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XPS studies of directly fluorinated HDPE: problems and solutions

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Abstract

X-ray photoelectron spectroscopy (XPS) applied to the study of fluorinated polymer surfaces presents several problems related both to peak assignment and to degradation. In this work, we analyse extensively the question of XPS peak assignments in this kind of surfaces. We conclude that in this kind of surfaces using binding energy differences between fluorine and carbon is better than using absolute binding energies. Also a useful relation between fluorine photoelectron energy vs. polymer composition expressed through the atomic ratio fluorine/carbon (F/C) was found. A protocol for data treatment is proposed and applied to a XPS study of the degradation induced by X-ray on high-density polyethylene surfaces modified by direct fluorination. Results obtained for the degradation, namely the atomic ratio F/C obtained by two different methods, combined with angle resolved X-ray photoelectron spectroscopy (ARXPS) were used to study the fluorine concentration profile in depth, producing self-consistent results.

1. Introduction

Interest on surfaces, knew a huge increase in the last 40 years [1,2]. Applications demanding thorough physical and chemical characterizations of surfaces include the fabrication of composite materials, semiconductor technology, biocompatible prosthesis, protection against corrosion, increase of impermeability, etc.

In order to understand real surfaces, a large number of techniques to create model organized films (monocrystalline thin films [3], self-assembled layers [4], namely Langmuir–Blodgett films [5]) and amorphous films (made by spin-coating, dipping, vacuum evaporation, etc.) were developed. And so were the techniques to modify/functionalise surfaces. For many applications, a decrease of surface energy is needed. For organic surfaces, this may be achieved by fluorination, direct (F_2 gas) or indirect [6] during which some of the hydrogen atoms are replaced by fluorine ones. The direct fluorination of polymers may be performed during blowing—in-line fluorination—or after moulding—post-mould fluorination.

One of the most powerful techniques to characterize

surfaces is the X-ray photoelectron spectroscopy (XPS), which may detect a few tens of molecular layers. However, one of its limitations is the degradation that X-rays may induce in organic materials especially in halogenated species, as is the case in fluorinated surfaces. Literature reports a lower degradation for the fully fluorinated polymer (polytetrafluoroethylene, PTFE, $(CF_2CF_2)_n$) when compared with the less fluorinated polymers as, for instance, the polyvinylfluoroethylene, PVF, $(-CHFCH_2-)_n$ [7]. However it is never zero. This limitation may be very awkward in the case where information about the elemental concentration as a function of depth is needed. In fact, XPS can be used in an angle resolved mode (ARXPS): spectra are acquired in several directions relative to the sample surface (take-off angle, TOA). As TOA decreases, a lower depth is sampled and, from the analysis of the evolution of spectra intensity as a function of TOA, relative concentration profiles for the elements present in the analysed film can be deduced at least qualitatively [8]. A relative XPS intensity decreasing (increasing) with decreasing TOA, is indicative of a concentration decreasing (increasing) towards the surface. Spectra acquisition for several take-off angles requires a long time of irradiation inducing necessarily some degradation. Therefore, the evolution of intensity as a function of TOA is the result of two effects. This may lead to

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erroneous interpretations of data if the degradation is not taken into account. For instance, for a 'post-mould' fluorinated film, where a fluorine concentration decreasing with depth or at least constant is expected, ARXPS results were compatible with a decreasing concentration towards the surface [9]. Authors assign this result to the influence of degradation of surface by the fluorination agent itself but, in fact, it may simply be due to a X-rays induced degradation of the fluorinated surface.

Another problem associated to the XPS analysis of polymer surfaces comes from the low electric conductivity of samples leading to surface charging. For unknown composition of insulating samples, the search for sound binding energy reference is difficult. A method usually employed is the partial coating of the surface with a very thin layer of gold and taking the Au 4f7/2 peak at 84 eV to correct for surface charging [10]. However, this method does not take into account the contact potential between the gold and the surface to be studied. This may introduce an error of the order of several tenths of eV [11]. The use of a 'flood gun' to neutralize the charge may increase the degradation of the surface and, any way, there is always a need of a binding energy reference [7].

In this work, XPS peak assignments are extensively discussed especially the relation between the fluorine photoelectron energy and the polymer composition. A protocol of data treatment is proposed and applied to a XPS study of degradation induced by X-ray on high density polyethylene (HDPE) surfaces modified by post-mould direct fluorination. Results obtained for the degradation combined with angle resolved X-ray photoelectron spectroscopy (ARXPS) are used for studying the fluorine concentration profile in depth for a same sample producing self-consistent results.

2. Experimental

The samples studied here were supplied by Ciba and by Solvay. They consisted of plaques of virgin HDPE 'post-mould' fluorinated in a home-made fluorination line as described elsewhere [12].

