Plasma Modification of Cellulose Derivatives as Biomaterials

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SYNOPSIS

A film of cellulose acetate was submitted to a cold plasma of tetrafluoromethane or of sulfur hexafluoride. The interactions of these cold plasmas and cellulose acetate lead to a material whose surface has been modified by fluorination. Comparison of CF_4 or SF_6 plasma treatment shows that fluorine atoms provided by each kind of plasma induce degradation and grafting of fluorocarbon radicals on the surface. As a consequence, the surface energy decreases and offers the possibility of a better response of plasma-modified cellulose derivatives used as biomaterials (e.g., hemodialysis membrane).

INTRODUCTION

A biomaterial, specifically a blood-compatible material, is a synthetic or natural polymer whose surface is in direct contact with biological components. When a foreign biomaterial is dipped in blood or tissue fluids, in a few seconds adsorption of biomolecules, cells (e.g., macrophage cells), usually proteins, takes place. This is followed in the next minutes or few hours by cellular interactions leading to a thrombus formation. Therefore, an ideal biopolymer does not adsorb any proteins[1,2] and also induces no activation of complementary system.[3]

The proteins adsorption depends greatly on the surface properties of the biomaterial: i.e., surface energy, surface composition, and surface morphology.

For example, Ikada et al.[2] show that a lower protein adsorption rate is obtained either with a biomaterial "superhydrophilic" (like polyethylene grafted with acrylamide, cellulose grafted with polyvinyl alcohol) or a biomaterial "superhydrophobic" such as perfluoro polymers. The surface of these biomaterials could be also modified with a simple chemical surface treatment that leads to a low protein adsorption rate.

Thus, a great deal of effort has gone into surface modifications.[4] Surface modification could proceed by the following procedures:

1. A physical deposition of other compounds (surfactants, etc.) to create a new surface chemistry in order to modify protein adsorption.[5]
2. A direct chemical modification (oxidation, hydrolysis, sulfonation, corona discharge, or plasma treatment) to create a barrier film that reduces undesirable diffusion of small molecules from the substrate (migration of adjuvants of biomaterials[6]) or control the rate of diffusion of drugs from the substrate.[7,8]
3. A chemical grafting of a different polymer (radiation graft copolymerization, plasma polymerization) to provide new surface chemistry for subsequent immobilization of molecules.[9,10]

In the hemodialysis field one of the most used membranes is a film or capillar tubes of cellulose or derivatives. During hemodialysis treatments, leukopenia is observed: A direct relation between this phenomenon and the complementary activation involving the hydroxyl groups of the cellulose backbone[11,12] has been proposed. Masking or substitution of the hydroxyl groups via plasma treat-

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ments (plasma polymerization or modification) should reduce the complementary activation. Corretge et al.[9] proposed grafting of poly(ethyleneglycol) on cellulose. The purpose of this publication and others[3] is to deal with fluorination of surfaces of cellulose and its derivatives through a cold plasma treatment and its consequence on the leukopenia and the complementary activation.

Cellulose and its derivatives have been treated in different plasmas for membrane permeability or textile applications.[13-18]

Argon, nitrogen, and air plasmas treatments lead to radical species in concentration depending on plasma conditions,[14-16] to new chemical groups or functions (ketone), and to a decrease of hydroxyl groups.[15,16] Degradation and crosslinking via hemiacetal bonds is proposed as a mechanism for these plasmas modifications.[18]

But, although the fluorination of cellulose or its derivatives is a promising research field for many bioapplications, little work has been done on this subject.[19]

EXPERIMENTAL

Plasma Equipment

The microwave plasma equipment previously described[20] is composed of three parts:

1. The excitation power is provided by a variable output (0–250 W) (P) microwave generator (433 MHz) that is coupled to the surfatron. The incidence power (P_i) and the reflected power (P_r) were measured with a power meter (Hewlett-Packard 435 B). The impedance is adjusted until the reflected power is the lowest ($P_r = 10^{-2}$ W). The glow is generated at the top of the reactor,

2. The reactor is a quartz cylinder of 500 mm length and 76 mm in diameter. The reactor is set up on a chamber used for the sample introduction. The sample substrate can be moved into or outside the plasma volume. The distance between the end of the visible part of the plasma and the substrate will be noted as z and the plasma length as l.

3. The pumping system is composed of a primary pump (CIT ALCATEL 2012) and an oil diffusion pump (CIT ALCATEL Crystal). The pressure (p) is measured with Penning and Pirani gauges down the plasma. The gas flow is controlled by MKS mass flow meters 1259 B.

The RF reactor is a ATEA device of 300 liters. The plasma was produced by an RF (13.6 MHz) capacitive excitation inside the reactor walls.

Surface Analyses

The SEM pictures are made on a Hitachi 52300 in the Département de Génie Mécanique, Institut Universitaire de Technologie, Université du Maine (Le Mans, France).

