Water Permeation of Polymer Films. IV. Teflon FEP

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Synopsis

The evaluation of the permeation parameters of water for Teflon FEP has shown that permeation is a dual mode process: Water is initially adsorbed onto the polymer surface in a layer; because the residence time of the layer is short, little is ultimately absorbed. The diffusion process is disrupted at the onset of molecular motion, at the glass transition, due to an increase in effective tortuosity. Variations of the permeation parameters with thickness suggest a skin, of total thickness near 25 μm, whose permeation parameters differ from those of the bulk.

INTRODUCTION

Processing difficulties with PTFE (polytetrafluoroethylene) led to the introduction of FEP, a copolymer of tetrafluoroethylene with some 15–20 mol % of hexafluoropropylene (HFP).[1-3] The introduction of a CF_3 branch lowers the density and crystallinity, as well as the glass transition temperature.

Indeed, a plot of the dynamic mechanical α (i.e., glass transition) peak temperature obtained at ~1 Hz, against mol % HFP[4] gave a plot having a smooth, monotonic decrease as the HFP content increased. In spite of this decrease, the activation parameters of the α peak are the same for both TFE and FEP,[5] indicating that the introduction of one CF_3 branch every 14 (or so) carbons has little effect on the glass transition motions themselves.

One of the unique features of fluoropolymers is their low surface tensions,[6] generally in the range of 15–25 dyn/cm. This results in a low work of adhesion between most polar liquids and these fluoropolymer surfaces (the work of adhesion for water on TFE and FEP is near 50 dyn/cm at 20°C) and is reflected in the energy of sorption, E_S.[7] Because the residence time of a molecule on a surface τ, is related to the energy of sorption[8]

$$\tau = 10^{12} \exp(-E_S/RT) \text{ s} \tag{1}$$

A higher value of E_S reflects a shorter residence time. For water on FEP, τ is in the neighborhood of 10^{-13} s.[7] Now, molecular motions also occur on this time scale so that, unless a water molecule fortuitously gains the bulk of the polymer by approaching between chains, it will be desorbed. This has been considered mathematically in a previous paper in this series,[7] where it was shown that the permeation of water through FEP was directly related to the extent to which the water covered the surface.

The present paper considers the actual permeation parameters, and how they are affected by the glass transition.

EXPERIMENTAL

Extruded DuPont Teflon FEP type 100 film was obtained from a vendor in thicknesses of 12.7, 25.4, and 50.8 μm. Permeation parameters were determined on a modified Dohrmann Envirotech Polymer Permeation Analyzer model PPA-1[9] in the temperature range 30–80°C and in the relative humidity range 20–95%. The low permeation rate necessitated the use of at least five samples at each thickness, repeating each condition several times. In this way, it was found that the range of values generally varied by a factor of about 2 at most, and formed a good Arrhenius plot straight line portion. When a value deviated noticeably, it was obvious, and the value was rejected and redetermined. Only in this way could extraneous data be noted and rejected, while giving a high statistical significance to the retained data.

The permeation coefficient P was obtained from the total instrument signal,[10] while the diffusion coefficient D was obtained from two stages during the permeation process: region 1, 10–40% of the process, and region 2, 40–70%. The solubility coefficient S and the concentration of sorbed water, C, were calculated from P and D. As noted,[7] X_1 (where X is the value of D, S, or C, while the subscript refers to the region in which it was measured) was found to differ from X_2, indicating a time-dependent process. C values over an extended relative humidity range, from which a Henry's law plot could be constructed, were evaluated only at 55°C.

While the permeation parameters at 25.4 μm were redetermined in this study, the data of the previous study[7] are also included. Although samples were taken from the same roll of material, the tables and figure indicate that differences exist between them. An analysis of the data and the experimental procedure indicates that these differences are caused by inherent difficulties in measuring these exceedingly low permeation values. For this reason, values at the various thicknesses, as well as differences between them, may only be considered semi-quantitatively, at best.

RESULTS

See that the data were found to fit the Arrhenius equation:

$$Y = Y_0 \exp(-E_Y/RT) \tag{2}$$

where Y is the observable, Y_0 is a constant, R is the gas constant, and T is the absolute temperature.