The XPS here used was a XSAM800 (KRATOS) X-ray Spectrometer operated in the fixed analyser transmission (FAT) mode, with a pass energy of 10 eV and the non-monochromatized Mg K_α X-radiation ($h\nu = 1253.7$ eV). Typical operating parameters were 13 kV and 10 mA, i.e. 130 W. Samples were analysed in ultra high vacuum (UHV), and typical base pressure in the sample chamber was in the range of 10^{-7} Pa. All sample transfers from the fluorination reactor to the analysis chamber were made under a nitrogen atmosphere. Samples were analysed at room temperature, at take-off angle relative to the surface (TOA) of $90-30°$. Spectra were collected with a step of 0.1 eV, and $60-90$ s of acquisition by sweep, using a Sun SPARC Station 4 with Vision software (Kratos). The curve

fitting for component peaks was carried out with a non-linear least-squares algorithm using Voigt profiles and Shirley background. Contributions for the spectra coming from the X-ray source satellites were also subtracted. No charge compensation was used. Binding energies were corrected by using a method described in Section 3 and based on the fact that fluorine binding energy is a function of the F/C ratio in fluorocarbon polymers. Studied photoelectron regions were C 1s and F 1s. For quantification purposes, sensitivity factors were 1 for F 1s and 0.25 for C 1s photoelectrons.

3. Results and discussion

3.1. Charge shift, fluorine behaviour and peak assignment

XPS peak assignment is usually based on absolute binding energy values. For charged samples, correction for charge shifts is needed. The use of external references (aliphatic carbon contamination, casual or on purpose) or spots of gold or silver poses problems as referred above (see Section 1). It is preferable to choose an internal reference. In the case of the present work, fluorine or one of the carbon components could be a good choice. Let us analyse with some detail the characteristics of XPS F 1s and C 1s regions to make the correct choice.

In Fig. 1, XPS C 1s and F 1s spectra for the surface of a post-mould fluorinated HDPE film (~ 1 mm thick) are shown.

The first striking difference between both regions is the fact that F 1s peak is very symmetrical and fittable with just a component, whereas in the C 1s region we can, by simple visual inspection, fit at least four components (the best fitting was achieved with five components as shown below in Fig. 4). This behaviour of the F 1s peak is a quite general one. In the literature [7], even for copolymers having fluorine atoms in quite distinct neighbourhoods, F 1s peak is always fittable by a single component (with comparable FWHM) whereas the C 1s peak needs as much components as the number of different neighbourhoods in the polymer. However, in different polymers, fluorine has different binding energies.

Table 1 shows the C 1s and F 1s binding energies (BE) values found in literature for the most common fluorinated polymers and shows a single value for the F 1s binding energy for each of them.

This behaviour of F 1s peak in copolymers is quite unexpected since partial charges calculations for copolymers using the most popular methods of calculation (see Appendix A for detailed explanation) yield different partial charges for fluorine in different neighbourhoods in a same copolymer. It seems that fluorine, due to its large electronegativity and small volume, presents important intermolecular neighbouring effects absent in the case of other atoms.
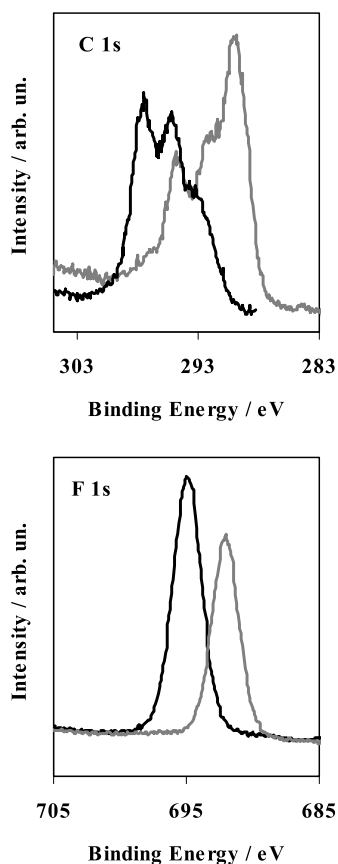
Fig. 1. Raw XPS C 1s and F 1s regions without charge shift correction for samples freshly introduced in the chamber (black line) and after 330 min of irradiation (gray line). Satellites were subtracted.

A parameter that measures the richness of the medium in fluorine and may be a good measure of the intensity of neighbouring effects is the atomic ratio F/C. From Table 1, we may verify that, for non-oxygenated polymers, $BE_{F\ 1s}$ is correlated to the degree of fluorine contents in the polymer i.e. with the F/C ratio as shown in Fig. 2.

