

Hydrocarbon Barrier Performance of Plasma-Surface-Modified Polyethylene

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SYNOPSIS

Plasma modifications were applied on the inner surfaces of high-density polyethylene bottles. The methods applied include Ar gas plasma treatment, plasma polymerization with tetrafluoroethylene (TFE), trimethylsilane (TMS) + O₂ (1 : 4), CH₄, and C₂H₂ monomers, plasma-induced acrylic acid grafting polymerization, and C₂H₂ plasma polymerization plus acrylic acid plasma polymerization. Solvent weight-loss data are reported primarily for the *n*-hexane/HDPE bottle system. The best permeation reduction factor of 0.03 was obtained with C₂H₂ plasma polymerization at a high energy level followed by acrylic acid plasma polymerization at a low energy level. C₂H₂ plasma polymerization at an energy level of 10¹⁰ J/kg and C₂H₂ plasma polymerization followed by acrylic acid grafting polymerization offer a similar permeation reduction factor of 0.07. A combination of improved surface polarity and tightness of the surface is responsible for remarkable reductions in permeation rates.

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INTRODUCTION

High-density polyethylene (HDPE) has been widely used as a material to fabricate industrial and household containers. HDPE containers, such as a gas tank of a car, have a number of advantages over metal counterparts such as lighter weight, no corrosion problems, and design freedom that makes an effective utilization of space possible. However, when HDPE containers are used to contain hydrocarbons such as gasoline, unlike a metal container, the permeation of hydrocarbons through the wall of a container is a serious concern with respect to pollution of the environment.

Permeation of a penetrant in a polyethylene follows the solution-diffusion mechanism through the homogeneous amorphous phase of the material. First, the liquid content dissolves into the polymer surface. Second, the dissolved penetrant passes through the amorphous region via the process of diffusion under the chemical potential gradient where it ultimately reaches the other surface. Third,

the penetrant evaporates into the ambient phase from that surface. The permeability P is therefore a function of both the solubility S and diffusivity D .

The solubility follows the principle of "a like dissolves a like" and can be expressed in term of Hildebrand's solubility parameter of the permeant and of the polymer. S can be considered to be inversely proportional to the absolute value of the difference between the solubility parameter of the polymer and of the permeant:

$$S = \frac{A}{|\delta_{\text{polymer}} - \delta_{\text{permeant}}|} \quad (1)$$

where the solubility parameter δ = (cohesive energy density)^{1/2}. A is a proportionality constant characteristic to a polymer. The solubility parameter of *n*-hexane is very close to that of polyethylene as shown in Figure 1, and the value of S is high for the system.

The diffusivity D is largely determined by the intermolecular interaction between the polymer itself, and D can be considered to be inversely proportional to the solubility parameter of the polymer as shown in eq. (2):

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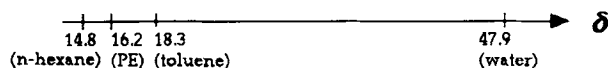


Figure 1 Schematic diagram of solubility parameter of permeants and polyethylene. Solubility parameter data are adopted from Ref. 1.

$$D = \frac{B}{\delta_{\text{polymer}}} \quad (2)$$

where B is a proportionality constant characteristic to a solvent. The nonpolar polyethylene has low value of δ_{polymer} and polyethylene belongs to highly permeable polymers.

In light of eqs. (1) and (2), the reduction of permeability of n -hexane through a polyethylene container can be achieved by placing a thin layer of a polymer which has higher δ_{polymer} than that of polyethylene, which will reduce D and S and, hence, P . Such an approach does not reduce the permeability of water as much as for nonpolar organic compounds, because the value of solubility parameter for water is very high (47.9) and the increase of δ_{polymer} decreases the difference appeared on the denominator of eq. (1).

Different barrier technologies have been developed to decrease the permeability of organic solvents. Among them, when the bulk properties of polyethylene remained unchanged, surface fluorination and sulfonation have been proved to be very effective in improving the barrier properties toward hydrocarbon solvents.²⁻⁷ However, the main disadvantages for fluorination is the use of fluorine, which requires transportation, storing, and use precautions, due to its highly corrosive nature, as sulfonation is the use of toxic chemical of sulfur trioxide, sometimes combined with chlorine, which is a potential environmental hazard.

Exposure of a polymer to a glow discharge plasma containing a source of fluorine atoms has been demonstrated in the literature to be an effective means of perfluorinating the surface layer. Preliminary studies by Anand⁸ showed that glow discharge fluorination of low-density polyethylene film significantly reduced the sorption rate of p -xylene into the film. A later report by Corbin et al.⁹ demonstrates the reduction of initial toluene permeation rates through fluorine (e.g., 5% F_2 /95% He, 5% F_2 /95% Ar, and 10% CF_4 /90% He) plasma-treated polyethylene film. The limited scope of their work and the intriguing results reported there motivated further study of applying

plasma-surface modification technology in this area.

In this fundamental study, the inner surfaces of 16 oz HDPE bottles were exposed to plasma treatment, plasma polymerization, and plasma-induced graft-polymerization with an intent to determine the effects of such plasma-surface modification on the permeation of polyethylene to n -hexane and toluene. Since we cannot change the cohesive-energy density of polyethylene, we can only change that of the surface or the plasma polymer layer.

In general, if the cohesive-energy density of the surface increases as a result of modification, it will decrease the value of the diffusion coefficient. However, the effect of change in the cohesive energy on the solubility depends entirely on the cohesive energy of the permeant. As shown in Figure 1, n -hexane has a lower solubility parameter than that of polyethylene. By increasing the cohesive energy of the polyethylene surface through plasma-surface modification by means of increasing the surface polarity, the denominators in eqs. (1) and (2) are increased, and, thus, both S and D are reduced and so is P .

Toluene, on the other hand, has a slightly higher solubility parameter than that of polyethylene. When the surface polarity of polyethylene is increased in such a way that the solubility parameter moves closer to that of toluene, S will unfavorably increase. To reduce the S of toluene in the polyethylene surface, the surface polarity of polyethylene must therefore be increased to a greater extent so that a larger difference between the solubility parameters of polyethylene and toluene is achieved. At the same time, D will also be reduced. With its larger molecular cross section and aromatic structure, toluene should present a smaller diffusion coefficient than that of linear hexane.

