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Surface modification of several carbon-based materials: comparison between CF_4 rf plasma and direct F_2-gas fluorination routes

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Abstract

Due to their extreme reactivity, fluorine and fluorinated gases may be used to modify the surface properties of numerous materials. In the following, the surface fluorination of some carbon-based compounds (graphite, graphitised carbon fibres, carbon blacks and elastomers) using CF_4 rf plasma technique and direct F_2-gas fluorination is proposed. From XPS studies, the different types of C–F bonding obtained in the materials after treatment have been correlated either to the physico-chemical characteristics of the pristine material or to the experimental parameters of the fluorination. Reaction mechanisms are proposed.

Keywords: Carbon blacks; Carbon fibres; Fluorine; Graphite; Nitrile gloves; rf plasma; Surface fluorination; XPS

1. Introduction

The outstanding characteristics of F_2 molecule, e.g. extreme reactivity and oxidizing power, and the utmost electronegativity of F^- ion, lead to very strong bonds between fluorine and most of the other elements of the periodical table. Therefore fluorine, fluorinated gases and fluorinated plasmas constitute exceptional tools for modifying the surface properties of materials. Several review papers and books have recently appeared on fluorinated carbon-based materials [1–5]. Many advantages of these methods can be indeed outlined, when compared to more conventional methods: low-temperature reactions (even at room temperature), chemical modifications limited to surface only without changing the bulk properties, possible non-equilibrium reactions. Depending on the type of starting materials and employed techniques, the improved properties may concern wettability, adhesion, chemical stability, permeation, electrical conductivity, biocompatibility, grafting, mechanical behaviour, etc.

The present paper deals with the effect of fluorination on the surface of several types of carbon-based materials: graphitised carbons, carbon fibres, carbon blacks, and finally nitrile–butadiene elastomer (nitrile gloves). The reaction processes have been carried out using either radio-frequency (rf) cold plasmas of fluorinated gases (CF_4, CHF_3) or direct fluorination by F_2-gas, pure or diluted in N_2. The mechanisms of surface fluorination will be proposed on the basis of the assignment of the different components of the XPS spectra.

2. Experimental procedure

2.1. Starting materials

2.1.1. Graphitised samples

Exfoliated graphite (Papyex) was obtained from Le Carbone Lorraine. Pitch-based fibres (P120 from Amoco, USA) and polyacrylonitrile (PAN)-based fibres from IPCL, India, were high-temperature treated (HTT) at around 3000 °C in order to increase the level of graphitisation.

2.1.2. Carbon black samples

A furnace carbon black (Corax N115 from Degussa) was chosen because it exhibits a fairly good crystallinity.

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The material was obtained at 1400 °C and was formed of particles with a mean size of 25 nm, the coherence length along the c-axis of the graphene domains being $L_c = 1.2$ nm. The surface area determined by BET technique was about 145 m^2/g and the active surface area (ASA), which represents a reactive fraction of the surface or aggregates as determined by the amount of oxygen adsorbed at 300 °C on materials previously degassed at 900 °C, was 8.8 m^2/g.

2.1.3. Nitrile–butadiene samples

Thin nitrile gloves from Mapa-Hutchinson, France, submitted to fluorination had a thickness of 100 μm. The materials comprised carboxylated nitrile–butadiene rubber latex (XNBR) having about 40% dry rubber content and inorganic additives such as zinc oxide (1–2%). The main polymeric components were poly(butadiene) (PBD) and poly(acrylonitrile) (PAN).

2.2. The fluorination procedures

2.2.1. Plasma-enhanced fluorination (PEF)

PEF experiments were carried out in a S.E. 80 Barrel Plasma Technology System. CF_4 gas was excited by an rf source at 13.56 MHz. The reactor consisted of two aluminium barrel electrodes which were coated with alumina. The inner electrode on which the sample was placed was connected to the rf source and the outer one was grounded. A primary vacuum was obtained by a 40 $m^3\ h^{-1}$ Edwards E2M40-type pump equipped with a liquid nitrogen condenser for the trapping of any residual gases. The gas was introduced in the inner part of the reactor and then dissociated by electron impacts occurring between the two electrodes. Neutral species and radicals diffused from this plasma zone to the center of the reactor where they reacted with the sample. The chamber was thermostatically controlled and maintained either at room temperature or at about 90 °C during the process. Taking into account previous experiments of PEF on various types of carbon materials [6], optimized conditions could be established with the following parameters: CF_4 gas flow rate: $Q \sim 10$ ml min^{-1}; total pressure: $p = 200$–300 mTorr; rf power: $P = 80$–100 W. After the fluorination treatment, the samples were generally handled and kept in a glove box under an Ar atmosphere.

2.2.2. Direct F_2-gas fluorination

Direct F_2-gas fluorination processes were performed at room temperature in a "fluorine line" using handling procedures previously described in [7]. The samples were set in a Ni boat which had been previously passivated. F_2-gas, generally 10% diluted in N_2 (Air Products) was used at room pressure. The reaction duration depended on the starting materials and in most cases did not exceed 60 min, in order to limit the fluorination to the surface only. At the end of the experiment, F_2-gas was eliminated from the reactor and substituted by N_2.

2.3. Use of XPS data for the assignment of the components of fluorinated carbon-based materials

2.3.1. XPS procedure

XPS analysis was performed with a VG 220 i-XL ESCALAB. The radiation was a Mg non-monochromatized source (1253.6 eV) at 200 W. Surveys and high-resolution spectra were recorded, then fitted with an Eclipse processing program provided by Vacuum Generators. Each C 1s component was considered as having similar full-width-at-half-maximum (FWHM), i.e. 1.3 eV. This procedure appeared to be the most reliable one, as previously proposed in investigations on fluorinated carbon materials [8]. A good agreement between the experimental curve and the full calculated envelope was obtained, which allowed explaining in addition subtle distinctions between the proportion of fluorinated components. As fluorinated materials are non-conductive, flood gun has been activated onto the samples to shift the high-resolution spectra in their normal range (i.e. 285–293 eV for C 1s).