The FTIR spectra are recorded on a FTIR Perkin-Elmer 1750, with a microcomputer 7700, transmission (20 scans), attenuated total reflexion (ATR, 200 scans, θ comprised between 30° and 60°) are used.

The electronic spectroscopy for chemical analysis (ESCA) has been developed by the Laboratoire de Physique des Couches Minces, Université de Nantes (Nantes, France).

Surface energies of samples have been calculated from the contact angle of distilled water, glycerol, and α-bromonaphthalene (volume: 4 μL) and from the Dupré relation[21] used as described in Ref. 22. Surface energies of different liquids are as follows:

$$\gamma_{H_2O} = 72.75 \text{ mJ/m}^2, \gamma^D_{H_2O} = 21.75 \text{ mJ/m}^2, \gamma^P_{H_2O} = 51.0 \text{ mJ/m}^2$$

$$\gamma_{gly} = 63.4 \text{ mJ/m}^2, \gamma^D_{gly} = 37.0 \text{ mJ/m}^2, \gamma^P_{gly} = 26.4 \text{ mJ/m}^2$$

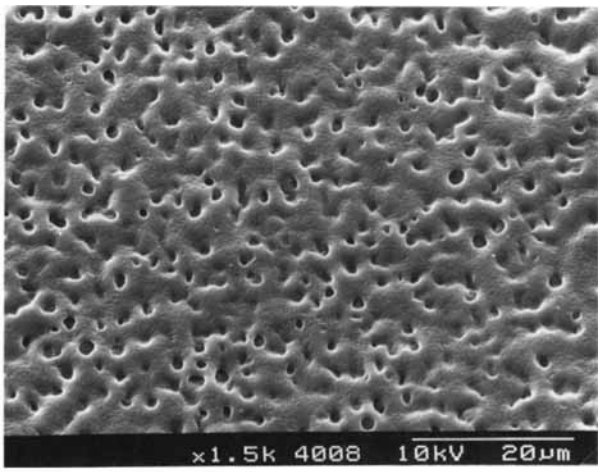
$$\gamma_{bro} = 44.4 \text{ mJ/m}^2, \gamma^D_{bro} = 43.6 \text{ mJ/m}^2, \gamma^P_{bro} = 0.8 \text{ mJ/m}^2$$

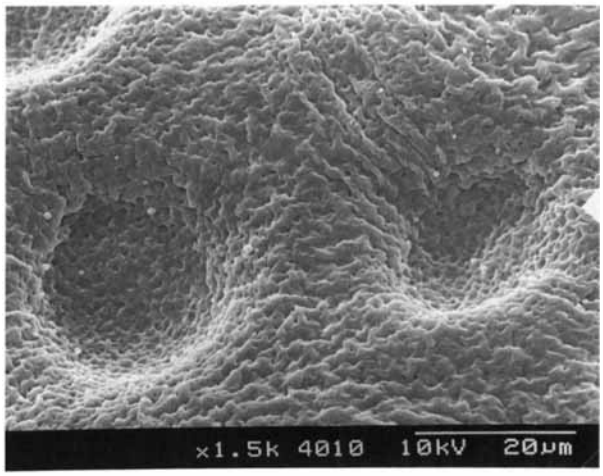
Film Preparation

The cellulose acetate (Aldrich, MW = 30 000, density = 1.30, acetylation yield = 39.8%) is dissolved in a mixture of acetone and water (23% of cellulose acetate, 67% acetone, 10% H_2O) at room temperature during 12 hs. Then 1 mL of this solution is spread on a glass slide previously cleaned with sulfochromic acid several times with H_2O and EtOH. The film (30 μm in thickness) is maintained at 40°C for 5 min, then dipped in ice for 1 h, and finally dipped in hot water (65°C) for 5 min, then dried.[23] One of the faces is mat and the other polished. The polished face seems to be more homogenous than the mat one.

Films of cellulose acetate of approximately 30 μm thickness could be also prepared with a dioxane solution[24] (15 g of acetate into 200 mL of dioxane). The film spread on glass slide was kept in H_2O for a few minutes at room temperature, then dried. Two mat faces are obtained. Keeping the solution in water for 12 h gives a transparent film.

SEM [Fig. 1(a)] shows a surface (mat face) with pores of 2 μm diameter, the biggest ones on the sur-





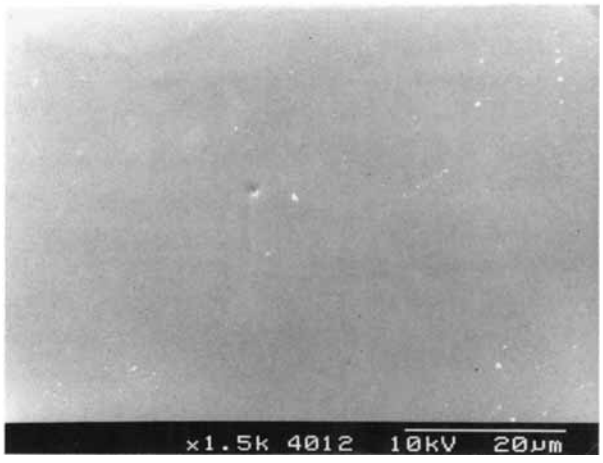


Figure 1 SEM of cellulose acetate films prepared in acetone (a) or in dioxane with fast evaporation (b), or slow evaporation (c).

