

Polyethylene Plasma Fluorination and Permeability Relationships to Methanol–Gasoline Mixtures

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SYNOPSIS

In the case of cold plasma fluorination we analyzed effects of the main processing conditions (power, exposure time, nature of gas, and number of fluorinated faces) on gasoline permeability of polyethylenes. Optimization of processing conditions gave us a permeability reduction of 30% compared to untreated polyethylene. XPS analysis of fluorinated specimens before permeation experiments shows the PE to be highly fluorinated at the surface with a F/C ratio up to 2. Fluorination appeared to be homogeneous over the disk surface with a concentration depth profile showing a step decline below the extreme surface. However, significant fluorination is achieved only up to a few tens of nanometers (20 to 30). A more interesting effect is the evidence for chain breaking during the process suggests the creation of short chain segments at the surface. These segments would be highly fluorinated but easily leached out by the diffusing molecules. Leeching seems more important with alcohol containing gasolines. These data show clearly that fluorination by cold plasmas in the conditions under studies has not a permanent effect. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Containers fabricated from polyethylenes provide a large number of design advantages over those made from metal or glass,¹ for instance, flexibility, low-cost fabrication, good resistance to corrosion, and breakage. These advantages explain the great interest of automotive and oil industries to produce containers (e.g., fuel tanks and pipes) in high-density polyethylene (HDPE). Unfortunately, polyethylene is highly permeable to the main constituents of gasoline² (i.e., hydrocarbons, oxygen, etc.). On the other hand, fluorinated polymers are not sensitive to usual solvents but their prices are prohibitive and their processing is elaborate, and also expensive. Thus, many attempts have been made to introduce fluorine by improved surface treatments of polyethylene and other polyolefines or polyesters. The new hydrocarbon emission standards for automobiles³ and particularly for fuel tanks have generated wide

interest in both the technical and economic aspects of production of highly impermeable containers and pipes. Fuel tank hydrocarbon emission standard proposed in 1992 by California Air Resources Board (CARB) limits the emission to 2 g/day even with methanol containing fuels. This limit includes volatiles from all parts of the car, so the limit on the tank itself is being set as low as possible and Solvay Automotive Inc. has proposed a lower limit around 0.2 g/day.³

In order to improve the resistance properties to gasoline–methanol mixtures, a great deal of work has been carried out in the last years in order to increase basic knowledge of transport phenomenon. Usually the permeation process is divided into three steps⁴: (1) sorption of organic liquids at the surface of the polymer, (2) entry and diffusion of the penetrant molecules, and (3) evaporation and transition of liquids into environment. Taking HDPE containers such as fuel tanks, this simple scheme illustrates, in addition to others factors, the dependency of diffusion rate and permeability on the following parameters⁵: (1) nature, partial pressure, and composition of the mixture; (2) percentage of crystalline

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phase, which is nonpermeable, and surface tension of the polymer. Each step of the permeation process can be modified by a controlled change in these parameters. For example, permeability can be reduced by establishing barriers in polymeric materials by means of fillers or protecting the surface to delay entry of solvents. In fact, this illustrates the three main techniques used to reduce the permeability of organic liquids mixtures through HDPE (and other polymeric materials): (1) fluorination or sulfonation of polymer surface,²⁻⁶ (2) coextrusion blow molding of HDPE-EVOH,⁷ (3) use of extruded or blow-molded blends of HDPE-PA.^{8,9} This article is focused on fluorination surface treatment of polyethylenes.

Direct fluorination of polymers such as polyethylene can be obtained in gas phase by fluorine diluted with an inert gas, or in liquid phase by fluorine dissolved in a perfluorinated solvent.¹⁰⁻¹⁵ A thick perfluorinated layer, in the range of 100 to 1000 nanometers, can be prepared with few polymer chains breaks.^{13,14} A correlation between the structure of polymer and critical surface tension obtained was also made.¹⁶ These processes has been associated with container blowing,¹⁷ or carried out separately¹⁸⁻²¹ in order to increase the barrier properties of PE to gasolines. A factor of 10 to 100 in reduction of permeability to hydrocarbons can be obtained.²²⁻²⁵ However, the presence of polar additives such as methanol or methyl tertio butyl ether (MTBE) in gasolines, significantly reduces the barrier properties.²⁶⁻²⁸

