

Surface Properties of Polymers Treated with Tetrafluoromethane Plasma

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Received 9 April 1996; received 12 May 1997

ABSTRACT: Polymer films of poly(ethylene terephthalate), polypropylene, and cellophane were surface treated with tetrafluoromethane plasma under different time, power, and pressure conditions. Contact angles for water and methylene iodide and surface energy were analyzed with a dynamic contact angle analyzer. The stability of the treated surfaces was investigated by washing them with water or acetone, followed by contact angle measurements. The plasma treatments decreased the surface energies to 2–20 mJ/m² and consequently enhanced the hydrophobicity and oleophobicity of the materials. The treated surfaces were only moderately affected after washing with water and acetone, indicating stable surface treatments. The chemical composition of the material surfaces was analyzed with X-ray photoelectron spectroscopy (XPS) and revealed the incorporation of about 35–60 atomic % fluorine atoms in the surfaces after the treatments. The relative chemical composition of the C 1s spectra's showed the incorporation of —CHF— groups and highly nonpolar —CF₂— and —CF₃ groups in the surfaces and also —CH₂—CF₂— groups in the surface of polypropylene. The hydrophobicity and oleophobicity improved with increased content of nonpolar —CF₂—, —CF₃, and —CH₂—CF₂— groups in the surfaces. For polyester and polypropylene, all major changes in chemical composition, advancing contact angle, and surface energy are attained after plasma treatment for one minute, while longer treatment time is required for cellophane. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1591–1601, 1997

Key words: plasma treatment; tetrafluoromethane; contact angle; surface energy; X-ray photoelectron spectroscopy; chemical composition; hydrophobicity; oleophobicity; treatment stability

INTRODUCTION

In many applications for polymers and fibrous materials, their hydrophobicity and barrier properties are of great importance. This includes applications such as packaging films, electrical cables, textiles, and nonwoven materials used in surgical gowns or drapes and protecting clothes. Hydrophobicity of polymers and fibrous structures can be obtained in many different ways,

with the use of fluorocarbon resins being a very common method for that purpose. In recent years, there has been increased interest in the use of plasma technology for surface modification of polymers. Plasma technology is a versatile method for surface treatments and can be used for designing surfaces with specific desired properties, without affecting the bulk properties.^{1–3} Plasma treatment is a dry processing method, with the small amounts of the reactive gases used making it an environmentally friendly process.

Plasma-based fluorination, using saturated fluorine compounds such as, CF₄, CHF₃, and C₂F₆, has been used to improve the water re-

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Journal of Applied Polymer Science, Vol. 66, 1591–1601 (1997)
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Table I Processing Conditions for Plasma Treatment with CF₄

Material	Power (Watt)	Pressure (mbar)	Time (min)
PET	150	0.2	1.0
PET	450	1.2	5.0
PP ^a	150	0.2	1.0
PP	250	1.2	2.0
Cellophane	150	0.2	1.0
Cellophane	450	1.2	5.0

^a PP, polypropylene.

pellency and barrier properties of polymers and textiles.^{2,4-7} These treatments have resulted in surface reactions, etching and deposition or polymerisation of the reactive plasma, depending on the type of fluorine containing monomer used.

In plasma processing, there are many different interactions taking place between the reactive plasma and polymer surfaces. The interactions depend on the gas and type of polymer used and the processing conditions such as time, power, and pressure. For the polymers, the chemical composition, crystallinity, and morphology are of great importance for the obtained results.^{8,9} To better understand the chemical reactions taking place in the plasma processing chamber, X-ray photoelectron spectroscopy (XPS) can be used to study the chemical composition in material surfaces. The XPS technique is surface-sensitive (1–10 nm) and makes it possible to obtain information on chemical bonding in the surfaces.

In this work, the aim has been to apply the plasma technology for increasing the hydrophobicity of polymer surfaces. Commercial films of poly(ethyleneterephthalate), polypropylene, and

cellophane were treated with tetrafluoromethane plasma under different time, power, and pressure conditions. The work includes studies on stability of the plasma-treated surfaces and the effect of the plasma treatment on chemical and physical properties of the materials.

EXPERIMENTAL

Materials

In these experiments, plasma treatment was performed on commercial films of poly(ethylene terephthalate) (PET), polypropylene, and cellophane. The PET material used was a Mylar film from DuPont with a thickness of 0.1 mm; the PP film was a 0.1 mm thick Protec-X104 from KWH Plast AB, Sweden; and the cellophane used was a 0.0419 mm thick film from Courtoulds Films, United Kingdom. Before the treatment, the films were cut into 1 × 2.5 cm sections and washed with ethanol.

Plasma Treatment

Plasma treatments were carried out in a commercial installation using Plasma System 440G from Technics Plasma. The substrates were treated with CF₄ plasma under different power, pressure, and time conditions, as shown in Table I. The plasma was produced with a high-frequency generator at the microwave frequency of 2.45 GHz.

