

Solvent Permeation in Plasma-Fluorinated Polyethylene

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Synopsis

Liquid-phase sorption data are reported for the toluene-polyethylene system. The effects of fluorine plasma and inert-gas plasma treatments of the polymer surface were investigated. The presence of a fluorinated surface layer reduces initial solvent permeation rates, but the enhanced barrier property is lost when irreversible morphological changes occur during polymer swelling. A combination of chemical and morphological factors appears to be responsible for the observed temporary reduction in permeability; crosslinking of surface macromolecules was not a significant factor for the particular cases investigated in this work.

INTRODUCTION

Surface fluorination of polyethylene with elemental fluorine has been reported to be effective at decreasing the permeation rate of organic solvents into the polymer.¹⁻⁴ Exposure of a polymer to a glow discharge plasma containing a source of fluorine atoms (e.g., F₂, CF₄, SF₆) has been demonstrated to be an effective means of perfluorinating the surface layer.⁵⁻⁹ Preliminary studies by Anand¹⁰ showed that glow discharge fluorination of low density polyethylene film significantly reduced the sorption rate of *p*-xylene into the film. The limited scope of Anand's work and the intriguing results reported there motivated further study of this phenomena. In this paper the solvent barrier properties of plasma treated low density (LDPE) and high density (HDPE) polyethylenes will be reported. The objective of our work was to conduct a series of experiments to determine the effects of various plasma treatments on the permeability of polyethylene to one representative solvent, toluene.

EXPERIMENTAL

The procedure used to determine the relative permeability of pristine and plasma-treated polyethylene was a straightforward liquid sorption measurement. A polymer sample (~6 cm²) was immersed in a solvent bath onto a submerged metal screen. Solvent temperature was controlled by a surrounding stirred water bath; a copper-constantan thermocouple was used to monitor the solvent temperature. The general experimental procedure involved immersing the polymer in the solvent, removing it at regular intervals (proportional to the square root of time), quickly (<5 s), drying

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it on tissue paper, weighing the sample, and then replacing it back into the solvent bath. A calibrated linear variable differential transformer (Schaevitz, Model FTD-G-10), which could detect changes of ± 0.0002 g, was used to obtain the specimen weights.

An inductively coupled radiofrequency (13.56 MHz) plasma was utilized to chemically modify the polymer surfaces.¹¹ The operating conditions employed were pressure of ≈ 2 torr (267 Pa), 50–100 W rf power, and a flow rate of 50 cm³(STP)/min. Gas compositions of 5% F₂/95% He, 5% F₂/95% Ar, and 10% CF₄/90% He were used to fluorinate the polyethylene in both glow and cage^{10,11} environments. Reaction time was also variable. In these experiments the polymer films were cut to size and placed on a polytetrafluoroethylene (PTFE) sheet at the bottom of the reactor or cage. After the preselected reaction time had passed, the rf power was turned off, the system was opened, and the polymer sample was turned over. The reaction was again performed for the same length of time to ensure that both sides and all edges of the film were fluorinated. If, for example, a polymer sample was reacted for 1 h on each side, then the time reported in later sections of this paper would be 1 h.

THEORY

Before presenting the results of this work, it is necessary to provide some background on the solvent sorption experiment. The starting point for analysis of this process is Fick's second law:

$$\frac{\partial C}{\partial t} = \text{div}(D \text{ grad } C) \quad (1)$$

where C is the local concentration of diffusant, t is time, and D is the diffusion coefficient. Next assume a slab geometry of half-thickness L which is infinite in length and width (i.e., neglect edge effects). The polymer slab is immersed in an effectively infinite bath of fluid, and the diffusion coefficient is assumed to be a constant, independent of the diffusant concentration. Rather than solve explicitly for concentration as a function of position and time, only the integrated flux of diffusant as a function of time, $M(t) = \int_{-L}^{+L} C(x,t) dx$, will be evaluated because this is the quantity measured in the sorption experiment. A solution to eq. (1) in terms of $M(t)$ is¹²

$$M(t) = 2M_{\infty}(Dt/L^2)^{1/2} \left\{ 1/\pi^{1/2} + 2 \sum_{n=0}^{\infty} (-1)^n i \text{erf } c[nL/(Dt)^{1/2}] \right\} \quad (2)$$

where M_{∞} is the equilibrium amount of diffusant as $t \rightarrow$ infinity. The form of this equation suggests that a plot of fractional equilibrium uptake, $Q(t) \equiv M(t)/M_{\infty}$ vs. $t^{1/2}$, should be linear at small times and that the diffusion coefficient can be calculated from the initial slope. Most of the data will be presented in this form.

