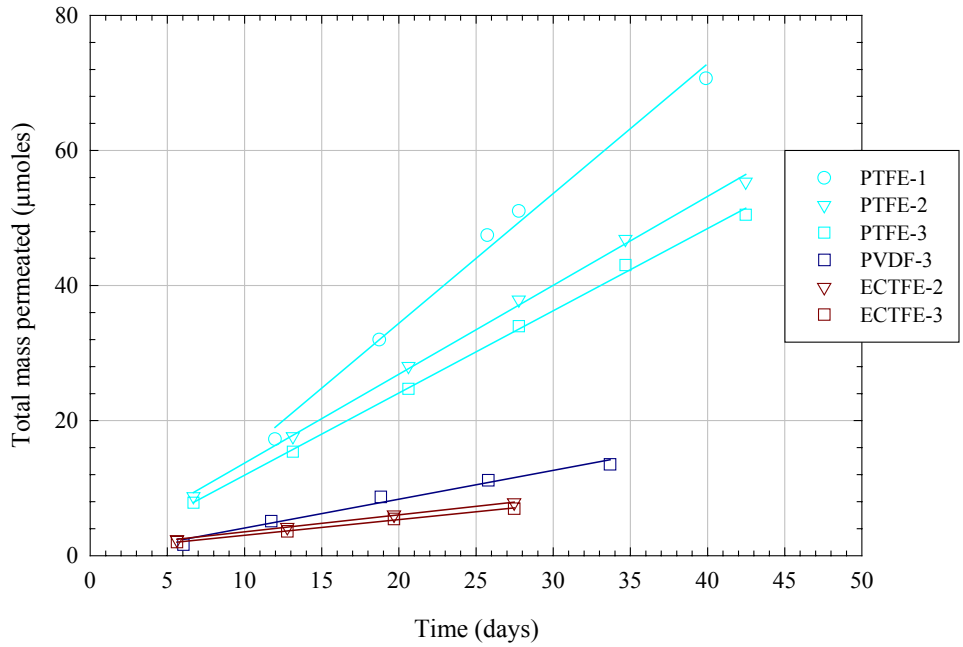


Figure 2b. HCl permeation rate measurements at 30°C (cont'd)



Overall, the acid mass collection rates from the PE 1000, PFA 940 HP, PFA 440 HP, Daikin PFA, and PTFE samples reached steady-state conditions at 30°C within a few days, while the PP samples required nearly two weeks, and the ECTFE and PVDF required more than 8 weeks. Surprisingly, the PP samples, which required nearly two weeks to achieve steady-state conditions, had the highest permeation rate of any of the materials evaluated. Although the objective was to measure steady-state permeation rates, some observations of the relative diffusivity and solubility of these materials may also be made. As stated earlier, the permeation rate of HCl through a polymer is

proportional to the product of the diffusion coefficient and the solubility of HCl in that polymer. The slow approach to steady-state suggests that the diffusivity of HCl gas in PP is low compared to all of the other materials except ECTFE and PVDF, even though the permeation rate was the highest of the materials tested. As a result, the solubility of HCl in PP must be rather high. Since ECTFE and PVDF took even longer to reach steady-state conditions, the diffusivity of HCl in these materials was very low compared to all of the other materials. Furthermore, we suspect the diffusivity and solubility of HCl in the other materials (various PFAs and PE) are rather similar.