face [Fig. 1(b)] of cellulose acetate–dioxane film could be interpreted as a result of dioxane evaporation from a viscous liquid. The topography of the transparent film, obtained from cellulose acetate–dioxane [Fig. 1(c)] seems to be uniform. All the samples have a fixed area of 15 cm^2.

Plasma Treatment

Before applying the usual process of treatment,[20] as the material is very hygroscopic, water remaining in the film must be removed, and the film must be kept in a dry atmosphere. Samples must be dried under vacuum for at least 1 h [Fig. 2α]. When the pressure is restored back to atmospheric, the concentration of adsorbed water reaches a constant value after 16 h [Fig. 2β].

Modification is studied as a function of the different parameters of the plasma: duration (t, mn), power (P_i, W), gas flow (D, sccm: standard cm^3/mn), and distance between the end of the visible part of the plasma and the sample (z, cm).

All the samples, before plasma treatment, are submitted to a primary pumping of 3 h then to a secondary pumping of 15 min at ambient temperature.

The degradation rate [degraded layer (μm)], described as the proportion of volatile products (oligomers, CO_2, H_2O) produced during the plasma treatment, is measured by weight difference between the untreated and treated samples.

RESULTS AND DISCUSSION

As described in previous studies,[25,26] the plasma modification of polymers can lead to functionalization and degradation. These different reactions will be characterized through different experiments and analyses and compared together with the idea of a potential biomedical application.

Influence of Degradation

On Surface Topography

The CF_4 plasma treated samples, prepared either from dioxane or acetone solutions, show a smoother surface than the blank one. The plasma treatment leads to uniform erosion and also probably a fluorinated layer (Fig. 3), as pores in treated samples seem to be smaller than in the blank sample.

On the Concentration of Low Molecular Weight Products

The degradation can be characterized by the formation of oligomers, some of them in the vapor phase, with others blown away with the gas flux.

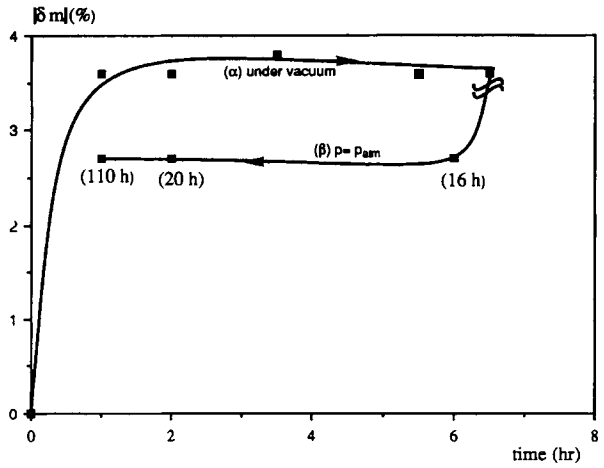


Figure 2 Dependence of the concentration of absorbed water in cellulose acetate: Iδm I = (initial weight of sample–final weight of sample)/initial weight of sample, (α) on time and pressure (p = 10^{-2} mbar) conditions under vacuum, (β) on time at atmosphere pressure.

When one of the plasma parameters (t, P, or z) is increased, the degradation of cellulose acetate film also increases (Fig. 4). But SF_6 plasma seems to be a more reactive plasma. The degraded layer can reach more than 5 μm thickness, and fragmented macromolecules may induce pollution in the medium (in vitro or in vivo) and toxicological consequences when used as a biomaterial like a hemodialysis membrane. Cellulose is a weak material and C—O, C—H bonds are probably dissociated via fluorine atoms substitution or addition as their strengths (C—O: 351–389 kJ/mol, C—H: 355 kJ/mol) are low. A mild treatment needs the following conditions: $t < 5$ min, $P_i < 100$ W, $z = 0$ cm (substrate at the end of the visible part of the plasma).

