

Water Permeation in Polymer Films. VII. Polyimide/Teflon FEP Laminates

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Synopsis

Permeation parameters were obtained for various commercial polyimide/Teflon FEP laminates. Permeation coefficients, predicted from data obtained separately on each component of the laminate, match closely those found experimentally. The diffusion and solubility coefficient values, which are not amenable to such predictions, demonstrate that closely similar permeation coefficient values may be obtained from widely different diffusion and solubility coefficient values.

INTRODUCTION

Polyimide film is commercially available in a laminate form, coated on one or both sides with Teflon FEP. This provides a convenient method of heat-sealing the polyimide, a process which might otherwise prove difficult. While some properties of such laminates are diminished from those of the polyimide alone, some other properties are improved. One of these is the reduction in water permeation.

In previous studies in this series, we established the water permeation properties of polyimide^{1,2} and Teflon FEP^{3,4} alone. They were shown to be vastly different in how they each permeate water. While the permeation coefficient P and solubility coefficient S of Teflon FEP are both significantly smaller than those of polyimide, the diffusion coefficient D is about the same. Thus, the desirably low permeation of water through Teflon FEP is due to its low solubility: the maximum concentration of water in Teflon FEP is $\sim 10^{-3}$ mol/mol of polymer repeat unit while, in polyimide it is 1 mol/mol of polymer repeat unit. The permeation also benefits from the residence time of the water molecule on the surface: For Teflon FEP, this residence time is on the order of a single molecular motion^{3,4} while, for polyimide, it is about 10^7 molecular motions,^{1,2} time enough for a favorable channel to open nearby for access to the bulk.

It was, therefore, anticipated that the permeation parameters of the composite would be significantly different from those of either component. Since the permeation coefficient of neither component was noticeably pressure-dependent, we did not expect the composite to constitute a permeability valve.⁵

EXPERIMENTAL

Polyimide film, coated on one or two sides with Teflon FEP, is commercially available as DuPont Kapton polyimide film type F. This designation is followed by three digits which are, in order, the thicknesses of Teflon, polyimide, and the Teflon on the other side, all in mils (25.4 μm). An initial 0 indicates that only one side of the polyimide is coated, while a 9 is used for 0.5 mil. Thus, the designation 019 refers to a 1 mil polyimide film coated on one side with 0.5 mil of Teflon FEP.

The instrument used to follow the permeation process was an extensively modified Dohrmann Envirotech Polymer Permeation Analyzer Model PPA-1.^{6,7} These modifications and the techniques used were previously discussed.^{1,4}

Measurements were carried out in the temperature range 40–70°C, at the single relative humidity of 50%. At least two experiments were made at each condition, each on a separate sample, after equilibrating for several hours.

RESULTS

Permeation data were obtained, in the cases of the nonsymmetrical laminates, for each side facing the water vapor source. In two cases, D and S differed slightly with the side facing the permeant; however, since the points were less than a factor of 2 apart, a difference easily accounted for by experimental error,² their average was used.

Similarly, as previously found for Teflon alone,^{3,4} the D values measured early in the permeation process were slightly larger than those measured later in the process while, for the S values, and the C values calculate from them, the opposite was true. This reflects a time-dependent condensation on the Teflon surface⁸: Because the rate of permeation must be a function of surface coverage by the permeant, this condensation variation is manifested as a time-dependent permeation process. While the differences in D and S values were consistent, they were also small (from nil up to 20%). Thus, here, too, the data were averaged. One should note, however, that this finding was independent of which side of the laminate faced the water vapor flow.

The permeation data are found in Table I, where both correlation coefficient and t -test showed that all the correlations had statistical significances of > 0.9995 . While the table also contains values for the entropy of activation for diffusion, determined from D_0 values,⁹ and they are positive, as expected for the diffusion process¹, their significance in the present case is not clear. Far clearer, and far more meaningful, are the actual permeation data, plotted in Figures 1–3.