2.3.2. Chemical shifts of C 1s and F 1s levels in fluorinated carbon-based materials

Schematic overviews of the binding energies (BE) of the various entities that can be found in fluorinated carbons and in fluoropolymers have been proposed [8]. The order of magnitude of the relative chemical shifts of C 1s and F 1s levels can be correlated to the nature of the bond that is formed between C and F. Fluorine has a very strong effect on the core level of the BE of the element to which it is bound. For example the shift in BE of a carbon atom bound to several fluorine atoms can be as high as 10 eV compared to the one of the reference: C–H_x bond in polymer or C in pristine carbon at about 284.5 eV. This important shift can be considered as a primary effect. When a C atom, not bound to fluorine, is first neighbour of another element bound to one or several fluorine atoms, an inductive (β) effect arises. The influence of this secondary effect has been evaluated to be roughly additive [8]. The primary BE shifts in C 1s level of CF_n groups ($n = 1$–3) correspond to the following ranges: 3–4.8, 6–7.5, 7.5–10 eV, according to the number of F atoms bound to the concerned C, i.e. one, two, or three, respectively. The importance of the inductive effect clearly appears from the differences in BE observed for a same carbon with different environments: for instance the C 1s BE of a C non directly bound to an F atom, but first neighbour of CF_n ($n = 1$–3) groups, is shifted of 0.6 ± 0.2 eV when the given C atom is bound to only one CF group, and of 1.4 ± 0.2 eV when its neighbours are either two CF groups or one CF_2 group.

For the F 1s core level, the BE shifts in C–F_n bonds are generally more limited. In fluorinated graphite and carbon blacks, the range is only of about 2 eV. In polymers, for CHF groups, F 1s BE increases by about 0.5 eV only when these groups are bound to another fluorinated C, as shown by the difference in BE between $(CHF–CH_2)_n$ and $(CHF–CHF)_n$

units [8]. The presence of an additional F on a C atom increases BE by about 1.0 ± 0.2 eV, as far as this group is not bound to another fluorinated C atom. This is the case for instance of CHF and CF_2 groups in PVF and PVDF, respectively. When the CF_2 groups are bound to other CF_2, as in PTFE, the addition of two F atoms increases BE by about 2 eV.

Finally, in these materials, F 1s BE ranges from 684.5–685.5 for ionic (inorganic) fluorides such as CaF_2, ZnF_2, to 686.0–686.7 eV for semi-ionic intercalated C–F bonds and 691–692 eV for CF_n ($n = 2, 3$) groups in “graphite fluoride” type structures.

3. Results and discussions

3.1. Fluorination of graphitised carbon materials

3.1.1. Graphite PEF

The main difference between graphitised samples and the other materials involved in this study is their better crystallinity, the coherence length along the c-axis of the graphene domains being around $L_c = 30$ nm for both the exfoliated graphite and the HTT pitch-based fibres, and around $L_c = 12$ nm for the HTT PAN-based fibres, whereas it is only of about 1 nm for N115 carbon blacks. This point drastically limits the number of surface defects with respect with those found in carbon blacks and also in polymers. This point also reduces the presence of the inductive (β) components in the C 1s envelope, because the domains are more homogeneously fluorinated. The number of components present in the XPS spectra is then much more limited.

In exfoliated graphite, PEF-treated with CF_4, the component at ca. 284.5 eV of the C 1s envelope remains unchanged relatively to pristine graphite (Fig. 1a). Due to an asymmetry towards higher BE, the fitting of the graphitic contribution (1) is split as usually into two components. This asymmetry, which is common in metallic samples is due to the interaction between the positive core hole created and the conduction electrons. The component (2) is due to C bound to hydroxyl or carbonyl groups and also to the inductive effect. In the case of graphite, this last contribution is weak because the number of reactive sites (i.e. surface defects and borders of graphitic domains) is limited. New components appear at higher BE: the weak component (3) around 287 eV can be associated with “semi-ionic” C(sp^2)–F bonds of F species intercalated in between the graphene layers [9]. At higher BE, the contributions can be assigned to covalent CF or CF_2 groups in which carbon, with an sp^3 conformation, is located either on the border of graphene particles or in domains with the $(CF)_n$ graphite fluoride type [2,10,11] (4, 5). The C 1s and F 1s BE and the relative amounts of the different components are given in Table 1. It should be noted that similar results have been obtained on natural graphite samples used as anodes of lithium-ion batteries [12]: once PEF treated, the anodes exhibit capacities higher than those of non-treated graphite and even higher than the theoretical capacity of graphite.

3.1.2. Graphitised carbon fibres PEF

C 1s and F 1s XPS spectra of various fluorinated pitch- or PAN-based fibres are collected in Fig. 2 and the BE and relative amounts of the most important contributions are grouped in Table 2. The influence of the morphology and the thermal treatment of the starting material is evidenced in Fig. 2, in which the XPS spectra of two different types of fluorinated HTT carbon fibres are compared with fluorinated non-HTT materials. Although the BE values of the main components are close to those found for fluorinated graphite, their relative amount is different. In PAN-based fibres, the higher intensity of the component at 285.6 eV (2) is due to C–O, C–N, C=N groups arising from carbonyl, nitrile and naphtyridine groups present in the starting material [6,13].