Treatment with fluorinated molecules, activated by electrical discharges, can replace direct reactions with diluted fluorine. In 1979, Amouroux et al.²⁹ activated low-density biaxially stretched polyethylene with Corona discharges in a variety of gases: air, air + N₂O mixture, difluoroethylene (CH₂CF₂), chlorotrifluoroethylene (C₂ClF₃), chlorotrifluoromethane (CClF₃), bromotrifluoromethane (CBrF₃), dichlorodifluoromethane (CCl₂F₂), or tetrafluoromethane (CF₄). Introduction of fluor atoms into the polymer reduces its wettability.³⁰⁻³² Perfluorination can also be obtained by dissociation of fluorine compounds such as CF₄, SF₆, by electrical discharges (i.e., corona, cold plasma, etc.). The modified surfaces had good barrier properties toward automotive fuels,³³ suggesting that the plasma discharges increases the fluorination rate of the polymers.³⁴ In 1982, use of CF₄, CF₃CClF₂, SF₆, or similar gases was proposed for container processing.³⁵ Gas is introduced in the container and is dissociated by a high-frequency electromagnetic field to obtain a plasma that

modifies the inner surface of the container. Corbin et al.³⁶ studied effects of plasma fluorination treatments on sorption of toluene in polyethylene and effects of an inert gas plasma treatment. The formation of a fluorinated layer reduces the initial solvent permeation, but the improvements to barrier properties are subsequently lost with irreversible morphological changes induced by polymer swelling, as deduced by XPS analysis. The authors proposed that the surface crosslink phenomenon is not a significant factor, and that chemical and morphological changes are responsible for the temporary reduction in permeability. Recently, Chasset et al.³⁷ studied cold plasma treatments of polymers. Treatment with nonpolymerizable molecules, such as CF₄ or SF₆, but also with polymerizable molecules, leads to modifications over a very shallow depth, less than 10 nm. Mournet³⁸ puts emphasis on the effect of argon on the efficiency of fluorine components grafted onto polyolefines and polyethylene terephthalate by corona discharges, at low or high pressures. The modified surfaces had good barrier properties toward automotive fuels, suggesting that plasma discharges increases the fluorination rate of PE.³³ Finally, Arefi³⁹ reviewed the analytical techniques (e.g., XPS, SIMS, contact angle) useful to study the surfaces of plasma treated polymers, and to characterise the plasma itself. By these means, fluorocarben (CF₂) is proposed as a reactive intermediate at normal pressure, during CF₄ + H₂ + Argon plasma treatment on polyethylene. The critical surface tension is strongly affected by the formation of a perfluorinated layer, but this layer is very thin, around 10 nm. Homogeneity of such layers appears to be sensitive to (1) swelling and deswelling in the subsurface of untreated polymeric materials, and (2) the presence of polar components in the gasoline composition. Thicker layers cannot be prepared as the polymeric surface is subject to polymeric chain breaking and damage.

In conclusion, it appears that plasma perfluorination of polyethylenes allows preparation of layers of 4 to 10 nm, which change significantly the wettability, adhesion (casing effect), and friction coefficient (surface effects). However, it appears that the literature data are not so convergent in terms of methanol containing gasoline reduction of polymers permeability. In these conditions, the following part of this work is focused upon the relationships between surface treatment of polyethylenes and variations to their permeability to alcohol containing gasoline.

Table I Polyethylenes Physical Characteristics

Polymer	\bar{M}_w	\bar{M}_n	Crystallinity (% w)	T_m (°C)
HDPE	241,000	10,500	75	132
MDPE	157,000	5,900	55	129

Molecular weight by GPC, crystallinity, and melting temperature by DSC.

EXPERIMENTAL

Materials

Polymers used are high-density polyethylene (HDPE) and medium-density polyethylene (MDPE) from FINA Co., where the respective physical characteristics are described in Table I. Pellets of both polymeric materials were compressed and molded at 200°C during 20 min at 20.10⁶ Pa and cooled to room temperature at 5°C/min to form plates of 2 mm of thickness.

