Water transport and condensation in fluoropolymer films

Charles M. Hansen and Lisbet Just

FORCE Institute, Park Alle 345, 2605 Broendby, Denmark

Received 18 December 2000; revised 1 March 2001; accepted 8 March 2001 Available online 5 September 2001.

Abstract

This report explores phenomena related to the undesired condensation of water in or under fluoropolymer films. Condensation of water in or under polymer films will occur when the local vapor pressure is higher than that corresponding to the local dew point vapor pressure. This can happen for any type of polymer film, including fluoropolymer films, even though solubility of water in the film may be extremely low. A “cold” substrate, for example, can readily lead to water condensation under a fluoropolymer film, and therefore to a reduction of adhesion or to complete delamination. These problems will not be so severe and may, indeed, disappear for acid-resistant fluoropolymer films exposed to hot and/or concentrated acids, such as sulfuric acid. The vapor pressure (activity) of the water in the acid is so reduced that condensation in or under the film will not occur at the usual temperatures encountered in practice.

Diffusion coefficients, permeation coefficients, and solubilities for water in selected fluoropolymers (PVDF, ETFE, ECTFE, PFA, MFA, FEP, and PTFE) have been measured at 90°C. The diffusion coefficients are greater than 3×10^{-7} cm^2/s at this temperature. This means that a change in the environment will result in a new equilibrium condition for absorption, desorption, and/or permeation in practical fluoropolymer coatings within a maximum of a day or so for all of the materials tested. Practical free film thicknesses near 2 mm were used.

Approximate diffusion coefficients have also been measured by a new technique at 20°C for comparison. When the environment changes, a new condition for equilibrium is established at room temperature after times varying from several days to 2 months in these experiments which used the same practical film thicknesses. The technique involves following release of dissolved tritiated water (HTO) from a film while it is immersed in a scintillation liquid (gel) in a glass counting vial. The counting rate increases to an equilibrium level in proportion to the extent of diffusion of HTO out of the sample.

Author Keywords: Fluoropolymers; Blistering; Permeation; Diffusion coefficients; Tritium

Article Outline

1. Introduction

Adhesion between a fluoropolymer coating and a substrate can be destroyed if there is water condensation at the substrate. Traditional methods to counteract the effects of such condensation include insulating the equipment to prevent large temperature gradients, having a good barrier topcoat, inclusion of barrier type pigmentation, such as flaky materials, and providing a means for good mechanical anchoring of the film by suitable sandblasting or other surface preparation. A special technique worthy of further consideration is providing voids within the film, and preferably close to, but not necessarily exactly at, the substrate [1]. Still another approach is to allow for relief of the internal liquid pressure by “holes” of some description going to and through the external film surface while still maintaining an intact primer layer at the substrate. Fundamental understanding of what is going on in terms of water transport in the fluoropolymer coatings of interest requires measurement of diffusion coefficients D, permeation coefficients P, and solubility coefficients S, of water for relevant conditions. Such measurements are reported in the following.

The focus of this study is on water transport at 90°C in films of the most commonly used fluoropolymers including:

PVDF

poly(vinylidene fluoride)

ETFE

poly(ethylene-*co*-trifluoroethylene)

ECTFE

poly(ethylene-*co*-chlorotrifluoroethylene)

PFA

poly(tetrafluoroethylene-*co*-perfluoroalkylvinyl ether)

MFA

poly(tetrafluoroethylene-*co*-fluoromethylvinyl ether)

FEP

poly(tetrafluoroethylene-*co*-hexafluoropropylene)

PTFE

poly(tetrafluoroethylene)

2. Experimental

An isotope method of analysis to follow the transport of water has been used with tritiated water (HTO) as a tracer. The amount of HTO in a given sample is found by measuring the radioactivity present with a scintillation counter. Calibration is required to find the actual amount of water in the sample. Water transport studies were done primarily at 90°C with some data at 20°C being included for comparison. It would have been desirable to work at higher temperatures, but this would require alternative equipment. A control experiment without the use of HTO was used to detect possible contamination or other interfering radiation. If pure water yields an apparent transport rate for HTO, then there is probably cross-contamination in the sample. These control values were so low in all cases that no corrections to the measured values were required.

These HTO techniques have been discussed earlier [2]. The terminology used in this report will simply be water, with the understanding that the HTO tracer technique has been used to follow the transport of the water.

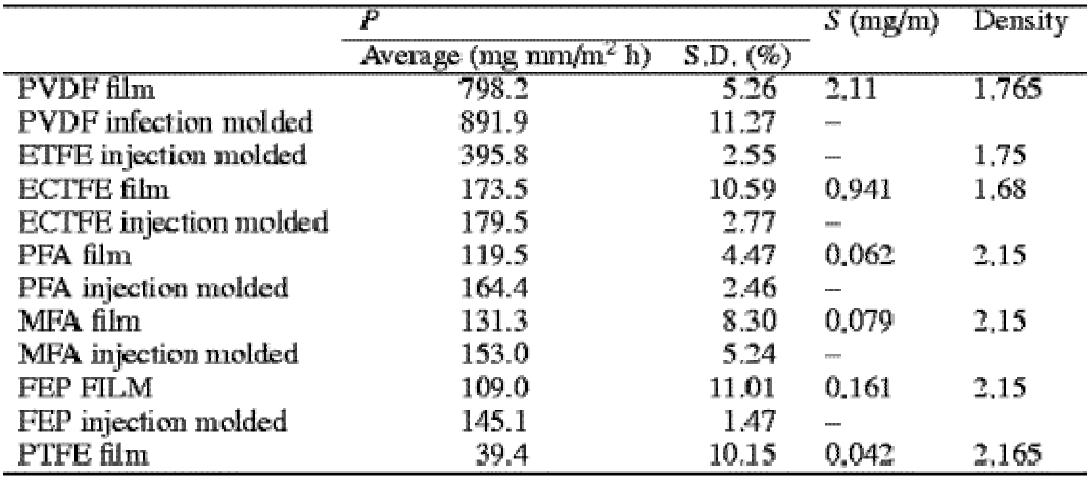
2.1. Permeation coefficients

Standard ASTM 5.0 cm permeation cups with some modification were used for the permeation experiments. The inlets and outlets have been replaced by mechanical sealing caps, and the scintillation glass vials can be screwed directly onto the cup. HTO was added to water to the desired specific activity and this water was then added to one side of a permeation cell. A scintillation glass vial partly filled with water-free glycerine was used to collect the water which had passed through the films. The free, exposed surface of the samples is a circle with a diameter of 5.0 cm. The film thicknesses were close to 2 mm, as it can be seen from the data presented below. The cells were stored in an oven at 90°C for the higher temperature experiments. The glycerine-filled scintillation glass vial in use was replaced with a new one at predetermined time intervals. Liquid nitrogen was used to cool the scintillation glass vial prior to exchange with the new one to make sure that all water vapor is condensed into the glycerine. Earlier studies have confirmed that this procedure does not give problems because of too high concentrations of water in the glycerine. This is confirmed once more in these studies since the same permeation coefficients are measured at equilibrium conditions, regardless of the duration of the collection time as long as this is not excessively long nor are the permeation rates too high. The permeation rate would fall with time if the amount of water in the glycerine became significant. This would mean that permeation coefficient would appear to be lower for longer collection times. Such experiments repeatedly showed that this has not been the case in the present study. Identical control experiments without the use of HTO showed that there was no need to correct for extraneous radiation or contamination.

Because of the relatively rapid diffusion rate of water in the films at this temperature, the sample intervals selected for the initial experiments did not allow an evaluation of diffusion coefficients from the permeation rates at the shorter time intervals. The intervals were more intended for certain determination of equilibrium permeation values at longer times. Standard deviations for such values were found to be between 2 and 4% in this study.

The permeation coefficients can be given in a variety of units. Table 1 reports about the data at 90°C in the units of (mg mm)/(m^2 h).