For HTT fibres, either ex-pitch or ex-PAN, the C 1s signals (Fig. 2a and b) do not show important changes with respect to the pristine materials. Very weak components at high BE are assigned to surface fluorinated domains and it

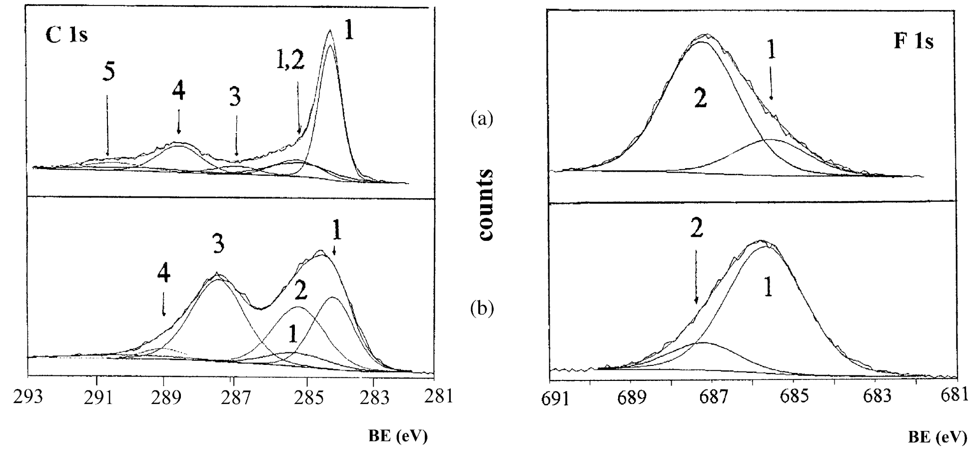

Fig. 1. Comparison of C 1s and F 1s XPS spectra of PEF-treated (a) and F_2-gas treated (b) graphite.

Table 1
C 1s and F 1s BE (eV) and relative amounts of C, F (%) at the surface of PEF- and F_2-gas treated graphite [the percentages are indicative only]

	PEF-treated graphite	F_2-gas treated graphite	Number and assignment of the components
C 1s	284.2 (42%)	284.1 (25%)	1: Graphitic C(sp^2)
	285.2 (7%)	285.1 (18%)	2: Asymm. comp., β effect, C–O, C–C(sp^3), C–H
	287.0 (4%)	287.4 (26%)	3: "Semi-ionic" C(sp^2)–F bond, C–O
	288.7 (11%)	289.1 (3%)	4: Covalent C–F bond (surface defects)
	290.6 (4%)		5: Covalent C–F (graphite fluorides), CF_2
F 1s	685.6 (7%)	685.7 (22%)	1: Semi-ionic F–C bond
	687.3 (24%)	687.3 (4%)	2: Covalent F–C bond

can be concluded that the reactivity of HTT fibres with plasma fluorination is limited to the utmost surface. The low fluorination rate is also confirmed by the weak F 1s signal (see Table 2). The F 1s envelope is composed of two components, the covalent one (BE = 688 eV) being much more important that the semi-ionic one (BE = 686–686.7 eV) which arises from a partial intercalation of fluorine species in between the graphene planes. The importance of the pre-treatment, is also evidenced: although the fluorination of as-received ex-pitch fibres (L_c = 10 nm) (Fig. 2c) gives results similar to those of the HTT ones, the C 1s spectrum of fluorinated as-received ex-PAN fibres (Fig. 2d) appears totally different. The starting materials exhibited ill-crystallised characteristics and contained numerous defects, with L_c = 2 nm only. The main components are now located at high BEs. Among the C 1s components associated with C–F bonds, that is for BE > 287 eV, the most intense is located at 288.5 eV (4) and corresponds to covalent CF groups mostly from C atoms located at the edges of the graphitic domains. Additional CF_2 (5) and even CF_3 (6) components are noted at 290.5 and 292.5 eV, respectively. The covalent nature of the C–F bonds is further confirmed by the F 1s spectra, the component at 687.7–688.2 eV being largely the most dominant one.