The difference in reactivity of CF_4 and SF_6 can be explained by the value of bond strength of C—F (552 kJ/mol) and S—F (343 kJ/mol). The sulfur hexafluoride bonds are weaker than those of the CF_4 molecule, and may produce more fluorine atoms, as has been shown by Picard et al.[27] The silicon etch in SF_6 plasma is recognized to be about one order of magnitude greater than in CF_4 plasma under the same conditions.[27] Fluorine atoms are the main etching species, produced by attachment, ionization, and dissociation of neutral species SF_6 and SF_4. As surface-modified derivatives of cellulose acetate are insoluble or poorly soluble in solvents used for SEC or viscosimetry measurements, no determination of the molecular weight of modified product is possible. As a first step, we chose filtration and toxicological tests as analytical reference.[3]

Nevertheless, with RF plasma treatment of hemodialysis membranes under mild conditions, no secondary effects (alteration of filtration properties, toxicologic consequences in vivo or in vitro tests) due to the presence of a degraded layer of cupro-

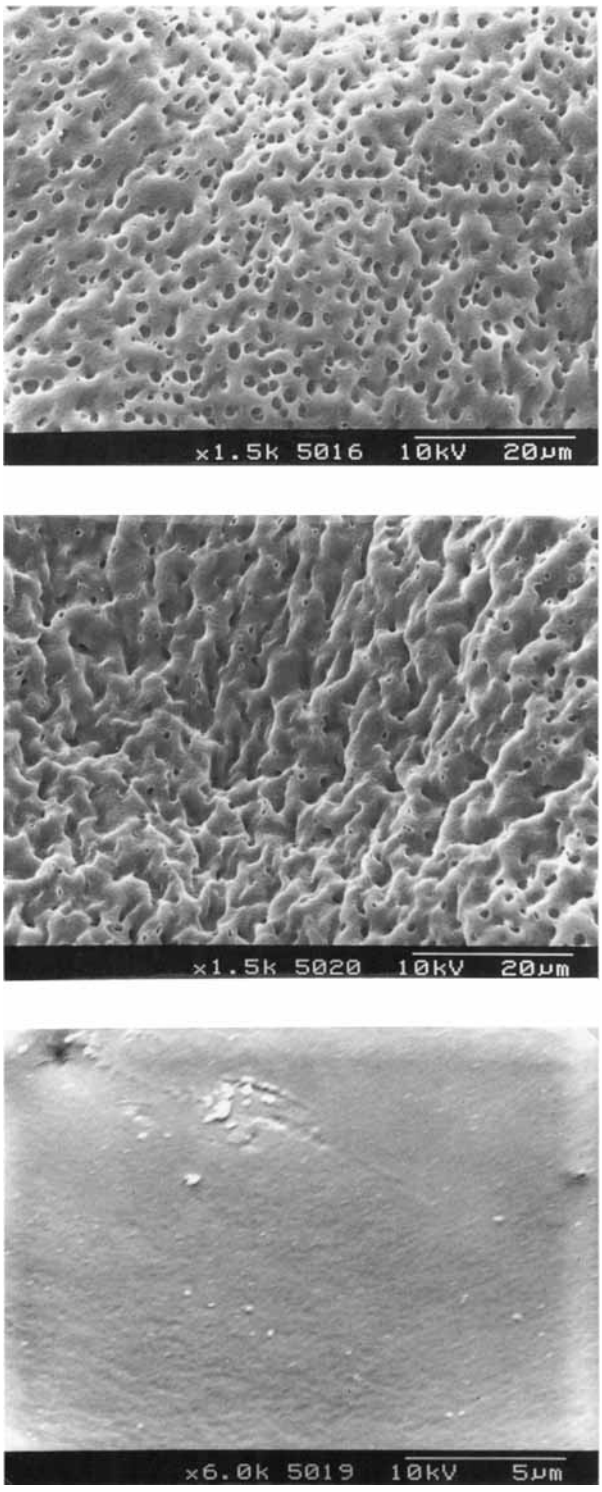


Figure 3 SEM of treated cellulose acetate films prepared in acetone (a), in dioxane with fast evaporation (b), or slow evaporation (c); DCF_4 = 15 sccm, Pi = 60 W, p = 0.2 mbar, l = 15 cm, z = 0 cm, t = 20 mn.