DISCUSSION

Using a previously derived equation for steady-state laminar flow, Barrer¹⁰ showed that the permeation coefficient for the laminate is related to that for each lamina as

TABLE I
Values of Permeation Constants at 50% RH

Parameter	Laminates			
	F019	F011	F031	F919
P_0 (std cc cm/cm ² s cm Hg) × 10 ⁶	1.832	1.515	0.6038	1.427
E_p (kJ/mol)	13.35 ± 1.05	13.69 ± 0.90	9.58 ± 1.30	13.17 ± 0.55
D_0 (cm ² /s)	1.087	0.0707	0.0747	3.174
E_D (kJ/mol)	53.05 ± 1.51	43.24 ± 2.93	45.19 ± 2.47	58.10 ± 4.35
(Δ) S_D^\ddagger at 40°C (J/mol K)	5.44	12.39	12.85	43.95
S_0 (std cc/cc cm Hg) × 10 ⁶	1.691	19.99	9.445	0.4171
E_S (kJ/mol)	-39.71 ± 1.63	-29.72 ± 3.14	-35.19 ± 2.22	-45.04 ± 3.77

$$\frac{l_{\text{total}}}{P_{\text{total}}} = \sum_i \frac{l_i}{P_i} \quad (1)$$

where l is thickness. The derivation, itself, is independent of the sequence of the lamina, as experimentally verified in the present case.

Using previously determined permeation coefficient data,^{1,4} predicted val-

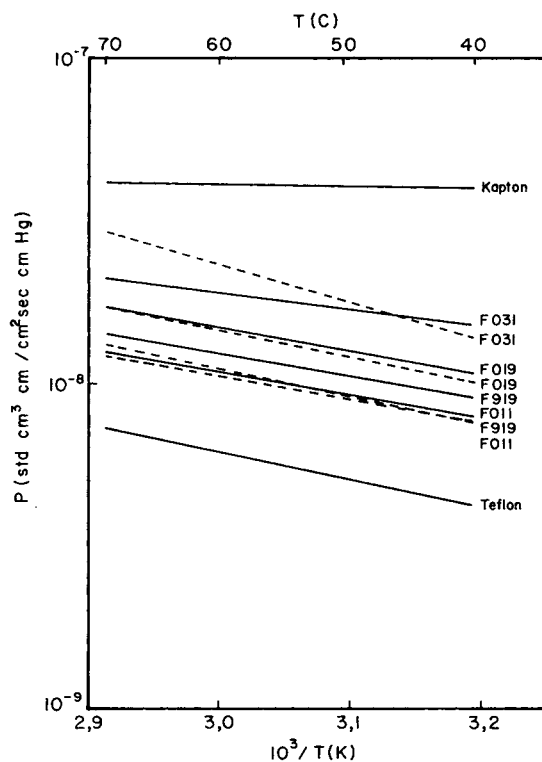


Fig. 1. Arrhenius plots of laminate permeation coefficients.

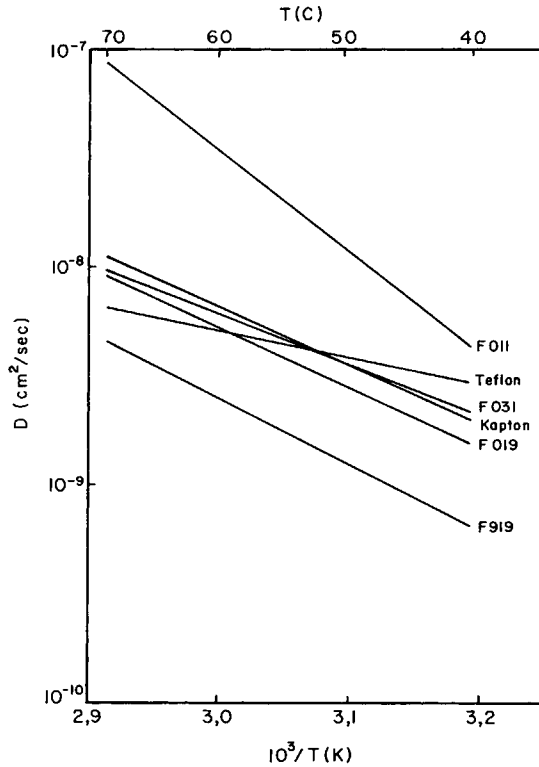


Fig. 2. Arrhenius plots of laminate diffusion coefficients.

ues were calculated* for all the laminates through eq. (1) and are found as dashed lines in Figure 1. Note that the order predicted is that found. Further, the actual and predicted data are close, showing the consistency and accuracy of the various sets of data for all three materials, as well as the predictive power of eq. (1).