Measurements (Analysis)

Advancing contact angle and surface energy were analyzed with a Cahn DCA 322 dynamic contact angle analyzer. The reported values correspond

Table II Advancing Contact Angles and Surface Energies of Untreated and CF₄-Treated Polyester

Material	θ_{Water}	$\theta_{\text{Methylene iodide}}$	γ_p (mJ/m ²)	γ_d (mJ/m ²)	γ (mJ/m ²)
Untreated	84	40	8	33	41
Plasma treated (1 min)	109	97	6	10	16
Washed with water	96	91	11	10	21
Washed with acetone	106	92	7	11	18
Plasma treated (5 min)	115	95	3	12	15
Washed with water	103	89	7	12	19
Washed with acetone	108	94	6	11	17

Table III Advancing Contact Angles and Surface Energies of Untreated and CF₄-Treated Polypropylene

Material	θ_{Water}	$\theta_{\text{Methylene iodide}}$	γ_p (mJ/m ²)	γ_d (mJ/m ²)	γ (mJ/m ²)
Untreated	100	66	4	24	28
Plasma treated (1 min)	140	112	<1	5	5
Washed with water	119	100	<1	8	9
Washed with acetone	139	112	<1	5	6
Plasma treated (2 min)	153	127	<1	2	3
Washed with water	130	105	0	7	7
Washed with acetone	149	120	<1	3	4

to the average of three measurements of the advancing contact angle. Typical standard deviations were 4–5°.

To investigate the stability of the plasma-treated films, they were washed in acetone and water, respectively, and analyzed in terms of surface properties.

Chemical composition in the substrate surface was analyzed with a Perkin-Elmer PHI 5500 XPS photospectrometer. A Mg K α (1253.6 eV) X-ray source was used, and the take-off angle was 45°. The pressure in the chamber was 10⁻⁹–10⁻⁸ Torr during data acquisition. The analyzed area was 0.8 mm in diameter, and the depth of analysis was approximately 30–40 Å. To evaluate the surface composition, the sensitivity factors used were according to the Perkin Elmer manual.

RESULTS

Wettability and Surface Energy

The effect of plasma treatment on wettability was followed by measuring the advancing contact

angle for water on a Cahn dca analyzer. The contact angle was also measured on treated materials washed with water or acetone to determine the stability of the treated materials. The surface energy (γ) of the samples was determined by measuring the contact angles for water and methylene iodide and then applying the harmonic–mean method. In some cases, the contact angles were too high, which required the use of the geometric–mean method.

The contact angles and surface energies for polyester are given in Table II. The contact angles for water and methylene iodide on untreated polyester are 84 and 40°, respectively. After the plasma treatment, the contact angles for these liquids increased considerably, the treatment thus improving both the hydrophobicity and the oleophobicity of the material. Washing the treated materials with water and acetone had only a minor effect on the contact angles for water and methylene iodide, indicating stable surfaces after the treatments.

The surface energy for the untreated polyester is 41 mJ/m². After the treatments with CF₄, the

Table IV Advancing Contact Angles and Surface Energies of Untreated and CF₄-Treated Cellophane

Material	θ_{Water}	$\theta_{\text{Methylene iodide}}$	γ_p (mJ/m ²)	γ_d (mJ/m ²)	γ (mJ/m ²)
Untreated	30	48	40	24	64
Plasma treated (1 min)	75	118	39	1	40
Washed with water	77	92	24	9	33
Washed with acetone	87	93	17	9	26
Plasma treated (5 min)	132	128	<1	2	2
Washed with water	117	95	<1	10	11
Washed with acetone	117	104	1	7	8

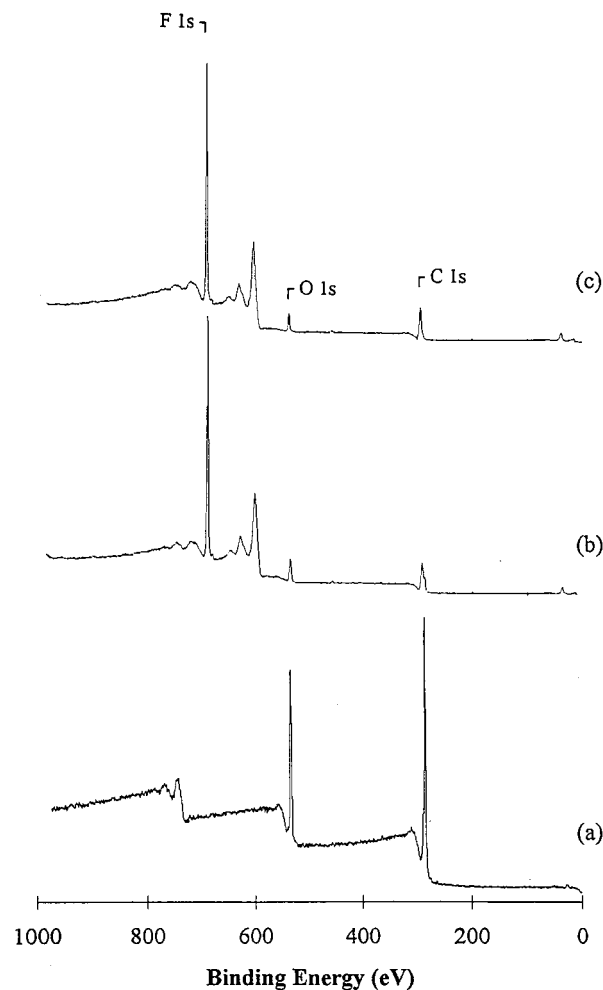


Figure 1 Survey scans for untreated and CF_4 plasma-treated PET: (a) untreated; (b) CF_4 plasma (1 min); and (c) CF_4 plasma (5 min).

surface energy decreased substantially to a value of $15\text{--}16\text{ mJ/m}^2$, indicating extensive incorporation of nonpolar groups in the surface after the plasma treatments. Washing the treated materials with water and acetone increased the surface energies slightly.