The line defined by the three empty squares in Fig. 2 has the equation:

$$BE_{F\ 1s} = -0.6(F/C)^2 + 3.32(F/C) + 685.43. \tag{1}$$

Since in surfaces here studied the contents of oxygen are

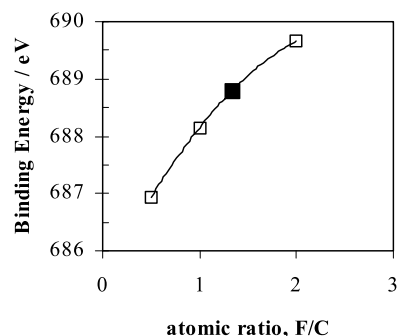Fig. 2. F 1s binding energy (□) as a function of atomic ratio F/C for polymers 1, 2 and 3 in Table 1. The full square is the point corresponding to VITON and fits exactly with the value predicted by Eq. (1).

negligible when compared to the fluorine and carbon contents, we may apply Eq. (1) as a polynomial interpolation to them. This allows deducing $BE_{F\ 1s}$ for each surface from the measured XPS F/C ratio, provided that the XPS F/C ratio is between 0.5 and 2. The difference between the value so computed and the experimentally measured one gives us the charge shift, which is then taken to correct the entire spectrum, namely the C 1s region.

However, even with the charge correction, the assignment of C 1s components is not easy given the large spread of binding energy for a given group.

In Table 2, differences between C 1s and F 1s binding energies are presented. This quantity shows to be a more useful tool for group identification since it is not affected by the charging of the sample. When a single fluorine atom is bound to a carbon atom, that difference is around 399 eV whereas for the carbon bound to two fluorine atoms, that difference decreases about 2 eV. For carbon bound to three fluorine atoms or two plus a very electronegative atom (oxygen, for instance) another decrease of about 2 eV occurs for that difference and, finally, for carbon bound to three fluorine atoms plus a very electronegative atom, another decrease of about 1 eV occurs. This is a tool that may be very important to assign the origin of the different components in the C 1s region especially when there is no reason to believe that a measurable amount of CH_2 sequences remain after fluorination to serve as a reference

Table 1
C 1s and F 1s binding energies values in eV for the most common fluorinated polymers [7]. Binding energy for fluorine in copolymers are presented in bold characters

	OCF_3	OCF_2	CF_3	CF_2	CF	CH_2	F	F/C
$(-CHFCH_2-)_n$					287.91	285.74	686.94	0.5
$(-CF_2CH_2-)_n$				290.9		286.44	688.15	1
$(-CF_2CF_2-)_n$				292.48			689.67	2
VITON[a]			293.86	291.77, 291.23[b]	289.82	286.77	**688.8**	1.333
$(-CH_2CH(OC(O)CF_3)-)_n$			292.65				**688.15**	0.75
FOM[c]	295.19	294.09	293.80	293.23	291.4		**689.08**	

[a] $(-CFCF_3CF_2-)_n(-CF_2CH_2-)_n$ with $x/y = 1/3$.
[b] The first value concerns the CF_2 groups in the perfluorinated block of the copolymer.
[c] $CF_3[(-OCFCF_3CF_2-)_n(-OCF_2-)_m-]_xOCF_3$.

Table 2
Differences between F 1s and C 1s binding energies, in eV, for polymers in Table 1

	OCF$_3$	OCF$_2$O	CF$_3$	CF$_2$	CF	CH$_2$
(−CHFCH$_2$−)$_n$					399.03	401.2
(−CF$_2$CH$_2$−)$_n$				397.25		401.71
(−CF$_2$CF$_2$−)$_n$				397.19		
VITON			394.94	397.03, 397.57[a]	398.98	402.0
FOM	393.89	394.99	395.28	395.85[b]	397.68[c]	

[a] The first value concerns the CF$_2$ groups in the perfluorinated block of the copolymer.
[b] In this polymer the group is really OCF$_2$C.
[c] In this polymer the group is really OCF(CF$_3$)CF$_2$.

(BE(C $1s_{CH2}$) = 285 eV). Moreover, fluorinated surfaces are not easily contaminated by hydrocarbons and anyway the problem of the contact potential remains.

Nevertheless, it is challenging trying to find absolute values for binding energies and, even with the assigning problem solved, attempts will be done for correcting BE for the charge shift based on Eq. (1).