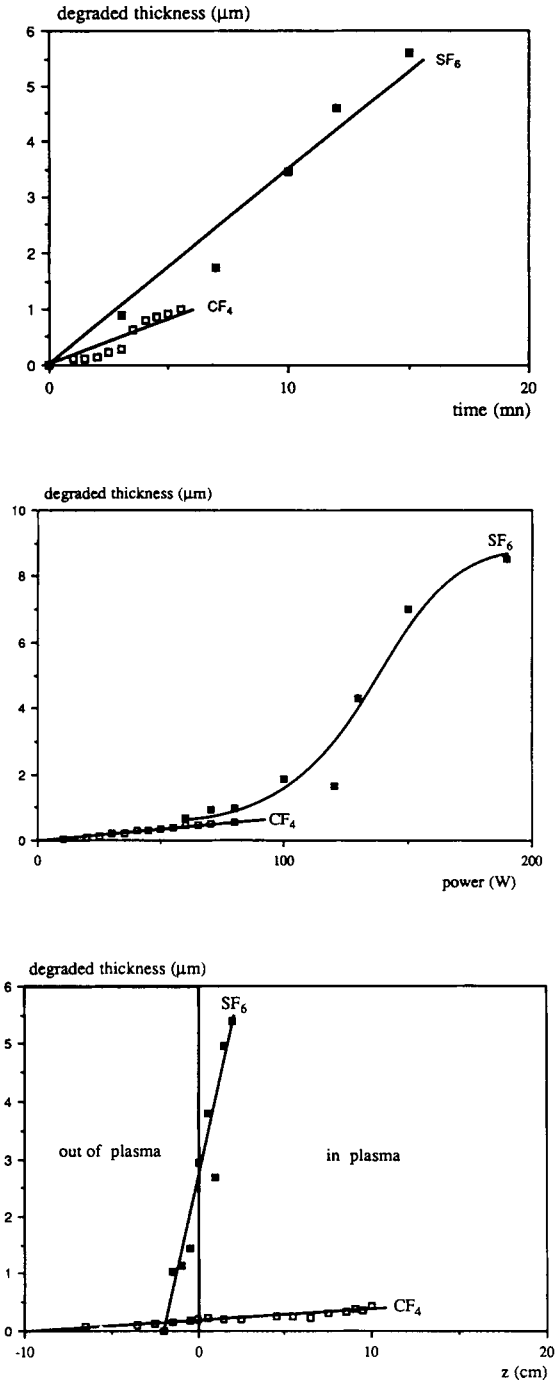


Figure 4 Dependence of degradation rate of cellulose acetate films on plasma parameters: degraded layer = initial thickness − final thickness = $(m_i/s.d) - (m_f/s.d)$, with s: surface of sample 15 cm^2, and d: cellulose acetate density: 1.3 (a) time (DSF_6 = 10 sccm, Pi = 100 W, l = 11 cm, z = 0 cm, p = 0.7 mbar, DCF_4 = 15 sccm, Pi = 40 W, l = 13.5 cm, z = 0 cm, p = 0.2 mbar); (b) power (DSF_6 = 10 sccm, p = 0.7 mbar, t = 5 mm, d = 8 cm, DCF_4 = 15 sccm, p = 0.2 mbar, z = 0 cm, t = 3 mn); (c) distance (DSF_6 = 15 sccm, p = 0.2 mbar, Pi = 40 W, t = 3 mn, l = 13.5 cm, DCF_4 = 15 sccm, p = 0.7 mbar, Pi = 40 W, l = 4 cm, t = 3 mn).

phane have been detected.[3] This could be explained by degradation with formation of volatile products of different chemical nature and in small quantities.

Influence of Functionalization

Characterization of this surface functionalization was by wettability measurements of ESCA analysis on cellulose acetate films and also on commercial hemodialysis membranes. An ATR–FTIR analysis approach will also be discussed.

On Water Adsorption

The CF_4 or SF_6 plasma treatments lead to a fluorinated layer. As it has a hydrophobic character, the layer should act as a barrier to hydrophilic liquid diffusion. The modified cellulose acetate film is an effective barrier to water adsorption [Fig. 5], the adsorption rate is divided by 3 when the sample surface is modified. As plasma modification takes place only on a thin layer (< 10 nm), it should say that water adsorption is a surface phenomenon.

On Surface Tension

Contact angle measurement can provide considerable insight into the character and properties of polymer surfaces, such as physical (surface polarity, group reorientation, and mobility) and chemical (new polar or apolar functions) interactions, even if some assumptions have to be made (the solid sur-

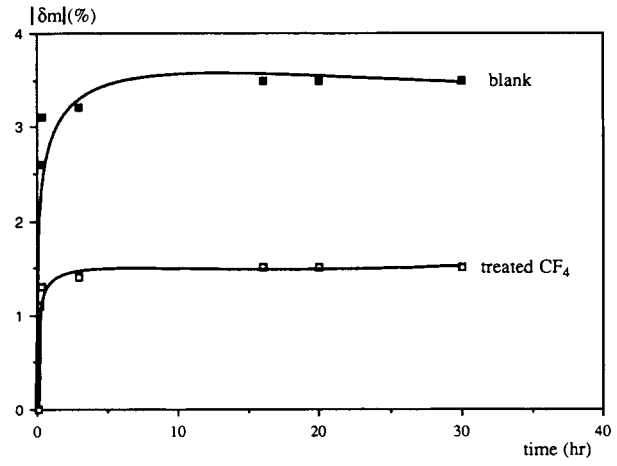


Figure 5 Dependence of the concentration of absorbed water in cellulose acetate treated: Iδm I = (initial weight of sample − final weight of sample)/initial weight of sample, DCF_4 = 15 sccm, Pi = 40 W, p = 0.2 mbar, t = 5 mm, l = 13.5 cm, z = 0 cm.