Low-temperature plasma treatment and plasma polymerization are relatively simple and environmentally benign processes, which consume the minimum amount of gas or monomer and are operated in a well-contained environment. Plasma polymer coating applies, in general, to only 5–50 nm of the layer, which is often negligibly small compared to the thickness of the substrate polymer. The permeation rate can be reduced, by such an ultrathin layer, to less than 5% of that for the untreated substrate. We present data which seem to confirm the effectiveness of plasma polymer coatings which reduce permeation rate of n -hexane and toluene which are used as model compounds for gasoline permeation study.

EXPERIMENTAL

High-density Polyethylene (HDPE) Bottle

The 500 mL HDPE bottles were purchased from the Environmental Sampling Supply Co. and used as received. The bottle wall thickness is approximately 1 mm and its height, 150 mm. The inner surface area exposed to solvent permeation is approximately 347.3 cm². Three bottles were subjected to each surface modification to minimize the influence of imperfections in the bottle wall.

Plasma Reactor

Figure 2 illustrates a schematic diagram of the reactor used for treating the inside surface of a bottle. This reactor consists of two independent vacuum systems, one for inside the bottle which is equipped with a monomer (or gas) feed-in system and another for the outside of the bottle including a glass vessel. The monomer inlet is a stainless-steel tube extending through a hole drilled in the center of the lid, which was screwed onto a bottle sample. The tube has a flat washer welded to it. When the tube was inserted in the hole, epoxy was used to seal the area between the flat washer and the lid. The end of the monomer tube was extended to 4.5 cm above the bottom of the bottle. A pair of ring-shaped copper electrodes connected to a 13.56 MHz radio-frequency (rf) power generator was wrapped around the Pyrex glass vessel.

Monomers (or gases) were introduced into the bottle through metering valves. The system pressure was given by a Baratron absolute pressure transducer (MKS) and was controlled by adjusting the mass flow rate with the metering valves. The mass flow rate was determined by measuring the system pressure increase over a given time interval using a Baratron absolute pressure transducer and then was converted to the flow rate (sccm).

Plasma Treatment

Argon, which was purchased from Airgas, Radnor, was used as the inert gas for plasma treatment. After Ar gas was introduced, glow discharge was initiated. The system pressures were maintained at 450 mTorr, the rf power ranged from 5 to 40 W, and treatment time ranged from 2.5 to 10 min.

Plasma Polymerization

Methane (CH₄) (Matheson), tetrafluoroethylene (TFE) (PCR Research Chemicals), acetylene (C₂H₂)

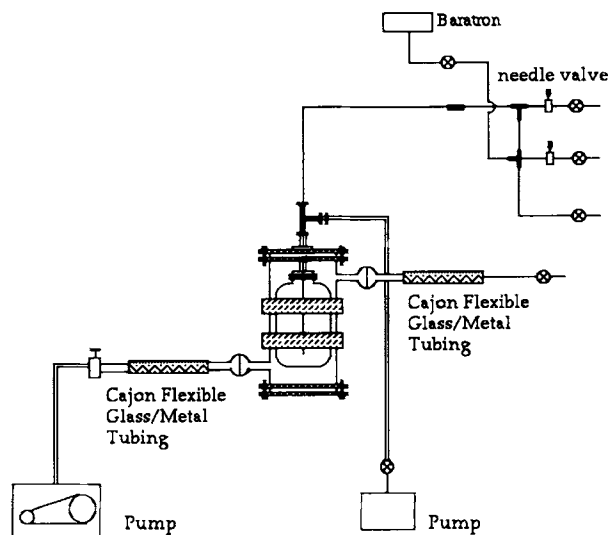


Figure 2 Schematic diagram of plasma reactor for bottle inner surface modification.

(Matheson), and trimethylsilane (TMS) (PCR Research Chemicals) monomers were used without further purification. Oxygen, purchased from AIRCO Inc., was used as a reactive gas.

The operating conditions employed were a system pressure of around 350 mTorr and rf power ranging from 5–90 W. The flow rate and deposition time varied with the selected monomers. Before admitting a second monomer for a second-layer plasma polymer deposition, the system was evacuated to a system pressure less than 15 mTorr.

Plasma-induced Surface Grafting Polymerization

Acrylic acid (Aldrich Chemical Co.) was used for grafting polymerization. Prior to its use, the precursor was transferred into a monomer reservoir and connected with the reaction system and then subjected to multiple freeze–pump–thaw cycles. After argon, which was purchased from Airgas, Radnor, plasma treatment, or acetylene plasma polymerization, the system was evacuated again to less than 15 mTorr of system pressure. Then, acrylic acid vapor was introduced and maintained (in a closed system) for a predetermined period of time.

Surface Characterizations

Water Contact Angle

After the plasma surface modification, parts of a bottle were cut into small coupons (0.5 × 0.5 cm) which provided a flat enough surface to measure the contact angle. Advancing water contact angles were

measured with the sessile drop (0.2 μL in volume) method at room temperature using a contact angle meter (Model G-I, Kernco Instruments Co., TX).

Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA spectra of treated and virgin HDPE bottle substrates were obtained using an electron spectrometer (Model 548, Physical Electronics, Eden Prairie, MN) with a $\text{MgK}\alpha$ X-ray source (1253.6 eV). The energy scale of the spectrometer was calibrated for the Au 4f level at 83.7 eV. Binding energies were referenced to the hydrocarbon C_{1s} core level peak centered at 285.0 eV. The surface compositions in terms of atomic ratio were determined.

Permeation-loss Rate Measurement

Solvent-loss rate evaluation was checked by total weight measurement. After being filled 20% with a solvent, a bottle was then thoroughly sealed with Teflon tape around the screw portion and a phenolic resin cap with a Teflon liner to ensure that the only means by which its contents could escape would be to permeate through the bottle walls. The sealed bottle was then placed in a 40°C oven with good air circulation. The bottle was periodically removed from the oven and, after a 30 min cooling at room temperature ($23 \pm 2^\circ\text{C}$), weighed using an analytical balance (METTLER AT 261 DeltaRange) having 0.001 g sensitivity. After the weighing, the bottles were put again in the test oven and maintained there until the next measurement. To avoid errors caused by surface imperfections, at least three bottle samples were prepared under the same plasma surface modification conditions and then were tested.