Plasma Treatments

An inductively coupled radiofrequency (13.56 MHz) plasma was used to chemically modify the polyethylene surfaces. The effects of the following operating conditions were examined: plasma power from 80 to 300 W, exposure time from 5 to 240 min, nature of gas (CF₄ and SF₆), number of fluorinated faces of samples, and crosslinking before fluorination of the specimen surface. Gas flow rate was kept constant at 50 cm³ (STP) and the pressure inside the plasma vessel was 267 Pa.

XPS Spectroscopy

XPS spectroscopy was performed with a Kratos XSAM800 spectrometer using a magnesium source. Specimen chamber vacuum was around 10⁻⁸ Torr (1.3·10⁻⁶ Pa) during analysis except during ion beam-assisted depth profile. Because of the insulating nature of the samples, static surface charging occurred. This was compensated via software before analysis by shifting the energy scale, so that the $[-CH_2-]_n$ form of carbon presented a C 1s binding energy of 284.6 eV.

Quantitative analysis was performed by integrating peak areas after background subtraction. Elemental sensitivity factors, calculated from Schofield ionization cross-sections and measurements of the spectrometer transmission function,⁴⁰ were verified on a range of clean reference samples (e.g.,

PTFE and PVDF). Because fluorinated polymer specimens are known to be sensitive to X-radiation,^{41,42} several successive analyses of the same sample were performed to determine whether X-ray-induced damage (e.g., loss of fluorine or modifications to carbon-fluorine bonding) was occurring, and analysis time were kept short enough to avoid this effect. From analysis of several samples obtained under identical conditions a precision of ±2% for an individual analysis was determined.

Depth profiles were obtained by repeatedly analyzing the surface and etching using a 2.5 keV ion beam with a current density of 6 A·cm⁻². Under these conditions, it was established that the rate of erosion of a metallic surface (NIST standard reference material No. 2135)⁴³ was 0.6 nm/mn. Because erosion rates of the materials studied here are not known and probably vary with the concentration of fluorine, this rate will be used here in order to estimate fluorination depth, but should not be taken as an absolute etch rate. Here again, it has to be noted that samples studied are sensitive to beam damage, which is more severe with ion beams than with X-rays.^{44,45} Variations in the F 1s and C 1s binding energies were observed during etching experiments, but because of the uncertain origin of these effects no attempt at determining molecular species was made for the ion etched samples.

As it is shown in Figure 1, 12 mm diameter disks were punched from the 60 mm diameter samples. In order to ascertain the homogeneity of the surface composition, disks were obtained from various parts of the original spacemen at the center (I), periphery (E), and median (M) positions. For each position both faces were analyzed. The XPS results are noted as follows: X_i with X = I, E, and M denoting the area of origin of the specimen with respect to the

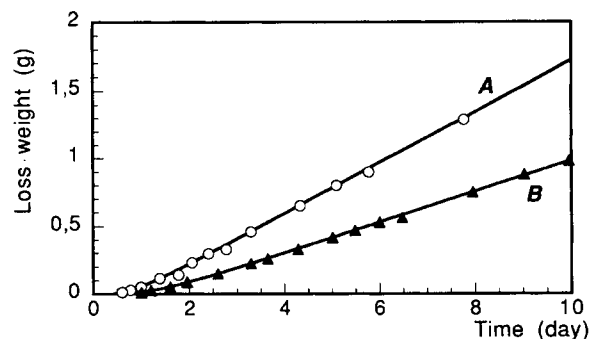


Figure 1 Variations of weight loss in function of time for (A) PEHD reference sample, and (B) after SF₆ fluorination (120 W, 240 mn) with C gasoline. Fitting of experimental data is obtained by equation 4.

original disk and $i = 1$ for surface in contact with the gasoline and 2 for evaporating surface.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

Permeability Measurements

The weight loss method was used on 60 mm diameter disks, cut from plates, to analyze the transport coefficients: permeability (P), Diffusion (D), and Solubility (S) at 55°C. The permeation cells consists of a partly circular aluminium vessel, filled with solvent, and closed by a polymer disc. Discs were in contact at 55°C with gasolines of different compositions: N 45/45/7/3 wt % of toluene/isooctane/ethanol/methanol and C 50/50 wt % of toluene/isooctane. The general experimental procedure is described elsewhere.⁴⁶ The values of permeability reported are a number average of three runs. Repeitions gave the standard deviation of the data (SD).