Table I Surface Tension and Its Dispersive Component (mJ/m²) of Modified Cellulose Acetate[a]

	CF_4		SF_6	
Time (mn)	E (mJ/m²)	E_d (mJ/m²)	E (mJ/m²)	E_d (mJ/m²)
0	49.1	38.3	49.1	38.3
1	56	50		
2	57	53.6	37.5	36.1
3	35.3	32.5	13.3	11.1
4	31.9	31.7	13.2	11.1
6	33.1	32.8	5.7	5.5
8	27.9	27.3	6.4	6.2
10	29.3	28.1	4.5	4.5
12			8.9	7.8
14			15.4	11.8
Power (W)	E (mJ/m²)	E_d (mJ/m²)	E (mJ/m²)	E_d (mJ/m²)
10	35.9	31.5	11.4	11
20	31.1	26.9	11.5	11.3
30	8.6	8.1	8.5	8.2
40	31.9	31.7	9.5	9.6
50	26.2	26.0	15.1	15.0
80	26.9	26.2		
z (cm)	E (mJ/m²)	E_d (mJ/m²)	E (mJ/m²)	E_d (mJ/m²)
+9.5	41.2	38.3		
+3.5	41.6	41.6		
+1.5			18.6	18.4
+1			8.1	7.7
0	31.9	31.7	13.2	11.1
−1			16.7	14.4
−2			20.2	14.8
−3.5	38.2	37.1		
−6.5	44.4	40.6		

[a] Same plasma as in Figure 6.

face must be rigid, highly smooth, and homogeneous).

The surface tension and its polar and dispersive components were calculated, but only the polar term variations with plasma conditions are represented in Figure 6 as it is the most important factor when a fluorination (creation of apolar groups on a polar surface) takes place. The other components have also been calculated: The dispersive one is relatively constant, whereas the global energy has the same evolution as the polar energy (Table I, Fig. 6) ($E = E_d + E_p$).

As shown by the degradation rate [Fig. 4(a), 4(b)], the SF_6 plasma treatment leads to a more drastic effect, and the polar surface tension decreases nearly to zero, more quickly than with CF_4 plasma when a higher duration or a higher power is applied [Fig. 6(a)–6(c)]. When the sample is in the afterglow zone or near the excitator, the polar energy is increasing again, showing a diminution of fluorination rate (when z is negative) or a degradation

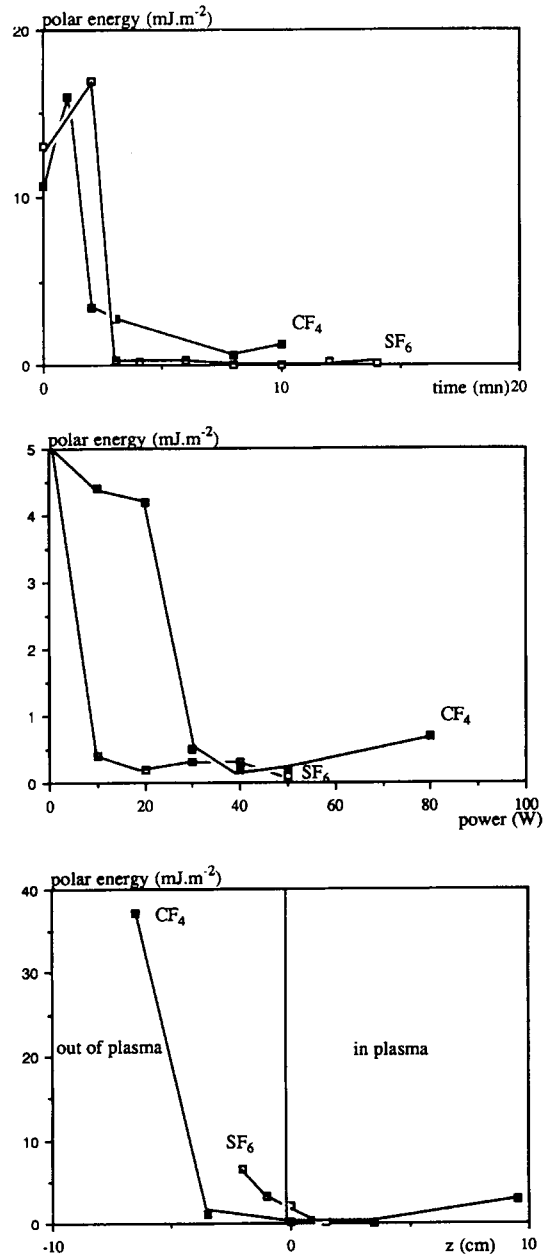
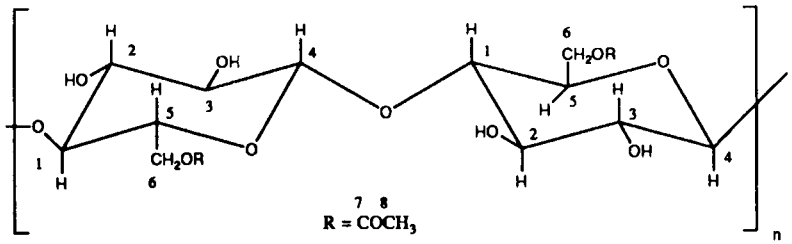