Calculation of Permeation Rate, Flux, and Reduction Factor

The initial transient state of permeation will merge to a steady-state process. In the absence of a plasticizing effect of the permeant, the time required to approach steady permeation can be estimated to be three times the diffusion time lag defined in eq. (3):

$$\tau = \frac{l^2}{6D} \quad (3)$$

The data for cumulative weight loss at time $tQ(t)$ can therefore be converted to approximate values of permeation rate r , in units of permeation weight loss (g) per day:

$$r = \frac{\Delta Q}{\Delta t} \quad (4)$$

and steady-state permeation flux, j :

$$j = \frac{\text{cumulative weight loss } Q \text{ at steady state}}{\text{time} \times \text{permeation area}} \\ = \frac{\text{slope of } Q \text{ vs. time at steady state}}{\text{permeation area}} \quad (5)$$

Since the same type of bottles were used throughout this work, permeation rate data were used mostly. The capacity of plasma-surface modification in reducing the overall solvent permeation rate was evaluated by the permeation reduction factor, Ψ , defined in eq. (6):

$$\Psi = \frac{\text{permeation flux of treated sample}}{\text{permeation flux of untreated sample}} \quad (6)$$

RESULTS AND DISCUSSION

It has been known that the thickness of plasma polymer coatings is an important factor of the permeability coefficient of plasma polymers in contrast to that for most conventional polymers in which the permeability constant is independent of the thickness. There exists a threshold value of thickness above which the permeability coefficient decreases drastically.^{10,11} Because of this reason, the thickness of the plasma polymer applied on the bottle was controlled so that the thickness does not exceed an arbitrarily set upper limit of 50 nm. For deposition thickness measurement, small pieces of a silicon wafer were placed on the inside wall of the bottle, and the thickness was measured by ellipsometry.

The thickness less than 50 nm is too small, compared to the thickness of bottle wall (ca. 1 mm), to justify the analysis based on the permeability of two-layer composite films. Therefore, no effort was made to measure the actual thickness of the plasma polymer layer for each experiment unless otherwise noted. Experimental conditions such as flow rate, discharge power, and treatment time are used as major parameters of experiments. Plasma polymerization performed in the low flow rate and low-pressure regime generally forms a flawless ultrathin layer unless the surface flaw of the substrate is too large to be covered by such an ultrathin film. Any reduction in permeation rate is the confirmation of a flawless plasma polymer layer.

In this study, our interest was focused on the comparison of different modification methods, i.e., plasma treatment, plasma polymerization, plasma-induced graft-polymerization, and combined surface modification methods. No strong effort was made concerning the details of the plasma conditions under each specific method.

The simple weight loss measurement yields an accurate enough permeation data from which the permeation rate and the time lag can be calculated. The data shown in Figure 3 are for untreated HDPE bottle. A cumulative weight loss of *n*-hexane is plotted vs. time. The permeation flux, calculated from eq. (5), is 8.6×10^{-7} kg/m²/s. The time-lag, the intercept of the linear region with the time axis, is 6 h. Then, the effective diffusion coefficient (\bar{D}) can be calculated according to eq. (3). A value of $\bar{D} = 7.7 \times 10^{-8}$ cm²/s was determined which compares favorably with the literature value¹² for the diffusion of *n*-hexane through an HDPE bottle sample testing at 40°C ($\bar{D} = 2.0 \times 10^{-8}$ cm²/s). The calculation of apparent *D* for the coated sample is considered to be a meaningless practice. Figure 3 and values calculated from the plot confirm that such a simple weight loss measurement is accurate enough to evaluate the reduction of the permeation rate by plasma polymer coatings.

Plasma Treatment by Argon Gas

It has been demonstrated that by treating polyethylene in an inert gas plasma will crosslink the surface region which is referred to as the CASING.¹³ Yasuda et al. used ESCA to analyze Ar plasma-treated polyethylene surfaces.¹⁴ Increased oxygen content on the polymer surfaces was found after treatment in an Ar plasma. This phenomenon was attributed to the post-treatment reaction of surface radicals created during plasma treatment with oxygen or moisture after exposure to air. Oxygen-containing moieties were thus introduced onto the polyethylene surface.

To determine if surface treatment would affect the overall permeation rate, several bottles were exposed to an argon glow for several minutes and subjected to *n*-hexane weight loss evaluation in a ventilating hood. Our testing results are shown in Figure 4 as plots of cumulative weight loss against time. (The leveling off is due to the total loss of liquid in a bottle.) The best permeation reduction factor [calculated from eq. (6)] is 0.27. Considering that no coating was applied in these cases, it is important to note that Ar plasma treatment alone can reduce the permeation rate significantly when the process is carried out under or near the optimum conditions.

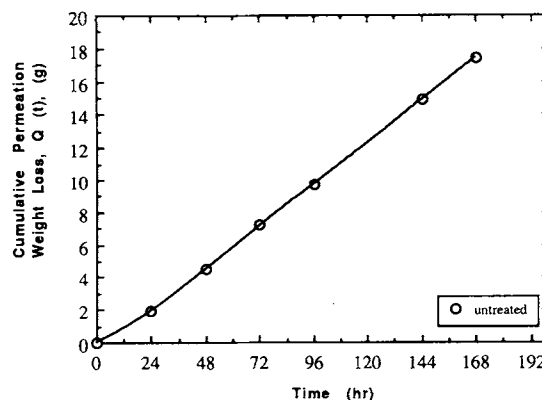


Figure 3 Cumulative weight loss *Q* over time. The 500 mL bottle is 20% full with *n*-hexane and at 40°C.

The results shown are reconfirmation of the CASING effect. Because polyethylene is a typical "crosslinking-type" polymer under irradiation, it is not surprising to see the CASING effect.

