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Surface properties of methacrylic copolymers containing a perfluoropolyether structure

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Abstract

New copolymers obtained by free radical copolymerization of methylmethacrylate (MMA) with a methacrylic monomer containing a perfluoropolyether structure (PFEUMA) were prepared. The products showed an excellent surface activity evidencing hydrophobic and lipophobic properties; the water contact angle of the films was always very high (>105°). Angle-dependent XPS analyses showed that the fluorinated monomer preferentially concentrates at the air surface and a fluorine gradient normal to the surface is present. A surface reorganisation was observed by changing the interface. The wettability increased when the films were dipped in water; after complete drying, the surface regained its hydrophobicity. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Methacrylate copolymers; Perfluoropolyether; Surface properties

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1. Introduction

Perfluorinated polymers show outstanding properties such as low surface tension, chemical inertness, thermal stability, together with a peculiar frictional, optical and electrical behavior [1]. The copolymerization of fluorinated with hydrogenated monomers allows us to obtain better processability reducing the cost. Several papers were published describing the preparation of new fluorinated copolymers and their properties [2–5]. Recently, some authors showed that a low amount of the perfluoroalkylethylmethacrylate monomer introduced in the chain is enough to lower the surface tension [4]. Other scientists obtained excellent results from a series of methacrylates with oligohexafluoropropeneoxide side groups having different length [6]. In fact it has been shown that the fluorinated groups are able to easily migrate to the surface and can form highly ordered layers having very low surface energy [7].

In the last few years, we obtained similar results investigating UV-cured acrylic networks [8–10] containing several fluorinated comonomers of the type $C_nF_{2n+1}R$–OCO–CH=CH$_2$ ($4 \le n \le 10$) at low concentration (<1% w/w). The films thus obtained showed a water contact angle higher than 100°, depending on the fluorinated monomer structure and its concentration. At the same time the bulk properties of the films were unchanged.

Moreover, interesting results were obtained studying the UV-curing of new difunctional and monofunctional methacrylic monomers having a perfluoropolyether structure [11,12]. When used as comonomers for hydrogenated acrylic systems, an excellent surface activity was observed even at a concentration lower than 0.5% w/w: advancing contact angles of 120° with water were measured [13]. The performance of these comonomers can be attributed to the perfluoropolyether chain, which is very flexible, highly apolar, hydro- and oleophobic without any crystallisation tendency [11].

Considering these points, the work was focused on the preparation of new copolymers with methylmethacrylate (MMA) and the monofunctional perfluoropolyether product (PFEUMA) having the following structure:

$$CF_3CF_2O\,(CF_2CF_2O)_m(CF_2O)_nCF_2CH_2OCONHCH_2CH_2\text{-}OCOC(CH_3){=}CH_2$$

where $m/n = 2$ and $M_n = 1079$. The copolymers were obtained in solution through a radical mechanism; they were used to prepare films whose surface properties were investigated.

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Table 1
Properties of the copolymers

Copolymer	% w/w PFEUMA in the copolymer	Intrinsic viscosity $[\eta]^a$ (dl/g)	T_{g1} (°C)	$T_{g2}{}^b$ (°C)
1	8.3	0.256	−121	+114
2	17.6	0.331	−130	+113
3	27.0	0.310	−120	+113
4	31.8	0.269	−129	+120

[a] In acetone, $T = 27$°C.

[b] T_g for the PMMA homopolymer = 116°C.

2. Experimental

2.1. Materials

PFEUMA monomer was synthesized on purpose through a series of complex reactions. The first step was the preparation of a peroxidic perfluoropolyether, by reacting tetrafluoroethylene with oxygen, in the presence of CF_3OF as an initiator. The obtained product consisted of a polymer chain where perfluoroether and peroxidic repeating units are randomly distributed. This product was subjected to catalytic hydrogenation; then it was treated with methanol, at room temperature, obtaining the ester derivative, which was reduced to the alcohol [14].