The contact angles and surface energies for polypropylene are given in Table III. The contact

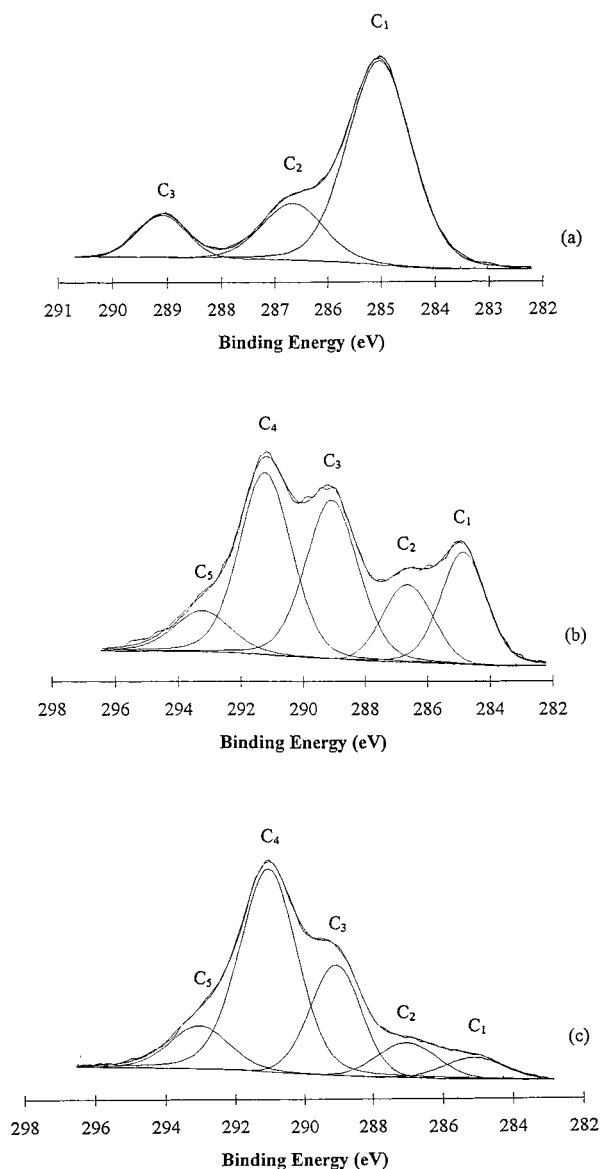


Figure 2 Line-shape analysis of the high-resolution C 1s spectra for untreated and treated PET. (a) Untreated: C₁, $-\text{CH}-/-\text{C}-\text{C}-$; C₂, $-\text{CO}-/-\text{COH}$; C₃, $-\text{COO}-$, (b) CF_4 plasma (1 min): C₁, $-\text{CH}-/-\text{C}-\text{C}-$; C₂, $-\text{CO}-/-\text{COH}$; C₃, $-\text{COO}-/-\text{CHF}-$; C₄, $-\text{CF}_2-$; C₅, $-\text{CF}_3-$; (c) CF_4 plasma (5 min); peak notations as in (b).

Table V Atomic Percent Composition in the Surface Determined by XPS for Polyester Treated with CF_4 Plasma at Different Processing Conditions

Sample	C%	O%	F%	O/C	F/C	F/O
Untreated	75	25	0	0.33	0.00	0.00
Plasma treated						
1 min	38	7	55	0.18	1.45	7.85
5 min	42	10	48	0.24	1.14	4.80

Table VI Relative Chemical Composition of C 1s Spectra of Polyester Treated with CF₄ Plasma

Sample	Relative Chemical Composition (%)				
	—CH—	—C—O—	—COO—/—CHF—	—CF ₂ —	—CF ₃
Untreated	71	19	10	0	0
Plasma treated					
1 min	18	12	29	33	8
5 min	5	8	23	53	11

angles for water and methylene iodide on untreated polypropylene are 100 and 66°, respectively. After the plasma treatments with CF₄ for 1 and 2 min, the contact angles for water and methylene iodide increased substantially, with the material becoming highly hydrophobic and

oleophobic. Washing the treated surfaces with water and acetone decreased the contact angles slightly.

The surface energy for the untreated polypropylene is 28 mJ/m². After the treatments with CF₄, the surface energy decreased to values of 5 and 3 mJ/m² after treatments for 1 and 2 min, respectively; thus, the surface became more nonpolar. The polar component of the surface energy is negligible after these treatments.