At long times, another solution to eq. (1) is preferred for computations:

$$Q(t) = 1 - (8/\pi^2) \sum_{m=0}^{\infty} \{ [1/(2m+1)^2] \exp[-D(2m+1)^2\pi^2t/4L^2] \} \quad (3)$$

which reduces to

$$\ln[1 - Q(t)] = \ln(8/\pi^2) + (-D\pi^2t/4L^2) \quad (4)$$

as $t \rightarrow$ infinity. Thus a plot of $\ln[1 - Q(t)]$ vs. t should be linear at long times and again the slope is directly proportional to the diffusion coefficient. Some of the data will be plotted in this format.

Finally, one can account for the 3-dimensional (3-D) nature of the polymer slab by including the solvent flux through the edges of the sample. This calculation will be done to determine if edge effects are significant. It can be shown¹¹ that the analogous 3-D solution to eq. (1) is

$$Q(t) = 1 - (512/\pi^6) \sum_{a=0}^{\infty} \sum_{b=0}^{\infty} \sum_{c=0}^{\infty} (e^{-\alpha(a,b,c,t)}) / (2a+1)^2(2b+1)^2(2c+1)^2 \quad (5)$$

where

$$\alpha(a,b,c,t) \equiv (D\pi^2t/4)[(2a+1)^2/E^2 + (2b+1)^2/W^2 + (2c+1)^2/L^2] \quad (6)$$

$a, b,$ and c are dummy variables; $E, W,$ and L are the half-length, half-width, and half-thickness of the polymer slab.

Before presenting the data, the assumptions made in the preceding analysis should be scrutinized. The postulate that the diffusion coefficient is independent of concentration will not be valid in this work because toluene is a swelling solvent for polyethylene. This will have a plasticizing effect within the polymer causing D to increase with C . The assumption that L (half-thickness) is a constant will not be strictly true; swelling of the polymer will cause L to increase slightly with C . Induction (time-lag) effects, due to relaxation processes within the polymer, have been reported for sorption in semicrystalline polymers.¹³ The effect of this phenomenon is that a plot of $Q(t)$ vs. $t^{1/2}$ will have a sigmoidal shape. Finally, irreversible morphological changes due to crystallite melting and/or reordering cannot be discounted because this has been observed in similar solvent-polymer systems.^{14,15} All of the above caveats suggest that we can expect deviations from ideal behavior in our experiments.

RESULTS AND DISCUSSION

The data shown in Figure 1 are for untreated LDPE (0.075 cm thick) immersed in a bath of toluene at 25°C; fractional equilibrium uptake is plotted vs. the square root of time. The equilibrium concentration of toluene was measured to be about 0.17 g solvent/g dry polymer. A manually drawn

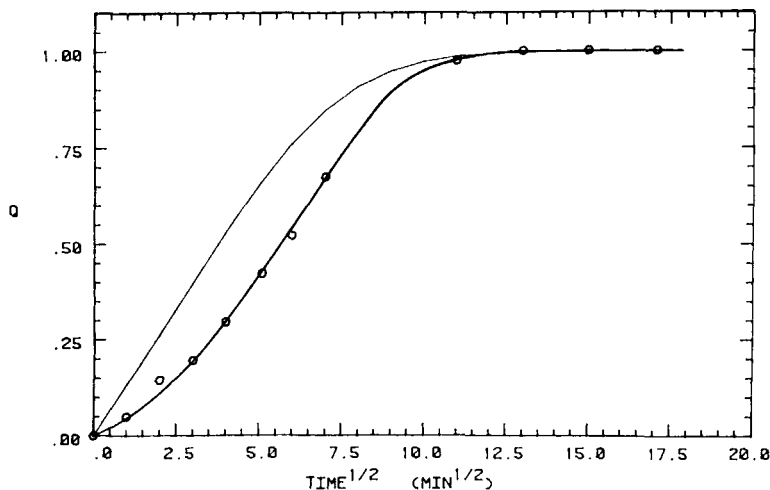


Fig. 1. Sorption data for toluene (25°C) and low density polyethylene compared to the predicted behavior calculated from eq. (3) using a value of $D = 3.1 \times 10^{-7} \text{ cm}^2/\text{s}$: (○) data (0.075 cm); (—) 1-D simulation.