However, a problem exists with the F/C ratio. In fact, F 1s photoelectrons have a smaller kinetic energy than C 1s photoelectrons and, therefore, give information about a smaller film thickness than the C 1s ones. For a situation where a non-constant concentration profile in depth is expected to exist, the F/C ratio computed by using the F 1s and C 1s areas and respective sensitivity factors do not represent the real average F/C ratio. Moreover, this ratio will also be distorted by the presence of surface contaminants and surface roughness. We can also compute the F/C ratio using exclusively the C 1s region. This will produce, in principle, a more realistic average value for F/C ratio. Let us take C 1s peak in Fig. 1. Its components have binding energies 403, 401.7, 399.7, 397.3 and 394.8 eV lower than the F 1s binding energy. From Table 2 we could assign the first (C 1s1) and second (C 1s2) components to CH$_2$ group in neighbourhoods poor and rich in fluorinated carbons respectively, the third one (C 1s3) to a CHF group, the fourth one (C 1s4) to a CF$_2$ group and the fifth one (C 1s5) to a CF$_3$ group. This allows us to compute a new F/C ratio F/C (C 1s):

$$F/C(C\ 1s) = f(C\ 1s3) \times 1 + f(C\ 1s4) \times 2 + f(C\ 1s5) \times 3 \quad (2)$$

where $f(C\ 1sx)$ is the ratio between the C 1sx component area and the total C 1s region area. The methodology here described for data treatment will be applied to the X-ray induced degradation of HDPE samples and its soundness tested.

3.2. X-ray induced degradation studies

For this study, a 'post-mould' fluorinated sample was used. A series of 76 spectra with an acquisition time of about 4 min were recorded keeping the sample position relative to the analyser at constant TOA = 90°. In each spectrum two regions were acquired—C 1s and F 1s—for about 2 min. The duration of X-ray irradiation was around 323 min. Fig. 1 shows XPS C 1s and F 1s regions for the sample freshly

introduced in the chamber and for the same sample after about 330 min of X-ray irradiation.

The first observation is a confirmation that, independently of the film composition measured by the atomic ratio F/C, a single, symmetrical F 1s peak was obtained. Its FWHM has a small decrease but very small compared to the change in F/C.

In Fig. 3, the change in binding energy and FWHM for the F 1s peak as a function of irradiation time are shown.

C 1s region was fitted with five peaks as shown in Fig. 4.

The difference between its binding energies and $BE_{F\ 1s}$ as a function of irradiation time is shown in Fig. 5.

From Fig. 5 and Table 2, we can easily identify C1 and C2 as CH$_2$ groups, C3, C4 and C5 as mono-, di- and trifluorinated carbons, respectively. This allowed computing ratio F/C (C 1s) as described above. Following the procedure described in the Section 3.1, the charge shifts were computed. Fig. 6(a) and (b) shows the evolution of the charge shift and the global F/C and F/C (C 1s) ratios as well as their ratio as a function of the irradiation time.

It is noticeable the decrease of charge shift as the sample loses fluorine. Qualitatively, it is an acceptable result since both the surface and the bulk resistivity are larger in PTFE than in HDPE [13,14]. However, an experiment made with another sample, covering two corners of the surface with silver, one in electrical contact with and the other one without electrical contact with the sample holder, yielded a constant difference between the two Ag $3d_{5/2}$ peaks (of 6 eV corresponding to the sum of the charge shift plus the contact potentials between silver and the polymer surface) showing that the charge shift is constant during irradiation. Thence,
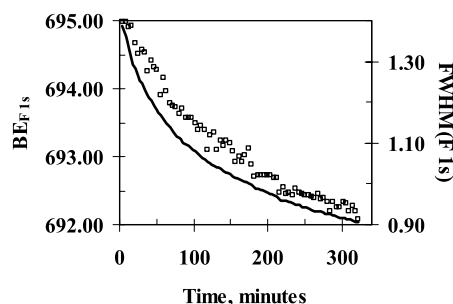

Fig. 3. Binding energy (full line) and FWHM (empty squares), in eV, for the F 1s peak as a function of irradiation time.
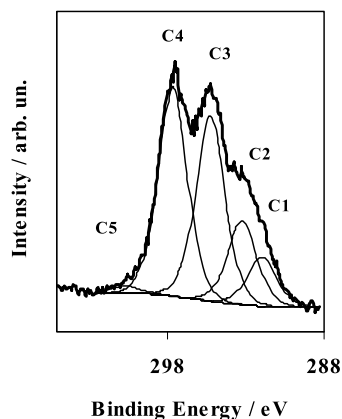
Fig. 4. XPS C 1s region (bold line) fitted with five components (normal line).

all the variation of F 1s binding energy must be ascribed to chemical shift. This means that either Eq. (1) does not describe correctly the variation of BE (F 1s) as a function of F/C or the F/C to be used is none of those here proposed. In fact, as we mentioned above, F 1s signal comes from shallower layers than carbon signal. It is expectable that the large variations of F/C occur near the extreme surface. Variations of F/C ratios are, in principle, much slower if they are averaged over a large depth than if they are averaged over a few layers near the surface. In fact, the escaping of fluorine atoms from the polymer is much faster near than far from the surface. That is precisely what is suggested by these results: F/C averaged over the mean depth from where the F 1s comes, should vary much more than values in Fig. 6(b) for, assuming Eq. (1) as valid, having a larger variation of $BE_{F\ 1s}$ as a function of time and, thence a constant charge shift. The method for calculating chemical shifts based on F/C ratio needs, then, homogeneous composition in depth to be applied.

