

Anomalous Permeation Observed in Fluoropolymer

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1. Introduction

Compatibility of polymeric materials governs their suitability for nearly all potential applications. An aspect of compatibility that is frequently important for fluoropolymers is their ability to isolate fluids by serving as a barrier to mass transport. This property is commonly expressed as permeability. In ideal cases, both solubility and diffusivity are constant at any given temperature and so the permeability is also a constant. However, in most cases involving organic liquids, these coefficients vary because of unfavorable physical phenomena, such as swelling, relaxation, deformation, and stress development in the matrix that occur simultaneously with diffusion and solution process. The penetrant absorbed by the polymer develops anisotropic swelling stress and promotes segmental motion of the polymer chains at any given temperature. In such cases, the permeability becomes a function of concentration, spatial coordinates, stress, and history of a sample.

The present work is focused on individual measurements of the lumped permeability of some organic liquids in several fluoropolymers in order to evaluate the systematic relationships between polymer structures and transport properties. The information gathered will lead to a quantitative basis for predicting the ability of the polymers to contain or isolate these substances. It may also reveal subtleties that are affected by processing conditions or formulation that may be a tool for product development.

2. Experimental

Permeation is observed under steady-state or quasi-steady state conditions. The permeation experiments were conducted in cup-shaped vessels made of 316 stainless steel and Carpenter 20. Each test of a liquid permeating through a polymer sample into air closely follows the current ASTM method for evaluating vapor transmission of volatile liquids. The mass of the permeation chambers is usually measured every four days using a Mettler 2000 microbalance with an accuracy of ± 1.0 mg.

3. Results and Discussion

Depending on the types of polymers, solvents, and processing properties (e.g., roll coating, orientation), different permeation behavior was observed.

3.1. Polymer and Solvent types

The modified fluoropolymers (ETFE, ECTFE, and PVDF) showed different permeation behavior for different types of solvents. For example, ECTFE turned out to be most susceptible to polar chlorinated hydrocarbons. On the other hand, PVDF was most susceptible to hydrogen (H)-bonding organics such as phenol and methyl ethyl ketone. ETFE exhibited intermediate resistance to polar and H-bonding organics among the modified fluoropolymers. The character of the interchain bonds in PVDF are more protonic, and those in ECTFE have the character of dipole-dipole interactions. ETFE has both characteristics, but the strength of interchain bonds is less than in PVDF in protonic character, and less than that in ECTFE in dipole-dipole interactions.

3.2. Effects of processing properties

Surface skin: The initial permeation rate in ECTFE film was very low, and the permeation rate increased very rapidly due to relaxation effects, as time proceeded. ECTFE films also exhibited other unusual behavior due to the existence of a dense, shiny skin that was possibly formed during manufacturing using a take-up roll, while the surface exposed to air became soft and dull. (Figure 2) The two different surfaces apparently have different properties. The shiny skin seems to be more tough and resistant to swelling stress than the dull side. This is illustrated by the onset of rapid relaxation of different time scales, depending on the types of penetrating solvents and the types of exposed surfaces.