curve is included to outline the trend in the data. The sigmoidal shape of the curve is a consequence of polymer mobility/relaxation phenomena as discussed previously. By estimating the slope of this curve in the linear region, an effective integral diffusion coefficient (\bar{D}) can be calculated. A value of $3.1 \times 10^{-7} \text{ cm}^2/\text{s}$ was determined which compares favorably to the literature value¹⁵ for the diffusion of *p*-xylene in linear polyethylene ($\bar{D} = 1.1 \times 10^{-7} \text{ cm}^2/\text{s}$). If our estimated value of \bar{D} is inserted into eqs. (2) or (3) a 1-dimensional (1-D) ideal simulation is obtained which is also included in Figure 1. The region of linearity is seen to be quite broad. Nonideal behavior is observed primarily at short times, where polymer relaxation times are equivalent to the experimental time scale.

The same data are replotted in Figure 2. In this graph, eq. (3), $\ln(1-Q)$ vs. time, is presented. Note that, at very long times, the simulation becomes

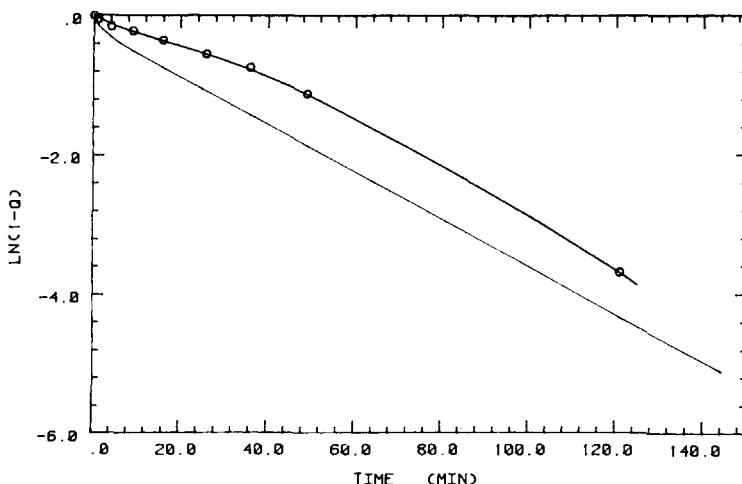


Fig. 2. Sorption data for toluene (25°C) and low density polyethylene compared to Equation 3 with $D = 3.1 \times 10^{-7} \text{ cm}^2/\text{s}$: (○) data (0.075 cm); (---) 1-D simulation.

linear whereas the slope of the data appears to steepen. Since the effective diffusion coefficient is directly proportional to this slope at long times, this implies that it is increasing with Q . Again, this is consistent with what is expected: The diffusion coefficient of a swelling solvent in a polymer should increase with concentration.

The data shown in Figure 3 were obtained with a different, thicker (0.15 cm) LDPE sample. The sigmoidal sorption curve is similar to the previous data shown in Figure 1. An effective integral diffusion coefficient was again estimated from the slope of the linear region of the curve and found to be $\approx 2.9 \times 10^{-7} \text{ cm}^2/\text{s}$, in good agreement with the previous value. Both 1-D and 3-D simulations were calculated for this sample. The 3-D curve lies above the 1-D curve because sorption occurring through the "edges" of the polymer contributes to the total mass flux in the former case. The difference between these two simulations is relatively small, and will be even less for thinner samples. Therefore, the remainder of the data were obtained with thinner (0.075 cm vs. 0.15 cm) polymer slabs and "edge" effects were neglected.

A direct comparison of the two sets of data shown in Figures 1 and 3 can be accomplished by using a reduced abscissa ($t^{1/2}/L$), and is presented in Figure 4. Ideally, the two curves should overlap. They are seen to be very similar in shape with nearly identical slopes in the linear intermediate regime.