It was immediately found that Arrhenius plots of both P and D were composed of two linear portions which intersected near 65°C. An example is seen in Figure 1. The actual data are found in Table I, where the generally higher statistical significances below the intersection temperature reflect the larger temperature range of the data ($\Delta T \approx 35$°C, compared with ~15°C above the intersection temperature). Since the Arrhenius equations above and below the intersection must be equal at the temperature of the intersection, one obtains this temperature by equating them and solving for T; values so obtained are found in Table II, and average to 63.2 $\pm$ 2.8°C, the T_g of FEP.[1–5]

The calculated values of S give a linear Arrhenius plot, indicating a P-D compensation. Figure 2 shows that both S_1 and S_2 decrease with increasing thickness, while Table I shows this to be due to decreases in both S_0 and E_S.
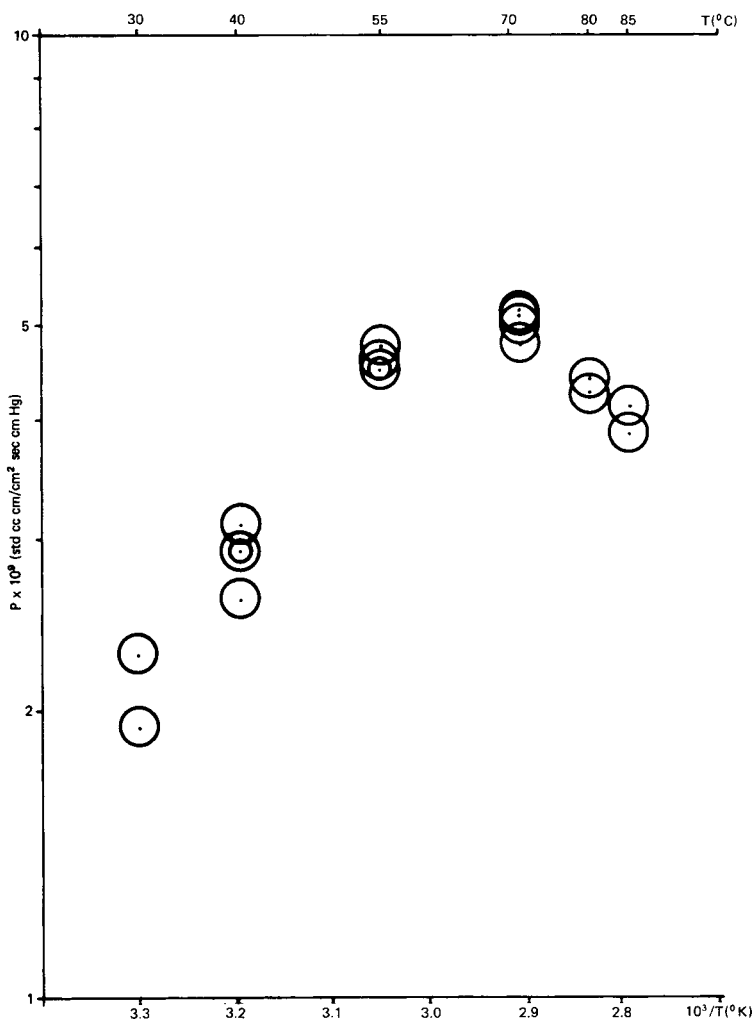
Fig. 1. An Arrhenius plot of the water permeation coefficient of 50.8-μm Teflon FEP.

This thickness effect is also indicated by the values of the entropy of activation for the diffusion process, $\Delta S_D^{\ddagger}$[11(a)]: as found in Table III, these values are negative, with the exception of those at 40°C for the 50.8 μm samples. As noted,[9] the actual permeation process should manifest positive values of $\Delta S_D^{\ddagger}$. [11(b)]

As previously shown,[7] Henry's law plots (C vs. % RH) are linear down to 20% RH but do not intersect the origin. This was interpreted as being due to the superposition of a Langmuir-like adsorption isotherm C_L, superimposed on a Henry's law isotherm C_H:

$$C = C_L + C_H \tag{3}$$

where

$$C_L = \frac{C_L' \times b \times (\%\ \text{RH})}{1 + b \times (\%\ \text{RH})} \tag{4}$$

