XPS and IR Analysis of Thin Barrier Films Polymerized from C_2H_4/CHF_3 ECR-Plasmas

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ABSTRACT: Thin fluorocarbon polymer films are prepared on PE-foils in low-pressure electron cyclotron resonance plasmas using ethylene (C_2H_4) and trifluoromethane (CHF_3) as monomers. The thin fluorinated hydrocarbon layers strongly reduces the permeability of polyethylene to alkanes. For example, the permeation of toluene was decreased by a factor of about 100 by a single, thin fluorocarbon layer. A further reduction of the permeation down to a factor of 1600 can be obtained by a multilayer coating. X-ray photoelectron spectroscopy and Fourier transform IR spectroscopy are used to characterize the plasma polymerized films. It is shown that the addition of CHF_3 to a C_2H_4 plasma leads to an increase of CF_3—, CF_2—, and CF— groups and to a decrease of CH_3— and CH_2— groups in the film. The chemical composition of the polymer layers and their toluene permeabilities are discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 717–722, 1997

Key words: plasma polymerized films; polyethylene; toluene permeability; infrared spectroscopy; x-ray photoelectron spectroscopy

INTRODUCTION

Low weight, plasticity and ease of processing makes polyethylene (PE) an attractive candidate for packing materials. Polyethylene foils, bottles, and containers are widely used in many industrial applications. However, PE is not sufficiently impermeable to various organic liquids.[1–4] The goal of this work is to demonstrate that a thin fluorinated hydrocarbon layer effectively improves the barrier properties of PE.

The permeation of a liquid through a polymeric material is generally due to activated diffusion and depends mainly on solubility and diffusivity of the permeated molecules in the polymer.[1,2] The permeation process by which a molecule perme-ates through a polymer film involves the following four stages. These are: (1) the absorption of the permeating species onto the surface of the polymer, (2) the solution of the molecules into the polymer matrix, (3) the diffusion through the polymer along a concentration gradient, and (4) the desorption of the molecules from the other surface of the polymer. According to the theory of activated permeation, it is assumed that if the solubility of the liquid decreases, the permeation through the polymer will also decrease.

It is well known that "chemical" fluorination of PE improves the barrier property towards many organic solvents.[5,6] The reaction of elemental fluorine and polyethylene yields a surface film resembling that of PTFE ("Teflon") in certain properties. In the case of fluorinated PE as polymer and organic solvents as permeants, the interactive forces between the surface coating and permeant molecules will be less than the cohesive forces between permeant molecules. The solvent
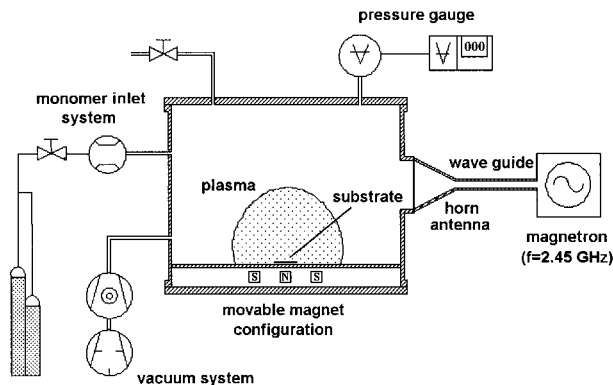

Figure 1 Plasma reactor.

will tend to aggregate and form clusters. This causes a decrease in solubility and a corresponding decrease in permeation.[1,2] This means that a surface treatment of PE affects only the first two steps of the permeation process—the absorption and the solution of the liquid in the polymer.

In this study, we apply plasma processing techniques to deposit a thin fluorocarbon layer on polyethylene to improve the barrier properties of PE toward toluene. CHF_3 and C_2H_4 are used as monomers. The chemical composition of the plasma polymerized films is determined by X-ray photoelectron spectroscopy and Fourier transform IR spectroscopy. The toluene resistance of the films is investigated by measuring their permeation rate.

EXPERIMENTAL

Thin polymer films were deposited on PE foils in an electron cyclotron resonance (ECR) plasma. The experimental setup is shown in Figure 1. The magnetic field strength of 0.0875 T required for the ECR heating at $f = 2.45$ GHz is produced by three rows of cobalt samarium permanent magnets. The magnets are mounted on a rectangular iron yoke in a closed racetrack configuration (magnetron device). The magnet system is installed at the bottom of a stainless steel chamber of 80 cm diameter and 80 cm height. The microwave power was radiated by a horn antenna from one side of the plasma chamber through a microwave transparent window into the plasma chamber. Details of the magnet configuration and the plasma generation mechanism is described in ref. 7.