The sorption data presented to this point have demonstrated that our simple experimental technique is successful at generating reproducible results consistent with previously published work. We now turn to experiments designed to monitor the effects that solvent sorption has on polymer structure. An untreated sample of LDPE was subjected to three consecutive sorption experiments. Between experiments the sample was dried at room temperature under vacuum to a constant weight. The data are shown in Figure 5. The second and third runs revealed progressively faster sorption

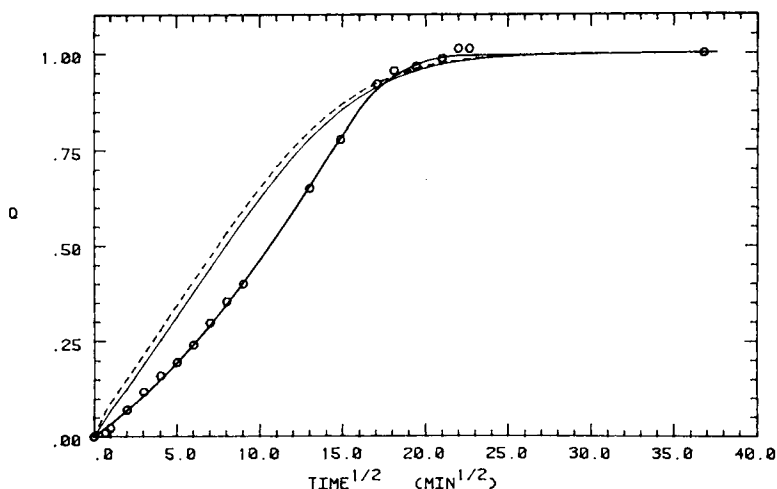


Fig. 3. Sorption data for toluene (25°C) and low density polyethylene using a thicker LDPE film. Predictions of eq. (3) (1-D) (—) and eq. (5) (3-D) (---) were calculated using a value of $D = 2.9 \times 10^{-7} \text{ cm}^2/\text{s}$; (○) data (0.15 cm).

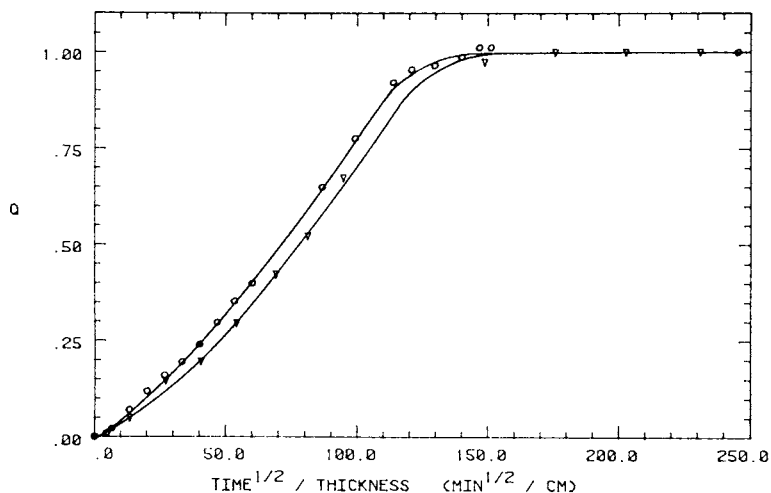


Fig. 4. Effect of sample thickness on the sorption experiments for toluene (25°C) and low density polyethylene: (○) 0.15 cm sample; (▽) 0.075 cm sample.

rates; however, the shape of the curves remains sigmoidal. The slopes in the linear regime are steeper for the second and third runs suggesting that D has increased. This agrees with the data reported by Michaels et al.¹⁴ and Baddour et al.,¹⁵ who employed solvent treatments to condition polyethylene membranes. The significance of these findings will be discussed later in the paper.

It has been demonstrated that treating polyethylene in an inert gas plasma will crosslink the surface region.¹⁶ To determine if this would have an effect on observed sorption rates, a sample of LDPE was exposed to a pure helium glow for 10 min and then subjected to the sorption experiment. The data shown in Figure 6 establish that this treatment does not significantly change the sorption rate of toluene; it is possible, however, that larger diffusant molecules may be affected by a crosslinked surface region.

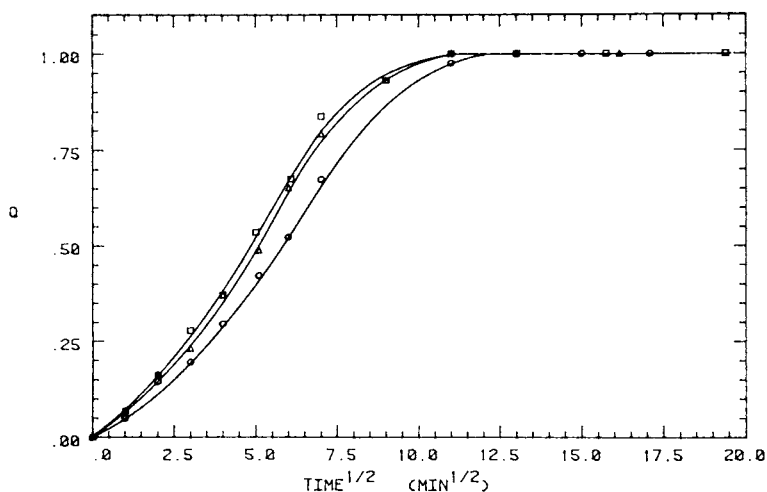


Fig. 5. Effect of repeated sorption/drying cycles for untreated low density polyethylene samples: (○) first run; (△) second run; (□) third run. (Toluene, 25°C.)