Permeability Data Treatment

The basic mathematical aspects of diffusion are extensively described in review papers and in textbooks.⁴⁶ Only some basic aspects of the permeation of liquids through polymeric membranes will be briefly discussed here. Permeation is a transport phenomenon that describes the passage of diffusing molecules through a polymer. The driving force is the concentration gradient. As we are more interested in the macroscopic permeability behavior of the polymeric membranes, comparing the relative effects of the different treatments, than by a study of the liquid-liquid interactions during diffusion process, the following hypotheses have been made: (1) diffusion of the solvent molecules is independent of the concentration, for instance, the mixture is considered as an homogeneous organic liquid, and (2) contact of the solvent and the polymeric surface is instantaneous. Under these conditions the transport phenomenon can be describe by Fick's laws in one dimension.

At initial time ($t = 0$) the membrane is free of gasoline ($C = 0$) and the concentration at the face through which the diffusing substance emerges is also zero. At $t > 0$ the concentration at the surface in contact with gasoline is C_1 . Under these initial and boundary conditions the solution of Fick's second law [Eq. (1)] is easily obtained by the method of separation of variables [Eq. (2)]. Here, L is the thickness of the membrane:

$$C_{x,t} = C_1 \left(1 - \frac{x}{L} \right) - \frac{2C_1}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi x}{L}\right) \exp\left\{-\left(\frac{n\pi x}{L}\right)^2 Dt\right\} \quad (2)$$

The amount of diffusing substance that passes through the membrane per unit area in time t is calculated by integrating Fick's first law with respect to time [Eq. (3)], by considering the gradient concentration at $x = L$ [Eq. (4)].

$$M_t = - \int_0^t D \left(\frac{\partial C}{\partial x} \right)_{x=L} dt \quad (3)$$

$$M_t = \frac{P_e}{L} \left\{ t + \frac{2L^2}{\pi^2 D} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \left[1 - \exp\left\{\left(\frac{n\pi x}{L}\right)^2 Dt\right\} \right] \right\} \quad (4)$$

Under the hypotheses described above, the permeability (Pe) coefficient is equal to $D \cdot C_1$, we used a two variables (D, Pe) multilinear regression in Eq. (4), on at least 30 experimental points defined by M_t and t . This original calculation gives the possibility to take into account the transient and the steady state regimes of diffusion. On the other hand, as we are only interested in the macroscopic permeation behavior of the polymeric membranes, the solubility coefficient was then calculated by Pe/D . It should be noted that in our case the permanent state is obtained rapidly (less than 3 days). Even if Figure 1 shows experiments up to 10 days, experiments up to 30 days have been conducted without modify the permanent flux of diffusing molecules through the polymeric membrane.

RESULTS AND DISCUSSION

Permeability Analysis

The different variables tested during cold plasma fluorination processing are noted as follows: plasma power (P), type of plasma gas (g) (CF_4 or SF_6), exposure time (t), and number of fluorinated faces of samples (nb) (one or two). The permeability data depend on the type of PE (i.e., high and medium density polyethylenes: HDPE and MDPE), gasoline (N, C) and the cold plasmas conditions (i.e., power and time). Table II shows the results obtained with

different values of P , t , g , and nb , for HDPE in contact with N and C gasolines. It is clear that the processing variables such as the nature of gas and the number of fluorinated faces have no influence on the relative permeability (i.e., HDPE/fluorinated HDPE). It seems on the contrary that P , t , and especially the composition of gasolines, have an effect. We observed a reduction with C gasoline while with N gasoline (10 wt % alcohol) we observe a slight increase of the permeability. This last original increase effect can be explained by the presence of shorter polymeric chain sequences becoming from the cold plasma fluorination treatment. Actually, these fluorinated chain sequences can increase the free volume of the polymer and, therefore, increase the rate of the diffusion processes and then the permeability level. Permeability analysis on MDPE following the same cold plasma treatments showed a similar behavior.