Table 1. Permeation coefficients and solubilities of water in selected fluoropolymers at 90°C



	P		*S* (mg/m)	Density
	Average (mg mm/m^2 h)	S.D. (%)		
PVDF film	798.2	5.26	2.11	1.765
PVDF infection molded	891.9	11.27	–	
ETFE injection molded	395.8	2.55	–	1.75
ECTFE film	173.5	10.59	0.941	1.68
ECTFE injection molded	179.5	2.77	–	
PFA film	119.5	4.47	0.062	2.15
PFA injection molded	164.4	2.46	–	
MFA film	131.3	8.30	0.079	2.15
MFA injection molded	153.0	5.24	–	
FEP FILM	109.0	11.01	0.161	2.15
FEP injection molded	145.1	1.47	–	
PTFE film	39.4	10.15	0.042	2.165

For more generality, the permeation coefficients in this type of units could be divided by the vapor pressure difference over the film (525.8 mm Hg or its equivalent 7.0×10^4 Pa at 90°C). This has not been done in the present report, since this was not necessary to reach the desired conclusions. The reported permeation coefficients can be used for other vapor pressure differences at the same temperature by multiplying by the ratio of the actual vapor pressure difference divided by the one used here. Vapor pressures for water at various temperatures can be found in standard reference works such as in [3].

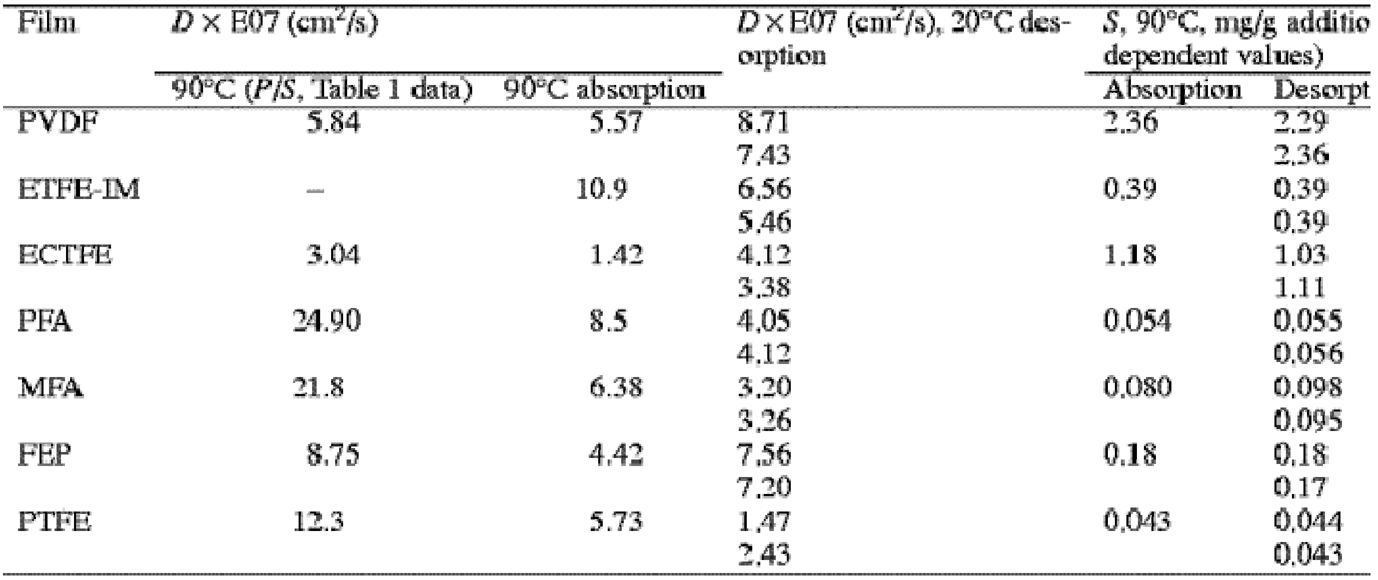
2.2. Solubility coefficients and diffusion coefficients

Absorption rates for water were measured by placing films of the respective polymers into HTO-labelled water at 90°C. The specific activity was regulated to a sufficiently high value to measure the small amounts of absorbed water as required. Amounts as low as 43±1ppm (for PTFE) could be measured and much lower values could also be determined, if such were required. The films were exposed for predetermined times. The shortest time measured for the initial experiments was 2 h, which was unfortunately too long for accurate determination of diffusion coefficients. Most of the films had already absorbed more than half of the equilibrium amount at this time, and the following sampling times were too long to allow accurate determination of the diffusion coefficients. After the predetermined exposure time, the films were removed from the water and rinsed quickly. They were then immersed in a suitable scintillation liquid (gel) at 20°C for counting the HTO activity in a scintillation counter. HTO diffuses out of the film and into the water-containing scintillation liquid, where decay events are counted. Samples are taken until the concentration of HTO in the scintillation liquid reaches a constant value, which then can be calculated back to an initial concentration in the film. Calibration is required, and samples were measured until the counting rate maintained a constant value, judged from successive measurements giving the same value at sufficiently long times to ensure that equilibrium had been established. Control measurements without the use of HTO were performed to detect any contamination or interfering radiation. No corrections were required for these reasons.

Measurements of transport coefficients at temperatures other than 90°C were desired. An approximate diffusion coefficient at 20°C was determined by analysis of data found in the scintillation counting technique. One could plot the approach to equilibrium as the HTO left the sample and entered the scintillation liquid (gel). The scintillation liquid was chosen for long-term stability properties. This was INSTA-GEL PLUS (Packard) which consists of 60% of 1,2,4-trimethylbenzene and 39% of ethoxylated alkylphenol, and two additives at concentrations less than 1%. Twelve milliliters of this material is mixed with 8 ml of water, heated to 35°C, and then allowed to cool to form a gel. The diffusion coefficient values found are approximate because there may be excess of water in the films from the temperature reduction from 90 to 20°C. Water solubility can be expected to be higher at higher temperatures [1 and 4], and rapid cooling to a lower temperature can release free water (uniformly?) within the film. The use of a gel as a collection medium in this type of work has been shown in the past as not posing a problem for this type of diffusion coefficient measurement.

S was taken as the average of the last measurements of the equilibrium absorption. These results are reported in Table 1. Three additional independent values for *S* (at 90°C) and a repeated set of experiments to find the diffusion coefficients at 90°C are found in Table 2. Duplicate determinations of the diffusion coefficient found by desorption of the HTO, as described below, at 20°C are also found in Table 2.

Table 2. Diffusion coefficients for water in selected fluoropolymers at 90 and 20°C



Film	$D \times$ E07 (cm^2/s)		$D \times$ E07 (cm^2/s), 20°C desorption	S, 90°C, mg/g additio dependent values)	
	90°C (P/S, Table 1 data)	90°C absorption		Absorption	Desorpt
PVDF	5.84	5.57	8.71	2.36	2.29
			7.43		2.36
ETFE-IM	–	10.9	6.56	0.39	0.39
			5.46		0.39
ECTFE	3.04	1.42	4.12	1.18	1.03
			3.38		1.11
PFA	24.90	8.5	4.05	0.054	0.055
			4.12		0.056
MFA	21.8	6.38	3.20	0.080	0.098
			3.26		0.095
FEP	8.75	4.42	7.56	0.18	0.18
			7.20		0.17
PTFE	12.3	5.73	1.47	0.043	0.044
			2.43		0.043

D can be calculated from the time required for one-half of the equilibrium amount to be absorbed (or desorbed), $t^{1}/_{2}$. The usual equation for this is

$$D = \frac{0.049(L)^2}{t_{1/2}}$$

With the film thickness for a free film *L*, in centimeters and with time in seconds, the units for the diffusion coefficient *D* are square centimeter per second, which are those used in this report. A plot of weight gain versus the square root of time is made to evaluate the experimental data. A straight line to a relative uptake close to 0.55 is expected for this type of plot when the diffusion coefficient is constant. The diffusion coefficient is most certainly constant within the experimental error at the low water concentrations involved in these studies.