For the deposition of fluorocarbon polymer films, ethylene (C_2H_4) is used as monomer together with mixtures of trifluoromethane (CHF_3). The flow ratio of C_2H_4/CHF_3 was varied from 0 to 100% by varying the partial flow rates of each component. For example, a C_2H_4/CHF_3 mixture containing 65% CHF_3 means a monomer composition of 65% CHF_3 and 35% C_2H_4 during the deposition process. The experiments were performed at pressures from 2 to 4 Pa. The microwave power of 3 kW is modulated with an on-off pulse cycle of 100 μs to 900 μs.

IR spectra of the plasma polymerized films were recorded on a Bruker IFS 48 spectrometer system using the KBr disc transmission mode. The plasma polymer films for these experiments were first deposited on glass substrates then scraped off by a razor blade. These plasma polymer "powder" was mixed with KBr and pressed into a disc using a hydraulic press. The XPS measurements were performed on a LH Max 200 system equipped with a $Mg(K\alpha)$ radiation source. The plasma polymerized films for the XPS experiments were prepared on Mo-coated glass substrates to minimize charging effects. The samples were exposed to air during their transfer from the plasma chamber to the XPS spectrometer.

To determine the barrier properties of the plasma polymerized layers, permeability measurements were performed using plasma-treated and -untreated polyethylene foils. A 110 μm thick, high density polyethylene foil of 0.955 g/cm³ density, supplied by BP Chemicals, was used. Permeability measurements of toluene were performed at 40°C. The permeation flux of toluene through the PE foils was measured as a function of time, using a Carlo Erba gas chromatograph with a flame ionization detector. The experimental setup is described in detail in ref. 8.

RESULTS AND DISCUSSION

Permeability Studies

The permeability of toluene across PE foils coated with a plasma-polymerized film was measured. Figure 2 shows the permeation flux density as a function of time for (a) an uncoated PE foil and for plasma polymerized films from C_2H_4/CHF_3 mixtures containing (b) 0% CHF_3, (c) 65% CHF_3, and (d) 92% CHF_3. Further, Figure 2 shows the permeation curve through a multilayer coating consisting of seven single films that were deposited on the surface of PE from different $C_2H_4/$
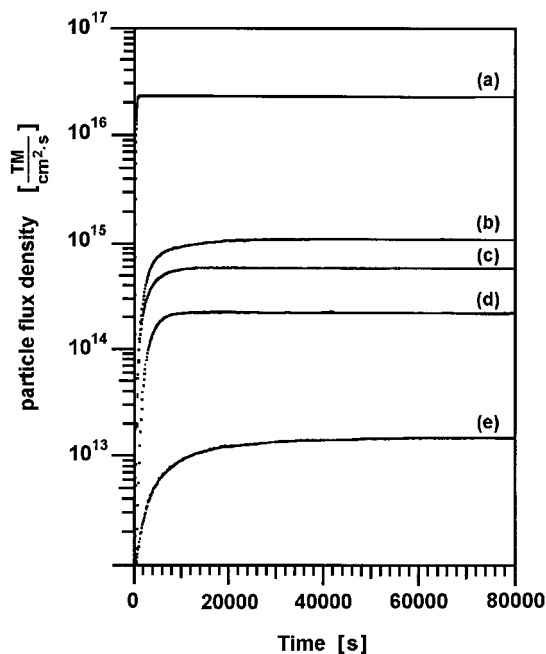
Figure 2 Toluene flux density as a function of time for (a) an uncoated PE foil and for (b) to (e) different plasma polymerized films on the surface of PE.

92%. These results indicates that a small amount of C_2H_4 is very effective in the improvement of the barrier properties. As shown in Figure 2, the deposition of a 300 nm thick multilayer leads to a significant reduction of the toluene permeability. The permeation of toluene through polyethylene is drastically reduced to $j_s = 1.44 \cdot 10^{13}$ TM/cm^{2}s. The multilayer coating consists of the following single films, beginning from the surface of polyethylene:

1. A 55 nm thick layer deposited from a pure C_2H_4 plasma.
2. A 40 nm thick layer from a C_2H_4/CHF$_3$ monomer mixture containing 50% CHF$_3$.
3. A 30 nm thick layer from a C_2H_4/CHF$_3$ monomer mixture containing 80% CHF$_3$.
4. A 30 nm thick layer from a C_2H_4/CHF$_3$ monomer mixture containing 88% CHF$_3$.
5. A 25 nm thick layer from a C_2H_4/CHF$_3$ monomer mixture containing 92% CHF$_3$.
6. A 25 nm thick layer from a C_2H_4/CHF$_3$ monomer mixture containing 97% CHF$_3$.
7. A 95 nm thick layer deposited from a pure CHF$_3$ plasma.