The raw product was a mixture of alcohol, diol and non-functionalized molecules. It was subjected to a chromatographic separation by using a column filled with silica gel [15]. Different fractions were collected; the product used in this work corresponds to the middle fraction having –OH functionality equal to 1.02, as confirmed by ^{19}F-NMR analysis. The fluorinated alcohol was reacted with isocyanate-ethyl methacrylate (EIM), according to the procedure described elsewhere [11]. The final product was fully characterized as reported in a forthcoming paper [16].

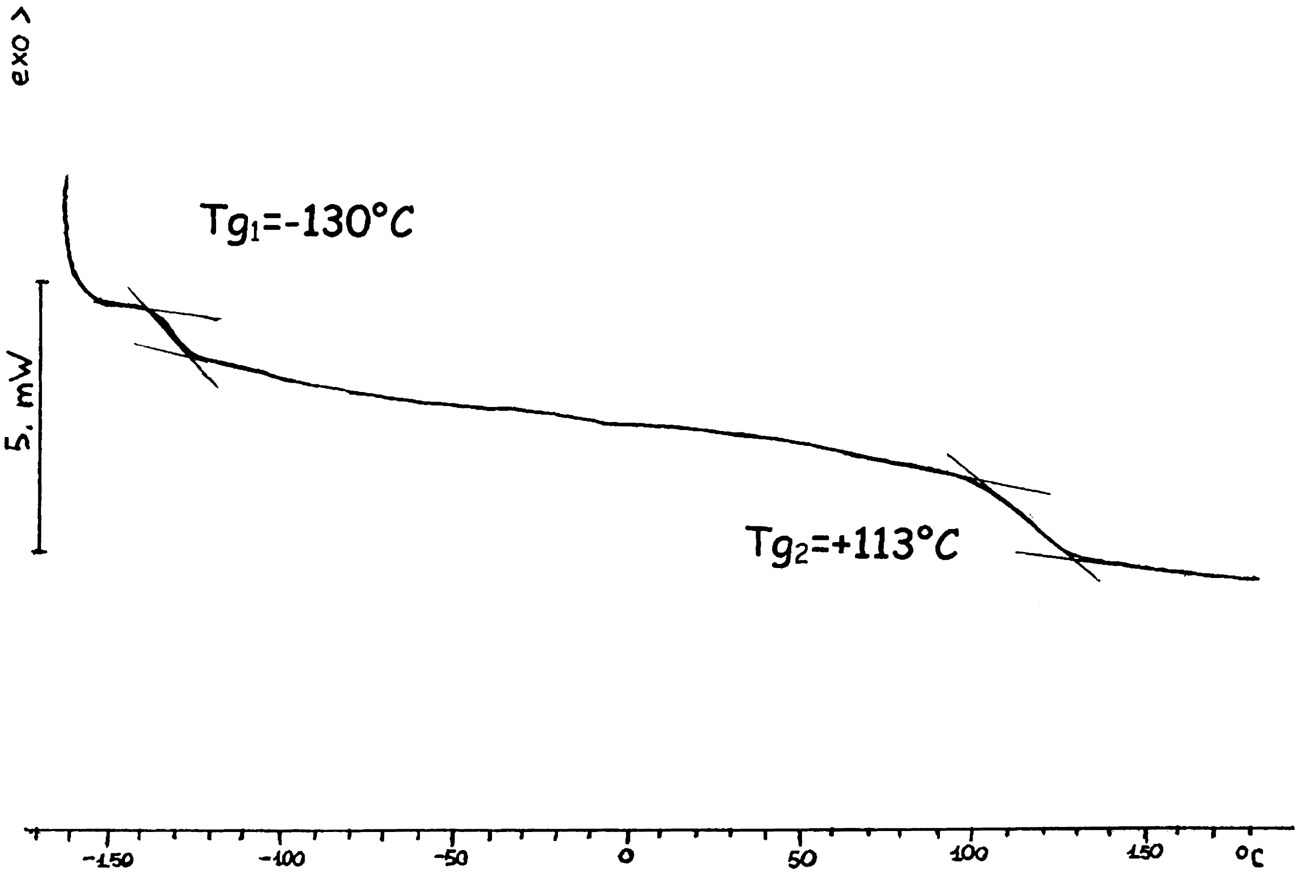

Fig. 1. DSC thermogram of MMA–PFEUMA copolymer (17.6% PFEUMA w/w).