The other interesting result is that F/C ratio is always larger when computed from the C 1s and F 1s regions than when computed from C 1s region alone. This is a clear indication that a fluorine concentration profile decreasing with depth exists having a typical dimension lower than the order of the magnitude of the maximum XPS analysis depth
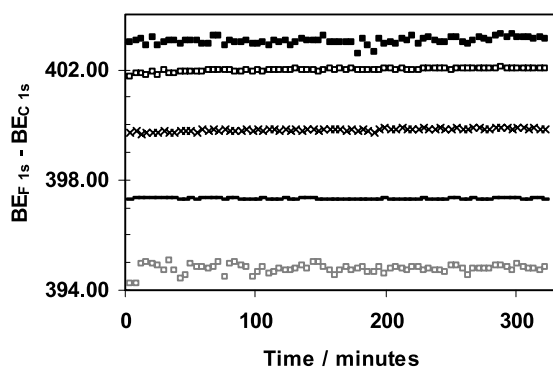

Fig. 5. $BE_{F\ 1s} - BE_{C\ 1sx}$ as a function of irradiation time. From top to bottom x = 1 to 5.
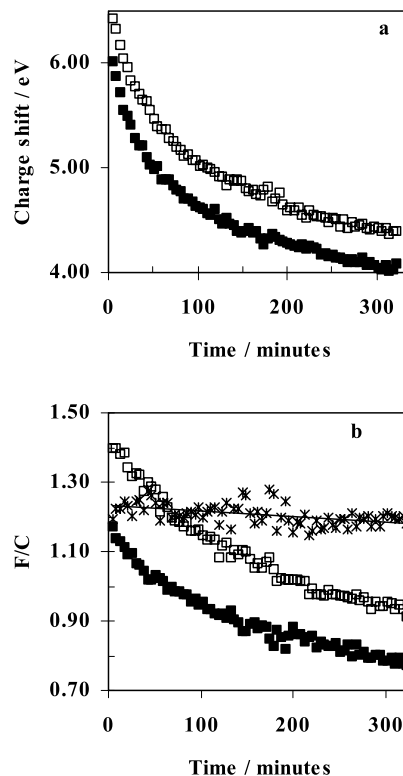

Fig. 6. (a) Charge shift as a function of irradiation time for F/C ratio computed from F 1s and C 1s areas (□) and from F/C ratio computed exclusively from C 1s region (■). (b) F/C ratio computed from F 1s and C 1s areas (□); computed exclusively from C 1s region (□); ratio between F/C and F/C(C 1s) (∗). A line was fitted to these last points giving the relation $y = 0.00016x + 1.2306$.

(~ 100 Å). We can even estimate that order of magnitude from the ratio between the two values.

Assuming that (i) fluorination does not change the number of carbon atoms per volume unit in the film; (ii) the concentration profile in depth (x) of monofluorinated (C_m), difluorinated (C_d) and trifluorinated carbon atoms (C_t) is proportional to $\exp(-x/l)$ where l is the typical dimension of the fluorinated layer, the same for all the profiles, we can find

$$\frac{\text{F/C}}{\text{F/C(C 1s)}} = \frac{\lambda_C + l}{\lambda_F + l} \tag{3}$$

where λ_C and λ_F are the effective attenuation length of the C 1s and F 1s photoelectrons, respectively. Taking for approximate values of λ_C and λ_F the inelastic mean free path computed from an expression proposed by Tanuma et al. for polyethylene [15]

$$\lambda = 0.14E^{0.79} \tag{4}$$

we get $\lambda_C = 31.2$ Å and $\lambda_F = 20.5$ Å.

This gives for the order of magnitude of the fluorinated layer thickness values ranging from 27 Å at the beginning of the analysis to 39 Å at the end. This increase in the order of magnitude of the depth with irradiation time is an evidence for a fluorine concentration profile decreasing towards the

bulk in the beginning. With the depletion of fluorine in the layers at the surface, the profile becomes more uniform and, thence, at larger times of irradiation it is characterised by a larger parameter *l*.

Finally, average composition of film as a function of irradiation time is shown in Fig. 7.