Figure 3a. HCl permeation rate measurements at 42°C

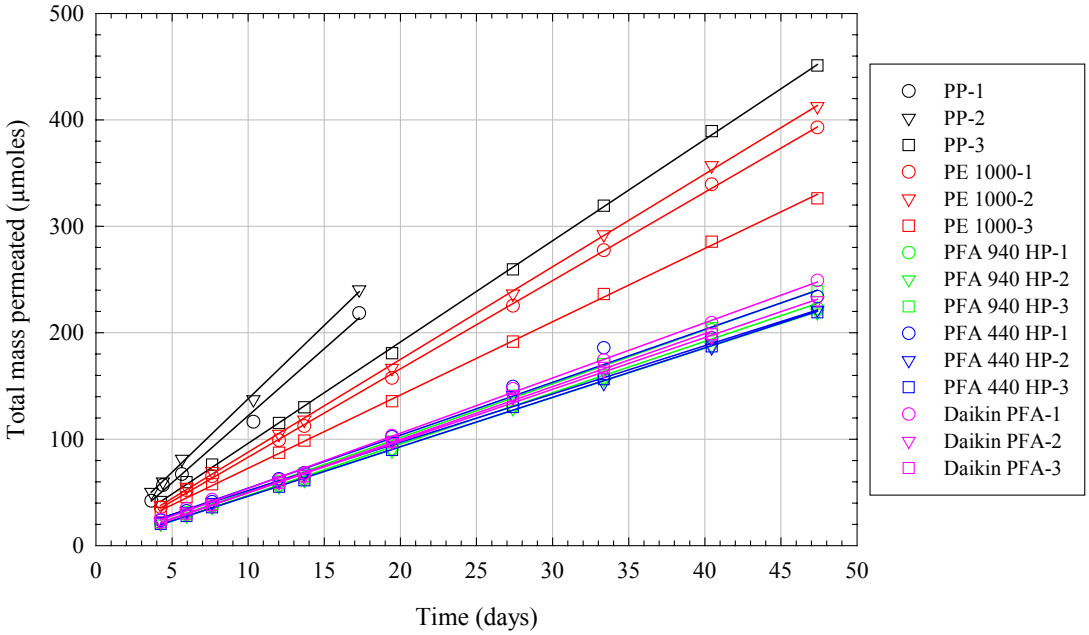


Figure 3b. HCl permeation rate measurements at 42°C (cont'd)