The materials were retested at 90°C with shorter time intervals to determine the diffusion coefficients with more accuracy that was allowed in the first set of experiments. At the same time it was decided to see whether our procedure allowed measurement of the diffusion coefficients at room temperature. The method used was to follow the desorption of HTO into the scintillation liquid, using the fully saturated samples as the starting points. There may be some question as to whether the true solubility at 90°C is the same as that of at room temperature. As discussed above, there may be an excess of dissolved water from the higher temperature equilibrium absorption which can appear as liquid water at the lower temperature on quenching. The solubility of water can be expected to be lower at lower temperatures. This phenomenon has been discussed in [1 and 4]. The desorption of water in the sample could be followed by the increase in counting rate in the scintillation counter. The diffusion of water (HTO) leaving the surface of the sample into an essentially aqueous gel media does not represent a significant barrier to its removal because the diffusion rate in the gel is very much larger than that in the polymer sample itself. The plot of desorbed amount of water versus the square root of time is expected to give a straight line. Exactly the same mathematics can be used to interpret these experiments as were used for the absorption studies. The half-time for desorption is used in the same equation reported above.

In the present case, D was also calculated using the relation

$$D = \frac{P}{S}$$

where P and S are measured in separate experiments, thus allowing the calculation of D (using consistent units, of course). These calculated values for D from P/S at 90°C are also listed in Table 2 for comparison.

3. Results

The experimental data are reported in Fig. 1, Fig. 2, Fig. 3, Fig. 4, Fig. 5, Fig. 6, Fig. 7, Fig. 8 and Fig. 9. Results calculated from these data are tabulated in Table 1 and Table 2.

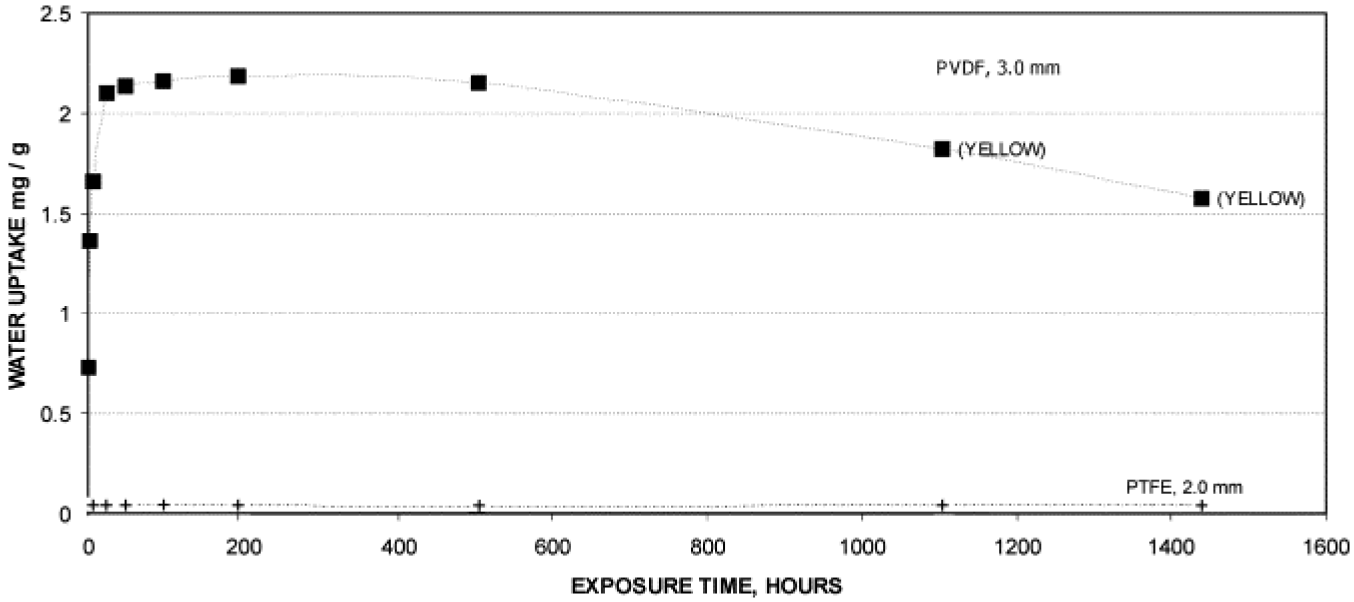


Fig. 1. Water uptake in selected fluoropolymers at 90°C. Initial studies for determination of required specific activity for the tracer HTO. Higher activity was used in subsequent work.

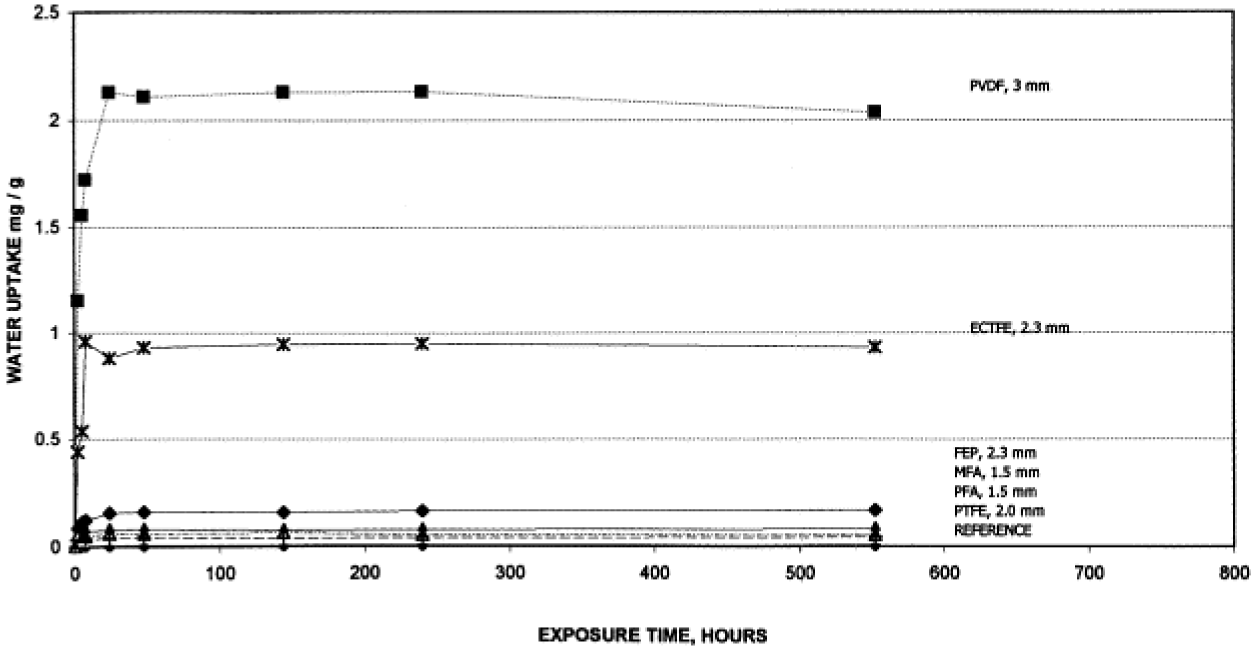


Fig. 2. Water uptake in selected fluoropolymers at 90°C to determine equilibrium uptake of water.