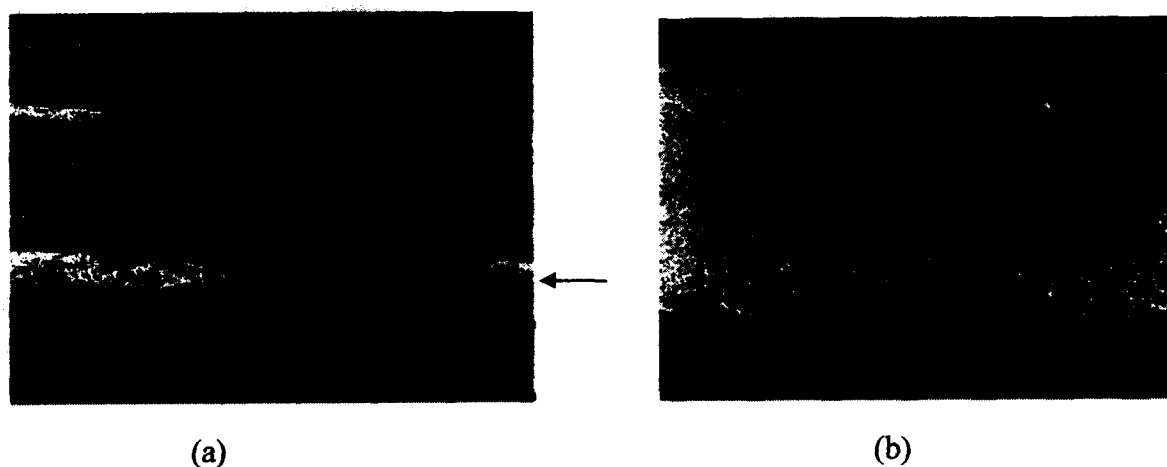


Figure 1. The cross sectional photograph by SEM: (a) ECTFE, (b) PVDF

Small and polar penetrants such as benzene and chlorobenzene induce the quicker onset of relaxation in ECTFE film, which results in the rapid increase of permeation rate during transient period, compared with large and nonpolar toluene, as shown in Figure 2. The exposure of the tough skin to the penetrant delays the onset of rapid relaxation in comparison to the dull side, as shown in Figure 3. In addition, the onset of rapid relaxation, especially when the shiny side was exposed to the penetrant, appeared with different time scales, e.g., the distribution of relaxation times, which are generally observed in glass transition phenomena. The steady-state permeation rate when the shiny side was in contact with the solvent was slightly less than that of the dull side, as shown in Figure. This probably indicates that the shiny side is less permeable and exhibits lower solubility

than the dull side.

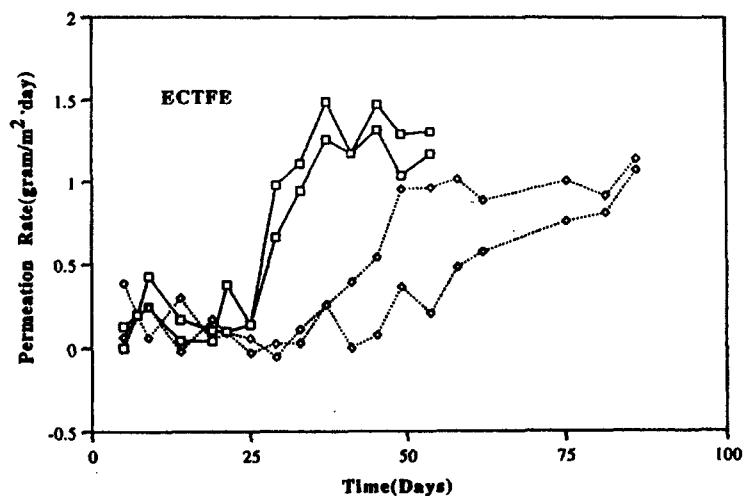


Figure 3. The transient permeation rate of aromatic solvents through ECTFE at 25°C (□: Benzene, 8: Toluene, O: Chlorobenzene).

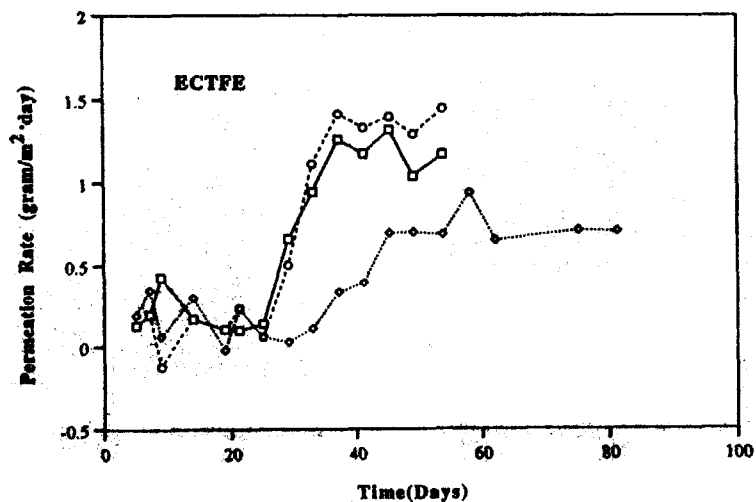


Figure 4. The comparison of permeation rates of benzene in ECTFE, when shiny side is exposed, and when the dull side is exposed at 25°C (□: Dull side, ◇: Shiny side).