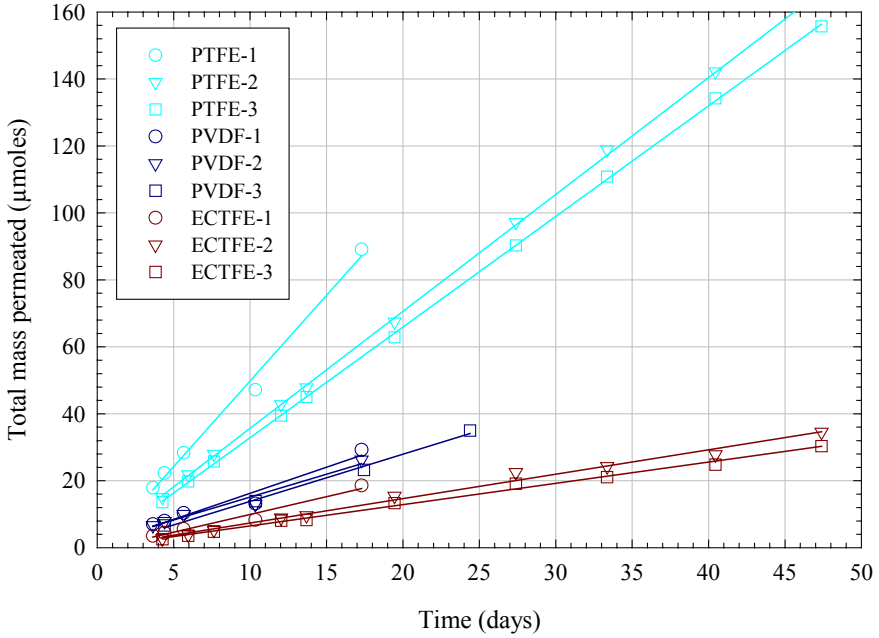


Figure 4a. HCl permeation rate measurements at 55°C

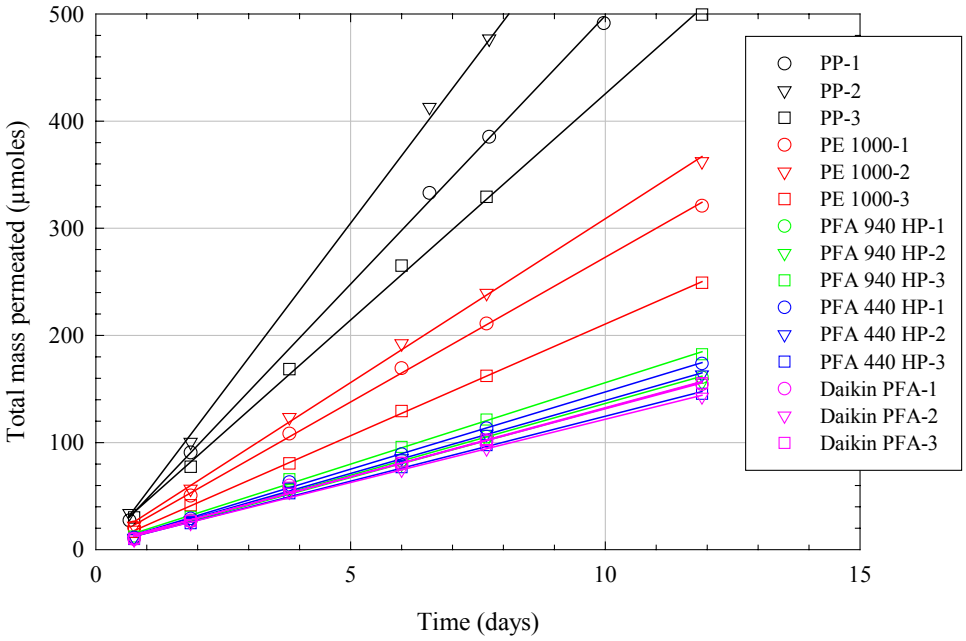
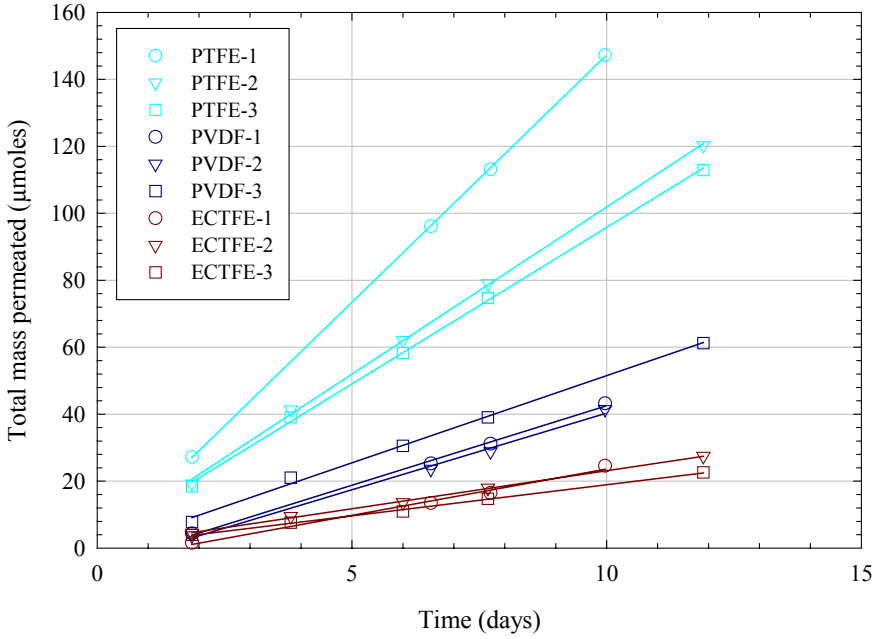


Figure 4b. HCl permeation rate measurements at 55°C (cont'd)