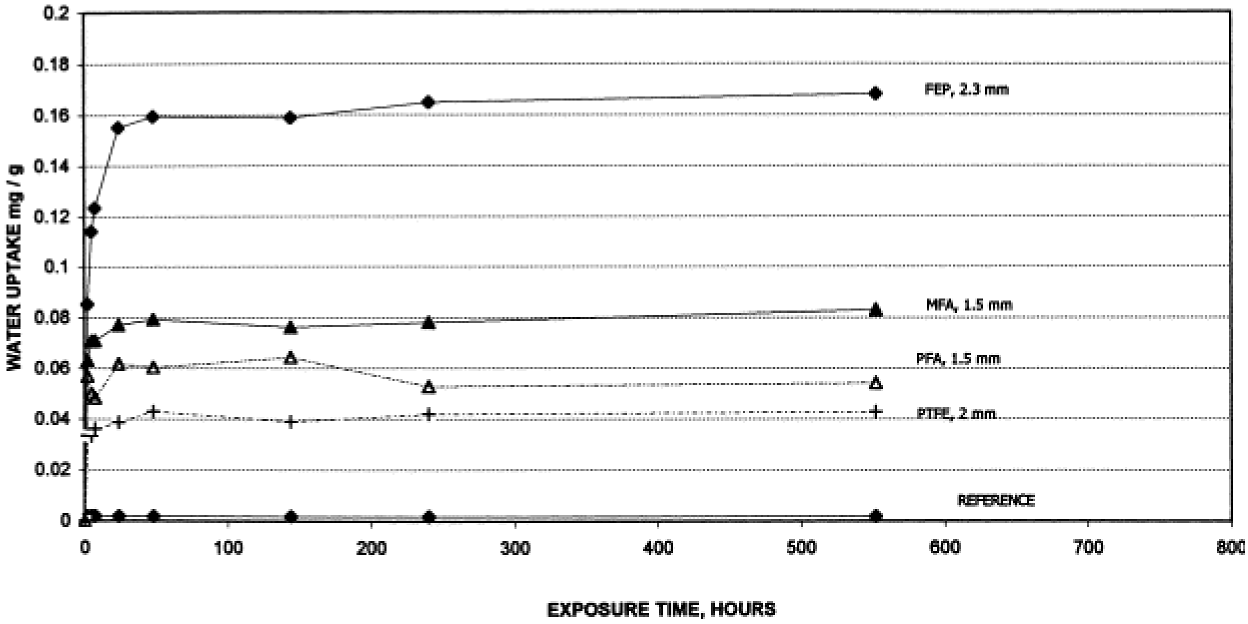


Fig. 3. Water uptake in selected fluoropolymers at 90°C to determine equilibrium uptake of water with expanded scale for same data reported in **Fig. 2**.

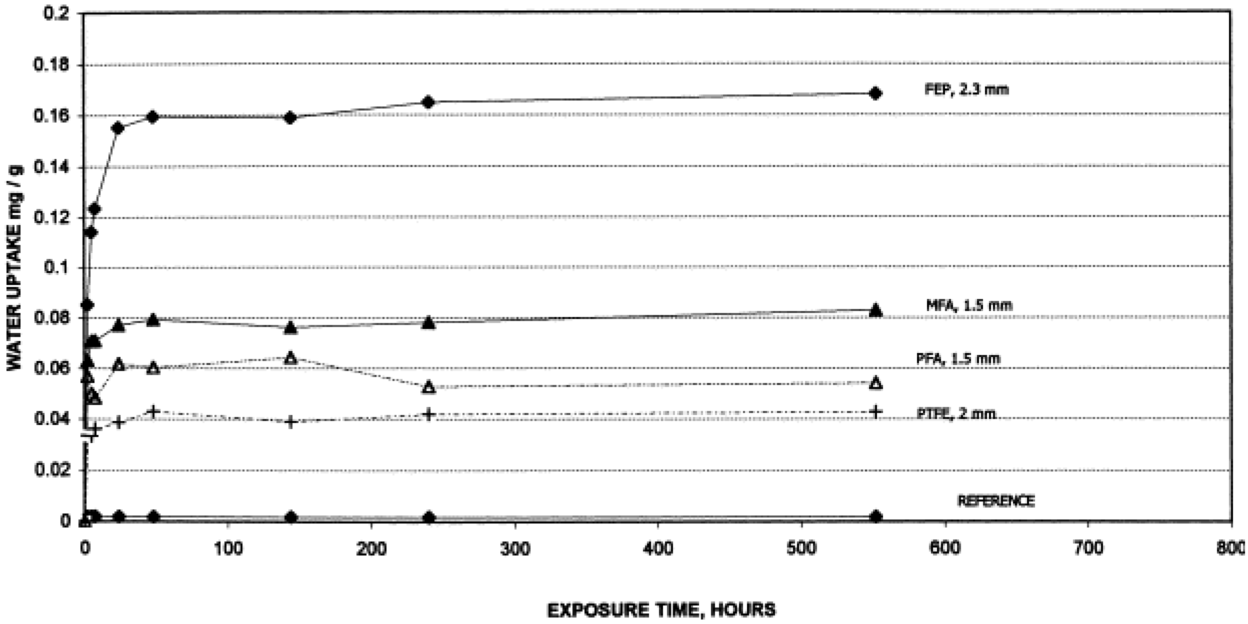


Fig. 4. Permeation rates for water at 90°C in selected fluoropolymer films to establish equilibrium values of permeation rates for calculating permeation coefficients as reported in **Table 1**.

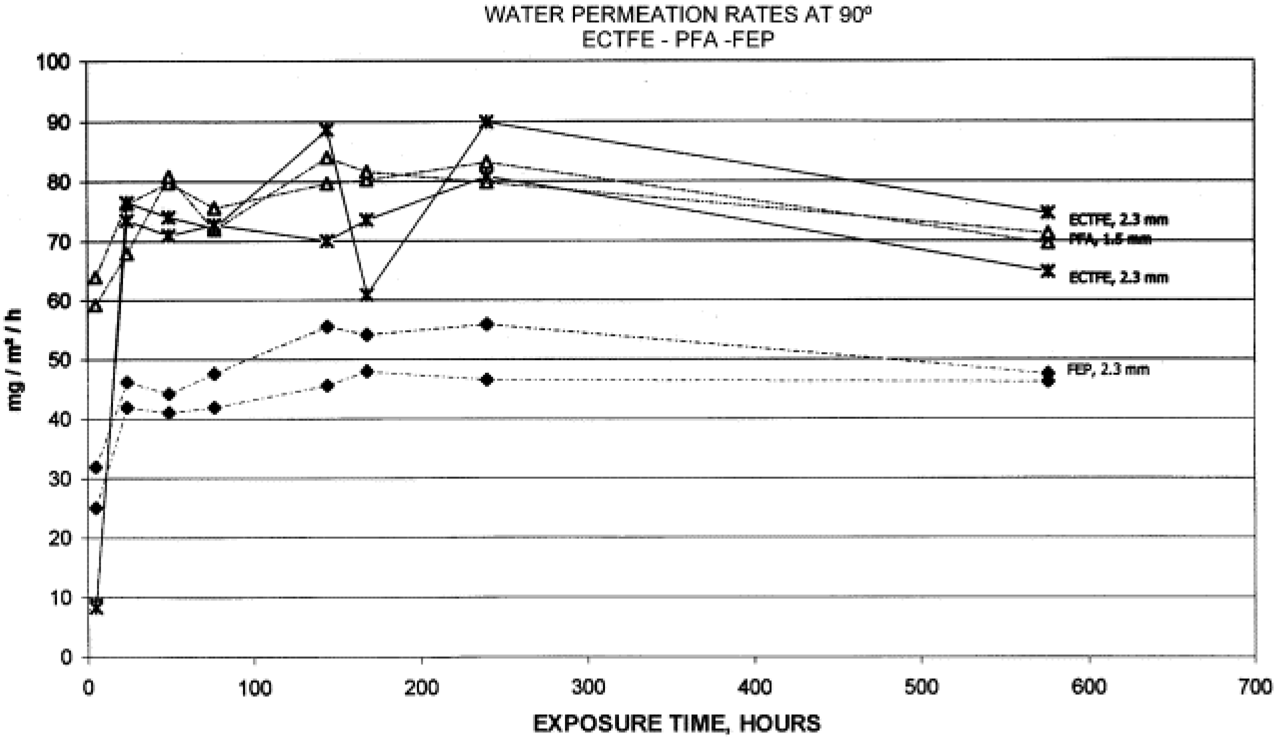


Fig. 5. Permeation rates for water at 90°C in selected fluoropolymer films to establish equilibrium values of permeation rates for calculating permeation coefficients as reported in **Table 1**.