Figure 6 Dependence of surface tensions of cellulose acetate films on plasma parameters: (a) time (DSF_6 = 7 sccm, p = 0.8 mbar, Pi = 100 W, l = 4 cm, z = 0 cm D_{CF_4} = 15 sccm, P_i = 40 W, l = 13.5 cm, z = 0 cm; (b) power (D_{SF_6} = 7 sccm, p = 0.6 mbar, t = 3 mm, d = 3 cm, D_{CF_4} = 15 sccm, p = 0.2 mbar, z = 0 cm, t = 3 mn); (c) distance (D_{SF_6} = 7 sccm, p = 0.6 mbar, P_i = 100 W, t = 3 mn, l = 4 cm, D_{CF_4} = 15 sccm, p = 0.2 mbar, P_i = 40 W, l = 13.5 cm, t = 3 mn.

Table II Analysis of ESCA Spectra



Cellulose Acetate				Cellulose Acetate Treated in CF_4 Plasma[a]				Cellulose Acetate Treated in SF_6 Plasma[b]				Cuprophane				Cuprophane Treated in CF_4 Plasma[c]			
Peak	Group	E_L (eV)[d]	X%	Peak	Group	E_L (eV)[d]	X%	Peak	Group	E_L (eV)[d]	X%	Peak	Group	E_L (eV)[d]	X%	Peak	Group	E_L (eV)[d]	X%
	8, 2, 3	285.3			8, 2, 3	285.3			8, 2, 3	285.3			8, 2, 3	285.1			8, 2, 3	285.1	
	6, 1, 5	286.8			6, 1, 5	286.8			6, 1, 5	286.8			6, 1, 5	286.8			6, 1, 5	286.9	
	4, 7	289.1			4, 7	289.1			4, 7	289.1			4, 7	288.5			4, 7	288.5	
C_{1s}	C–CF_x		70	C_{1x}	C–CF_x	287.5	46	C_{1s}	C–CF_x	287.5	46.5	C_{1s}	C–CF_x		68.5	C_{1s}	C–CF_x	288.5	60
	CF				CF	288.0			CF	288.0			CF				CF	to	
	CF_2				CF_2	290.5			CF_2	290.0			CF_2				CF_2	292.3	
	CF_3				CF_3	292.2			CF_3	291.8			CF_3				CF_3	292.3	
O_{1s}		533.2	30	O_{1s}		534.8	15	O_{1s}		533.5	13	O_{1s}		531.2	31.5	O_{1s}		533.1	34
F_{1s}				F_{1s}		685.1	39	F_{1s}		689.1	40.5	F_{1s}				F_{1s}		686.6	6

[a] D_{CF_4} = 15 sccm, P_i = 50 W, p = 0.2 mbar, l = 13.5 cm, z = 0 cm, t = 5 mn.
[b] D_{SF_6} = 7 sccm, P_i = 100 W, p = 0.8 mbar, l = 5 cm, z = 0 cm, t = 10 mn.
[c] RF plasma, P = 500 W, t = 15 mn.
[d] Bond energy corrected of charge effect.

effect more important than the modification (when z is positive) as the ionic bombardment is increasing [Fig. 6(c)]. A duration of 2 min [Fig. 6(a)] or a power of 10 W (SF_6 plasma) or 30 W (CF_4 plasma) lead to a minimum polar surface tension.

On Surface Structure Determined by ESCA Analysis

The ESCA analysis has been performed not only on cellulose acetate films treated in CF_4 or SF_6 plasmas but also on cuprophane films treated in CF_4–RF plasma, this material being used as a hemodialysis membrane (Table II and Fig. 7).

The microwave plasma treatment induces a high fluorination yield [CF_4 plasma: 39% (F_{1s}), SF_6 plasma: 40.5% (F_{1s})]. The grafted fluorinated layer on the surface of cellulose acetate film is composed of a mixture of CF, CF_2, and CF_3 groups. As a consequence of the treatment, the oxygen concentration is decreased (15 instead of 30%).