and

$$C_H = k \times (\%\ \text{RH}) \tag{5}$$

TABLE I
Permeation Values for Teflon FEP at 50% RH

	Thickness (μm)			
	12.7	25.4[b]	25.4	50.8
Below intersection				
P_0 (std cc·cm/cm²·s·cm Hg)	$4.78_5 \times 10^{-6}$	5.03×10^{-6}	2.13×10^{-6}	6.59×10^{-5}
E_P (kJ/mol)	18.3 ± 3.6	18.5 ± 1.2	16.2 ± 3.1	26.2 ± 1.7
Statistical significance[a]	>0.9990	>0.9995	>0.9995	>0.9995
D_{01} (cm²/s)	1.15×10^{-4}	5.86×10^{-5}	2.48×10^{-4}	198
E_{D1} (kJ/mol)	23.7 ± 3.1	18.7 ± 5.1	23.5 ± 3.1	57.9 ± 4.8
Statistical significance[a]	>0.9999	>0.9995	>0.9995	>0.9995
D_{02} (cm²/s)	$1.02_5 \times 10^{-4}$	8.03×10^{-5}	9.74×10^{-4}	62.8
E_{D2} (kJ/mol)	24.0 ± 2.1	20.6 ± 7.1	$28.0 \pm 5.1_5$	54.9 ± 3.6
Statistical significance[a]	>0.9999	>0.9900	>0.9995	>0.9995
Above intersection				
P_0 (std cc·cm/cm²·s·cm Hg)	4.21×10^{-11}	7.83×10^{-11}	3.52×10^{-11}	2.11×10^{-11}
E_P (kJ/mol)	-14.6 ± 7.9	-13.4 ± 7.8	$-14.8 \pm 7.9_5$	-15.6 ± 1.8
Statistical significance[a]	>0.9000	>0.9000	>0.9995	>0.9995
D_{01} (cm²/s)	9.47×10^{-11}	7.36×10^{-10}	2.68×10^{-10}	3.83×10^{-5}
E_{D1} (kJ/mol)	-15.1 ± 8.7	-12.8 ± 6.0	-15.2 ± 12.9	$15.0 \pm 3.3_5$
Statistical significance[a]	>0.9000	>0.9500	>0.7500	>0.9975
D_{02} (cm²/s)	2.82×10^{-11}	1.88×10^{-9}	4.79×10^{-10}	9.69×10^{-5}
E_{D2} (kJ/mol)	-11.7 ± 6.1	-9.6 ± 16.9	-12.9 ± 15.7	18.0 ± 6.3
Statistical significance[a]	>0.9000	>0.6000	>0.7500	>0.9750
S_{01} (std cc/cc·cm Hg)	0.648	1.39	0.0126	1.29×10^{-6}
E_{S1} (kJ/mol)	1.7 ± 2.1	6.9 ± 2.1	-6.4 ± 1.8	-28.1 ± 1.2
Statistical significance[a]	>0.7500	>0.9950	>0.9990	>0.9995
S_{02} (std cc/cc·cm Hg)	0.201	0.224_5	0.00509	3.14×10^{-6}
E_{S2} (kJ/mol)	-2.0 ± 1.6	$1.1 \pm 2.8_5$	-9.6 ± 2.5	-25.8 ± 0.8
Statistical significance	>0.7500	>0.6000	>0.9995	>0.9995

[a] From both t-test and correlation coefficient
[b] Ref. 7.

TABLE II
Intersection Temperatures[a]

Intersection of	Thickness (μm)			
	12.7	25.4[b]	25.4	50.8
P	66.2	73.4	65.5	65.7
D_1	59.6	62.8	66.0	60.2
D_2	62.2	68.0	65.2	58.1

[a] In °C.
[b] Ref. 7.

C'_L, usually called the saturation constant, is the maximum concentration of the Langmuir-like isotherm, b is usually called the affinity constant, and k is the solubility constant. At sufficiently high relative humidity ($\geq 20\%$, in our case), $b \times (\% \text{ RH}) \gg 1$, and

$$C = C'_L + k \times (\% \text{ RH}) \tag{6}$$

Values of C'_L and k are found in Table IV. While the variation of C'_L with thickness is uncertain, this appears due to difficulties inherent in the measurement of such small values of the permeation parameters. For example, in our previous study,[7] which used another sample 25.4 μm thick, C'_{L1} and C'_{L2} were somewhat lower than in the present case, as seen in Table IV. Thus, their values are probably not known to better than a factor of, say, 2.
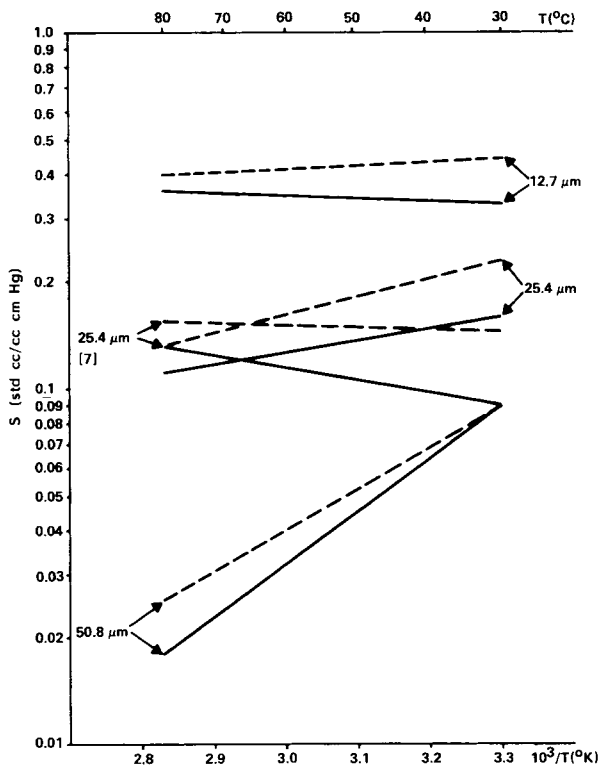