CHF$_3$ mixture ratios [curve (e)]. Table I shows the results of permeation experiments, with the steady-state permeation flux j_s tabulated as a function of the C_2H_4/CHF$_3$ mixture composition. The j_s value decreases from $2.34 \cdot 10^{16}$ Toluene Molecules/cm^{2}s (TM/cm^{2}s) for the uncoated PE to $1.13 \cdot 10^{15}$ TM/cm^{2}s for the plasma polymer from pure C_2H_4. The addition of CHF$_3$ to the C_2H_4 plasma leads to a further reduction of toluene permeability. As shown in Table I, j_s decreases from $5.96 \cdot 10^{14}$ TM/cm^{2}s for a plasma–polymer from a C_2H_4/CHF$_3$ mixture containing 65% CHF$_3$ to $j_s = 2.25 \cdot 10^{14}$ TM/cm^{2}s for a CHF$_3$ concentration of

IR Studies

Figures 3 and 4 show infrared spectra of polymer films formed by plasma deposition from the seven C_2H_4/CHF$_3$ gas mixtures to elucidate the chemical composition of the multilayer coating. Spectrum (a) in Figure 3 shows the FT–IR spectrum of PE and spectrum (b) shows the FT–IR spectrum of the first film of the barrier layer, plasma polymerized from pure C_2H_4. By comparing these IR spectra it can seen that the plasma-polymer-

Table I   Film Thickness, Toluene Permeation Rate, and Retention Coefficient of Different C_2H_4/CHF$_3$ Films Plasma Polymerized on PE

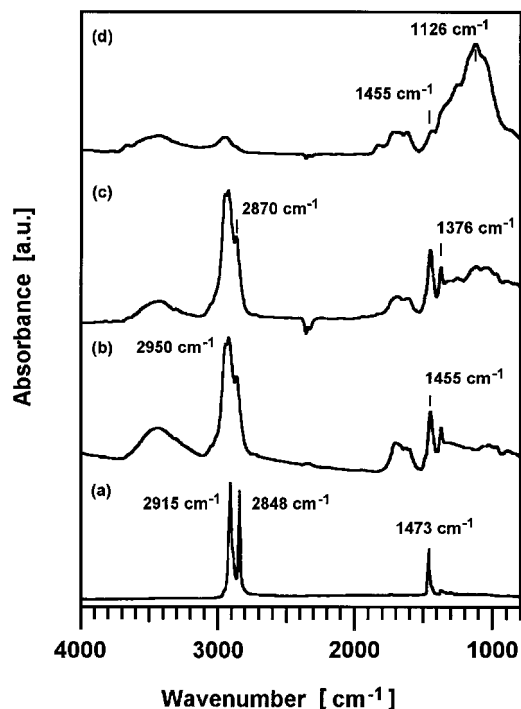| Monomer Composition of the Barrier Layer	Film Thickness	Stationary Permeation Flux [TM/cm^2 s]	Retention Coefficient
PE, uncoated	—	$2.34 \cdot 10^{16}$	—
C_2H_4/CHF$_3$-mixture containing 0% CHF$_3$	100 nm	$1.13 \cdot 10^{15}$	20.7
C_2H_4/CHF$_3$-mixture containing 65% CHF$_3$	100 nm	$5.96 \cdot 10^{14}$	39.3
C_2H_4/CHF$_3$-mixture containing 92% CHF$_3$	100 nm	$2.25 \cdot 10^{14}$	104
"multilayer"	300 nm	$1.44 \cdot 10^{13}$	1625

Figure 3 IR spectra of the multilayer plasma polymerized on the surface of PE (part 1). For details, see text.

ized ethylene (PPE) film shows some absorption bands similar to those of PE, for example, the CH$_3$ antisymmetric stretching band at 2925 cm^{-1} and the CH$_2$ symmetric bending band at 1455 cm^{-1}. The absorption band at 2950 cm^{-1} in the IR spectrum of the PPE film is due to stretching vibrations of CH$_3$ groups and the absorption band at 1376 cm^{-1} is due to CH$_3$ bending vibrations.[9,10] The stretching vibrations of C=C double bonds in the PPE film result in the absorption band at 1610 cm^{-1}. The absorption bands at 3400 cm^{-1} and 1705 cm^{-1} correspond to stretching vibrations of hydroxy (—OH) and carbonyl (C=O) groups, respectively. The incorperation of oxygen might be attributed to (a) reactions with water vapor or oxygen both being present in the process chamber during the treatment, or (b) to a reaction with atmospheric oxygen or water vapor after the removal of the PPE film from the vacuum chamber.