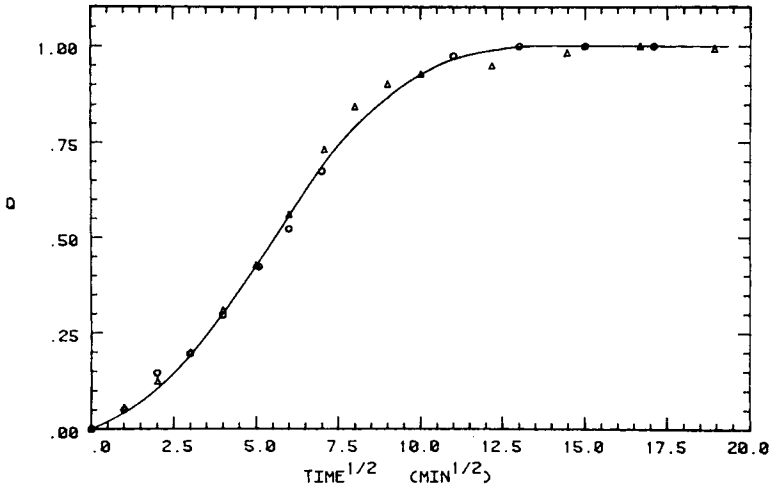


Fig. 6. Comparison of the sorption of toluene (25°C) into untreated low density polyethylene and into a specimen of the same polymer whose surfaces had been crosslinked in a helium plasma: (○) untreated (0.075 cm); (△) helium glow 10 min.

When LDPE film is fluorinated in a plasma (glow or cage) environment with 5% F₂/95% He, the sorption rate is initially retarded as demonstrated by the data shown in Figure 7. The initial rate of solvent permeation is much less in the fluorinated samples than in the untreated polymer. However, after a delay or induction period, relatively rapid sorption occurs in the treated polymers, and the same equilibrium value is eventually reached. The shapes of the curves are again quite similar; the effect of fluorine treatment can be approximated by a time translation of the curves. The fact that the slopes in the linear regime are all about the same implies that the initial improvement in barrier properties is completely ineffective after the induction period. For comparison, when a sheet of PTFE is subjected

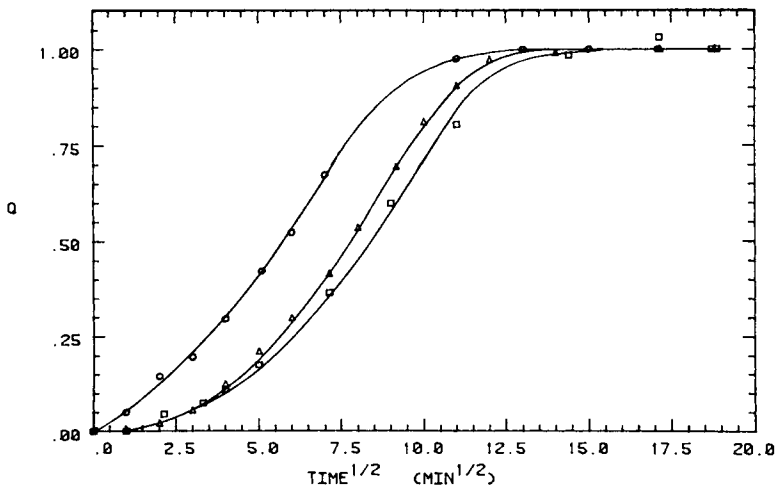


Fig. 7. Influence of plasma surface fluorination with F₂/He on the sorption behavior: (○) untreated (0.075 cm); (△) F₂/He glow 10 min; (□) F₂/He cage 1 h. (Toluene, 25°C.)