Fig. 2. Arrhenius plots of the water solubility coefficients of various thicknesses of Teflon FEP.

TABLE III
Entropies of Activation for Diffusion[a]

Thickness (μm)	Determined from	At 40°C	At 70°C
12.7	D_{01}	−41	−120
	D_{02}	−42	−170
25.4[b]	D_{01}	−45	−160
	D_{02}	−44	−130
25.4	D_{01}	−35	−150
	D_{02}	−23	−150
50.8	D_{01}	78	−50
	D_{02}	69	−40

[a] In J/mol·K.
[b] Ref. 7.

Knowing the density and thickness, one may calculate the surface area. From this and C'_L, one may calculate the number of molecules/Å^2. As in Ref. 7, this, plus an estimate of the area occupied by a water molecule ($\sim$9.65 Å^2), permits the calculation of the number of water monolayers on the film surface. This is found in Table V. Although, as stated above, the absolute value of C'_L is not known precisely, one must note that C'_{L2} is invariably greater than C'_{L1}. (The earlier data,[7] based on a single sample, suggested that $C_{L1} = C_{L2}$. The accumulation of data in which C_{L2} is invariably greater than C_{L1} now shows that suggestion to have been in error.) That is, the coverage increases with time.

Such an increase with time does not appear to be the case with C_H. This is seen in Table VI, calculated at 100% RH: while the previous study,[7] using a single thickness, found $C_{H1} < C_{H2}$, the present data show that C_H is actually invariant with time.

DISCUSSION

In a previous study on water permeation into polyimide,[9] no surface water layer was formed, and it was shown that, rather than

$$E_S = \Delta H_{cond} + \overline{\Delta H}_{mix} \tag{7}$$

where ΔH_{cond} is the molar heat of condensation and $\overline{\Delta H}_{mix}$ (sometimes small enough to be disregarded) is the partial molar heat of penetrant–polymer mixing, it is more appropriate to write

$$E_S = \Delta H_{ads} + \overline{\Delta H}_{mix}, \tag{8}$$

where ΔH_{ads}, the molar heat of adsorption, has replaced ΔH_{cond}. In the present case, the Langmuir-like surface layer indicates that eq. (7) is the more appropriate. Now, steam tables indicate that ΔH_{cond} is in the range of −(41.4–43.7) kJ/mol in the temperature range used, while $\overline{\Delta H}_{mix}$ is always positive. Thus, $\overline{\Delta H}_{mix}$ clearly cannot be disregarded in this case. Further, as seen in the E_S values in Table I, $\overline{\Delta H}_{mix}$ decreases dramatically between 25.4 and 50.8 μm.

Using the E_S values, eq. (1) gives the residence time of water on the Teflon surface. These are found in Table VII where, reflecting the E_S values, τ appears to depend on thickness, particularly between 24.4 and 50.8 μm. In order to elucidate the role of changing surface properties, if any, surface tensions were evaluated using the method of Kaelble.[12] This technique uses a contact angle

TABLE IV
Values of the Terms in the Henry's Law Plot at 55°C

	Thickness (μm)			
	12.7	25.4[a]	25.4	50.8
C'_{L1} (g water/g polymer) $\times 10^4$	1.67	0.38	1.22	0.289
k_1 (g water/g polymer $\times$ % RH) $\times 10^6$	8.06 ± 0.84	2.69 ± 0.22	2.24 ± 0.33	0.558 ± 0.037
C'_{L2} (g water/g polymer) $\times 10^4$	2.10	0.59	2.35	0.384
k_2 (g water/g polymer $\times$ % RH) $\times 10^6$	9.32 ± 1.41	3.19 ± 0.25	1.60 ± 0.51	0.504 ± 0.051

[a] Ref. 7.