Plasma Polymerization

One of the distinctive chemical features of plasma polymers is the presence of a high concentration of trapped free radicals. After exposure to air, trapped free radicals will react with oxygen, and, thus, there is a concurrent increase in the carbonyl group concentration as observed by infrared spectroscopy.¹⁵ Although the stable free-radical concentration and longevity will vary depending on the choice of monomer, such a feature will increase surface polarity and decrease the solubility of nonpolar organic solvents.

The data of permeation rate (weight loss/day) of *n*-hexane through TFE, TMS + O₂ (1 : 4), CH₄, and C₂H₂ plasma-treated bottle samples are plotted in Figures 5–8. Atomic ratios from ESCA, water contact angle, and diffusion time lag, together with the optimum data pertinent to the solvent-weight loss, are listed in Table I.

TFE Plasma Polymerization

Tetrafluoroethylene (TFE) plasma polymerization was chosen since the conventional (nonplasma) fluorine treatment of polyethylene is one of best surface modifications to reduce gasoline permeation through HDPE. As shown in Figure 5, all the deposition conditions reduce the overall *n*-hexane permeation rate; however, the optimum reduction is higher than that obtained by Ar plasma treatment.

From the viewpoint of solubility described by eq. (1), TFE does not seem to be a good candidate for

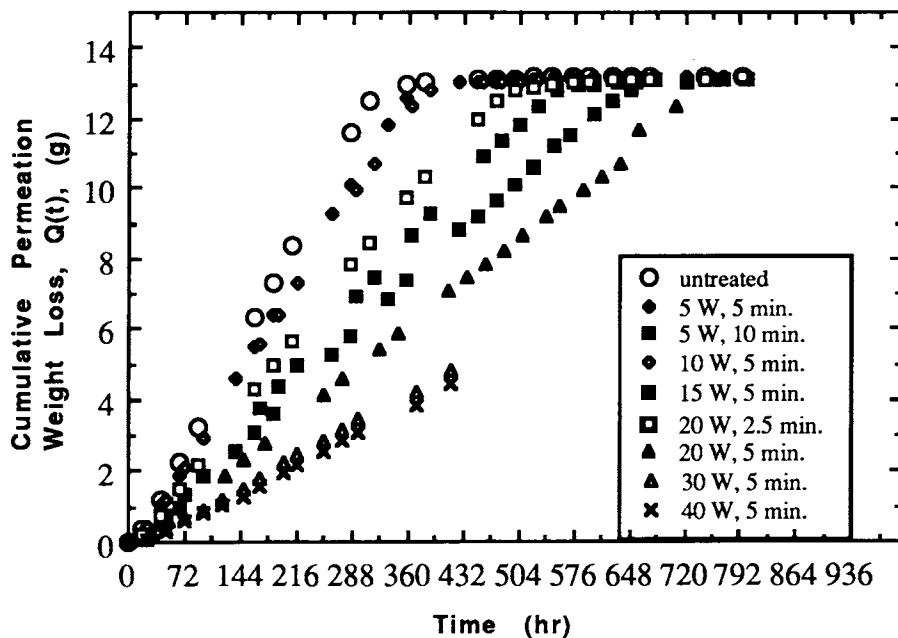


Figure 4 Cumulative weight loss Q over time for Ar plasma-treated bottles. The 500 mL bottle is 20% full with *n*-hexane and at room temperature. For all the Ar plasma treatments, the system pressure was maintained at 450 mTorr.

this purpose. It also confirms that the bulk characteristics of crystalline PTFE cannot be obtained by an amorphous plasma polymer of TFE, i.e., the plasma polymer of TFE is not a polytetrafluoroethylene.

The optimum permeation rate obtained at 50 W of rf power drops to one-half of the untreated one. The permeation rate increased at 70 W, which was anticipated due to excessive fragmentation and ablation caused by F plasma at higher wattage.

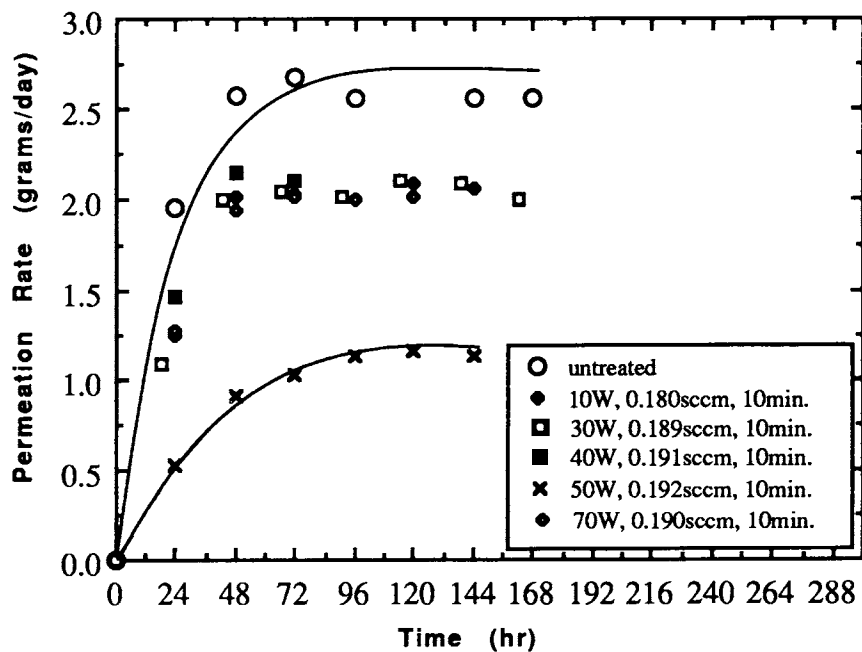


Figure 5 Permeation rate of hexane through 500 mL bottles with TFE plasma polymerization on the inner surface. The bottle is 20% full with *n*-hexane and at 40°C.