Table 2
Water contact angle on the fluorinated copolymers

Copolymer	% w/w PFEUMA in the copolymer	θ_{adv}[a] (°)	θ_{rec}[b] (°)	Hysteresis (°)
PMMA homopolymer	–	80	60	20
1	8.3	109	57	52
2	17.6	106	66	40
3	27.0	111	59	52
4	31.8	105	56	49

[a] θ_{adv} = advancing contact angle.
[b] θ_{rec} = receding contact angle.

MMA (99%, Aldrich) was distilled under N_2. 1,1,2-trichlorotrifluoroethane (Delifrene), α,α,α-Trifluorotoluene (99.5%) and 2,2′-azobisisobutyrronitrile (AIBN) were purchased from Aldrich and used as received. The water used for the contact angle measurements was doubly distilled ($\gamma = 72.1$ mN/m at 20°C). The *n*-hexadecane (Aldrich) had a surface tension of 27.2 mN/m.

2.2. Polymerization reactions

The polymerization reactions were carried out in 50 ml glass bottles with Teflon-coated screw caps. The monomers were introduced into the bottles at the desired molar ratio and dissolved in 1,1,2-trichlorotrifluoroethane or trifluorotoluene obtaining homogeneous solutions. Then AIBN (0.8 mol% with respect to the monomers) was added and the solutions treated with N_2 for ca. 10 min. The bottles were introduced in a thermostatic bath and shaked at 60°C. The polymers were coagulated by addition of an excess of methanol, filtered and dried under vacuum. The monomer conversion was in any case less than 30%. The complete procedure is reported in a forthcoming paper [16].

2.3. Polymer characterization

The copolymers were characterized by elemental analysis of the fluorine. FTIR analyses were performed by means of a Mattson Genesis Series II Instrument. Viscosity measurements were performed with a Cannon–Fenske capillary viscometer; acetone was used as a solvent at 27°C.

DSC thermograms were recorded by means of a Mettler DSC 30 instrument, in the temperature range from −160 to 150°C with a heating rate of 20°C/min.

Table 3
n-Hexadecane contact angle on the fluorinated copolymers

Copolymer	% w/w PFEUMA in the copolymer	θ_{av}[a] (°)	θ_{rec} (°)	Hysteresis (°)
1	8.3	64	50	14
2	17.6	64	48	16
3	27.0	67	47	20
4	31.8	68	47	21

[a] θ_{av} for the PMMA homopolymer = 15°.

Table 4
Dependence of the contact angle on the film substrate for a PFEUMA/MMA copolymer (17.6% PFEUMA w/w content)

	θ_{av} (°)	
	Glass	HDPE
Air side	100	100
Substrate side	75	95

Table 5
Advancing contact angle (°) of the fluorinated copolymers as a function of the number of immersion cycles in water

No. of immersion cycles	θ_{av} (°)			
Copolymer	1	2	3	4
1° cycle	101	106	108	105
2° cycle	99	80	103	96
3° cycle	98	71	95	92

2.4. Film preparation

Thin films were prepared by dipping microscopy cover slides in the polymer solutions (1% w/v in acetone). The immersion rate was 20 μm/s. The films obtained were less than 1 μm thick, as determined by ellipsometry.

Thicker films (about 50 μm) were prepared by coating glass plates or HDPE substrates with the polymeric solutions (5% w/v) and drying them in air at 25°C for 24 h.

Before the coating procedure, the cover slides and the glass plates used as a substrate were treated at 500°C for a couple of hours, then carefully cleaned with acetone and dried.