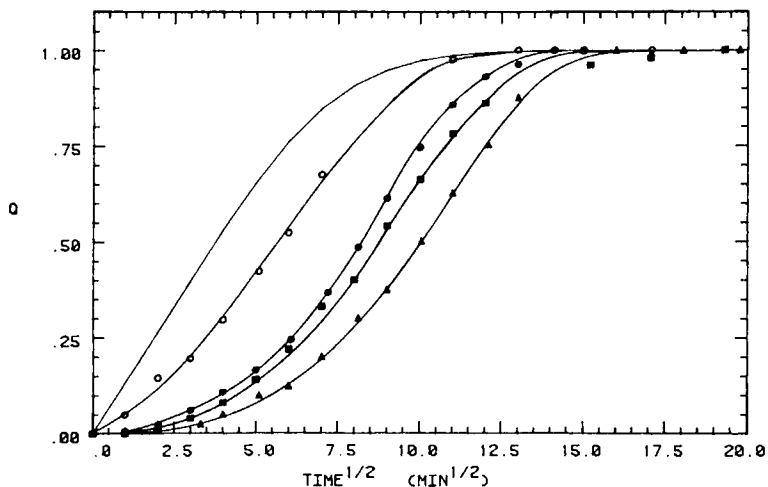


Fig. 8. Influence of the depth of surface fluorination with a F_2/Ar plasma on the sorption behavior: (—) 1-D simulation; (○) untreated (0.075 cm); (●) F_2/Ar glow 10 min; (■) F_2/Ar cage 1 h; (▲) F_2/Ar cage 2 h. (Toluene, 25°C.)

to the same sorption experiment, the value of Q remains essentially at zero, i.e., negligible sorption is detected.

Similar results are obtained with 5% $F_2/95\%$ Ar plasma treatments of LDPE (Fig. 8). If fluorination is carried out to a deeper level, then the induction time increases, as evidenced by a comparison of one and two hour cage experiments. An interesting observation is that, for all fluorinated samples shown in Figures 7 and 8, no solvent uptake is observed after 1 min. This may be a consequence of wetting phenomena. The toluene does not visually appear to wet the fluorinated LDPE during this period. This observation was also reported by Anand¹⁰ in his experiments. The data of Figure 8 have been replotted on an $\ln(1-Q)$ vs. t basis (Fig. 9). The terminal

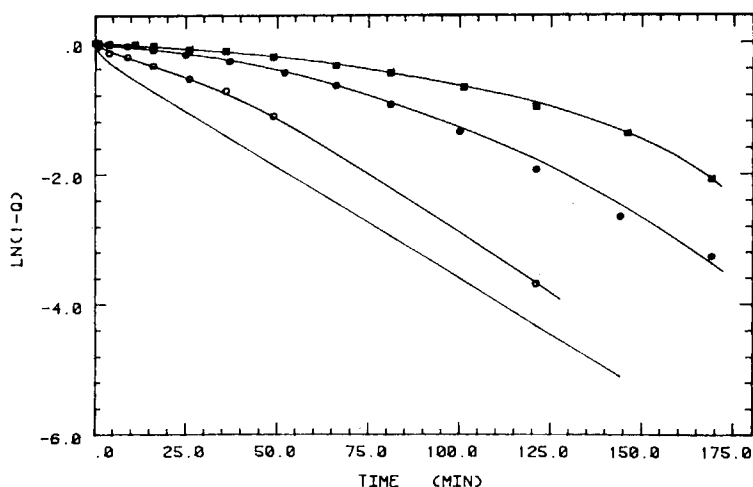


Fig. 9. Evidence for increasing diffusion coefficient with increased toluene (25°C) uptake for surface treated and untreated polymer; $D = 3.1 \times 10^{-7}$ cm²/s in simulation: (—) 1-D simulation; (○) untreated (0.075 cm); (●) F_2/Ar glow 10 min; (■) F_2/Ar cage 2 h.