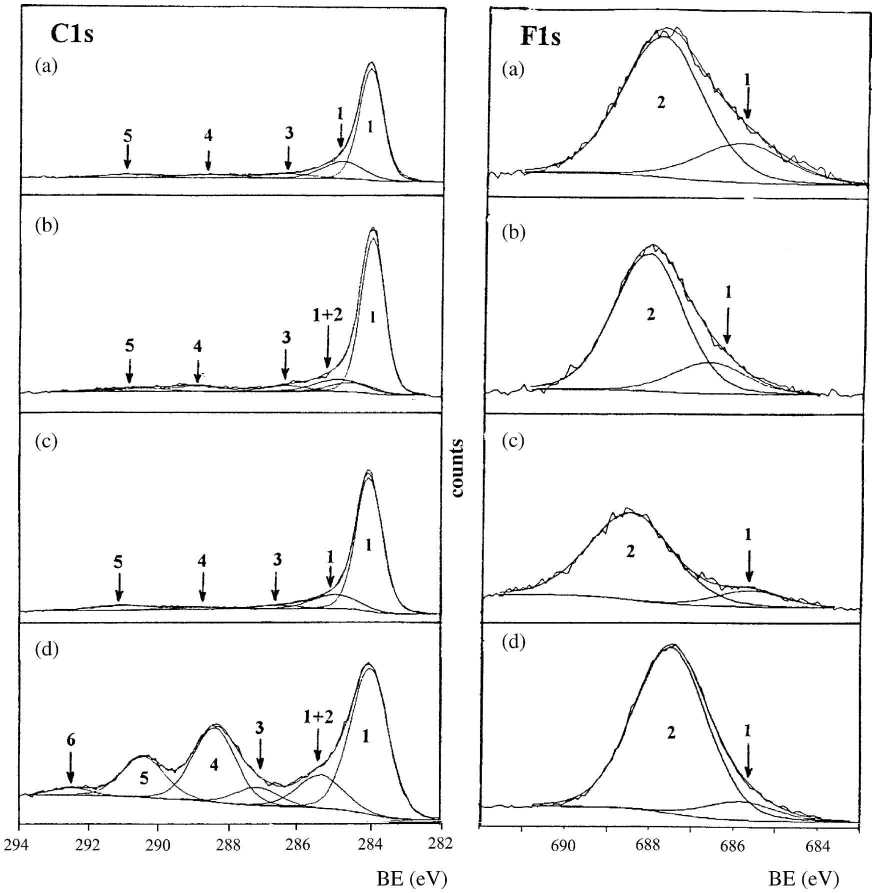

Fig. 2. C 1s and F 1s XPS spectra of PEF-treated HTT ex-pitch fibres (a), HTT ex-PAN fibres (b), as-received ex-pitch fibres (c), as-received ex-PAN fibres (d).

Table 2
C 1s and F 1s BE (eV), relative amounts of C, F, O (%), and F/C ratio at the surface of PEF treated ex-pitch or ex-PAN fibres, either HTT or as-received

	HTT ex-pitch P120 fibres	HTT ex-PAN IPCL fibres	As-received ex-pitch P120 fibres	As-received ex-PAN fibres	Number, assignment of the components
C 1s	284.1 (78%)	284.0 (73%)	284.2 (56%)	284.1 (26%)	1: Graphitic C(sp^2)
		284.6 (7%)		285.5 (7%)	1/2: C–H, C–O, C–OH, *C*–CF
	286.5 (6%)	286.5 (4%)	287.2 (5%)	287.3 (3%)	3: “Semi-ionic” C(sp^2)–F, C–O
	288.7 (5%)	289.0 (5%)	288.5 (10%)	288.5 (15%)	4: Covalent CF (surface defects)
	290.9 (4%)	290.5 (3%)	290.5 (3%)	290.5 (8%)	5: Covalent CF (graphite fluorides), CF_2
		291.6 (2%)	292.1 (2%)	292.5 (1%)	6: CF_3
F 1s	686 (1%)	686.7 (1%)	686.0 (4%)	686.3 (3%)	1: Semi-ionic F–C bond
	687.9 (4%)	688.2 (4%)	687.4 (15%)	687.7 (32%)	2: Covalent F–C bond
O (%)	1.4	0.6	1.8	2.5	
F/C	0.05	0.05	0.25	0.58	

3.1.3. F_2-gas fluorination and discussion

Although the same components are present in F_2-treated graphite, a drastic change in the relative intensities is observed (Fig. 1b and Table 1) with respect to the previous results. The semi-ionic component C 1s (3) relative to intercalated species is now the main peak of C–F bonds. In the F 1s spectrum, the inversion of components (2) and (3) is also consistent with this trend. It can be noted that the increase of component C 1s (2) is due to sp^2 carbons of graphene layers which are next to carbon bound to fluorine (inductive effect). In both cases the C-to-F ratio at the surface is roughly similar: 2.2 for PEF versus 2.8 for F_2-gas but in the latter case the amount of fluorine is important even in the core of the material.

For F_2-gas treated fibres, the reaction proceeds rapidly to the heart of the fibre. As shown in Fig. 3c, for short F_2 fluorination times (15 min), the C 1s and F 1s spectra are similar to those of PEF-treated fibres for both HTT ex-pitch or ex-PAN precursors (Fig. 2a and b) and the present species are covalent C–F bonds [see F 1s (2)] involving C atoms located on the edges of the graphitic domains. For 1 h fluorination (Fig. 3b), the intercalation of these graphitic domains proceeds [C 1s (3) and F 1s (1)], with the help of surface hydroxyl groups which favour the intercalation of fluorine. Similar results are observed for HTT ex-PAN fibres F_2-gas fluorinated for 1 h (Fig. 3d). Finally the reaction goes to completion, the materials being fully intercalated, as shown by the presence of predominant “semi-ionic” C 1s

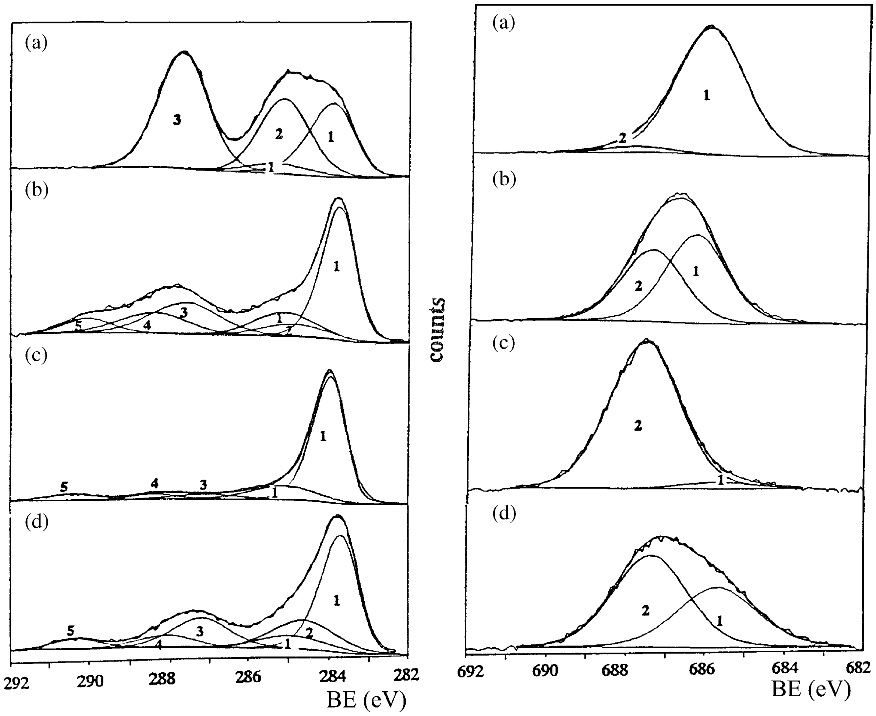

Fig. 3. Influence of the F_2-gas treatment duration on the C 1s and F 1s XPS spectra of HTT ex-pitch fibres: (c) 15 min, (b) 1 h, (a) 2 h, (d) F_2-gas treatment (1 h) of HTT ex-PAN fibres.