2.5. Film characterization

Contact angle measurements were made by using a Cahn balance DCA322, according to the Wilhelmy technique at an immersion rate of 153 μm/s. Wettabilities were also measured with a Kruss G1 goniometer by means of the

Table 6
XPS data for the fluorinated film of a PFEUMA/MMA copolymer (17.6% PFEUMA w/w content)

	Fluorine concentration (F atom %)
Calculated value of the copolymer	3.87
Calculated value of the PFEUMA comonomer	39.1
Experimental value at t.o.a. = 10°	30.7
Experimental value at t.o.a. = 45°	16.7

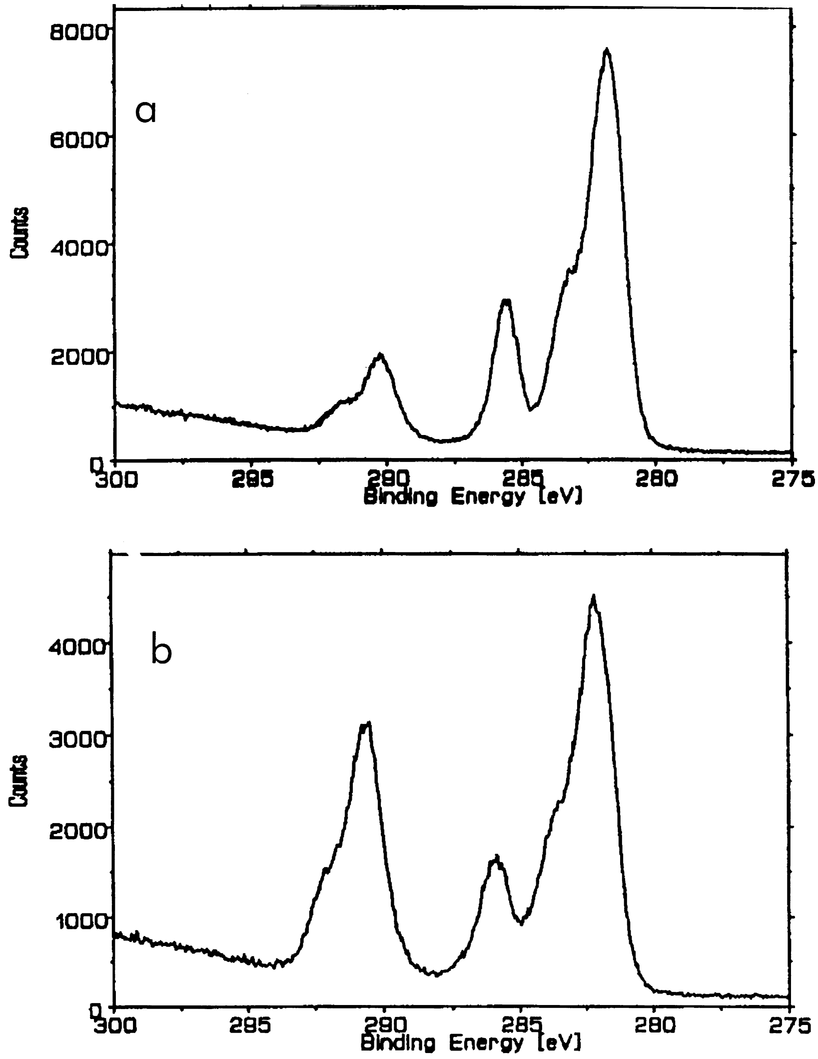

Fig. 2. XPS spectra, C1s signals: take-off angle = 45° (a) 10° (b).

sessile drop method. The solvents used were double distilled water and *n*-hexadecane.

When the films were subjected to a water treatment, the coated slides were dipped for a length of 12 mm in the liquid, at a rate of 30 μm/s and then withdrawn at the same speed. The cycle was repeated three times. After each cycle the contact angle was determined.

XPS spectra were recorded using a SCIENTIA ESCA 300 spectrometer, equipped with a high-power rotating anode and a monochromatized AlK_α X-rays source ($h\nu = 1486.6$) with high transmission electron optics and a multichannel detector. The electron take off angles (t.o.a.) selected for the analyses were 45 and 10° relative to the sample surface.