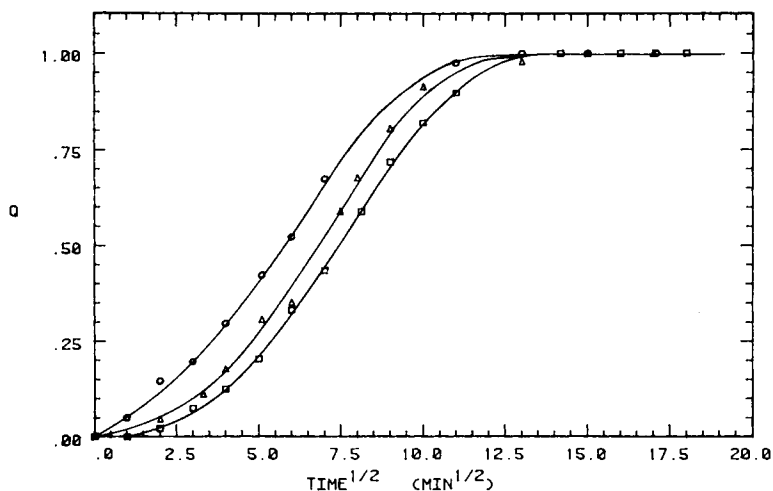


Fig. 10. Sorption behavior of low density polyethylene treated in plasmas containing CF_4 as the fluorine atom source: (O) untreated (0.075 cm); (Δ) CF_4/He glow 10 min; (\square) CF_4/He cage 1 h. (Toluene, 25°C .)

slopes are not constant except in the simulated case. Again, the steepening of the slopes implies that the effective diffusivity of the solvent is increasing with diffusant concentration as expected.

Treatment of LDPE with 10% $\text{CF}_4/95\%$ He in plasma environments is not as effective as F_2 plasma reactions at reducing the sorption rate of toluene; however, the trends in the data are similar (Fig. 10). The glow treated sample was dried under vacuum after the sorption experiment had reached equilibrium and the experiment was redone. This was then repeated a third time. The trends in the data shown in Figure 11 mimic the untreated LDPE results of a similar series of sorption experiments (Fig. 5). In fact, when the two sets of data are directly compared (Fig. 12), the second and third runs of the untreated and fluorinated samples are nearly identical.

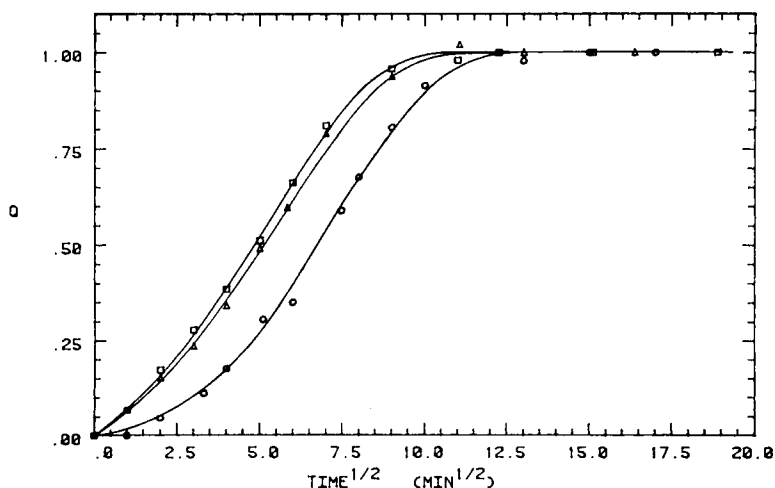


Fig. 11. Effect of repeated sorption/drying cycles for plasma surface fluorinated low density polyethylene samples (CF_4/He): (O) first run; (Δ) second run; (\square) third run. (Toluene, 25°C .)

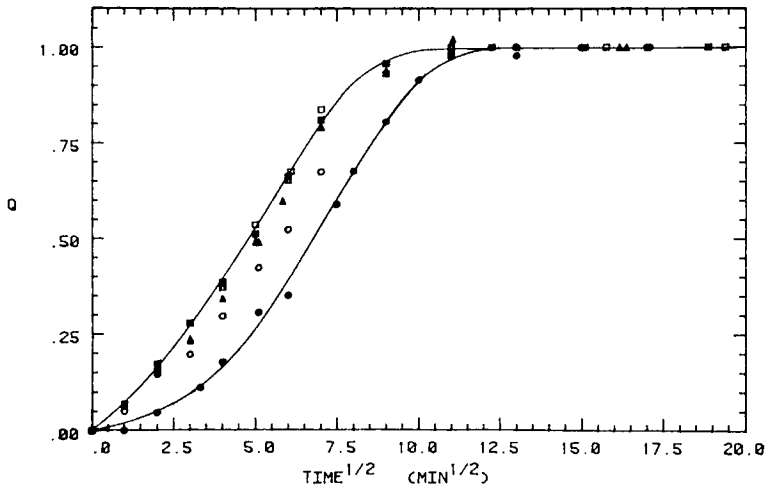


Fig. 12. Comparison of the data in Figures 5 and 11. Untreated: (○) first run; (△) second run; (□) third run. CF_4/He : (●) first run; (▲) second run; (■) third run. (Toluene, 25°C.)