Considering the low levels of permeability reduction obtained we decided, in a second step to set the cold plasmas processing variables (i.e., $g = \text{SF}_6$ and $nb = 2$) and drive the permeability analyzed in C gasoline. We note that increasing exposure time and plasma power leads to a decrease of the permeability coefficient (Table III). The best treatment conditions are given by a relatively low power and long time exposure, for example, with soft or gentle treatment conditions as mentioned in the review. Hence, it appears that an optimum exist at around 120 W and 240 mn. Under these conditions we obtained a 35% reduction to HDPE permeability. It should be noted that the same permeation tests were performed on a PVDF sample and gave us a permeability of $5.10^{-10} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ in N gasoline, which is very far from the permeability of HDPE, whether fluorinated or not.

A more interesting result is that the reduction of permeability is mainly due to the decrease of the rate of transportation (e.g., diffusion). In this case, we can expect that fluorination by cold plasmas treatment has created a thin less permeable layer (much less than $5.10^{-10} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$) at the extreme surface of the sample. The same permeation tests, in C and N gasolines, were twice performed on a HDPE sample conditioned as follow: 120 W and 240 mn and dried under vacuum at 60°C for 4 h. We checked that these drying conditions did not modify the crystalline characteristic of the polymer. The experimental permeability obtained are, respectively, for C gasoline: 1.4 and $2.2 \times 10^{-8} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ and for N gasoline: 1.7 and $2.3 \times 10^{-8} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$. These data clearly show the effect of gasoline content, and particularly the alcohol influence, upon the permeability of PE. On the other hand, these data imply that the decrease of permeability involved by cold plasmas fluorination, in the conditions under studies, is not permanent. So, we analyzed the surface of the above-mentioned samples in order to quantify the depth of fluorination and the quality of this type of treatment.

XPS Analysis

The results of XPS analysis of the surfaces obtained are presented in Table IV (atomic concentrations of fluorine, carbon, and oxygen for the various areas analyzed). Table V shows fluorine concentrations as a function of etch time, and, thus, of depth, for typical samples. The distribution of fluorine over the 60 mm diameter is schematised in Figure 2 before permeation tests (reference sample) and after permeation of N or C gasoline.

Table II Permeability Measurements vs. Cold Plasma Conditions

P (W)	Cold Plasma Conditions			Permeability ($10^{-8} \text{ g} \cdot \text{cm}^{-1} \cdot \text{sec}^{-1}$)	
	t (min)	g	nb	N Gasoline	C Gasoline
80	10	CF_4	1	2.3	2.2
80	30	SF_6	1	2.5	2.2
120	10	CF_4	2	2.5	
120	30	SF_6	2	2.3	
120	120	SF_6	2	2.3	1.5

(P) for plasma power, (t) plasma exposure time, (g) type of plasma gas, and (nb) number of treated surface of HDPE.

Table III Transport Coefficients of PE Treated by SF₆ Fluorination in C Gasoline

Polymer	SF ₆ Fluorination		C Gasoline		
	P (W)	t (min)	Solubility (g · cm ⁻³)	Diffusion (10 ⁻⁸ · cm ² · sec ⁻¹)	Permeability (10 ⁻⁸ · g · cm ⁻¹ · sec ⁻¹)
HDPE			0.24	9.2	2.2
	120	30	0.31	7	2.2
	120	120	0.22	6.8	1.5
	120	240	0.24	5.9	1.4
	300	5	0.27	7	1.9
	300	15	0.26	8	2.1
MDPE			0.35	8.3	2.9
	300	5	0.24	8	1.9
	300	15	0.16	13	2.1

(P) for plasma power, (t) plasma exposure time.