3. Results and discussion

3.1. Characterization of the PFEUMA–MMA copolymers

Typical copolymers were prepared by radical polymerization process in solution, by using either Delifrene or α,α,α-trifluorotoluene as solvent [16]. The solubility of the copolymers was checked by direct observation of the transparency of the solutions. Acetone, MEK, fluorinated solvents were found to be the best solvents. These results indicate the true copolymeric nature of the products: in fact acetone and MEK are the typical solvents of PMMA, but do not solubilize the fluorinated polymers; Delifrene and α,α,α-trifluorotoluene, on the contrary, are compatible with the fluorinated polymers.

Viscosity measurements were performed on the copolymer solutions in acetone: their specific viscosity showed a linear dependence on the concentration. The data of the intrinsic viscosity are given in Table 1.

As far as the thermal properties are concerned, all the copolymers show two distinctive glass transition regions indicating their biphasic structure. Two glass transition values were obtained: T_{g1}, at very low temperature, corresponds to the fluorinated segments; T_{g2}, which is related to the hydrogenated moieties, is close to that of the pure

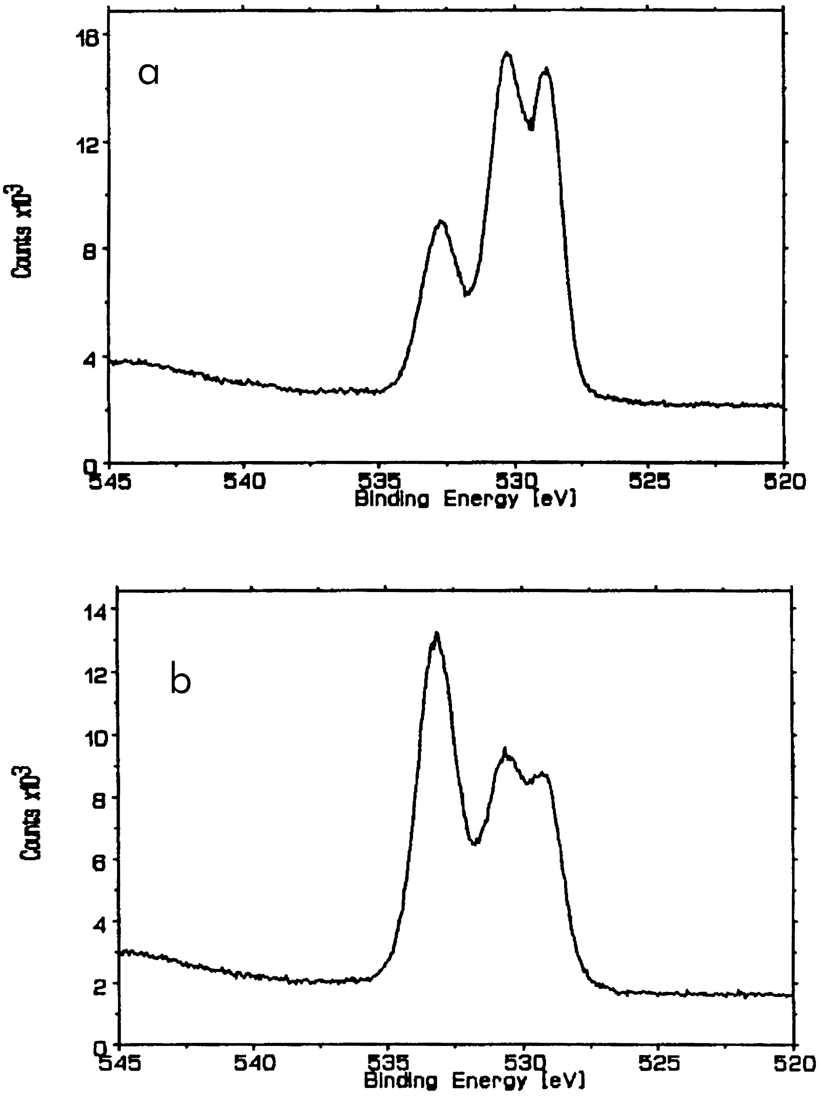

Fig. 3. XPS spectra, O1s signals: take-off angle = 45° (a) 10° (b).