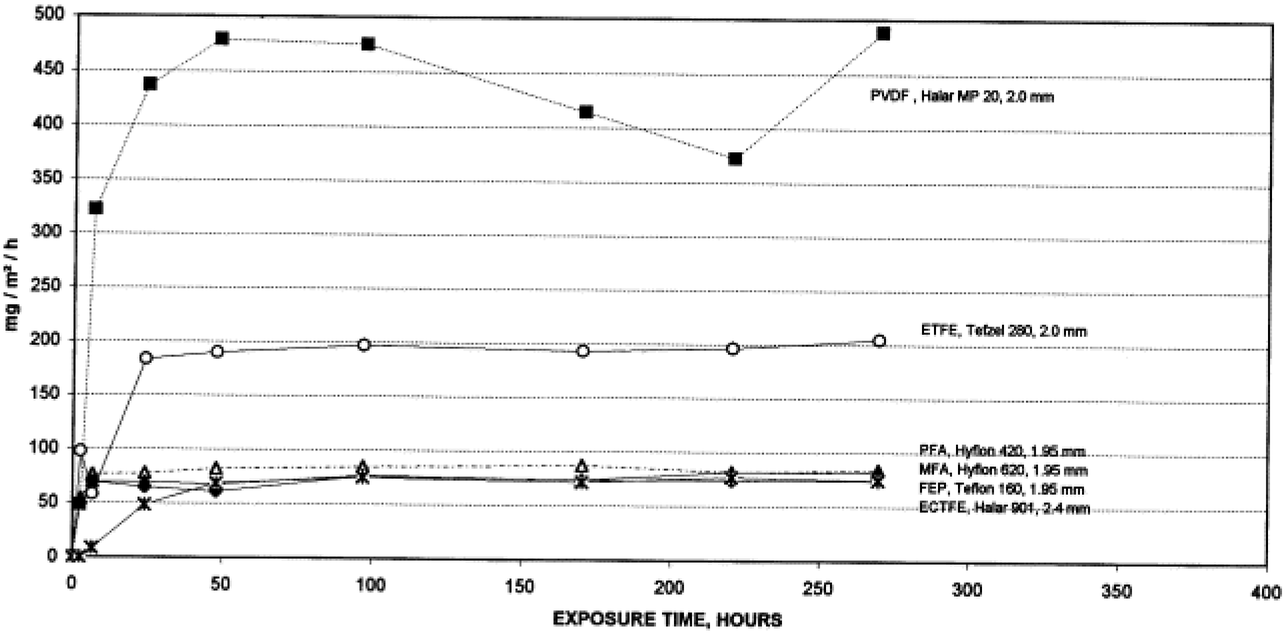


Fig. 6. Permeation rates for water at 90°C in selected fluoropolymers which were

injection molded. Data used to establish equilibrium values of permeation rates for calculating permeation coefficients as reported in **Table 1**.

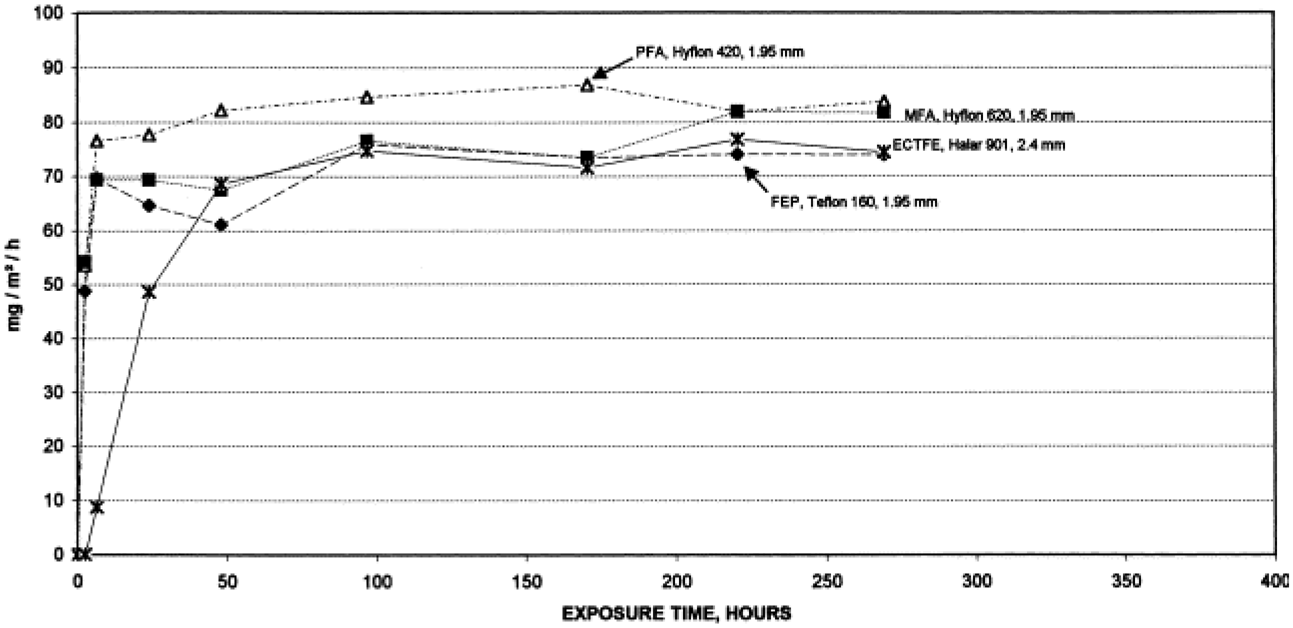


Fig. 7. Permeation rates for water at 90°C in selected fluoropolymer films which were injection molded. Data used to establish equilibrium values of permeation rates for calculating permeation coefficients as reported in **Table 1**.

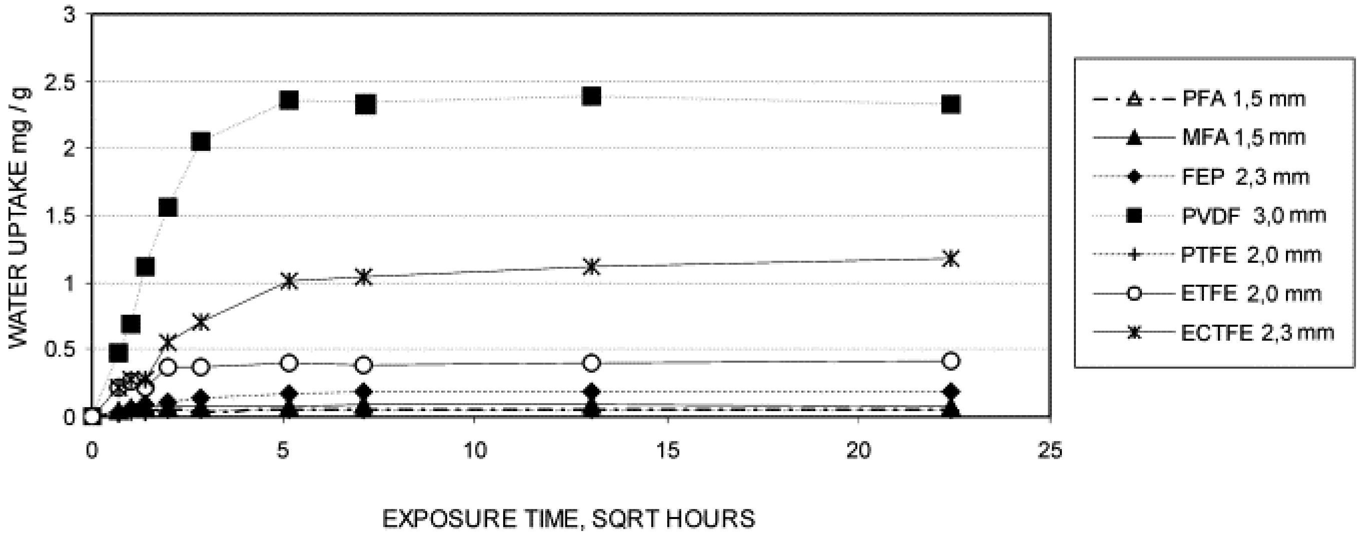


Fig. 8. Water uptake as a function of the square root of time in selected fluoropolymers at

90°C to determine diffusion coefficients from the time required for one-half of the equilibrium amount to be absorbed.