This quantitative analysis shows that the amount of trifluorinated carbon (C5) remains almost constant during the irradiation. There is just a small increase in the early stages of irradiation. The monofluorinated carbon (C3) has a small decrease in the beginning but keeps constant for larger irradiation times. Inversely, difluorinated carbon (C4) amount decreases monotonically with time. Concomitantly, a large increase in the amount of unfluorinated groups (C2 + C1) occurs. These results show that, at least after the first minutes, for each carbon a single bond is destroyed transforming difluorinated carbon into monofluorinated and monofluorinated into unfluorinated at the same rate. During the first minutes, the decreasing of the amount of monofluorinated carbon suggests that its degradation is faster than the degradation of difluorinated ones confirming literature results. After the first minutes, the constancy of the amount of monofluorinated carbon shows that a balance exists between the rate of disappearance of CF species and of appearance both by degradation of CF_2 species or by recombination of C and F radicals.

3.3. Angle resolved XPS

As already mentioned in Section 1, this kind of studies although very useful to know the elements and/or functional groups concentration profiles, may give misleading results when the X-irradiation induces degradation. One method of avoiding the degradation interference on ARXPS results could be the prior degradation study of the sample. The relative amount of a given element or group disappearing by degradation at a given time should be added to the amount measured in the ARXPS experiment after the same time (dose) of exposure. The problem with this methodology for the kind of samples here studied is that they are heterogeneous. Since the degradation studies and the ARXPS
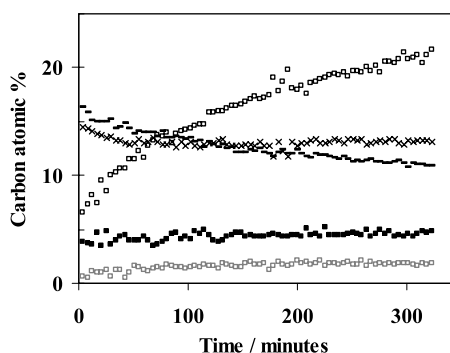
studies need two different pieces of a same sample, we can never guarantee that the piece of sample where the degradation was studied has exactly the same composition as the piece where ARXPS experiments were done. This led us to adopt the following methodology: with a piece of the sample, degradation studies were accomplished to compute the order of magnitude of the degradation suffered by the different groups in the sample (Section 3.2). ARXPS experiments were done with decreasing TOA followed by increasing TOA. Correction for degradation was done by fitting to the results a degradation law of the type $F/C = a + b \exp(-t/t_0)$ where t_0 is the characteristic time of degradation that minimises the sum of quadratic deviations between measurements made for a same TOA in the decreasing and increasing sequences. Rates of degradation so deduced had the same order of magnitude as the ones directly deduced. Fig. 8(a) shows the raw experimental results for F/C, the transformed data and the fitted curve based on the fluorine concentration profile shown in Fig. 8(b).

In the case of this film, degradation parameters extracted from the fitting to empty squares in Fig. 6(b) were exactly the same needed to minimize the difference between decreasing and increasing angles measures: $F/C = 0.87 + 0.55 \exp(-t/150)$ where t is the irradiation time in minutes. A schematic profile was fitted to corrected values and yields a characteristic depth of the order of 40 Å, the same order of magnitude found above by another method. The depletion noted at the extreme surface is, in principle,

Fig. 7. Carbon components at.% as a function of irradiation time: (■) C1; (□) C2; (×) C3; (–) C4 and (□) C5.
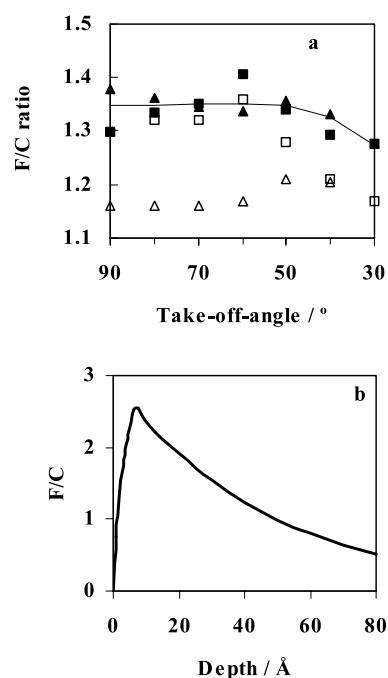

Fig. 8. (a) Angle resolved XPS results for F/C: empty symbols correspond to raw data and full symbols to corrected values for the degradation. Squares correpond to values measured for increasing angles and triangles for decreasing values. Analysis angles are measured relatively to the normal to the surface. Line was fitted using the F/C profile in depth displayed in (b).

caused by X-rays. In fact, prior to the analysis, the sample is irradiated for a few seconds to find the best sample position for analysis.