Overshoots: Overshoot was exhibited during some permeation experiments with ECTFE as shown in Figure 4. This anomalous behavior was not detected clearly at room temperature, but at 45 and 75 °C it was clearly observed. After the permeation rate reached its maximum, it leveled off and dropped to a lower, steady value. This phenomenon implies that the relaxation process, during transient permeation, creates a supersaturated space which can accommodate penetrants into the polymer matrix, but which is not thermodynamically stable (possibly in microvoids that are subsequently annealed). The overshoot of the permeation rate cannot be explained by the

mechanism of Case II sorption. The overshoot may originate from a combination of structural factors due to chemical composition and processing conditions. It may also be evidence of microvoids that initially convey material, but which shrink as the polymer swells.

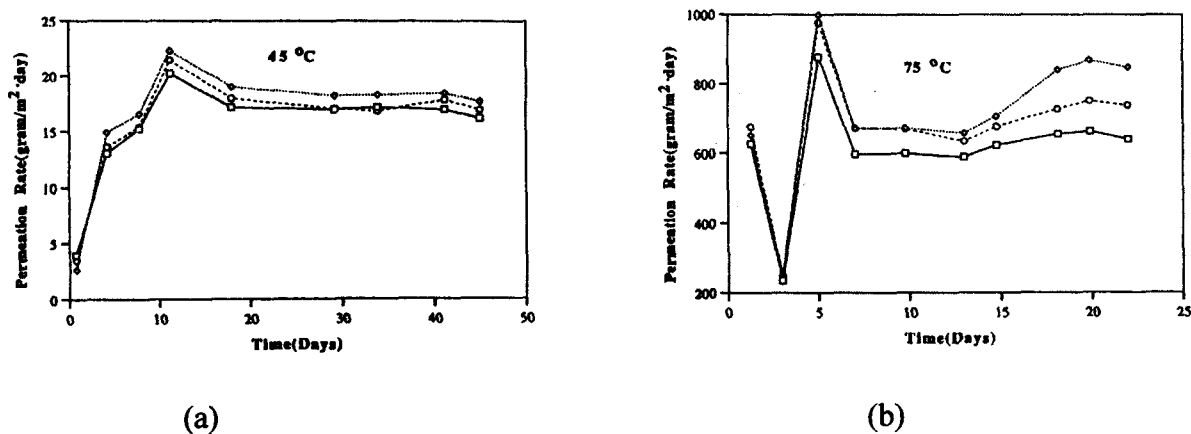


Figure 3. Overshoots in transient permeation of ECTFE-benzene system at 45°C and 75°C (□: Sample 1, ○: Sample 2, △: Sample 3).

4. Conclusions

Exposure of semicrystalline fluoropolymer films of different thickness to various liquid phase penetrants at several temperatures exhibited a broad range of trends that correspond to their chemical, physical, and processing properties. The increase of polar intersegmental attraction produced a high cohesive energy density and resulted in good mechanical and barrier properties. An unfortunate result, however, from the standpoint of stability of barrier characteristics was that non-Fickian diffusion was induced by the relaxation-controlled disruption of relatively weak intersegmental bonds due to solvent plasticization, which eventually resulted in the increase of permeability of partially fluorinated polymers. To overcome this disadvantage, it may be possible to modify some processing conditions to promote generation of a tough skin or a greater degree of orientation. The existence of a tough skin retards the relaxation process by inducing low solubility and low diffusivity.

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