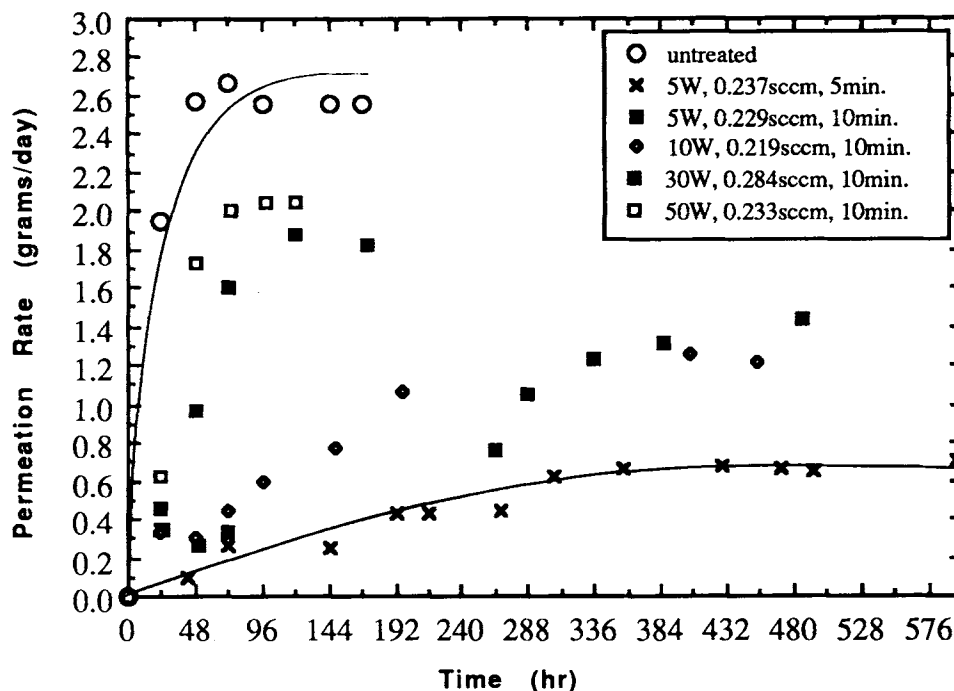


Figure 6 Permeation rate of hexane through 500 mL bottles with TMS + O₂ (1 : 4) plasma polymerization on the inner surface. The bottle is 20% full with *n*-hexane and at 40°C.

TMS/O₂ (1 : 4) Plasma Polymerization

The interesting feature of organosilicon plasma polymerization is that the nature of plasma-deposited polymers can be shifted from organic to inorganic by controlling the plasma parameters (in general, the higher the energy input, W/FM, the more inorganic the nature of the film).¹⁶ It was reported that O₂ etched away the organic pendant groups such as —CH₃ groups, which reduced the carbon content in the polymer, created an inorganiclike phase, and greatly increased the average number of Si—O bonds.¹⁶⁻¹⁹ The higher the concentration of O₂ and the higher the energy input, the more inorganic features has the film.

These features would seem suitable for barrier applications, since inorganic silicates, such as glass, is not permeable to any organic solvent. The drawback of high W/FM and O₂ concentration is that the produced film is usually highly stressed and cracks can be formed, which limits the barrier capacity of the plasma polymer coating.

As shown in Figure 6, plasma polymerization conditions have a great effect on the barrier performance of TMS/O₂ (1 : 4) plasma polymers. A relatively impermeable film was fabricated at lower rf power (flow rate fixed), and, thus, the lower the energy input, the shorter the deposition time. Under

the lowest power and shortest deposition time, the diffusion time lag was increased to 348 h. Such a long diffusion time-lag is certainly due to a very tight surface structure. A reduction factor of 0.26 was obtained under such an optimum plasma condition. This is definitely due to the tight surface structure, since 78° of the water contact angle indicated little improvement in surface polarity.

Methane and Acetylene Plasma Polymerization

In plasma polymerization of methane, free radicals are formed only by the hydrogen detachment, yielding plasma polymers containing the least number of trapped free radicals. In contrast, for acetylene plasma polymerization, diradicals are formed as the main source of free radicals and lead to plasma polymers with the highest number of trapped free radicals. The consequence of such a high concentration of trapped free radicals is that a large amount of oxygen-containing moieties was formed on the surface, even though the original monomer had no oxygen-containing functions. The O/C ratio of the acetylene plasma-polymerized surface can be 11 times as high as that of virgin polyethylene and six times that of methane plasma polymer, as listed in Table I. The improved polarity was directly showed by the low water contact angle of 68° for the acet-

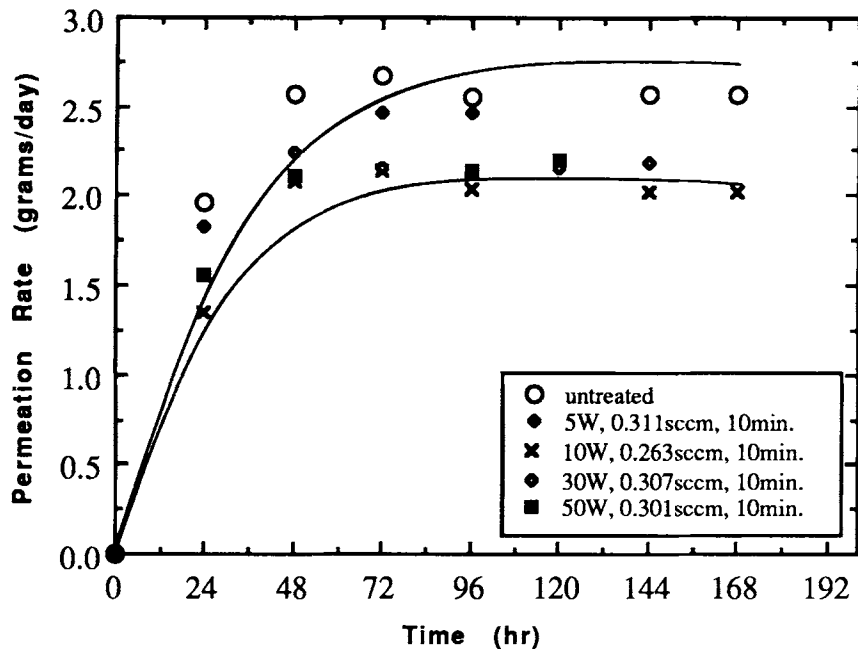


Figure 7 Permeation rate of hexane through 500 mL bottles with CH_4 plasma polymerization on the inner surface. The bottle is 20% full with *n*-hexane and at 40°C .

ylene plasma-polymerized surface, while no essential change occurred for that of methane. Under the optimum conditions, the overall diffusivity of a plasma-polymerized polyethylene with acetylene is nearly 1/20 of methane.