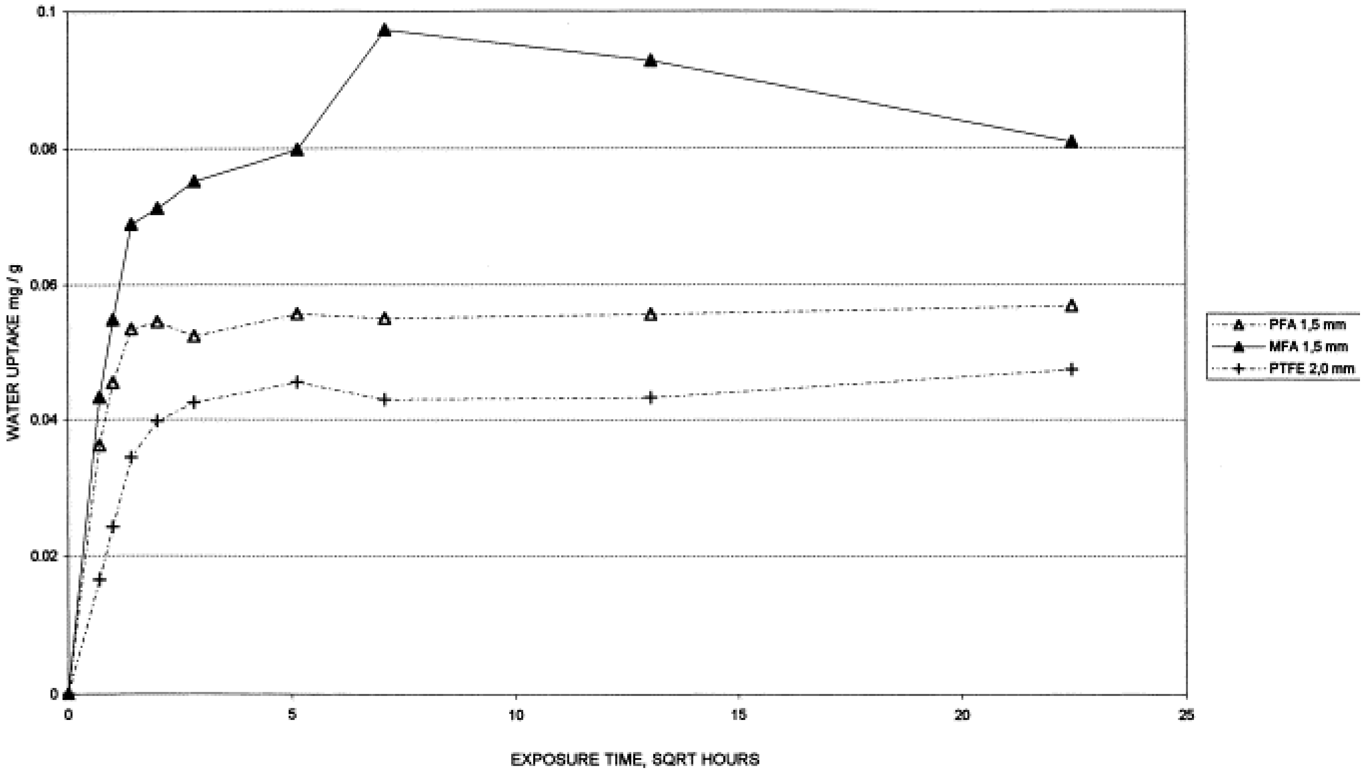


Fig. 9. Water uptake as a function of the square root of time in selected fluoropolymers at 90°C to determine diffusion coefficients from the time required for one-half of the equilibrium amount to be absorbed.

Fig. 1 reports data for the initial studies using PVDF and PTFE films to determine how much HTO was required to get the specific activity of the test liquid high enough for the small amounts of water to be detected. The data for PTFE showed that the specific activity was not high enough to measure the equilibrium uptake of 43±1 ppm as accurately as desired. This was corrected in subsequent experiments.

Fig. 2 reports water uptake data for all the films tested in the initial absorption studies. The samples were unfortunately not taken at optimum intervals to allow accurate diffusion coefficient measurements. These data are fully sufficient to determine the equilibrium solubility of water at the 90°C test temperature. Fig. 3 reports some of these same data for those films with uptake curves which are so compressed and low in value that it is difficult to distinguish between them in Fig. 2.

Fig. 4 and Fig. 5 report the measured permeation rate for various fluoropolymer films in mg/(m^2 h). The equilibrium rate in these curves was used to calculate the permeation coefficients reported in Table 1. The units used in Table 1 are (mg mm)/(m^2 h).

Fig. 6 and Fig. 7 report the measured permeation rates for various fluoropolymer specimens which were injection molded to flat films in mg/(m^2 h). The equilibrium rate established in these curves was used to calculate the permeation coefficients reported in Table 1. The units used in Table 1 are (mg mm)/(m^2 h).

The data in Fig. 8 and Fig. 9 allow the determination of the diffusion coefficients at 90°C. The plot of relative uptake versus square root of time is used. As discussed above, the method used to calculate the diffusion coefficient requires the half-time for equilibrium uptake, and this can be done by extrapolation or interpolation on the plots or in the tabulated data leading to them. The results are reported in Table 2.

Plots of desorption of HTO as a function of the square root of time were made for the desorption of water (HTO) into the scintillation liquid (gel) at 20°C, (See Fig. 10, Fig. 11 and Fig. 12). The diffusion coefficients estimated from these desorption measurements are also reported in Table 2. Equilibrium was established after 2 months for the films requiring the longest times. The procedures used to interpret these data are the same as those described above. Duplicate determinations were made. The effect of gel retarding diffusion of HTO has been evaluated as negligible, since these diffusion coefficients are far greater than those measured for diffusion in the polymers themselves.

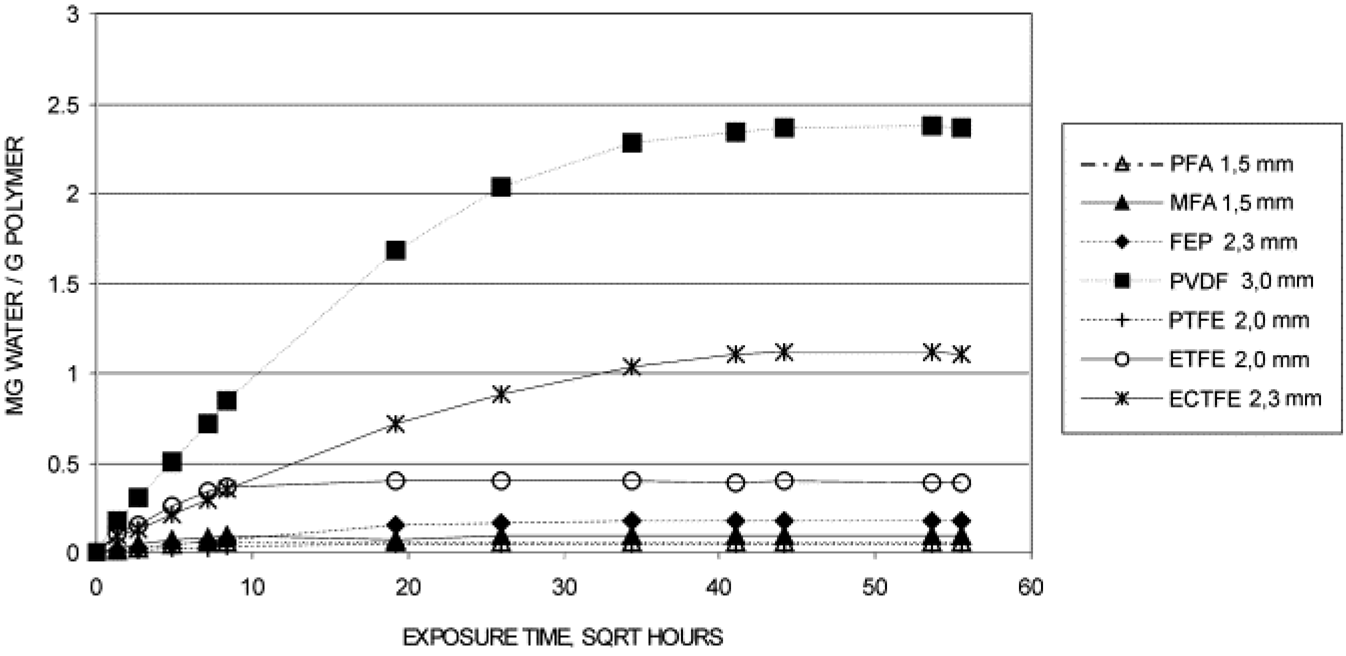


Fig. 10. Water diffusion out of selected fluoropolymer films at 20°C to determine diffusion coefficients from the time required for one-half of the equilibrium amount to be desorbed.