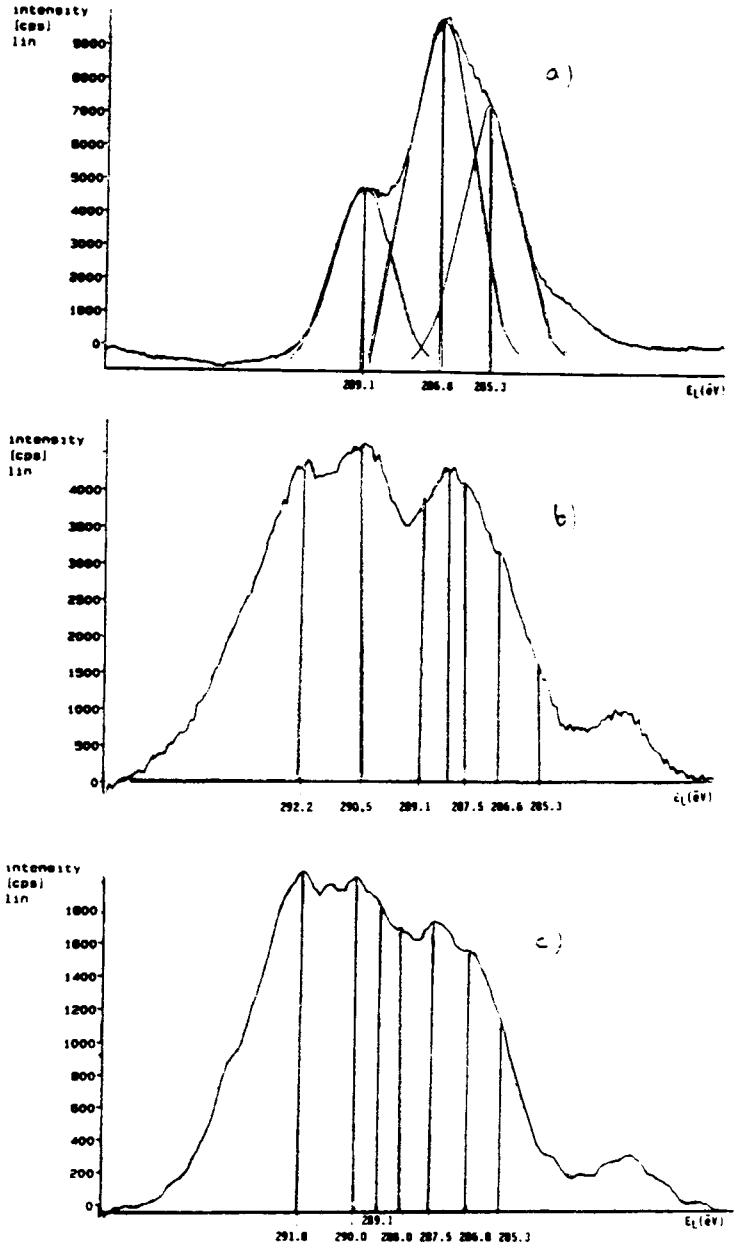


Figure 7 ESCA spectra of (a) cellulose acetate, (b) cellulose acetate treated in CF_4 plasma, (c) cellulose acetate treated in SF_6 plasma (same plasma conditions as in Table II).

The cuprophane film treated in RF plasma under such conditions and leading to a good hemodialysis test[3] has a fluorinated surface with a minor fluorine concentration (6%), but sufficient for a biomedical application. When changing the X-ray beam position from 0° to 50°, the fluorine concentration is nearly constant (6–8%); the subsurface is also modified. This treatment induces also an oxidation mechanism since the oxygen concentration is increasing, probably due to a postreaction or impurity interactions in the plasma phase.

Concerning the balance between concurrent reactions, degradation and fluorination, ESCA analysis can give the thickness of fluorinated layer (f):

$$f = \lambda \ln \frac{I_{C_{1s}} \text{ blank}}{I_{C_{1s}} \text{ treated}}$$

with λ = attenuation length of C_{1s} peak (λ = 1.6 nm using Mg Kα radiations), and I = intensity of C_{1s} peak.

The fluorinated layer thicknesses were found to be of the same order of 1 nm (0.88 nm in SF_6 cellulose acetate, 0.60 nm in CF_4 cellulose acetate, and 0.63 nm in CF_4 cuprophane). These results show that fluorinated layer deposition is a minor phenomenon in respect to degradation (0.7 μm in CF_4 atmosphere, 3.3 μm in SF_6 atmosphere).

On Surface Structure Determined by ATR–FTIR

The ATR–FTIR analysis is sometimes a simple and useful technique for surface modification characterization.[20,25,26] However, the complexity of the cellulose acetate film does not allow the direct application of such a spectrometric analysis. A derivation of modified and unmodified sample spectra emphasizes the appearance of new peaks that are not yet attributed. Further investigations are in progress not only on modified cellulose acetate and on use of FTIR and ESCA spectroscopy but also on model molecules and use of ESCA and SIMS spectroscopy and chromatography (SFC).

CONCLUSION

Modification of cellulose acetate films with CF_4 or SF_6 plasmas leads to a fluorinated layer. The modified materials can be used as a biomaterial (hemodialysis membrane), but this study emphasizes the importance of reactions concurrent to fluorination such as degradation. As for a biomedical application, by-products must be avoided. CF_4 plasma treatment seems to be well adapted for biomedical applications, rather than SF_6 plasma treatment, as degradation is a minor reaction. The plasma–material interaction mechanisms are not really cleared up and much work has to be carried out on plasma modification of model compounds of cellulose acetate.

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