This suggests that irreversible restructuring has occurred both within the polymer bulk and in the fluorinated surface layer. X-ray photoelectron spectroscopy (ESCA) carbon 1s spectra of the CF_4/He glow treated sample before and after a swelling/drying cycle are presented in Figure 13. These spectra verify¹¹ that the fluorinated layers are *chemically* similar in both cases; a slight increase in the hydrocarbon peak (285 eV) is noted for the swelled/dried surface. Thus the sorption process evidently causes permanent *morphological* changes within this fluorinated region which eliminate its enhanced barrier properties.

A final set of experiments utilized HDPE (0.075 cm thick) as the polymer substrate. The sorption experiments were performed at 40°C in toluene because the equilibrium concentration of toluene in the HDPE at 25°C was relatively low (0.03 g toluene/g dry polymer). At 40°C the equilibrium uptake was about 0.075 g toluene/g dry polymer. The data are summarized in Figure 14. Again helium glow treatment alone does not reduce the measured

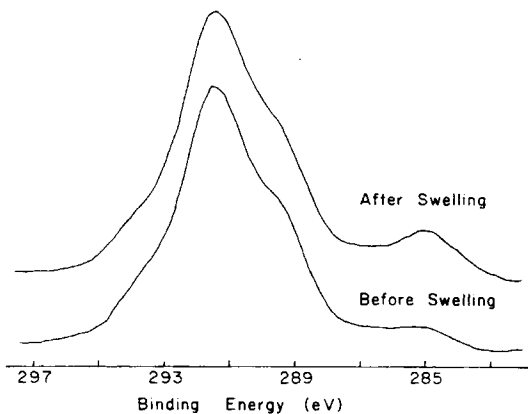


Fig. 13. ESCA C_{1s} spectra of CF_4/He treated low density polyethylene before and after a toluene swelling/drying cycle.

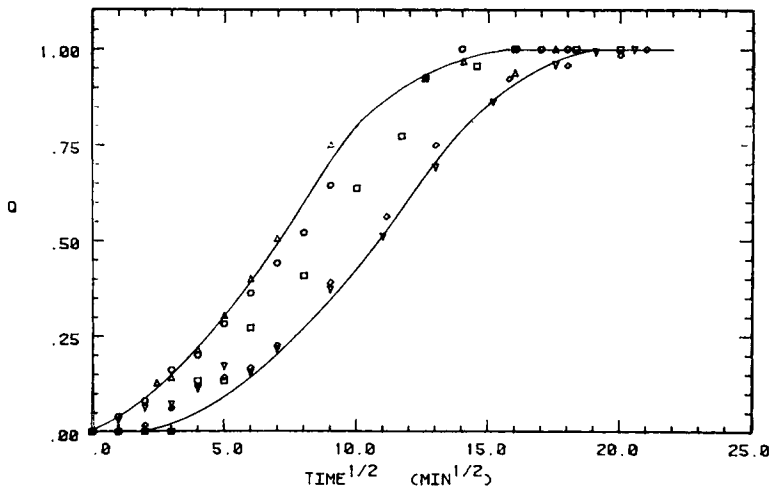


Fig. 14. Effect of surface fluorination on the sorption behavior for the case of toluene (40°C) and high density polyethylene: (○) untreated (0.075 cm); (△) He glow 10 min; (□) CF₄/He cage 1 h; (◇) F₂/Ar cage 1 h; (▽) F₂/Ar cage 2 h.

sorption rate. The fluorinated HDPE samples are seen to behave as the fluorinated LDPE samples did. Thus both the LDPE and HDPE plasma fluorinated films studied in here exhibit transient impermeability to toluene.

CONCLUSIONS

The general conclusion which can be drawn from these sorption experiments is that glow and cage fluorination of polyethylene surfaces results in a pronounced reduction in the initial permeation rate of toluene. This enhanced barrier property is transient in nature. Treatment for a long period of time in the cage environment generally extends the induction period. Repeated experiments with the same fluorinated sample (after drying) established that irreversible morphological changes occurred such that the fluorinated layer was no longer capable of improving impermeability after the initial sorption experiment. ESCA experiments verified the chemical permanence of the fluorocarbon surface layer and thus morphological changes appear to be responsible for the loss of enhanced barrier properties; crosslinking does not seem to be a significant factor in the particular cases studied.

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