(3) and F 1s (1) contributions (Fig. 3a) for HTT ex-pitch precursors F_2-treated for several hours.

The major difference between the two methods is that PEF treatments concern only a very thin layer, as shown by the rapid decrease of the F content after Ar sputtering. In graphitised materials, the bonding between C and F are essentially covalent and the predominant species involve C atoms located on the edges of the graphitic domains; almost no intercalation occurs. On the other hand the F_2-gas method yields a deeper fluorination and rapidly gives rise to F-intercalated materials. In the case of natural graphite anodes, PEF treatment leads to a rather constant surface fluorination ($<10\%$), whatever the size of graphite particles, whereas F_2-gas method gives higher fluorination rates and deeper penetration [14]. It appears therefore that the PEF method better ensures an efficient protective coating of graphitised materials by the formation of a very thin layer which does not affect the bulk properties of the materials.

3.2. Fluorination of carbon blacks

3.2.1. Furnace carbon black PEF

Due to their high specific surface area, that ranges from a few m^2/g to several thousands m^2/g, carbon blacks react thoroughly in PEF conditions. The reactivity of various types of carbon blacks with F_2-gas and other fluorinated reagents has been recently investigated [8,15]. N115 carbon black has been chosen for the present study because it exhibits intermediate surface area of 145 m^2/g. The fitted high-resolution C 1s and F 1s XPS spectra of PEF-treated N115 carbon black are given in Fig. 4 for as-received and activated (heated in air at 500 °C for 2 h) samples. When the materials are activated, the amount of fixed F increases due to an increase of the density of reactive surface sites arising from the increase of porosity (see for instance variation of component C 1s (6)). In order to take into account the total envelope of the C 1s spectra 10 components are required, as described in [8]. The assignments for C and F atoms involved in each component are shown in Table 3. For C 1s envelope, there are two major peaks. The peak at lower BE (1) located at 284.5 eV corresponds to non-functionalised C(sp^2) and C(sp^3) atoms that are not affected by fluorination. The area of component (1) represents 42% of the total area of the C 1s envelope and can be taken as an internal reference. The peak C 1s (6), which is located at 288.6 eV and which is the most important component of C–F bonds, can be assigned to carbon atoms that are covalently linked to a fluorine atom at the surface, border or sub-superficial zones of the graphitic domains of carbon blacks without any change in the sp^2 conformation of carbon (Type I structure). The four components which are located in between components C 1s (1) and (6) correspond to C atoms that are not directly bound to F atoms, i.e. the β inductive effect, evaluated to about 0.6 ± 0.2 eV for each F atom [8] and roughly additive. As a matter of fact, the chemical shift of F 1s core level is less dependent on the x value of CF_x groups than the C 1s core level and in Type I fluorinated structures, F atoms belonging to either CF, CF_2 or CF_3 groups contribute to the same component [F 1s (6), at 687.6 eV]. The component C 1s (7) at 289.8 eV corresponds mostly to CF groups of Type I with CF_2 groups as nearest neighbours. The peak C 1s (8), located at 290.7 eV, can be attributed to CF_2 groups of fluorinated structure of Type I, whose F atoms again contribute to F 1s (6), and also to CF groups of polyalicyclic perfluorinated structures of Type II, in which C(sp^3) atoms form puckered layers, similar to those of covalent graphite fluorides $(CF)_n$ [2,11]. F atoms of CF, CF_2 and CF_3 groups belonging to these structures of Type II contribute to the same component, F 1s (8) which is shifted by 2.0 eV relative to F 1s (6). Shoulder peak C 1s (9) and

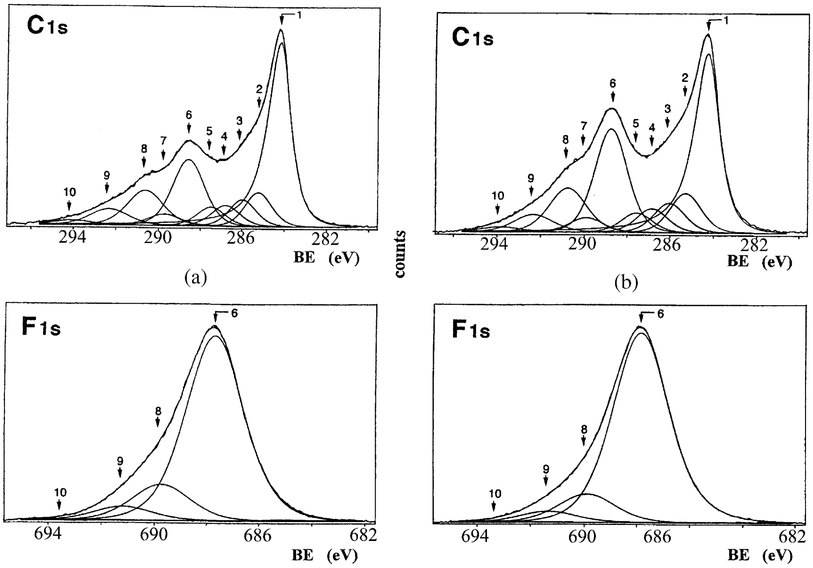

Fig. 4. C 1s and F 1s XPS spectra of PEF-treated furnace carbon black [as-received (a) and activated (b) N115].