PMMA (Table 1). In Fig. 1, a typical DSC thermogram of a copolymer containing 17.6% PFEUMA w/w is reported: the presence of the two afore-cited glass transitions is evident. A similar biphasic structure is already present in the PFEUMA monomer thermogram, which will be described elsewhere [16]. Moreover, it was also observed in other fluorinated copolymers containing perfluoropolyether chains [5,11].

The results of Table 1 indicate that the T_g values of the fluorinated and hydrogenated phases are independent on the copolymer composition and similar to the values obtained for the homopolymers. They indicate the absence of miscibility between the two phases.

3.2. Film preparation and surface properties evaluation

Thin films (less than 1 μm) of the different copolymers were prepared through the dip coating technique. The films were perfectly transparent. Therefore, as the products have a biphasic structure and the fluorinated and hydrogenated segments have very different refractive indices, their transparency suggests that the dimensions of the separated domains (containing fluorinated structures) are smaller than the visible light wavelength (nanophases).

Interesting results were obtained by the investigation of the surface properties of the films. In Tables 2 and 3, the results of contact angle measurements with water and hexadecane are collected. They show that the surfaces are, respectively, highly hydrophobic and oleophobic.

With a typical copolymer having 17.6% PFEUMA w/w content, some thick films were prepared by solvent casting, using acetone solutions (5% w/v). The substrate used was either a glass slide or a HDPE plate. The films were peeled off the substrate and the contact angles were measured on both sides (Table 4). The contact angle measured on the polymeric surface in contact with glass has a value close