Although similar equations are not available for diffusion and solubility coefficient data, there is no reason to think they are any less precise. It is, therefore, interesting to note that laminates having the identical materials in the identical thicknesses but in different orders (F011 and F919) can have similar permeation coefficients, over a significant range of temperatures, while both diffusion and solubility coefficients differ by an order of magnitude.

Clearly, both D and S respond to the permeant in different ways. Thus, although ΔS_D^\ddagger may be calculated from D_0^9 and τ , the residence time for water on the surface, from ΔE_s^{11} , their values are some undetermined combination and have little present significance.

It is not difficult to rationalize why the permeation coefficients should be independent of which side faced the flow of water vapor: The concentration drop of the permeant across each lamina is independent of sequence.^{5,10} Thus, after a short time into the permeation process, during

* Because of the unavailability of permeation coefficient data for 76.2 μm polyimide film, data for 50.8 μm film were used.

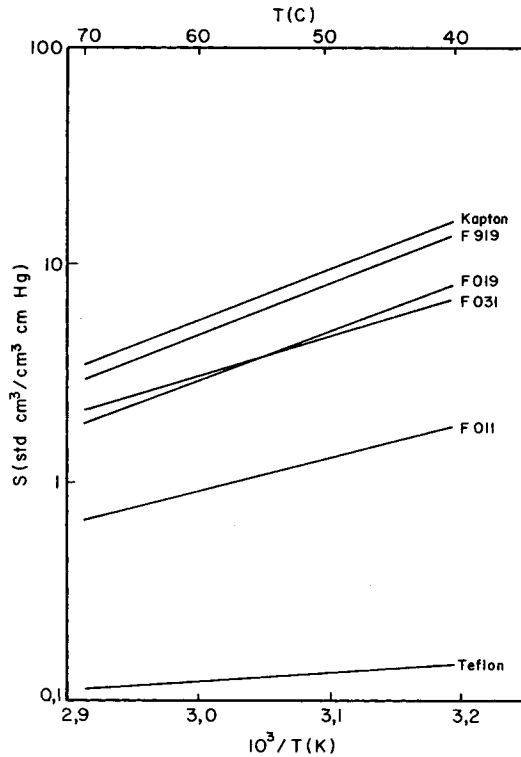


Fig. 3. Arrhenius plots of laminate solubility coefficients.

which equilibrium is attained, the concentration drop across a lamina stabilized to the same value irrespective of the side facing the permeant.

It is, however, more difficult to rationalize the independence of the solubility coefficients. In order to do so, one must recall that S is bulk-modulated for polyimide^{1,2} and surface-modulated^{3,4} for Teflon. Thus, for the present findings to be so, each lamina must not only operate independently, it must operate in a manner identical to that of each component operating alone.^{1,4} That is, the Teflon surface, for example, must present the same barrier to water permeation independent of its sequence in the laminate. In this light, it is interesting to note that two methods of polyimide/Teflon manufacture have been reported: in one,¹² an aqueous Teflon dispersion is applied to a silane-treated polyimide film, followed by heating, while, in the other,¹³ polyimide and Teflon films are calendered after being treated by electrical discharge to increase initial adhesion. One might reasonably expect that (1) polyimide film would exert an influence on the formation of the interfacial surface from an aqueous dispersion with which it was in contact¹⁴ and (2) the surface properties of films produced through the coalescence of aqueous dispersions would be different than those produced through extrusion. Since neither is evident, as attested to by our ability to calculate the P values from those of the individual components, the data appear consistent with the latter method of manufacture.

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