TABLE V
Monolayers of Water on Film Surface at 55°C

Calculated from	Thickness (μm)			
	12.7	25.4[a]	25.4	50.8
C_{L1}	14.8	6.8	22.0	10.2
C_{L2}	18.5	10.5	41.4	13.5

[a] Ref. 7.

plot to evaluate γ^d and γ^p, the dispersive and polar components of the surface tension; these sum to give the total surface tension γ. The statistical significances of the Kaelble plots were all > 0.9750, as determined from both t-test and correlation coefficient. Surface tension values in Table VIII show that, while γ^d may vary with thickness (the estimated precision is 1.0–1.5 dyn/cm), its variation *in the thickness range of the present experiments* is too small to be detectable. Thus, changes in E_S appear to be due solely to changes in $\overline{\Delta H}_{mix}$, the bulk term.

A large surface contribution from the condensation term is also evident in the P values. One may evaluate the surface layer resistance to permeation using the equation[13]

$$1/P(L) = 1/P_\infty + (r_1 + r_2)/L \tag{9}$$

where $P(L)$ is the permeation coefficient at thickness L, P_∞ is that at infinite

TABLE VI
The Bulk Concentration[a] of Water in Teflon at 55°C/100% RH

	Thickness (μm)			
	12.7	25.4[b]	25.4	50.8
$C_{H1} \times 10^3$	4.48	0.27	1.24	0.31
$C_{H2} \times 10^3$	5.18	0.32	0.89	0.28

[a] In mol water/mol polymer repeat unit.
[b] Ref. 7.

TABLE VII
Water Residence Times[a]

Determined from	Thickness (μm)			
	12.7	25.4[b]	25.4	50.8
E_{S1}	5.2×10^{-13}	7.0×10^{-14}	1.2×10^{-11}	4.8×10^{-8}
E_{S2}	2.1×10^{-12}	1.0×10^{-12}	4.0×10^{-11}	2.0×10^{-8}

[a] In s.
[b] Ref. 7.

TABLE VIII
Surface Tensions[a,b] at 20°C

Thickness (μm)	γ^d	+	γ^p	=	γ
12.7	15.9_5		0.8_5		16.8
50.8	16.5		1.0_5		17.5_5
127	17.6		0.7		18.3
254	18.2_5		1.7		19.9_5

[a] In dyn/cm.
[b] Precision, ±1.0–1.5 dyn/cm.

thickness, and $(r_1 + r_2)$ is the sum of surface layer resistances. The present results gave nonlinear plots of $1/P(L)$ vs. $1/L$ at both 40°C and 70°C, both plots having negative slopes. The reason for this is that, while the component of P which reflects penetrant migration is expected to fit eq. (9), the present data also include a Langmuir-like component, which does not. Unfortunately, unlike the Henry's law plot, no obvious method exists for separating them.

This contribution from the condensation term is also evident in the D values because D_0 is also a composite. For this reason, the $\Delta S_D^\ddagger$ values in Table III contain a negative component due to clustering on condensation[7] and a positive component due to bulk diffusion.[9-11] Table III also demonstrates a thickness effect: there is a marked increase in $\Delta S_D^\ddagger$ between 25.4 and 50.8 μm. Since the number of monlayers of water does not appear to vary with thickness (Table V), this suggests that increases in $\Delta S_D^\ddagger$ are due to increases in the bulk diffusion component. The near identity of $\Delta S_D^\ddagger$ values at 12.5 and 25.4 μm indicates that the extrusion process by which this material is manufactured produces a skin, the sum of whose thicknesses is at least 25 μm. This skin permeates water differently than the bulk of thicker samples.

It is interesting to note that, while Arrhenius plots of S are linear with $1/T$, those of D and P form two straight lines which intersect at T_g. What this means is that, while the solubility coefficient is continuous across T_g, both the diffusion and permeation coefficients suffer an abrupt change there. This can be rationalized in the following way: The onset of long range motions at T_g affects the ability of the water to permeate by increasing the tortuosity of the path the water molecules must take, although this has no effect on the amount of water sorbed. A recent paper on oxygen permeation through Teflon[14] found that Arrhenius plots of P and D (and, therefore, S) were linear with $1/T$. This, together with an E_S value of $\sim$−8.5 kJ/mol and an inability of the permeant to condense onto the surface, indicates little polymer–permeant interaction. This suggests that the changes in P and D at the T_g are due to specific interactions, perhaps between the water dipole and that of the C—F or C—CF$_3$ groups.

The time dependence of the permeation parameters was noted earlier. Although rare, it is not unknown (see Ref. 15 and references therein). A recent paper[15] indicates that this may be due to a time-dependent condensation of water onto the polymer surface: The rate is proportional to the extent of surface still uncovered. This would be expected for Teflon, which is known to have a Langmuir-like water layer on its surface, whose diffusion is also time-dependent and proportional to the extent of coverage.[7]

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