Table 3
Assignment of the XPS C 1s and F 1s components of PEF fluorinated carbon black (activated N115)

Component	BE (eV)	Assignment
C_1	284.5	Non-functionalized C(sp^2) and C(sp^3) atoms, not affected by fluorination
C_2	285.5	Aliphatic non-functionalized C(sp^3) in a non-fluorinated environment Non-functionalized C(sp^2) in β position to one F atom
C_3	286.3	Non-functionalized C(sp^2) or C(sp^3) in β position to one or two F atom(s), respectively C(sp^2) bound to an oxygen atom (phenol, phenyl ether)
C_4	287.1	Non-functionalized C(sp^2) or C(sp^3) in β position to two or three F atoms, respectively Oxygenated C(sp^3) in a non-functionalized environment (CH_x–OH, or C–O–C)
C_5	287.8(1)	Oxygenated C(sp^3) in β position to a F atom Non-functionalized C(sp^3) in β position to at least three F atoms C(sp^2) ''semi-ionic'', bound to intercalated F atom (very week contribution)
C_6	288.6(2)	C(sp^2) covalently linked to an F atom in Type I structure
C_7	289.9(3)	CF groups of Type I structure in β position of CF_2 groups
C_8	290.7(3)	CF_2 groups of Type I structure CF groups of Type II structure
C_9	292.4(4)	CF_3 groups of Type I structure CF_2 groups of Type II structure
C_{10}	294.1(4)	CF_3 groups of Type II structure + Plasmon effect
F_6	687.6	F atoms in Type I structure
F_8	689.6(1)	F atoms in Type II structure
F_9	691.1(1)	F atoms in Type II structure with charge effect
F_{10}	693.5(1)	F atoms in Type II structure with higher charge effect

(10) correspond mostly to CF_n groups of Type II and are associated with components F 1s (9) and (10) [see Table 3]. The Type II zones are strongly affected by charge effect.

3.2.2. F_2-gas fluorination and discussion

The structure of carbon blacks is much more complex than the graphitised sample one and because of the very high surface area, the numerous defects are readily accessible by both PEF- and F_2-gas methods. The latter method leads therefore to results similar to the PEF one, and same assignments and conclusions can be thus proposed.

From the analysis of the XPS spectra of fluorinated carbon black samples we can conclude that the fluorine atoms, fixed at the surface and in the sub-superficial zone of the particles, are covalently linked to carbon atoms. The majority of the structures of the fluorinated islands present at the surface are of Type I, a structure in which the planar (sp^2) conformation of carbon in the graphene layers is preserved. However some fluorinated islands of Type II structure also exist at the surface and some of them show a significant charge effect.

3.3. Fluorination of elastomers

3.3.1. NBR elastomers PEF

PEF treatments using CF_4 in rf plasma conditions at room temperature do not bring drastic modifications in C 1s spectra of NBR elastomers, as shown in Fig. 5a. The main peak located at 284.6 eV, can be assigned to CH_n bonds of unfluorinated pristine co-polymers (PBD, PAN). The weak component which is noted on the lower BE side of the C 1s envelope, and fitted at about −1 eV relative to this peak arises from the presence in the samples of different types of hydrocarbon surface pollution and non-fluorinated domains with different degrees of charging effect. The high-energy shoulder which is found between 287 and 289 eV is mostly due to carboxyl and carbonyl groups whose BE fall in the 287–288.5 eV range. Small amounts only of C–F bonds are formed and are attributable to CHF–CHF groups. Among the three contributions of the F 1s spectrum, the two major components can be attributed to ''ionic'' fluorides, in which fluorine is bound to inorganic elements that are present in the elastomer: CaF_2, ZnF_2, or complex fluorides, whereas the weaker one at 687.3 eV (2) (10%) corresponds indeed to the formation of C–F bonds.

The effect of thermal activation is illustrated in Fig. 5b, which shows C 1s spectra of the surface of NBR gloves treated in a CF_4 rf plasma at 90 °C. An important increase of the surface fluorination is noted from the elemental analysis, with a mean F/C ratio reaching 1.6. In this case, the C 1s spectra exhibit two clear maxima: one at a BE similar to that of the starting material, and another one with a shift of +6.8 eV. If we take a similar procedure as previously used for carbon blacks, this second maximum (7) can be assigned to CF_2 groups with first C neighbours bound to one F atom, for instance CF_2–CHF groups. Another feature of the spectrum which is consistent with an increase of surface fluorination is the presence of two more contributions at higher BE. The one with a shift at +8.0 eV (8) corresponds to CF_2 groups with CF_2 (or CF_3) first neighbours, or to CF_3