The contact angles and surface energies for cellophane are given in Table IV. The contact angles for water and methylene iodide on untreated cellophane are 30 and 48°, respectively. Treating this material for 1 min with CF₄ increased the contact angle for water and methylene iodide substantially. The advancing contact angles for water increased slightly after washing with water and acetone, indicating removal of polar groups from the surface. Treatment for 5 min resulted in substantial increase in the contact angles for both water and methylene iodide, and the material became highly hydrophobic and oleophobic. The contact angles were only slightly lowered after washing in water or acetone, indicating only moderate removal of nonpolar groups on washing.

The surface energy for the untreated cellophane is 64 mJ/m². After the plasma treatment for 1 min in CF₄, the total surface energy decreased to 40 mJ/m², with the surface becoming more nonpolar. The polar component of the surface energy is similar, while the dispersion component decreased from 24 to 1 mJ/m². However, after washing the surfaces with water or acetone, the surface energies decreased to 33 and 26 mJ/m² as a result of removal of plasma produced polar groups from the surfaces.

After treatment for 5 min, the surface energy decreased substantially to a value of 2 mJ/m², showing extensive incorporation of nonpolar groups in the surfaces. Washing the materials with water and acetone removed some of the nonpolar groups,

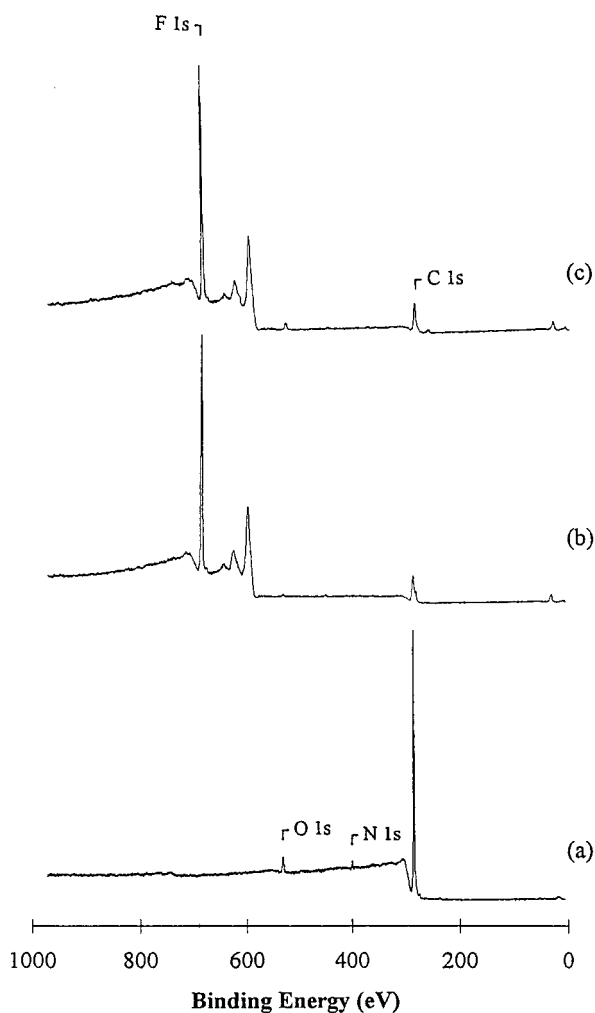


Figure 3 Survey scans for untreated and CF₄ plasma-treated polypropylene: (a) untreated; (b) CF₄ plasma (1 min); and (c) CF₄ plasma (2 min).

Table VII Atomic Percent Composition in the Surface Determined by XPS for Polypropylene Treated with CF₄ Plasma at Different Processing Conditions

Sample	C%	O%	N%	F%	100O/C	F/C	F/O
Untreated	95	3	2	0	3.16	0.0	0.00
Plasma treated							
CF ₄ (1 min)	39	1	0	60	2.56	1.54	60.00
CF ₄ (2 min)	37	3	0	60	8.10	1.62	20.00

with the surface energy increasing slightly to values between 8 and 11 mJ/m².

Analysis of Chemical Composition in the Surface with XPS

The chemical structure of the material surfaces was analyzed by XPS. Figure 1 shows survey scans of clean untreated and CF₄ plasma-treated PET surfaces for 1 and 5 min, respectively. An increase in the intensity of the peak for F 1s is observed after the plasma treatments in CF₄. Table V shows the atomic percent composition in the surface for untreated and plasma treated polyester. There is a substantial incorporation of fluorine atoms in the surface after the treatment for 1 min, with the fluorine content reaching 55 atomic %. The O/C ratio decreases after the treatment, while the F/C and F/O ratios reach values of 1.45 and 7.85, respectively. Treatment for 5 min gives a little lower fluorine content of 48 atomic %, lower F/C and F/O ratios, and higher O/C ratio compared to treatment for 1 min.