Comparing the data shown in Figures 7 and 8, any plasma polymerization parameter with acetylene offered a better reduction in permeation rate than did the optimum value obtainable with methane. However, a superior reduction ratio was obtained

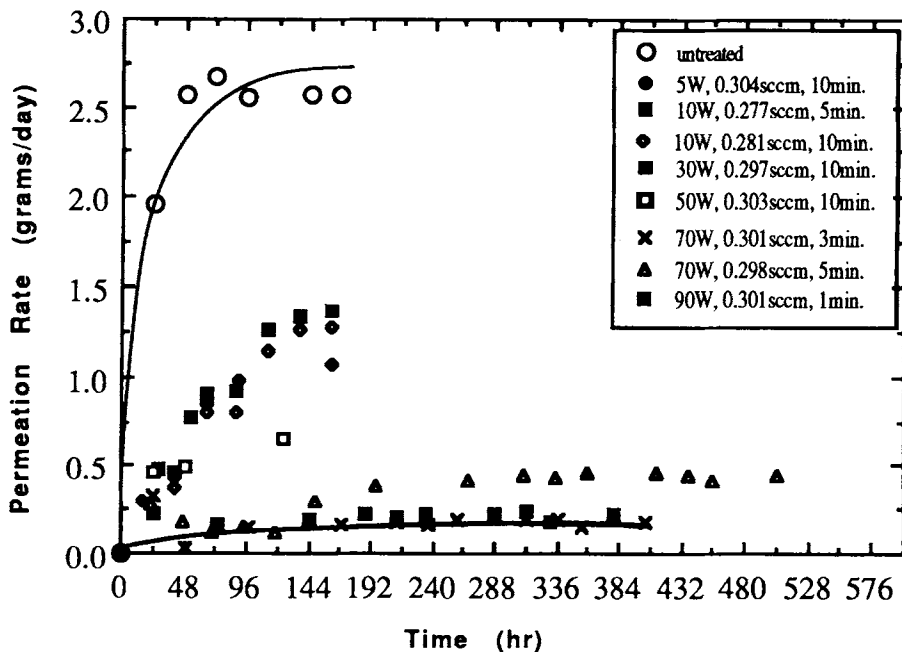


Figure 8 Permeation rate of hexane through 500 mL bottles with C_2H_2 plasma polymerization on the inner surface. The bottle is 20% full with *n*-hexane and at 40°C .

Table I The Best Results Obtained by Different Surface Modification Methods

	Permeation Rate (g/day)	Permeation Flux (kg/m ² s)	ψ^a	Diffusion Time Lag (h)	Water Contact Angle (Degree)	O _{1s} /C _{1s}	O/C Factor ^b
Untreated	2.58	8.60E-07	1	6.0	93.0	0.011	1.00
TFE (50 W, 0.192 sccm, 10 min, 450 Å)	1.09	3.60E-07	0.42	16.0	110.0	0.028	2.52
TMS/O ₂ (1 : 4) (5 W, 0.237 sccm, 5 min, 450 Å)	0.68	2.30E-07	0.27	348.0	70.0		
CH ₄ (10 W, 0.263 sccm, 10 min, 450 Å)	2.05	6.80E-07	0.79	8.0	91.0	0.066	5.93
C ₂ H ₂ (70 W, 0.301 sccm, 3 min, 120 Å)	0.18	6.0E-08	0.069	155.0	68.0	0.126	11.33
C ₂ H ₂ (70 W, 0.312 sccm, 5 min) + AA grafting for 30 min (120 Å)	0.17	5.80E-08	0.067	120.0	75.0	0.131	11.78
C ₂ H ₂ (70 W, 0.304 sccm, 5 min) + AA (1 W, 0.136 sccm, 5 min) (500 Å)	0.076	2.50E-08	0.029	105.0	0.0	0.397	35.69

^a Permeation reduction factor given by eq. (6).

^b (O/C of plasma treated surface)/(O/C of untreated surface).

when the input energy level was beyond 10¹⁰ J/kg of energy input.

Plasma-induced Surface Grafting Polymerization

A direct chemical bonding of polar functional groups such as carboxyl or carbonyl to the substrate would be an efficient way to reduce the solubility of organic solvents in the inner surface of HDPE bottles. Acrylic acid is one of the monomers most easily grafted to the plasma-treated polymer surface.

When a polymeric material is subjected to an inert gas plasma treatment, or to plasma polymerization, free radicals are formed on the substrate surface or mostly in the plasma polymer layer. If the substrate is maintained in a vacuum, these free radicals are fairly long-lived (up to several hours in some cases) and highly reactive. By making use of them, two different processes of grafting were used in this study.

The first approach was to expose the substrate to an Ar glow discharge for a short period of time. Then, the power was turned off, the remaining Ar gas pumped out, and vapor of acrylic acid immediately admitted to the reaction chamber. The surface free radicals were then available for free-radical addition polymerization. With the first approach, polymerization can start only at the surface of plasma-treated material, and precautions are required to prevent a decay of the surface free radicals.

The second approach was to expose the substrate to acetylene plasma polymerization; the vapor of acrylic acid was admitted afterward in a similar manner to the first approach. With this approach, considerable amounts of a concentration of long-lived trapped free radicals were available in the acetylene plasma polymer layer. This is consistent with the high concentration of oxygen-containing groups after air exposure. Furthermore, free radicals trapped in a plasma polymer are generally rather stable and difficult to destroy due to the relatively tight network structure. For instance, the presence of free radicals in the acetylene plasma polymer was even observed 15 months after exposure to air.¹⁵ The free-radical concentration of such an acetylene plasma polymer is then reduced to 13% of the value observed immediately after plasma polymer deposition and exposure to air.

As shown in Figure 9, the second approach offers a much more efficient way to reduce the overall hexane permeation rate. The high ratio of O/C and long lag time are also noticeable in Table I.