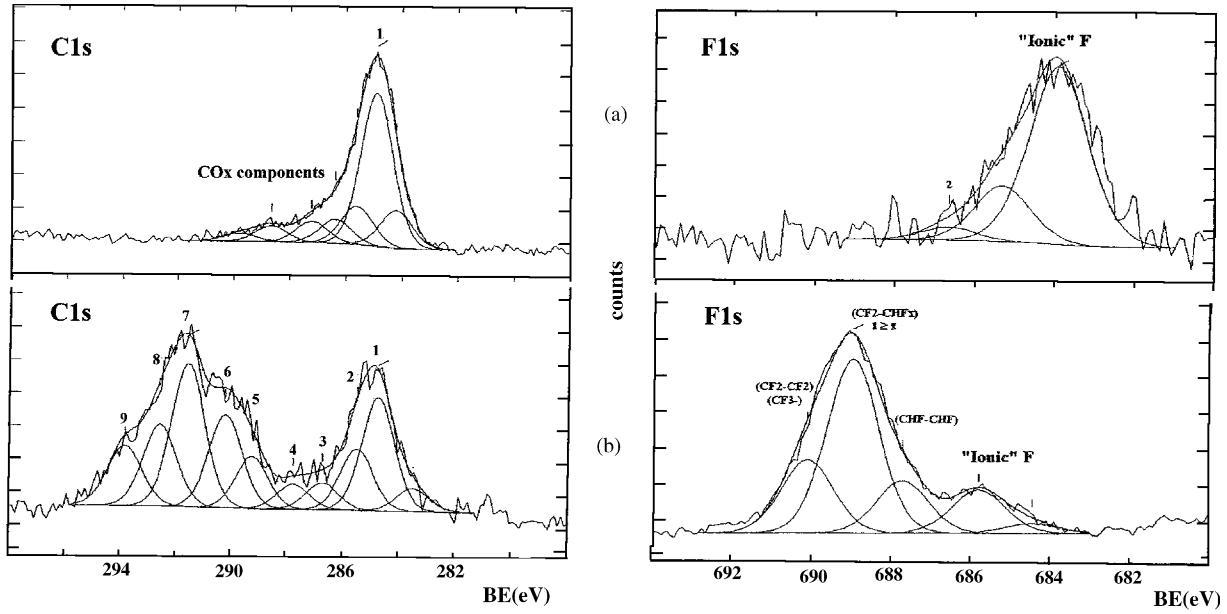

Fig. 5. C 1s and F 1s XPS spectra of NBR sample PEF-treated at room temperature (a) and at 90 °C (b).

groups with non-fluorinated neighbours. The contribution with a shift of 9.1 eV (9) can be assigned to terminal CF_3 groups with fluorinated neighbours. It can be noted that most of BE are shifted of 0.8 eV relative to the room-temperature experiments due to a higher fluorination level and an increase of the insulating character of the sample. The assignments of the different components are given in Table 4. The same trend is found in the F 1s spectrum, as shown in Fig. 5b. Although the amount of inorganic fluorides is more or less similar (12%), the maximum value of the envelope corresponding to the F–C components is shifted of several eV towards higher BE. As previously stated, the value of the maximum at 688.7 eV should correspond to CF_2–CH_2, or CHF–CF_2 units. At lower BE, the CHF–CHF component at 687.3 eV is weaker (15%). In addition, a further component occurs from the fitting procedure at 689.8 eV, which can be assigned to perfluorinated CF_n groups, in particular PTFE-like CF_2–CF_2 units and terminal CF_3 groups.

Table 4
Assignment of the XPS C 1s components of fluorinated NBR elastomer

No.	Chemical bond	BE (eV)
1	CH_n	284.5
2	$\mathit{C}H_2$–CHF	285.2–285.6
3	$\mathit{C}H_2$–CF_2	286.5
4	CHF–CH_2, CHF–CHF	287.5–288.0
5	CHF–CF_2	290.0
6	CF_x–$\mathit{C}F$–$CF_{x'}$ (x, x' = 2, 3), $\mathit{C}F_2$–CH_2	289.8–290.0
7	$\mathit{C}F_2$–CHF	290.7–291.3
8	CF_2–CF_2	292.3
9	$\mathit{C}F_3$–CF_x	293.6

3.3.2. F_2-gas fluorination and discussion

Direct F_2-gas fluorinations have been performed at room temperature using 10% F_2 diluted in N_2 (Fig. 6a). In these conditions, the F 1s peaks have considerably increased, with a mean F/C atomic ratio reaching 1.2 for samples treated during 30 min. The high-resolution C 1s spectra exhibit an envelope spread over 10 eV. The unfluorinated component at 284.6 eV has decreased. At higher BE the maximum of the envelope is now located at 288.1 eV. This value is similar to those of CHF–CHF groups in poly(vinylene fluoride) and it can be assumed that the main effect of room temperature F_2-gas fluorination is to open the double bond of PBD with a subsequent addition of a F atom on both C atoms. A second maximum is located at a chemical shift of +5.5 eV, which could be attributed to (CF_2–CH_2) units coming from the substitution of F for H, or alternatively C–F bond with highly fluorinated neighbours, such as CF_2 groups or terminal CF_3 groups. The two further contributions (+6.7 and +8 eV) can be assigned to CF_2–CHF and CF_2–CF_2 groups, respectively.

The F 1s peak, shown in Fig. 6a, is displaced of about 4 eV toward higher BE, when compared with that of room-temperature PEF experiments. The FWHM is also much larger, reaching 3 eV, which points out the presence of several contributions. The inorganic part of the spectrum (CaF_2, ZnF_2) with components at BE = 685 eV is very weak and corresponds to less than 10%. The maximum of the peak, at 687.6 eV, can be ascribed to a F–C bond with first carbon neighbours presenting also C–F bonds, i.e. (CHF–CHF) groups, which is in good agreement with the C 1s spectrum (see component 4 in Table 4). The contribution at intermediate BE, that is 686.5 eV, should correspond to F–C bonds with non-fluorinated C neighbours, i.e. (CHF–CH_2) groups. On the other side, the contribution at highest BE,