High-resolution scans of the C 1s region for untreated and plasma treated PET is shown in Figure 2. Line-shape analysis by peak deconvolution shows that the C 1s spectrum for untreated PET contains three distinct peaks at 284.7, 286.6, and 288.8 eV. These peaks can be assigned to the carbon atoms of the phenylene ring, the methylene carbon atoms singly bonded to oxygen, and the ester carbon atoms, respectively.¹⁰ After the plasma treatment with CF₄, the C 1s spectrum shows five distinct peaks. The peaks at 288.8, 291.0, and 293.0 eV can be assigned to —CHF—/—COO—, —CF₂— and —CF₃ groups, respectively¹⁰; while the peaks at 284.7 and 286.6 eV arise from —CH— and —C—O— groups, respectively. After the treatment for 5 min, the intensities for the peaks at 284.7, 286.6, and 288.8 eV decrease; while the intensity for the peaks at 291.0 and 293.0 eV increases.

Table VI shows the changes in relative chemical composition of the C 1s spectra in the surface

of polyester after the plasma treatments. Comparing the chemical composition of the materials treated for 1 and 5 min shows that there is a relative increase in the content of the nonpolar —CF₂— and —CF₃ groups, while the content of —CHF— groups and polar —COO— groups decreases.

The polypropylene samples were treated for 1 and 2 min. Figure 3 shows survey scans of clean untreated and plasma treated PP surfaces. An increase in the intensity of the peak for F 1s is observed after the plasma treatments in CF₄. Table VII shows the atomic percent composition in the surface for untreated and plasma-treated polypropylene. These scans show that the untreated polypropylene surface contains a minor amount of oxygen and nitrogen. There is an extensive incorporation of fluorine atoms in the surface after the treatment for 1 min, with the fluorine content reaching 60 atomic %. The O/C ratio decreases after the treatment, while the F/C and F/O ratios reach values of 1.54 and 60, respectively. Treatment for 2 min gives the same fluorine content of 60 atomic %, higher F/C and O/C ratios, but lower F/O ratio, compared to treatment for 1 min.

High-resolution scans of the C 1s region for untreated along with CF₄ plasma-treated PP is shown in Figure 4. Line-shape analysis by peak deconvolution shows that the C 1s spectrum for untreated polypropylene contains three distinct peaks. The peak at 285.0 eV can be assigned to the C—H carbons, and the two small peaks at 286.4 and 287.7 eV are due to carbons bonded to oxygen and nitrogen.¹⁰ After the plasma treatment with CF₄, the C 1s spectrum shows five distinct peaks. The peaks at 287.0, 289.0, 291.0, and 293.0 eV can be assigned to —CF₂—CH₂—, —CHF—, —CF₂—, and —CF₃ groups, respectively; while the peaks at 285.0 eV arises from —CH— groups.¹⁰ All nitrogen groups disappear after the plasma treatments. The oxygen content in the surface decreases after the 1 min treatment but increases again after treatment for 2 min.