4. Conclusions

The behaviour of the F 1s and C 1s regions in XPS of fluorinated organic surfaces was analysed in order to choose one of them as an appropriate internal reference to correct for the charge shift in binding energy for these surfaces. The usual reference, the aliphatic carbon at 285 eV is inappropriate because in heavily fluorinated surfaces we cannot assure the existence of a measurable amount of aliphatic CH_2 sequences. Fluorine is then a possibility since for each polymer, a single peak is obtained even in the case of copolymers where fluorine is in different neighbourhoods. The atomic ratio between fluorine and carbon, F/C, shows a correlation with the fluorine binding energy, which covers simultaneously homo and copolymers, at least for non-oxygenated polymers. This correlation was tentatively used to infer charge shifts in surfaces. The method was applied to the study of the X-ray induced degradation in post-mould fluorinated samples in laboratory conditions. It predicted a decrease of the charge shift with the irradiation time. However experiments with samples having two silver films on different points of the surface, one grounded and the other one floating, showed that in this kind of surfaces the charge shift is constant with irradiation time. The failure of the method is consistent with the existence of a decreasing profile in the fluorine. The order of magnitude of the characteristic depth of the profile was deduced from the degradation studies and confirmed by ARXPS studies. Simultaneously, it was shown that for fluorinated polymer with unknown composition, the assigning of carbon components in XPS is better based on binding energy differences relatively to F 1s binding energy than in binding energy absolute values.

Appendix A

The change in binding energy of a given photoelectron ejected from an atom i, known as XPS chemical shift, $(\Delta BE)_i$, is related to the change in partial atomic charge, Δq_i, relatively to the same atom in the standard state by:

$$(\Delta BE)_i = (BE)_i - (BE)_{i0} = k_i q_i + 2E_0 a_0 \sum_{j \neq i}^{n} q_j / R_{ij} \qquad (A1)$$

where $(BE)_i$ is the binding energy of the photoelectron i in the molecule under study, $(BE)_{i0}$ is the binding energy of the photoelectron i in the standard compound, k_i is a proportionality constant, R_{ij} is the distance of atom j to the atom i, $E_0 = 1$ Ry and $a_0 = 1$ bohr. The partial atomic charge, q_i, can be estimated by several methods including ab initio calculations as used by Duke et al. [16] specifically for fluorinated polyethylenes having obtained very poor agreement with experimental results.

One of the most popular way of estimating partial charges on atoms is the use of the Sanderson formalism with the modified approach proposed by Carver [17]. The Sanderson method for calculating partial charge q_i is based on the principle of electronegativity equalization, which supposes that charge reorganization occurs in the molecule so that it is characterized by an average electronegativity SR_m called molecular stability ratio. This average SR_m is the geometric mean of the elementary electronegativities: $(\prod_{j=1}^{n} SR_j)^{1/n}$ [18]. Partial charges, q_i on atoms are then computed by:

$$q_i = \frac{SR_m - SR_i}{\Delta SR_i} \qquad (A2)$$

where SR_i is the Sanderson electronegativity of atom i and ΔSR_i is a normalization factor given by $1.57\sqrt{SR_i}$ [19]. This method has a disadvantage: it does not allow differentiating atoms having different neighbourhoods. Carver et al. [17] proposed a modification of the method viewing the molecule as a collection of groups instead of viewing the molecule as a collection of atoms which allows for the calculation of different partial charges for a given element accordingly with its neighbourhood. They found that this method produced binding energy charge values comparable to the more sophisticated quantum methods and claim that charges so computed, contain already the potential contribution (the last term in Eq. A1) which allows for an ease calculation even without knowing the precise molecular geometry. This method was applied by Sastry [20] to a large collection of organic molecules and found that for more than 50 organic compounds, the C 1s binding energy was correlated with the carbon partial charge by:
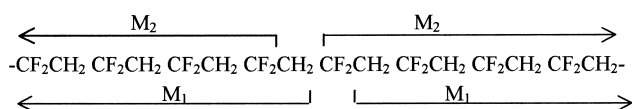
$$BE_{C\,1s} = 286.2 + 26q_C \qquad (A3)$$

We have applied the method to the fluorinated homo-polymers presented in Table 1 assuming infinite chains. Values for SR were H, 2.592; C, 2.746; F, 4.000 and for ΔSR were H, 2.528; C, 2.602 and F, 3.140 [19].