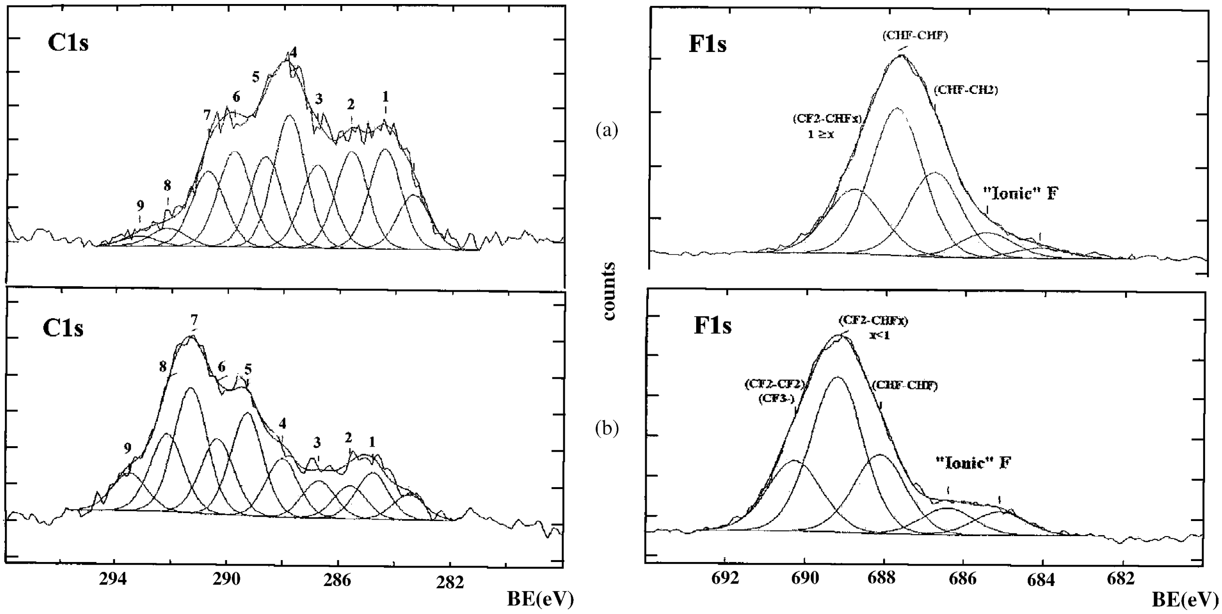

Fig. 6. C 1s and F 1s XPS spectra of NBR sample fluorinated by F_2-gas at room temperature (a) and at 90 °C (b).

that is 688.8 eV, can be assigned to C–F bonds with CF_2 groups as first neighbours or alternatively to CF_2 groups with CH_2 or CHF units as first neighbours (unfortunately the only literature data on F 1s BE of (CF_2–CHF) groups (BE = 690.1 eV) [16] is known to be too high [8]. This component would therefore correspond to components (5) to (7) of the C 1s spectra in Figs. 5 and 6 and Table 4.

The effect of thermal activation can be clearly noted from Fig. 6b, which corresponds to C 1s and F 1s spectra of the surface of NBR gloves treated at 90 °C with 10% diluted F_2-gas for 15 min only. In this case, the amount of fluorinated surface has further increased relative to room temperature fluorination, with F/C atomic ratio of 1.86, and a lower amount of pristine co-elastomer. The C 1s spectrum has similar features than that obtained for plasma fluorination at 90 °C, with a weaker signal of the unfluorinated material. The strongest component (7) can be now assigned to CF_2 groups that are surrounded by C–F groups with a BE shift of +6.5 eV. The two components at higher BE can be again attributed to perfluorinated CF_2–CF_2 units and terminal CF_3 groups. The F 1s spectrum is roughly similar to the one of plasma-treated materials at 90 °C (compare Fig. 5b and Fig. 6b).

The above results clearly show that in the fluorination of NBR rubbers several mechanisms can be observed depending on the fluorination conditions [17]. The comparison between the two fluorination routes points out that at room temperature a better efficiency is observed for the direct F_2-gas treatment. An addition reaction takes place at the (CH=CH) double bonds of the PBD, leading to (CHF–CHF) units. C–F bonds are the species most found at the surface, perfluoro-groups CF_n being in a lower amount. Whatever the fluorination method, thermal activation yields an increase of the amount of surface perfluoro-groups that finally leads to a coating mostly formed of perfluorinated (CF_2) groups, with some terminal –CF_3 groups.

4. Conclusions

As concluding remarks, it has been shown with the preceding examples that it is possible to modify the nature of the fluorinated film which is formed on the surface of several types of carbon-based materials: graphite, graphitised ex-pitch and ex-PAN carbon fibres, carbon blacks and elastomers, by acting either on the nature of the physical characteristics of the host material or on the fluorination conditions. In the case of graphitised carbon materials, the PEF method gives an efficient coating by the formation of a very thin layer which does not affect the bulk properties of the material, whereas the direct F_2-gas method gives higher fluorination rates and deeper penetration. On the other hand, in highly disordered structures such as carbon blacks, the numerous defects are readily accessible by both methods, because of the very high surface area of the materials and therefore similar results and assignments can be proposed for both PEF- and direct F_2-gas methods. In the fluorination of NBR rubbers, several mechanisms have been observed. However, whatever the fluorination method, thermal activation yields an increase of the amount of surface perfluoro-groups that finally leads to a coating mostly formed of perfluorinated (CF_2) groups, as in PTFE. Concerning the physical properties that can be improved, we can quote:

- the electrical conductivity of graphitised carbons and HTT carbon fibres;

- the electrical permittivity of carbon blacks, because of the formation of a fluorinated insulating layer on the surface of the particles which increases the repulsion effect;
- the increase in hydrophobicity/passivation properties of nitrile rubbers associated with a decrease in permeation.

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