After the treatment for 2 min, the intensities

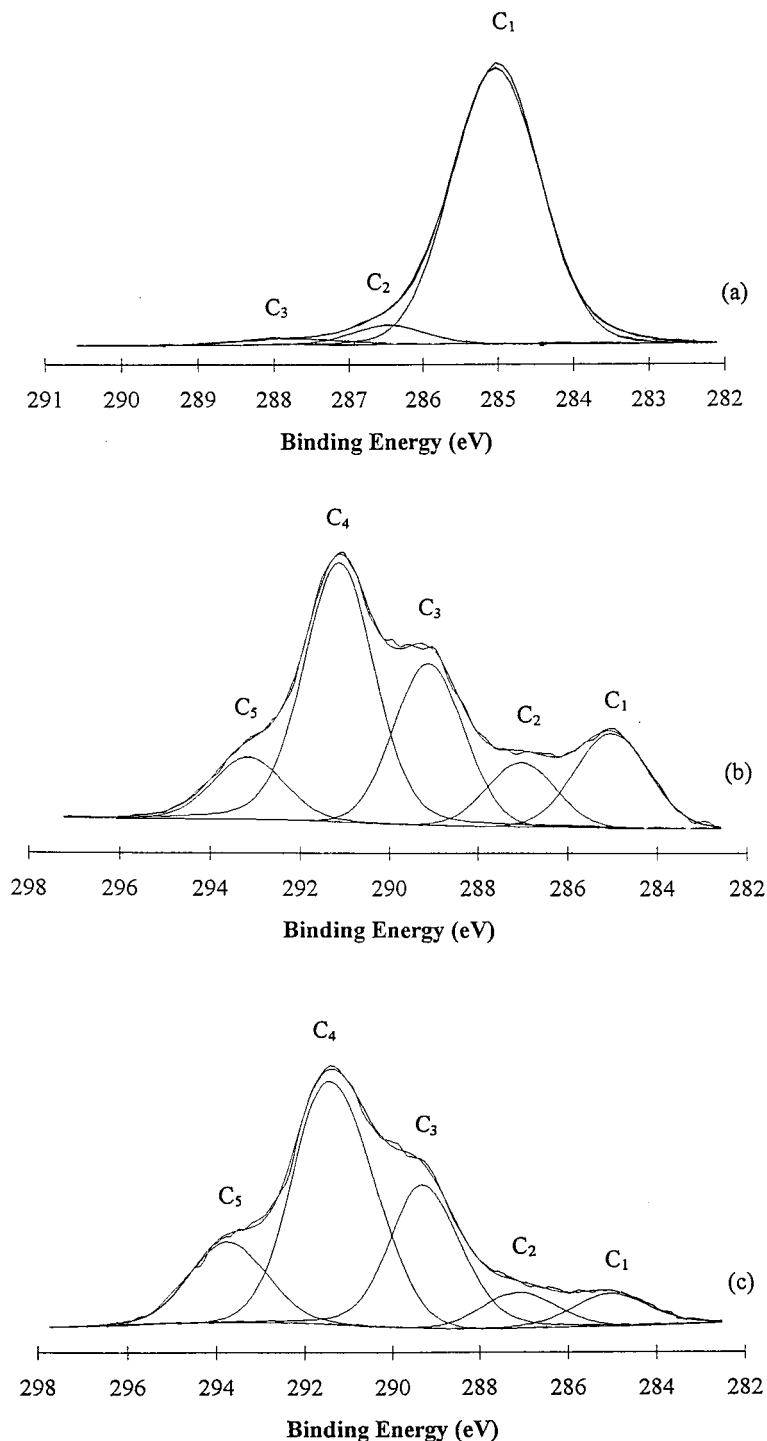


Figure 4 Line-shape analysis of the high-resolution C 1s spectra for untreated and treated polypropylene. (a) Untreated: C₁, $-\text{CH}-/\text{C}-\text{C}-$; C₂, $-\text{CO}-/\text{COH}$; C₃, $-\text{COO}-$; (b) CF₄ plasma (1 min); C₁, $-\text{CH}-/\text{C}-\text{C}-$; C₂, $-\text{CF}_2-\text{CH}_2$; C₃, $-\text{CHF}-$; C₄, $-\text{CF}_2-$; C₅, $-\text{CF}_3$; (c) CF₄ plasma (2 min); peak notations as in (b).

for the peaks at 285.0, 287.0, and 289.0 eV decreased; while the intensity for the peaks at 291.0 and 293.0 eV increased.

The relative chemical composition of the C 1s spectra is shown in Table VIII. Comparing the chemical composition of the materials treated for

Table VIII Relative Chemical Composition of C 1s Spectra of Polypropylene Treated with CF₄ Plasma

Sample	Relative Chemical Composition (%)				
	—CH—	—C—O—/—CF ₂ —CH ₂ —	C=O/—CHF—	—CF ₂ —	—CF ₃
Untreated	93	5	2	0	0
Plasma treated					
1 min	15	9	24	42	10
2 min	6	6	26	47	15

1 and 2 min shows that there is a relative increase in the content of —CHF—, —CF₂—, and —CF₃ groups; while the content of —CF₂—CH₂— groups decreases.

Figure 5 shows survey scans of clean untreated and plasma-treated cellophane surfaces. An in-

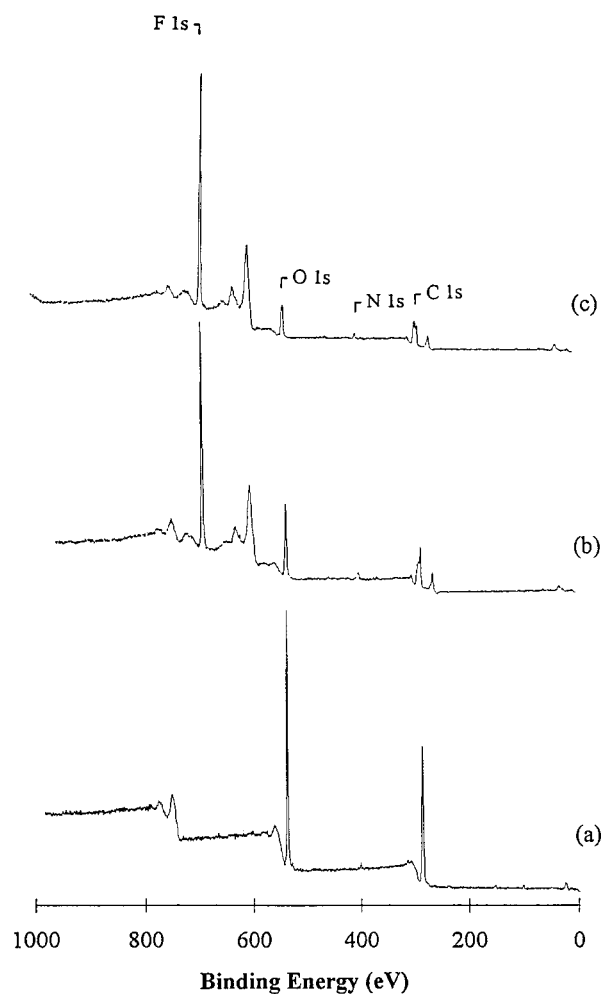


Figure 5 Survey scans for untreated and CF₄ plasma-treated cellophane: (a) untreated; (b) CF₄ plasma (1 min); (c) CF₄ plasma (5 min).

crease in the intensity of the peak for F 1s is observed after the plasma treatments in CF₄. Table IX shows the atomic percent composition in the surface for untreated and plasma-treated cellophane. There is a substantial incorporation of fluorine atoms in the surface after the treatment for 1 min, with the fluorine content reaching 35 atomic %. The O/C ratio decreases after the treatment, while the F/C and F/O ratios reach values of 0.88 and 1.59, respectively. Treatment for 5 min increases the fluorine content to 46 atomic % and increases the F/C, F/O, and O/C ratios, compared to treatment for 1 min.