The following six films of the multilayer were deposited from different C$_2$H$_4$/CHF$_3$ mixture ratios. The IR spectra (c) and (d) in Figure 3 and the IR spectra (e) to (h) in Figure 4 show the change in the chemical composition of the plasma polymer films. As CHF$_3$ is introduced to the C$_2$H$_4$ plasma, a broad absorption band in the IR spectra of the resultant polymers appears. Obviously, the

broad absorption band in the region between 1350 cm^{-1} and 800 cm^{-1} is a superposition of several overlapping vibration modes having different vibration frequencies.[11,12] The broad absorption band includes stretching vibrations of CF$_3$—, CF$_2$—, and CF— groups from different CFH— compounds such as (CF$_2$)$_2$—(CH$_2$)$_2$, (CF$_2$)$_2$—CH-(CH$_3$)—(CH$_2$), CF$_2$—CH$_2$, and CHF—CH$_2$.[13] The intensity of the absorption bands in the region between 1350 cm^{-1} and 800 cm^{-1} increases with increasing CHF$_3$ concentration in the gas mixture, whereas the intensity of the CH$_3$— and CH$_2$— absorption bands decreases.[11,14] These changes in the IR spectra indicate that the polymer prepared from the C$_2$H$_4$/CHF$_3$ mixtures contain C—H groups as well as C—F groups. When the C$_2$H$_4$/CHF$_3$ ratio is increased to 97%, the absorption bands of the C—H vibration modes at 2950 cm^{-1}, 2930 cm^{-1}, 2870 cm^{-1}, 1455 cm^{-1}, and 1376 cm^{-1} disappear. The outer film of the multilayer is plasma polymerized from pure CHF$_3$ and shows a "simple" spectrum involving a strong absorption band at 1230 cm^{-1}. This spectrum indicates that the polymer from pure CHF$_3$ mainly consists of fluorocarbon chains and can be described as a polytetrafluorethylene ("Teflon") like film.
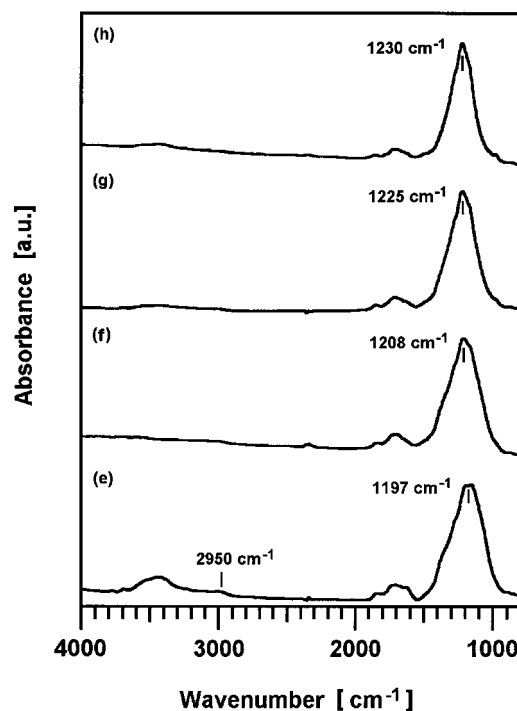

Figure 4 IR spectra of the multilayer plasma polymerized on the surface of PE (part 2). For details, see text.
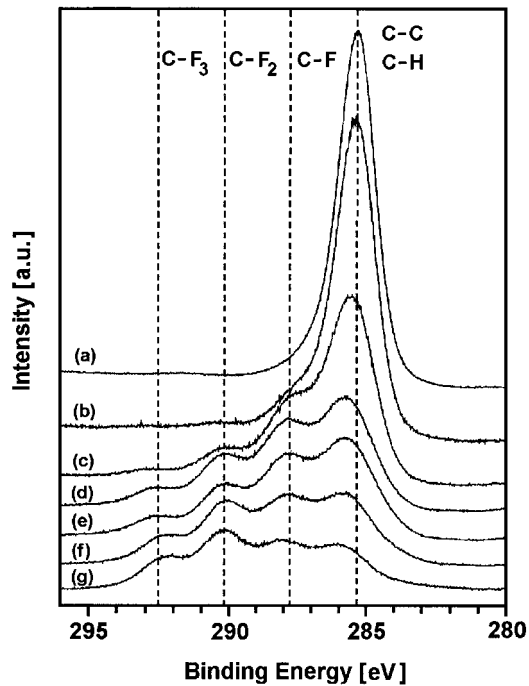
Figure 5   C(1s) photoelectron peaks in the XPS spectra of the multilayer coating.