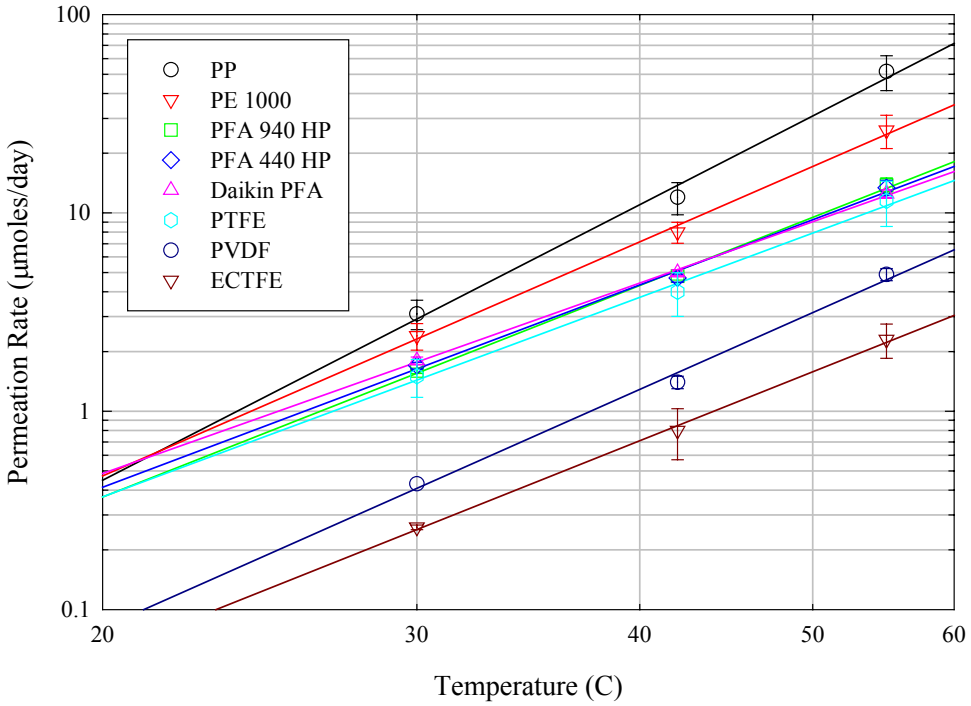


Upon removal of the samples from acid, visual observation of the samples revealed discoloration of some of the samples due to exposure to HCl. The PVDF samples turned a dark brown color and the ECTFE samples turned a tan color. No color change was observed with any of the other materials evaluated.

Figure 5 presents the mean permeation rates through each material as a function of temperature on a log-log plot. The error bars represent ± one standard deviation from the mean. The slopes of the permeation rate versus temperature curves were similar for all of

the test materials. ECTFE had the lowest permeation rate of the eight materials tested. The permeation rates of the various PFA materials were similar to each other and about six times higher than the permeation rate of ECTFE. The permeation rates of PP and PE 1000 were more than an order of magnitude higher than ECTFE, while PVDF was only about two times higher than ECTFE. These data suggest that the permeation rates approximately doubled every 8°C increase in temperature.

Figure 5. Permeation rates of each material as a function of temperature



The permeation coefficient for each material was calculated using equation 1. The mass flow rate used to calculate the permeation coefficient of the material with equation 1 is simply the slope of the mass collected versus time curve determined once steady-state had been achieved from Figures 2-4. The vapor pressures of HCl over 35% HCl at various temperatures are presented in Table I. The area available for diffusion in the test cell was 15 cm^2 and the thickness of each sample was 1.5 mm.

$$P = \frac{MT}{P_v A} \qquad (1)$$

where: M = Mass flow rate
P = Permeation coefficient
P_v = Gas vapor pressure
A = surface area available for diffusion
T = material thickness

Table I. Vapor pressure of HCl over 35% HCl at various temperatures

Temperature (°C)	HCl vapor pressure over 35% HCl (mm Hg)
30	140
42	270
55	530

[1] Values interpolated from data in reference.

The permeation coefficients measured for each material are presented in Table II. The table includes the permeation coefficients measured from each sample at each temperature. Mean and standard deviations for each material are also presented. Figure 6 presents the mean permeation coefficients of each material as a function of temperature on a log-log plot. The error bars represent ± one standard deviation from the mean.

Table II. Permeation coefficient results for each material at three temperatures

Permeation Coefficient (cm^3(g)-mm/M^2-day-atm)					
Material	Sample 1	Sample 2	Sample 3	Mean	Std. Dev.
30°C					
PP	380	440	320	**380**	60
PE 1000	310	320	240	**290**	44
PFA 940 HP	190	190	200	**190**	5.8
PFA 440 HP	220	210	200	**210**	10
Diakin PFA	230	210	210	**220**	11.5
PTFE	230	170	160	**190**	38
PVDF			52	**52**	
ECTFE		32	30	**31**	0.9
42°C					
PP	790	870	600	**750**	140
PE 1000	520	550	430	**500**	62
PFA 940 HP	310	290	320	**310**	15
PFA 440 HP	310	280	290	**290**	15
Diakin PFA	330	310	320	**320**	10
PTFE	320	220	210	**250**	61
PVDF	98	86	89	**91**	6.3
ECTFE	67	45	40	**51**	14
55°C					
PP	1610	2000	1360	**1660**	320
PE 1000	870	980	670	**840**	160
PFA 940 HP	430	410	490	**440**	42
PFA 440 HP	460	440	390	**430**	36
Diakin PFA	410	380	410	**400**	17
PTFE	480	320	310	**370**	95
PVDF	150	150	170	**160**	12
ECTFE	89	74	60	**74**	14

Table III shows the permeation coefficient of each material relative to the permeation coefficient of ECTFE, which had the lowest permeation coefficient of the materials

tested, at all three temperatures. The permeation coefficients of the various PFA materials were about six times higher than the permeation coefficient of ECTFE. The permeation coefficients of PP and PE 1000 were more than an order of magnitude higher than ECTFE, while PVDF was about two times higher than ECTFE. These ratios were essentially independent of temperature for all of the materials except PP. The permeation coefficient of PP relative to ECTFE increased with increasing temperature.