High-resolution scans of the C 1s region for untreated and plasma-treated cellophane is shown in Figure 6. Line-shape analysis by peak deconvolution shows that the C 1s spectrum for untreated cellophane contains three distinct peaks at 285.0, 286.6, and 288.1 eV. The peak at 285.0 eV is due to various low-molecular-weight hydrocarbon contaminants in the surface of the cellophane, —CH—/—C—C—. The peak at 286.6 eV originates from carbon atoms bonded to a single oxygen atom, —C—O—; while the peak at 288.1 eV originates from carbon atoms bonded to two oxygen atoms or from carbonyl groups, —O—C—O—/C=O. After the plasma treatment with CF₄, the C 1s spectrum shows five distinct peaks. The peaks at 289.8, 291.7, and 293.6 eV can be assigned to —CHF—, —CF₂—, and —CF₃ groups, respectively; while the peaks at 286.6 and 288.1 eV arise from the glucose anhydride units. After the treatment for 5 min, the intensities of the peaks at 289.8, 291.7, and 293.6 eV increase; while the intensity for the peaks at 286.6 and 288.1 eV decreases.

Table X shows the changes in relative chemical composition of the C 1s spectra for the surface of cellophane after the plasma treatments. Comparing the chemical composition of the materials treated for 1 min and 5 min shows that the content of the nonpolar —CF₂— and —CF₃ groups

Table IX Atomic Percent Composition in the Surface Determined by XPS for Cellophane Treated with CF₄ Plasma at Different Processing Conditions

Sample	C%	O%	N%	F%	O/C	F/C	F/O
Untreated	62	37	1	0	0.60	0.00	0.00
Plasma treated							
CF ₄ (1 min)	40	22	3	35	0.55	0.88	1.59
CF ₄ (5 min)	37	14	3	46	0.38	1.24	3.29

increases comparatively more with time than the content of —CHF— groups.

DISCUSSION

This work shows that plasma treatment with tetrafluoromethane decreases the surface energy and thus enhances the oleophobicity and hydrophobicity of polyester, polypropylene, and cellophane. For polyester and polypropylene, all major changes in chemical composition, advancing contact angle, and surface energy are attained after plasma treatment for 1 min; while longer treatment time is required for cellophane.

The atomic percent of fluorine in the polyester surface is lower for the material treated for 5 min compared to the material treated for only 1 min. This should result in higher surface energy for the material treated for 5 minutes. However, the content of —CF₂— and —CF₃ groups is higher after the longer treatment time, so the surface energy is similar for both processing conditions. All major changes in physical properties are therefore attained after 1 min of plasma treatment.

For polypropylene, all major changes in chemical and physical properties are attained after 1 min of plasma treatment. However, there is a slight decrease in the surface energy after plasma treatment for 5 min, although the fluorine content of the surface is the same. The reason is the in-

creased content of the nonpolar —CF₂— and —CF₃ groups.

For cellophane, the total surface energy decreases after plasma treatment for 1 min following the incorporation of fluorine atoms in the surface. After treatment for 5 min, there is a further increase in the atomic percent of fluorine and the content of nonpolar —CF₂— and —CF₃ groups in the surface, and the surface energy decreases.

CONCLUSIONS

In this work, the effect of plasma treatment with tetrafluoromethane on the surface properties of polyester, polypropylene, and cellophane has been studied. Contact angles for water and methylene iodide and surface energy were analyzed with a dynamic contact angle analyzer. These treatments increase the hydrophobicity and oleophobicity of the materials and form surfaces with very low surface energies of 2 to 20 mJ/m².

The chemical structure of the material surfaces was analyzed by XPS. XPS analysis revealed an extensive incorporation of fluorine-containing groups in the surface, with the amount of fluorine reaching values of 35 to 60 atomic %. Line-shape analysis of the C 1s spectrum by peak deconvolution shows the formation of —CHF—, —CF₂—, and —CF₃ groups in the surfaces of poly(ethyleneterephthalate) and cellophane and —CF₂—CH₂—, —CHF—, —CF₂—, and —CF₃ groups

Table X Relative Chemical Compositions of C 1s Spectra of Cellophane Treated with CF₄ Plasma

Sample	Relative Chemical Composition (%)					
	—CH—	—C—O—	—O—C—O—	—CHF—/—CF—CF ₂	—CF ₂ —	—CF ₃
Untreated	30	53	17	0	0	0
Plasma treated						
1 min	0	40	16	16	20	8
5 min	0	27	8	17	31	17