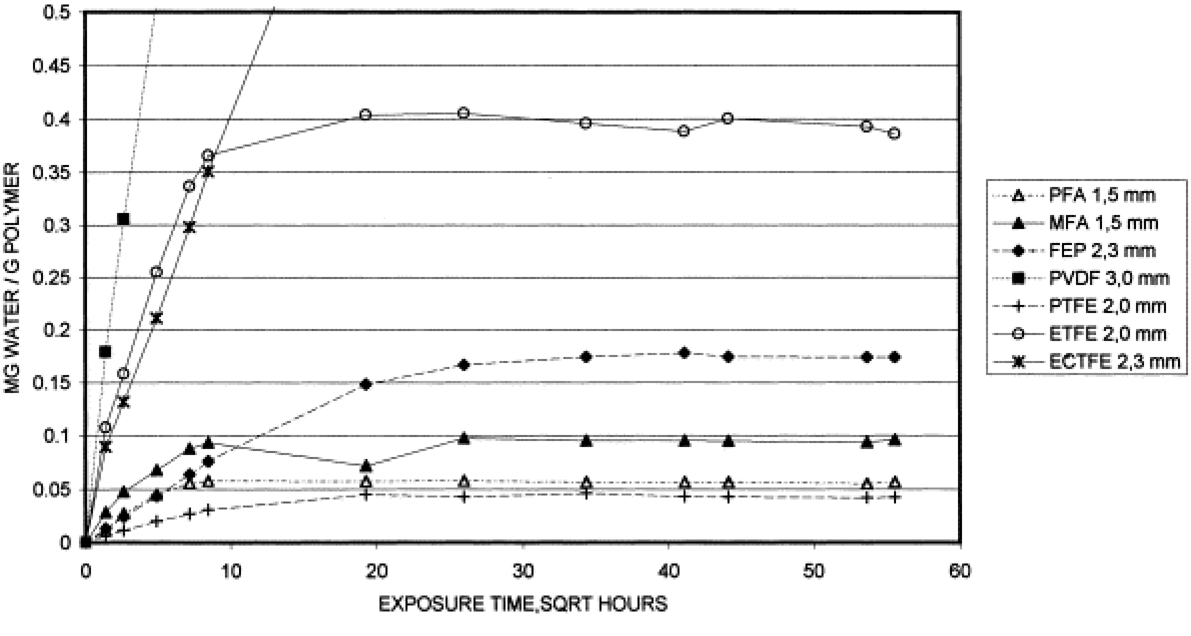


Fig. 11. Water diffusion out of selected fluoropolymer films at 20°C to determine diffusion coefficients from the time required for one-half of the equilibrium amount to be desorbed.

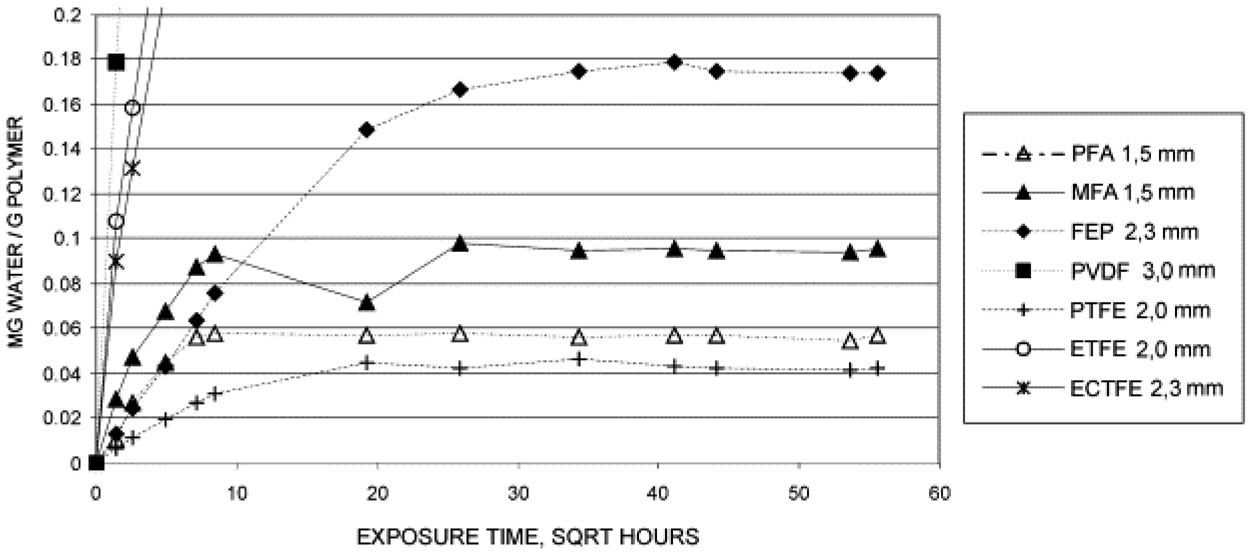


Fig. 12. Water diffusion out of selected fluoropolymer films at 20°C to determine diffusion coefficients from the time required for one-half of the equilibrium amount to be desorbed.

4. Discussion of results

Permeation and solubility coefficients have been reported on measurements made at 70 and 80°C by Conde [5] for some of the same fluoropolymers. Solubility coefficients are reported in this source as being 2.7 mg/g for PVDF. This study finds 2.1 mg/g at 90°C. The agreement is good. For PTFE, PFA, and MFA, Conde reports solubility coefficients as being <0.5 mg/g. The measured values reported here are about 10 times lower than this upper limit, as reported in Table 1 and Table 2. The standard deviation of our measurements for a given experiment is between 2 and 4% of the measured values, even in the low range, where 43±1 ppm water was found in PTFE. The permeation rates reported by Conde are about the double of those reported here for PTFE, PFA, and MFA with values for PVDF being between 458 and 750 versus our values of about 800–900, all in (mg mm)/(m^2 h). The agreement here is not as good as for the solubility coefficient(s), but is satisfactory considering differences in sources of materials with the different treatments possible, the difference in techniques, and other unknown factors.

In each case, where the comparison is possible, the injection-molded films gave higher permeation coefficients compared with the standard films. The reason for this is not evident from this study.

The results vary between the highest P (798.2 mg mm/m^2 h) and S (2.28 mg/g $_{\mathrm{av.}}$) values for PVDF to the lowest P (39.4 mg mm/m^2 h) and S (0.043 mg/g $_{\mathrm{av.}}$) for PTFE. The diffusion coefficients are highest for ETFE at 90°C (10.9×10^{-7} cm^2/s) as it can be seen from the data in Table 2. ECTFE has the lowest diffusion coefficient at 90°C which is 1.42×10^{-7} cm^2/s as it can be seen in Table 2. There is a factor of more than 10 between these extreme values in the fluoropolymers studied. The approximate diffusion coefficients for PVDF are the highest at 20°C (8.07×10^{-9} cm^2/s $_{\mathrm{av.}}$) with those for PTFE (1.85×10^{-9} cm^2/s $_{\mathrm{av.}}$) being the lowest. Here the difference between the extremes is only a factor of 4.4.

5. Discussion of consequences of the results

Undesired condensation of water in a polymer film or at a substrate will occur when the local vapor pressure is higher than that corresponding to the local dew point vapor pressure. Such condensation can lead to the loss of adhesion or to catastrophic delamination. The point of condensation should preferably not be within the film. The absolute best situation would be that there is no condensation whatever. No condensation is expected in the case of exposure to the solutions of concentrated sulfuric acid as discussed below. Several of the methods which can be used to reduce the condensation problem relate to the transport coefficients for water.

The permeation, diffusion, and solubility coefficients measured in this study allow estimates of the behavior of fluoropolymer films exposed to water at elevated temperatures. The equilibrium absorption to saturation is very quickly accomplished with the time required being on the order of magnitude of at most 1–2 days at 90°C, and sometimes much quicker. The rate of permeation measured in the studies can be used to make some estimates of how much water can enter a fluoropolymer film under given conditions. A sample calculation is given in the following example.

5.1. Porous films

A discussion of how rapidly a porous film will saturate is given in the following. An 1 mm thick film with an arbitrarily chosen porosity of 10% is used for this purpose. The permeation coefficient used is for PFA at 90°C. This example starts with a hypothetical (and in practice — impossible) vapor pressure difference of 526 mm Hg with a correction for the actual substrate temperature and corresponding water vapor pressure being given later. The example uses:

An assumed permeation coefficient (PFA) of 120 mg mm/m^2 h.