Acetylene Plasma Polymerization/Acrylic Acid Plasma Polymerization

An alternative way to grafting was polymerization. Acrylic acid contains a carboxyl group, as well as a double bond which can proceed conventional addition polymerization. It was reported²⁰ that plasma

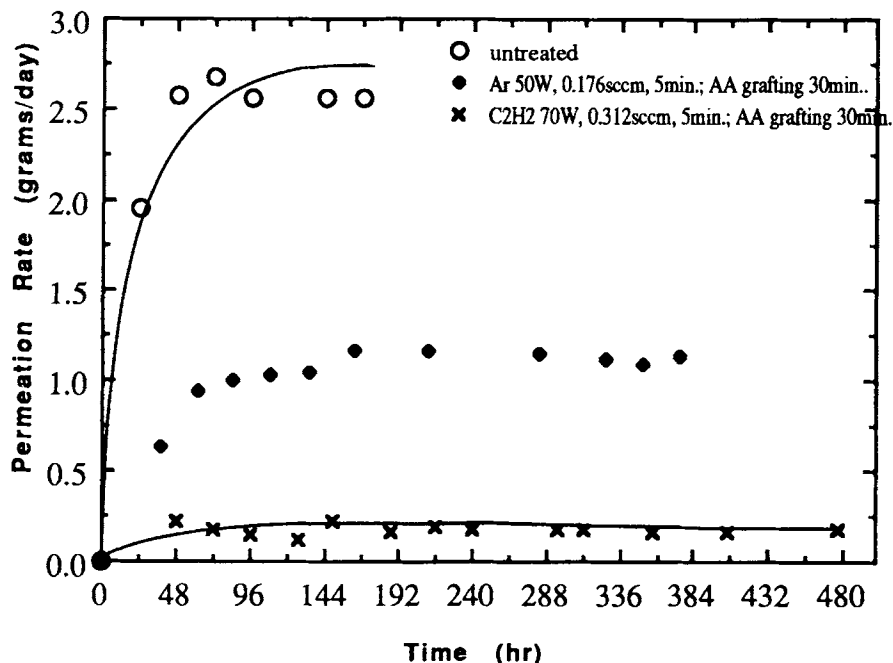


Figure 9 Permeation rate of hexane through 500 mL bottles with plasma-induced grafting polymerization on the inner surface. The bottle is 20% full with *n*-hexane and at 40°C.

polymerization of a low vapor pressure monomer at extremely low W/FM is characterized by the retention of the functional groups of the starting monomers. Under this condition, both plasma-state and

plasma-induced surface grafting polymerization are expected to occur simultaneously. Plasma polymerization of acrylic acid at low W/FM was carried out right after acetylene plasma polymerization.

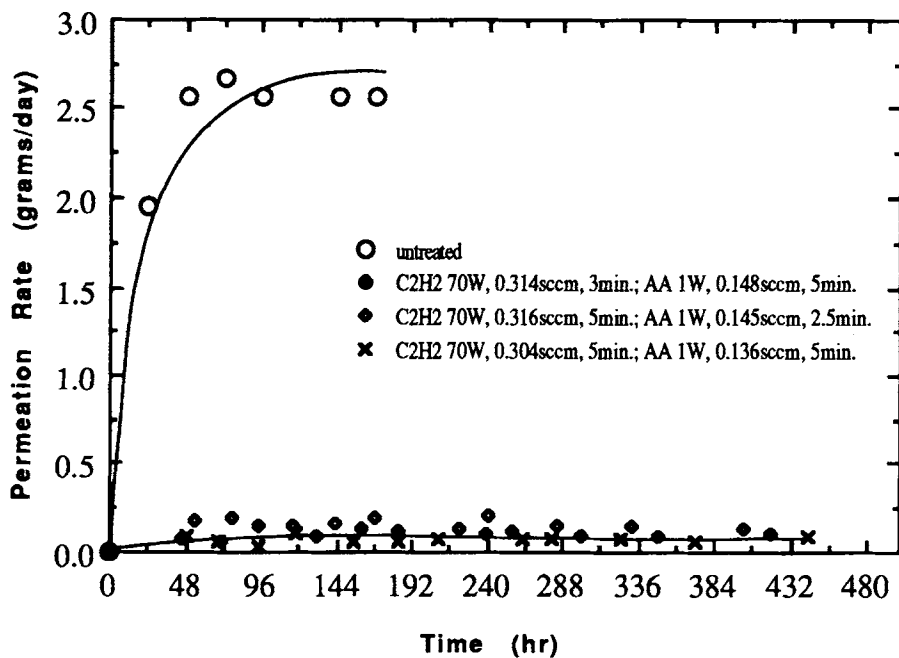


Figure 10 Permeation rate of hexane through 500 mL bottles with C_2H_2 plasma polymerization/acrylic acid plasma polymerization on the inner surface. The bottle is 20% full with *n*-hexane and at 40°C.