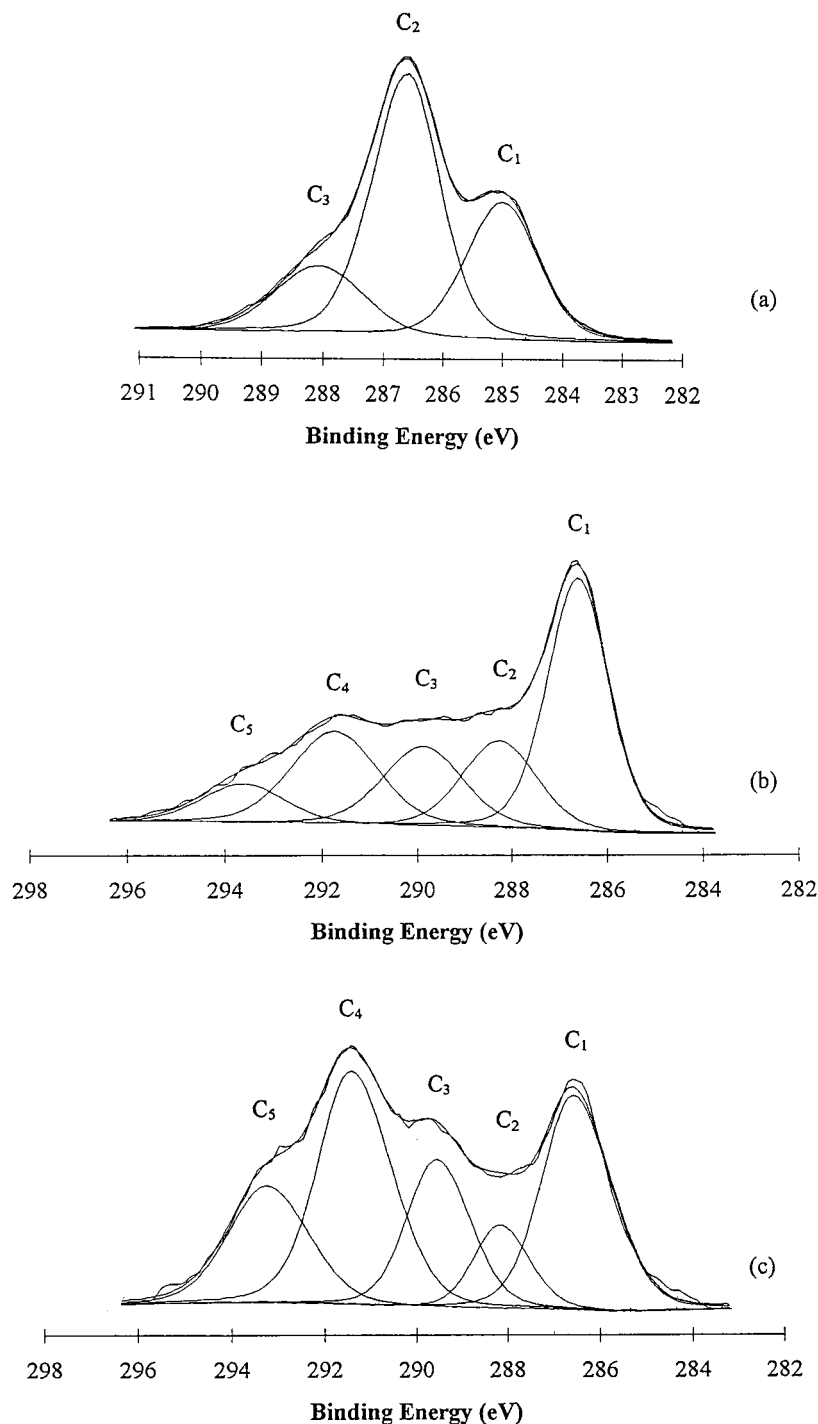


Figure 6 Line-shape analysis of the high-resolution C 1s spectra for untreated and treated cellophane. (a) Untreated: C₁, —CH—/—C—C—; C₂, —C—O—; C₃, —O—C—O—/C=O; (b) CF₄ plasma (1 min): C₁, —C—O—; C₂, —O—C—O—/C=O; C₃, —CHF—; C₄, —CF₂—; C₅, —CF₃; (c) CF₄ plasma (5 min); peak notations as in (b).

in the surface of polypropylene after the plasma treatments.

For polyester and polypropylene, all major

changes in chemical composition, advancing contact angle, and surface energy are attained already after plasma treatment for 1 min; while

longer treatment time is required for the cellophane. For cellophane, the total surface energy decreases from 64 to 40 mJ/m² after treatment for 1 min. After treatment for 5 min, there is a considerable increase in the atomic percent of fluorine and content of nonpolar —CF₂— and —CF₃ groups in the surface, and the surface energy decreases to 2 mJ/m².

Washing the treated surfaces with water or acetone affects the contact angles negligibly, indicating relatively stable surfaces.

The authors thank Anne Wendel at the Department of Polymer Technology, Chalmers University of Technology, for assistance with XPS measurements. We also thank Simonetta Granello and Birgitta Lindsjö, IFP, for experimental assistance and Jörgen Ohlsson, IFP, for valuable discussions.

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