Samples before Permeation

Analysis of different areas from a fluorinated reference sample showed virtually constant fluorine levels of 65 (± 2) at % on both faces (Table IV, Fig. 2). A part from fluorine and carbon (at around 35 at %), the only other element detected was oxygen, at a level of around 1.5 at %. The carbon 1s region shows several forms of carbon to be present at the surface of these samples (Fig. 3). Approximately one-tenth of the carbon detected is in the original [—CH₂—]_n form. Some of this may be surface contamination. The major carbon form present has a binding energy of 291 eV with other contributions at 289.1 eV and 293.2 eV. The C1s binding energy is very sensitive to local bonding in this type of polymer, showing effects due to bonding of neighboring carbons.^{39,40} The binding energies observed here correspond respectively to [—CF₂—CHF—]_n, [—CF₂—CFH—]_n chain segments and to CF₃— end groups. The presence of the latter form in significant quantities may indicate that chain breakage occurs during the fluorination process. Because of the errors involved in quantifying multiple peak simulations, and because many different bonding situations may be simultaneously present, it was not considered possible to determine a model of the surface "monomer" composition.

Fluorine levels fell dramatically following ion etching, reaching 20 at % after 15 mn etch time and falling below 10 at % for etch times above 45 mn (Table V). Only trace levels, perhaps due to simultaneous ion implantation of fluorine, were detected above 200 mn etch times. Referring to etch rates determined on metal samples, the fluorination thickness

is, thus, of the order of a few tens of nanometers for these samples.

Samples after Permeation

Fluorine levels were much lower and much less homogeneous for samples examined after permeation experiments had been performed. Analysis of the inner side of the PE after exposure to N gasoline revealed 5 to 8 at % fluorine (Fig. 2, Table IV). Figures for the outer face were on average higher and, in addition, showed a marked trend to higher values towards the disk edge, reaching 20 at % fluorine at the periphery. Exposure to gasoline C had similar though slightly less marked effects, the outer face showing 13 at % fluorine at center, rising to 26 at % at the edge.

Although the effect of carbon to fluorine bonding is visible in the C1s region (a low intensity peak at 291 to 292 eV binding energy showing that such bonds do remain) the dominance of the [—CH₂—]_n form prohibited any detailed investigation of the type of bonding present after permeation. Oxygen was detected in all samples at a level of between 9 and 12 at %. Reaction with the oxygenated components of the N gasoline is not considered to be a source, as no significant difference in the levels was detected between the two gasolines used. It is more likely that surface chemistry modifications, during the permeation experiment, render the surface more reactive to atmospheric oxygen.

CONCLUSION

XPS analysis of the samples before permeation experiments shows the PE to be highly fluorinated at

Table IV XPS Analysis of HDPE Surface

Position	Face Analyzed						
	Inner Face			Evaporating Face			
	E	M	I	E	M	I	I
Without Gasoline							
F	65	63	66	65	62		65
C*	34	35	34	35	36		34
O	1	2			2		1
N Gasoline (10 wt % Alcohol)							
F	6	5	8	22	11		8
C	85	86	80	68	80		84
O	9	9	12	10	9		9
C Gasoline							
F	13	12	13	26	25		11
C	77	78	76	65	66		79
O	10	10	9	9	9		10

Atomic percentages of fluorine (F), carbon (C*) and oxygen (O), at the center (I), periphery (E), and median (M) of disk specimen.

the surface. Fluorine is incorporated in a variety of local environments, the most abundant being of the $[-CF_2-CHF-]_n$ type. There is also evidence for chain breaking during plasma fluorination. Chain breakages occurring during the plasma treatment could result in a high density of short chain segments at the surface. The samples appeared to be homogeneous over the disk surface. The fluorine concentration depth profile showed a steep decline below the extreme surface, significant fluorination being achieved only up to a few tens of nanometers

depth. Optimization of the processing variables thus leads to an homogeneous film of fluorinated polyethylene of around 20 to 30 nm thickness. The fluorinated layers have broadly a chemical formula intermediate between $[-CF_2-CHF-]_n$ and $[-CF_2-CH_2-]_n$, which implies a permeability to N gasoline somewhere between 10^{-13} and $10^{-10} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$. A simple calculation, based upon lamellae models and the thickness of the fluorinated layers obtained in this work, shows a permeation of around $2 \times 10^{-13} \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$. A permeability re-

Table V XPS Analysis of the Fluorination Depth of HDPE for Different Types of Gasoline and Faces (*) of Specimen

Etch Time (mn)	F ^a (%)	Face Analyzed		
		F ^b (%)	F ^b (%)	F ^c (%)
		M ₁	M ₂	M ₂
0	65	5	17	25
15	20	3	9	8
30	12	2	3	4
45	8	1	2	2
75	5	1	1	1
105	4	1	1	1
165	3			
225	2			

(*) For ^a reference sample, ^b after permeation of N gasoline, and ^c of C gasoline.

duction of only around 30% is achieved because fluorinated layers is very thin.