For $(-CF_2CF_2-)_n$, there is a single kind of carbon and a single kind of fluorine atoms and thence, the electronegativity equalization principle gives immediately:

$$SR_m = (SR_C^n SR_F^{2n})^{1/3n} = (SR_C SR_F^2)^{1/3} = (2.746 \times 4^2)^{1/3}$$

$$= 3.5286$$

For $(-CF_2CH_2-)_n$, we can divide the molecule into groups CF_2, CH_2 and M1 and M2:

$$\overset{\displaystyle \overleftarrow{\hspace{3cm} M_2 \hspace{3cm}}}{\underset{\displaystyle \underleftarrow{\hspace{3cm} M_1 \hspace{2.5cm}}}{\text{-CF}_2\text{CH}_2 \ \text{CF}_2\text{CH}_2 \ \text{CF}_2\text{CH}_2 \ \text{CF}_2\text{CH}_2}} \quad \overset{\displaystyle \overrightarrow{\hspace{3cm} M_2 \hspace{3cm}}}{\underset{\displaystyle \underrightarrow{\hspace{3cm} M_1 \hspace{2.5cm}}}{\text{CF}_2\text{CH}_2 \ \text{CF}_2\text{CH}_2 \ \text{CF}_2\text{CH}_2 \ \text{CF}_2\text{CH}_2\text{-}}}$$

Since we assume infinite chains, which is, in principle, a good approximation for fluorinated HDPE, M1 and M2 are the same for all the points of the chain and, thence, we have:

$$SR_{CF_2} = (SR_C SR_F^2 SR_{M_1}^2)^{1/5}, \qquad SR_{CH_2} = (SR_C SR_H^2 SR_{M_2}^2)^{1/5}$$

$$SR_{M_1} = (SR_C SR_H^2 SR_{M_2}^2)^{1/4} \text{ and } SR_{M_2} = (SR_C SR_F^2 SR_{M_1}^2)^{1/4}$$

We can, then, derive:

$$SR_{CF_2} = SR_C^{1/3} SR_F^{34/75} SR_H^{16/75} = 3.2170 \text{ and} SR_{CH_2}$$

$$= SR_C^{1/3} SR_H^{34/75} SR_F^{16/75} = 2.899$$

Using Eq. A2, we could compute all the charges and check for the neutrality of the molecule. By the same procedure, we have also computed the charges in carbon and fluorine atoms in $(CHFCH_2)_n$. Obtained correlations are summarised in Fig. A1.

Fig. A1 shows that correlation here obtained for carbon is very close to the one obtained by Sastry despite the approximations made (infinite chains). The correlation for F 1s is also good.

For copolymer VITON, calculations are much more difficult since they give different results depending on the sequence of monomers. Anyway, for extreme situations—infinite blocks of $(-CFCF_3CF_2-)$ and $(-CF_2CH_2-)$ or one monomer of $(-CFCF_3CF_2-)$ and three of $(-CF_2CH_2-)$—the extreme charges for F 1s are, respectively (-0.25, -0.12) and (-0.25, -0.14). This would give a spread of binding energy for F 1s of the order of magnitude of 1.5 eV (taking into account the correlation found in Fig. A1). This spread of energy could not produce an F 1s peak like the one presented as the experimental result in Ref. [6]. It seems that fluorine, due to its large electronegativity and small volume, presents important intermolecular neighbouring effects not predictable by neither the modified Sanderson method nor by the most common ab initio methods. It is a good challenge for theoretical groups.
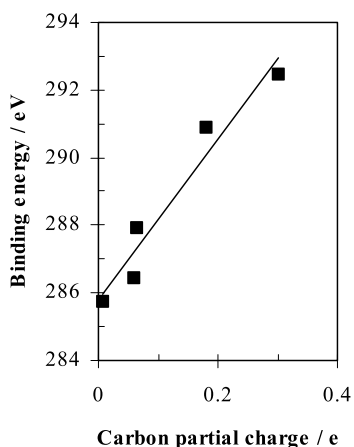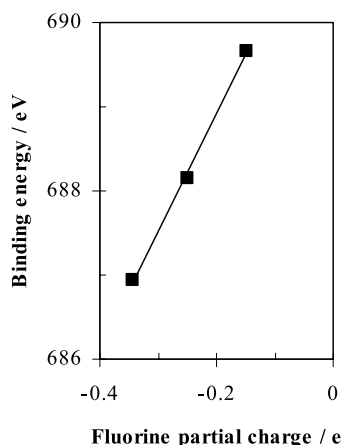

Fig. A1. Correlations between XPS binding energy and carbon and fluorine partial charges calculated using the modified Sanderson formalism for homopolymers in Table 1. Fitted lines are: $BE_{C\ 1s} = 285.76 + 23.916 q_C$ and $BE_{F\ 1s} = 681.73 + 14.0 q_F$.

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