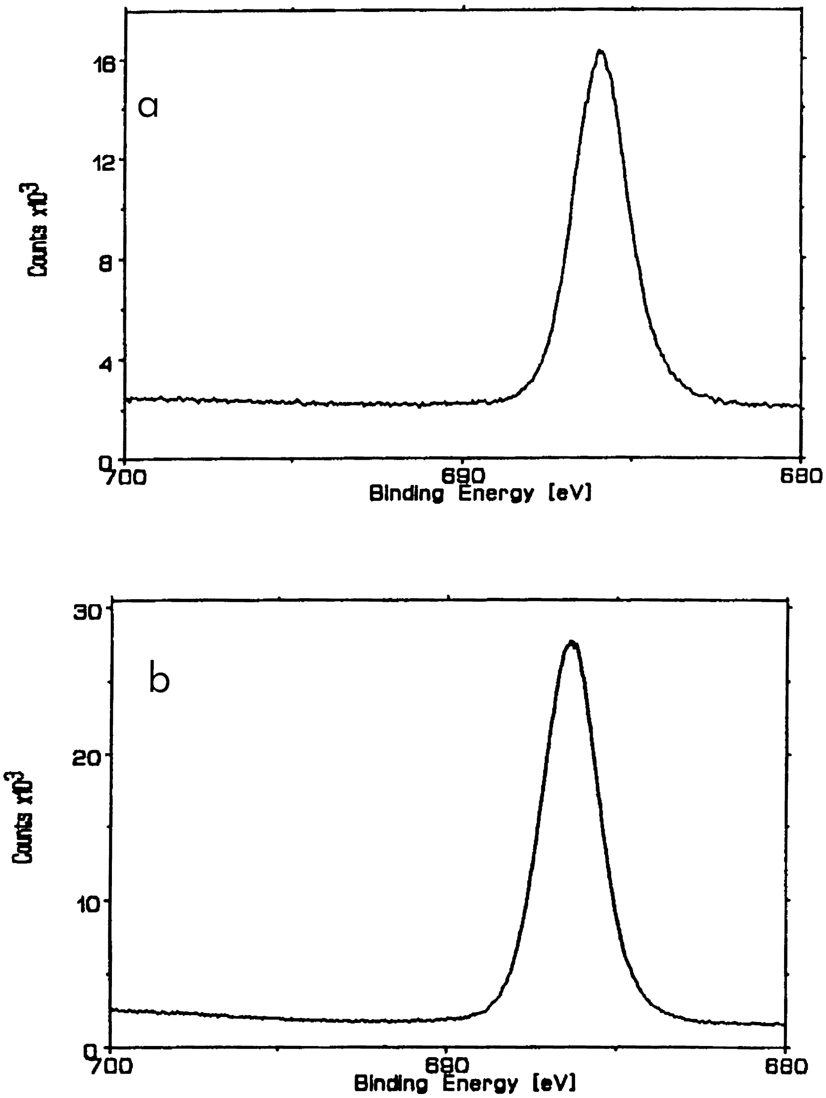

Fig. 4. XPS spectra, F1s signals: take-off angle = 45° (a) 10° (b).

to the pure PMMA, while the opposite side is found very hydrophobic. By using a non-polar material, such as HDPE, both sides of the film are hydrophobic. We can conclude that the substrate influences the film wettability depending on its polarity [8].

The surface composition can also change when in contact with different environments. This phenomenon is discussed in the literature [17].

Table 5 gives the results obtained measuring the wettability of the copolymeric films after a different number of cyclic immersions in water. We can note that, by increasing the number of immersions, the contact angle decreases. Therefore, a change of the surface properties of the copolymers occurs when the films are dipped in water. After drying, the films slowly regain their hydrophobicity, meaning that the surfaces rearrange and expose again the fluorinated units toward the air interface.

3.3. XPS investigation

The surface composition of the film obtained from the copolymer containing 17.6% PFEUMA w/w was determined by means of an XPS analysis. The survey spectra obtained at two different take-off angles reveal as expected the photoelectronic peaks of carbon, nitrogen, oxygen and fluorine [18]. The C1s peak in the spectrum recorded at a take-off angle of 45° (Fig. 2a) shows three main components corresponding to the aliphatic and the α-carbon atoms and to the CF_2 and CF_3 contributions. The intensity of the signals changes when the C1s spectrum is recorded at t.o.a = 10° (Fig. 2b): there is a strong enhancement of the component due to the fluorinated carbons at higher binding energies. Moreover, the shoulder of this signal, assigned to the perfluoromethyl group [12], increases and indicates its preferential concentration at the very surface of the air-side of the film.

Concerning the O1s spectra at t.o.a. = 45° and t.o.a = 10° (Fig. 3a and b, respectively), both show two distinctive signals corresponding to the oxygen of the hydrogenated segments (at lower binding energy) and to the OCF_2 units of the perfluoropolyether chain. The ratio between the intensity of the two peaks decreases in moving towards the surface (t.o.a = 10°), evidencing the predominance of the fluorinated monomer.

Also the fluorine signal present in the spectra recorded at different t.o.a. (Fig. 4a and b) shows the existence of a gradient in the concentration of the PFEUMA. The quantitative analyses are reported in Table 6: a concentration gradient from the surface towards the bulk is evident, the surface enrichment in fluorine is nearly of one order of magnitude and corresponds to a surface concentration of the monomer equal to 78% w/w. The results are in agreement with those recently obtained by investigating UV-cured films containing small amounts of perfluoropolyether structures [12].

4. Conclusions

The characterization of the MMA–PFEUMA copolymers clearly indicates their biphasic structure, which consists of fluorinated domains dispersed in the hydrogenated matrix. The films formed were completely transparent, indicating the presence of nanophases. The surfaces of the copolymers were found very hydrophobic and lipophobic, indicating the selective concentration of the fluorinated segments at the air surface, as confirmed by XPS analysis. Surface reorganization phenomena were observed in contact with water; the surface properties changed as a function of the environment to which the films were exposed. These modifications were found reversible; they can be attributed to the high mobility of the perfluoropolyether chain in the PMMA matrix.

Acknowledgements

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