XPS analysis show that permeation experiments modify strongly composition and homogeneity of the surface. Fluorine concentration falls by at least a factor of three. In addition, there is a tendency for the disk center to be more severely depleted in fluorine by a factor of six or more compared with the original value. This reduction in the surface fluorine concentration, together with the low thickness of the fluorination layer, are equally coherent with the observed lack of major modification to permeability.

The fluorine is clearly removed from the sample surface by contact with the gasolines, but it seems unlikely that breaking of carbon-fluorine bonds would take place. The oxygenated gasoline appears only marginally to have more affinity towards the fluorination layer than the toluene/isooctane mixture. The high surface density of short chain segments could more easily explain the removal of fluorine. These short chains would be both highly fluorinated and more easily leached out by the diffusing molecules than the long PE chains. These conclusions from XPS analysis of the HDPE surface, before and after permeation, explain the low reduction of gasoline permeation obtained by plasma treatment performed in this work.

A more interesting results, which is in accordance to our objective, are: (1) the presence of CF_3 end groups at the surface of polymeric membranes, and (2) performing the permeation experiments has itself a dramatic effect on the composition and ho-

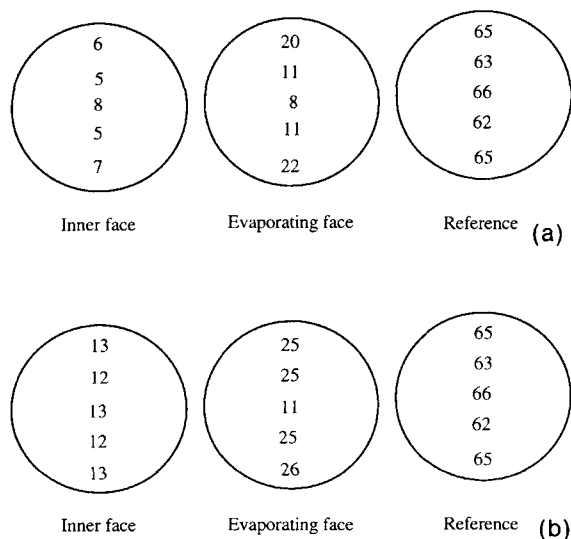


Figure 2 Variations of fluorine concentration (atomic percentage) over the 60 mm main diameter of samples for (a) N gasoline and (b) C gasoline.

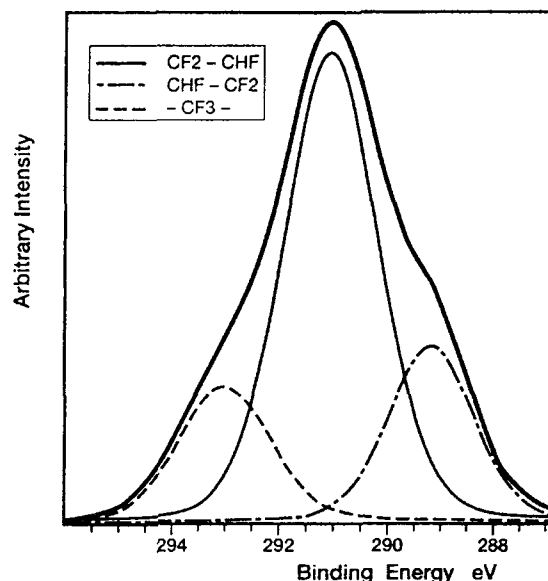


Figure 3 XPS C_{1s} of CF_4 treated medium density reference polyethylene.

mogeneity of the surface. Mainly, the permeability reduction is dependent upon the composition of gasolines. In all cases, this reduction obtained, in the conditions under study, should be not permanent.

The authors wish to thank M. Hulot and C. Boudou for their assistance in cold plasma treatment and in the acquisition of permeability data, respectively.

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Received May 17, 1995

Accepted March 30, 1996