An assumed thickness of 1 mm.

An arbitrarily assumed porosity of the film of 10%.

An assumed average film temperature of 90°C.

An assumed substrate temperature giving negligible water vapor pressure.

Using a basis of 1 m^2: The amount of water (density assumed to be 10^6 $\mathrm{g/m}^3$) required to fill the voids is:

$$\mathrm{Voidwater}=\mathrm{porosity}\times\mathrm{filmthickness}\times\mathrm{density}\times\mathrm{area}=0.11\ \mathrm{mm}\times10^{-3}\mathrm{m/mm}\times10^{6}\ \mathrm{g/m^3}\times\mathrm{m^2}=100\ \mathrm{g}$$

$$\mathrm{Uptakerate}=120\ \mathrm{mgmm/m^2\ h}\times1\ \mathrm{m^2/mm}=120\ \mathrm{mg/h}=0.120\ \mathrm{g/h}$$

$$\mathrm{Time}=100\ \mathrm{g}/0.120\ \mathrm{g/h}=833\ \mathrm{h}=35\ \mathrm{days}$$

It is of course recognized that the actual time would be somewhat less since the voids are distributed throughout the film rather than being located at its interface with the metal, but the order of magnitude is correct. The time required to saturate the experimental films was a matter of hours.

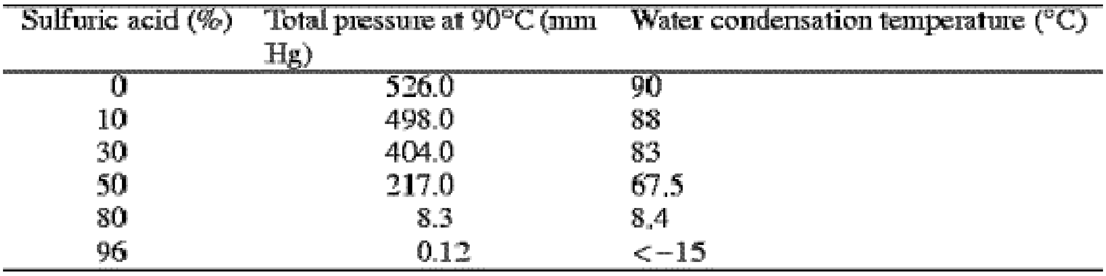
The previous example can be easily extended for different percentages of voids. If the 10% void content is found only in 20% of the film located nearest the substrate, the amount of water necessary to saturate the film is reduced by a factor of 5. The time required is also reduced by a factor of 5. Conversely, increasing the percentage of voids increases the time required to saturate the film proportionately, but other practical problems may be encountered. Doubling the film thickness means twice as much water is required, but the permeation rate is also cut into half, so there is a factor of 4 difference in the time requirement. The time required to fill the voids would become 140 days for the conditions in the fictitious example given above. Doubling the permeation rate will cut this time in half. Reducing the water vapor pressure difference will extend this time.

If the temperature of the substrate is about 87°C, the corresponding water vapor pressure is 473 mm Hg. This means that the vapor pressure difference in the above example is reduced by a factor of 10 (since the vapor pressure itself was assumed as essentially zero, corresponding to the experiments). This more realistic condition will increase the time to reach saturation by a factor of 10, and the time requirement is extended about a year. The vapor pressure driving force increases rapidly with the lower substrate temperatures, and the time requirement until condensation fills the voids shortens accordingly. There are many variations which can be considered.

5.2. Acid and salt solutions

Sulfuric acid solutions have special interest for fluoropolymer coatings since some of these are very resistant to the acid itself. The question of the behavior of water can then become critical in understanding performance. Data on the vapor pressure of water at various temperatures are given in standard reference books such as [3]. Standard reference books [3] also include data for the vapor pressure of water (approximately equal to the total vapor pressure in this discussion) at various sulfuric acid concentrations and at various temperatures. Conditions at 120°C are used as a theoretical example for this discussion. The vapor pressure of water at this temperature is 2 atm. The vapor pressure of water in a 50% sulfuric acid solution is 670 mm Hg at this temperature. If the coating or metal substrate surface maintain a temperature greater than 96.5°C (the temperature at which the vapor pressure of water is 670 mm Hg), then no condensation will occur. Other comparisons for other acid concentrations are clearly possible. The water vapor pressure differences between acid conditions and the temperature at the substrate can be used to establish the driving force for water diffusion or permeation in all cases. As the temperature (or percentage of acid) increases above 120°C, it becomes more and more unlikely that the substrate temperature will be lower than that at which condensation can occur. Table 3 gives some examples using a temperature of acid about 90°C as reference for the solutions, and shows the temperature within the coating or at the substrate where condensation can be expected.

Table 3. Expected water condensation temperatures for sulfuric acid solutions at 90°C



Sulfuric acid (%)	Total pressure at 90°C (mm Hg)	Water condensation temperature (°C)
0	526.0	90
10	498.0	88
30	404.0	83
50	217.0	67.5
80	8.3	8.4
96	0.12	<−15

Similar conditions exist for the solutions of sodium chloride. The saturation amount (33%) keeps a relative humidity close to 75% at all temperatures below 100°C. Thus at 90°C, the vapor pressure is 0.75 times 526 or 394.5 mm Hg. This corresponds to the vapor pressure of water at 82°C. Condensation can be expected if the film or substrate has a lower temperature than this. If it is assumed that the reduction of vapor pressure is linear with salt concentration, it can be calculated that the condensation temperature for a 10% sodium chloride solution at 90°C is about 88°C.

6. General considerations

These examples show that the temperature within the film and at the metal substrate is critical for condensation phenomena. The driving force for the transport of water to the substrate will be the vapor pressure difference between the water in the solution (here 90°C) and the vapor pressure of the water at the prevailing substrate temperature, assuming that the water does not condense in the film itself. This can happen if the local temperature is less than that corresponding to the vapor pressure of water in the solution.

It is beyond the scope of this report to cover the various situations which may be encountered or devised that remove condensed (void) water from a film. The transport coefficients reported above can be used in this respect. The diffusion coefficients will be the same for absorption or for desorption. A danger exists that water will vaporize more rapidly than it can diffuse out of the film if the temperature is raised too rapidly.

7. Conclusion

Permeation coefficients, diffusion coefficients, and solubilities for water have been measured at 90°C in many different types of fluoropolymers. Approximate diffusion coefficients for selected fluoropolymers have been measured at 20°C. Equilibrium amounts of water are absorbed in practical fluoropolymer films within a maximum of a day or so at 90°C, and equilibrium permeation conditions are also established within this period of time. The amounts of water entering the films after relatively short time exposures demonstrate that a strategy for maintaining effective adhesion of these fluoropolymer coatings to metal substrates must make use of other effects than film barrier properties in order to be acceptable in the long run. One way to accommodate the excess of water which may/will be found in such films due to condensation within the film, is to provide suitable voids in which the condensed water may reside.

The special case of exposure to concentrated solutions of sulfuric acid is discussed clearly to show that condensation within the polymer film is not expected for practical operating temperatures above 120°C.

Acknowledgements

The fluoropolymer films were supplied by Christian Strøbech, Accoat gruppen, to whom we also thank for helpful discussions.

References

1. C.M. Hansen. *Prog. Org. Coat.* **26** (1995), p. 113. SummaryPlus | **Full Text + Links** | PDF (596 K) | View Record in Scopus | Cited By in Scopus (13)

2. H. Welding, S.H. Poulsen, C. Ursin, in: Proceedings of 11th International Conference on Electricity Distribution, CIRED, Liege, Belgium, 1991.

3. J.H. Perry, C.H. Chilton, S.D. Kirkpatrick (Eds.), Chemical Engineer's Handbook, 4th Edition, McGraw-Hill, New York, 1963, p. 43 (Chapter 3).

4. C.M. Hansen, Hansen Solubility Parameters — A User's Handbook, CRC Press, Boca Raton, FL, 1999, p. 81, 97, 98.

5. M. Conde, Nordisk Korrosion, Vol. 3, No. 1, Swedish Corrosion Institute, Stockholm, 1999, p. 8.