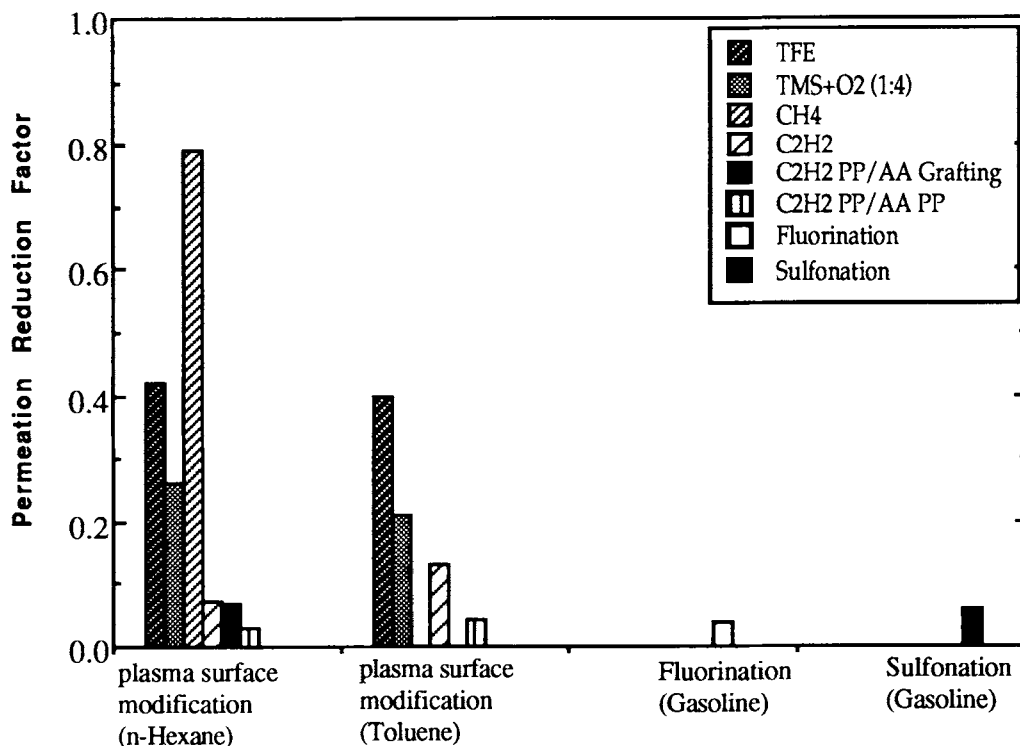


Figure 11 Permeation reduction factor of organic solvents through 500 mL HDPE bottles without and with plasma surface modification at optimized conditions. Bottles are 20% full and at 40°C.

As shown in Figure 10, permeation rates were reduced by nearly two orders of magnitude. This is attributed to an extremely polar surface (O/C ratio = 35.7), together with a tight structure of acetylene plasma polymer (diffusion time lag was increased to 105 h).

Mechanism of Permeation Rate Reduction

The best reduction factors obtained by different methods of surface modification are compared in Figure 11 for both *n*-hexane and toluene and compared with conventional surface modifications, i.e., fluorination and sulfonation. In the present work, the best and significant hexane barrier performance was obtained with acetylene polymerization followed by acrylic acid plasma polymerization at low-energy input, with which the permeation reduction factor of 0.03 was obtained. Since *n*-hexane is used as a model case for gasoline permeation, the value is compared with gasoline barrier characteristics of fluorinated and sulfonated HDPE bottles. The results seem to indicate that plasma methods can produce as good a barrier as these two conventional surface modifications provide. Because gasoline is

not a well-defined liquid, the direct comparison is not warranted.

All plasma-modified bottles are also much less permeable to toluene than is virgin polyethylene. However, acetylene polymerization with or without further acrylic acid deposition does not offer as significant permeation reduction factor as for *n*-hexane. On the contrary, TFE and TMS + O₂ (1 : 4) plasma polymerization are more efficient for toluene than for *n*-hexane. In other words, a tight surface leads to more reduction in the toluene permeation rate than in *n*-hexane; a highly polar surface leads to a more significant reduction in the *n*-hexane permeation rate than in toluene.

For comparison purposes, in Figure 11, the gasoline permeation reduction factors measured by Kathios et al.⁷ were also included. In their work, 16 oz HDPE bottles provided by the Air Products Corp. with a wall thickness of approximately 1 mm were used for permeation rate measurement. The bottles were 20% filled. The permeation reduction factor Ψ was expressed as the ratio of the liquid permeation flux of solvent blend A media-modified by barrier technology $j_A^{BT}(\text{kg}/\text{m}^2 \text{ s})$ and the liquid permeation flux of the solvent blend through media j_A (kg/m^2

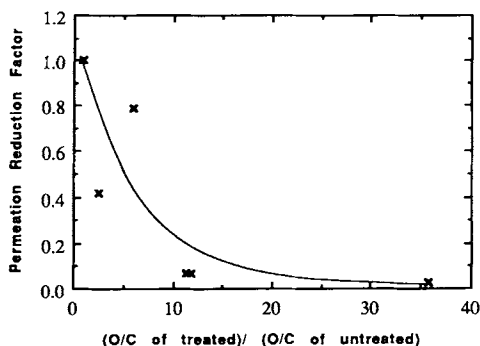


Figure 12 Correlation between permeation reduction factor with the ratios of (O/C of modified surface)/(O/C of untreated surface).

s). Therefore, except for the difference of the permeant, their experimental environment (40°C testing temperature, 20% full 16 oz HDPE bottle) and bottle parameters are comparable with ours.

Of all their methods tested, the optimized and superfluorination provide the best permeation resistance to all gasoline-alcohol fuel blends. The values of Ψ for gasoline are 0.04 for optimized fluorinated 16 oz HDPE bottles and 0.06 for standard sulfonated 16 oz bottles.

Both surface polarity and tightness have a great influence on the barrier performance of the plasma-modified surface against hydrocarbons as discussed above. The improvement in surface polarity can be estimated from the oxygen-containing polar group concentration on the surface. Surface chemical analysis such as ESCA does not provide information pertinent to the tightness of a plasma polymer layer. In this article, the main purpose of ESCA was to estimate the polarity change of the inner bottle surface by measuring the change in the atomic ratio of O_{1s}/C_{1s} and, therefore, to confirm our basic concept, i.e., improved surface polarity obtained from plasma surface modification is one of the key factors in reducing the permeation rate of nonpolar hydrocarbons.

In Figure 12, the optimum permeation reduction factor with plasma treatment, plasma polymer deposition, plasma-induced surface grafting polymerization, and two layers of plasma polymer deposition were plotted against the O/C improvement factor defined as (O/C of treated surface)/(O/C of untreated surface). The clear tendency is that the higher the O/C improvement factor, or the higher the surface polarity, the higher the permeation reduction factor for *n*-hexane.

The tightness of the surface can be estimated from the increase in diffusion time lag. As shown in

Table I, all the optimum conditions lead to significant increases in the diffusion time lag. On the other hand, an improvement in the tightness alone does not determine the overall effectiveness of permeation reduction as indicated by the case of the TMS + O₂ (1 : 4) plasma-polymerized polyethylene surface. By the same token, an increased polarity alone cannot be the key factor as indicated in the case of benzene permeation.

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