XPS Studies

XPS measurements were performed in order to characterize the film surfaces in view of the composition and the chemical state of the elements. Besides the signals originating from the presence of C and F atoms at the surface, a small oxygen signal was detected and attributed to the air exposure. The C(1s) and F(1s) signals were measured in detail. In order to quantify the F/C ratio at the surface of the differently prepared films, the peak areas were corrected by the analyzer transmission function and the different atomic sensitivity factors for C(1s) and F(1s) photoelectrons.

The content of F in the film increases with increasing CHF_3 flow in the C_2H_4/CHF_3 gas mixture during the preparation. The film prepared in pure CHF_3 atmosphere contains about 55% F (Fig. 6). The chemical state of differently bonded C atoms can be studied by analyzing the C(1s) signal. It can be divided into several peaks corresponding to C atoms bonded in different chemical surroundings (Fig. 5) such as CF_3, CF_2, CF, C—CF_x, and C—C and/or CH.[15,16] At the surface of the film prepared in pure C_2H_4 only one C(1s) peak can be detected indicating the presence of only C—C and CH bonds [Fig. 5(a)]. With increasing amounts of CHF_3 in the reaction gas [Fig. 5(b)– (f)] more and more higher fluorinated carbon

species can be detected with XPS, these are probably C—F_x compounds. The change and shift of the C—C carbon peak [Fig. 5(a)–(g)] is assumed to be related to the increasing amount of several C—CF_x bonds in the polymer.[15] The intensity of the C—C and C—CF_x is then correlated to the chain length and/or the number of cross bondings between the chains of the "polymer." The film prepared with pure CHF_3 as monomer [Fig. 5(g)] exhibits a strong signal from CF_2 bondings indicating a preferred incorporation of this compound in the resulting film. In the films investigated here, the amount of C—C and C—CF_x bondings is small compared to films prepared with mixed monomers or with other preparation conditions.[17]

CONCLUSION

It is shown that a thin fluorocarbon layer deposited from C_2H_4/CHF_3 plasmas is an effective means to improve the toluene barrier properties of PE. The steady state permeation flux j_s decreases from $2.34 \cdot 10^{16}$ TM/cm^2s for the uncoated PE to $j_s = 2.25 \cdot 10^{14}$ TM/cm^2s for the plasma polymer from a C_2H_4/CHF_3 mixture containing 92% CHF_3. A further significant reduction of the permeation flux to $j_s = 1.44 \cdot 10^{13}$ TM/cm^2s is obtained by a multilayer coating. IR and XPS measurements show that the first film of the barrier layer consists mainly of CH_3— and CH_2— groups and can be described as a PE-like film. The following five films of the barrier layer contains CH— groups as well as CF— groups. The F content of the films increases with increasing CHF_3 concentration in the C_2H_4 plasma. The outer film of the barrier
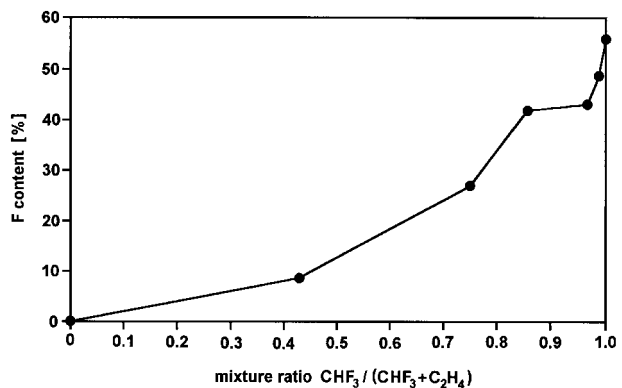

Figure 6   F/C ratio of the multilayer coating depending on the CHF_3 content in the several preparation steps.

layer consists mainly of fluorocarbon chains and can be described as a "Teflon"-like film.

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