Figure 6. Permeation coefficients of each material as a function of temperature

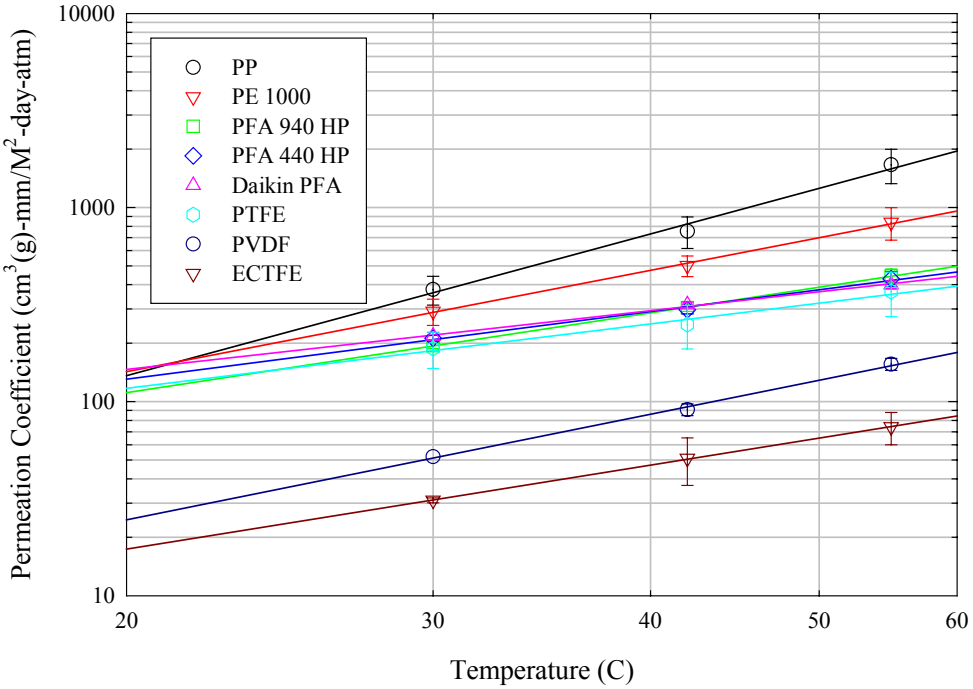


Table III. Permeation coefficients of various materials relative to ECTFE

Permeation Coefficients Relative to ECTFE			
Material	30°C	42°C	55°C
PP	12.2	14.7	22.4
PE 1000	9.4	9.8	11.3
PFA 940 HP	6.1	6.1	6.0
PFA 440 HP	6.8	5.7	5.8
Diakin PFA	7.1	6.3	5.4
PTFE	6.1	4.9	5.0
PVDF	1.7	1.8	2.2

Conclusions:

HCl permeation rates through the following polymers were measured at 30°C, 42°C, and 55°C: PP, PVDF, PTFE, ECTFE, Daikin AP-211SH PFA, Dupont PFA 440HP, Dupont PFA 940HP, and PE 1000. Permeation coefficients of each material were calculated as a function of temperature. The permeation coefficients of the various PFA materials were similar and were about six times higher than the permeation coefficient of ECTFE. The

permeation coefficients of PP and PE 1000 were more than an order of magnitude higher than ECTFE, while PVDF was about two times higher than ECTFE. These results were essentially independent of temperature for all of the materials except PP whose permeation coefficient increased faster with temperature than the other materials.

References:

1. John H. Perry, (1963), Chemical Engineers' Handbook 4th Edition, McGraw-Hill, New York, NY, p 3-61.

Appendix A

Examples of HCl permeation rate measurements at 30°C for each material (includes non-steady-state results)