



Trade Science Inc.

# Materials Science

An Indian Journal

Full Paper

MSAIJ, 7(2), 2011 [69-77]

## Electron emission spectra of radiatively carbonized PVDF films

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Received: 24<sup>th</sup> September, 2010 ; Accepted: 4<sup>th</sup> October, 2010

### ABSTRACT

The samples of poly(vinylidene fluoride) (PVDF) film was exposed to long term AlK<sub>α</sub> radiation, electrons and ion bombardment with the aim of surface carbonization. An influence of secondary electrons on the electron emission spectra of PVDF film and its carbonized derivatives has been studied. Original routines of the CKVV and C1s spectra shape parameterization for PVDF and its dehydrofluorinated derivatives have been developed and carefully described. Analysis of C1s and C KVV lineshape has revealed obviously different electronic structure of carbonized layers derived from PVDF via two kinds of radiative treatment. In case of Ar<sup>+</sup> bombardment the sp<sup>2</sup>-bonds predominate. The Al K<sub>α</sub> irradiation leads to some other form(s) of carbon, but additional ion bombardment transforms them into species with predominating sp<sup>2</sup>-bonding. The most puzzling result of this study is that both photons and ions produce the same depth gradient of fluorine in the layers of carbonized surface accessible for XPS analysis.

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### KEYWORDS

PVDF;  
XPS;  
Radiative carbonization;  
Ion bombardment.

### INTRODUCTION

The degradation of the poly(vinylidene fluoride) (PVDF) surface induced by X-rays, electrons, and/or ion bombardment has been observed in numerous studies<sup>[1-7]</sup>. In some of them mass spectrometry was used to reveal the nature of species being eliminated from the degrading surface, whereas fluorine, hydrogen, HF, but no carbon-containing molecules were detected<sup>[4]</sup>. These facts confirm the formation of a surface layer enriched with carbon, and this kind of degradation was

coined a “radiative carbonization”<sup>[6]</sup>.

Radiative modification of PVDF surface is prospective in a lot of aspects. At first, this is a route to achieve new and potentially useful physical and chemical properties of the well-known material, thus extending its applications into new fields. For instance, one should expect the conductivity of a carbonized layer to be higher than that of its polymeric precursor<sup>[8]</sup>. This opens up opportunity for creation of conducting and/or semiconducting nanofilms on elastic and transparent dielectric substrates for micro- and nanoelectronic and photonic

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devices.

Secondly, equal amounts of hydrogen and fluorine in starting PVDF provide a potential for creation of one-dimensional carbon structures in the form of polyynes and/or cumulene chains. As radiation-induced elimination of HF occurs due to random interactions of impinging photons or bombarding particles with a polymer chain, the fragments of “naked” carbon chains are formed after long exposure and/or high doses. Being structural parts of original PVDF chains, these fragments are covalently bonded to  $\text{CF}_2$  or CF species remaining due to incomplete dehydrofluorination or intrinsic defects existing in the polymer macromolecules (ca. 7-15% of residual fluorine<sup>[6,7]</sup>). These moieties may play a stabilizing role by keeping the carbonized fragments of neighboring chains apart from each other, thus preventing linear carbon from an immediate collapse. Quasi-1D carbon attracts special interest both in academic and practical aspects. On the one hand it may serve as a model substance to study the physics of low-dimensional solids, which predict unique transport, optical, and magnetic properties. On the other hand one-dimensional carbon (carbyne) and carbynoid structures are considered to hold promise for a variety of technical applications, e.g. in optics, micro- and nanoelectronics, medicine and in some other branches of science and technology<sup>[9]</sup>. Finally, an additional treatment of these quasi-stable one-dimensional carbon structures may provide an opportunity for further modification of atomic arrangement, depending on the nature and intensity of the impact. One can expect the formation of nanoscaled carbon chains, graphite- or diamond-like clusters, or, most probably, a complex combination of different types of carbon valence states. The proportion of each of these phases, depending on the radiation dose, can affect specific properties of the modified polymer surface. Thus, the identification of the valence state of carbon atoms and possibility to control it by changing external conditions seems to be promising not only to study the degradation mechanism but in various practical aspects as well. The deformation character of a film during radiative carbonization suggests the interatomic distances to become shorter<sup>[6]</sup>, but the types of arrangement in the carbonized surface layer could not be unambiguously identified and have yet to be dealt with.

The aim of the present study is to reveal both similar and peculiar features of the electron structures of species formed on the surface of PVDF films by the irradiation with soft X-rays ( $\text{Al K}_{\alpha}$ ) accompanied by secondary electrons of different energies and by an unfocused  $\text{Ar}^+$  flux with energies of 600 and 720 eV. The XPS technique has proved to be an appropriate tool for studying different groups of emitted electrons as well as for modifying PVDF surface *in situ*<sup>[5]</sup>.

## EXPERIMENTAL

Partially crystalline film of PVDF Kynar (type 720, thickness 50  $\mu\text{m}$ ) produced via a blow extrusion technique (Atofina, France) was used in this study. Compared to amorphous PVDF, the polymer chains in Kynar are oriented and thus more ordered. Based on large inter-chain spaces in crystalline PVDF (approx. 0.5 nm), one can assume that the probability of cross-linking during the carbonization process should in this case be appreciably lower. These spacings seem to be sufficient to prevent an immediate collapse after the formation of one-dimensional fragments of “naked” carbon resulting from the dehydrofluorination of PVDF. Taking into account that the formation of double and triple carbon-carbon bonds induced by the photon or ion irradiation is due to the coupled elimination of fluorine and hydrogen atoms, the process of radiative degradation of PVDF should be referred to as dehydrofluorination. However, we can neither directly analyze the content of hydrogen nor monitor its changes with the use of electron spectroscopy techniques. Therefore, we will use hereafter the term defluorination.

The electron emission spectra were excited and measured using a home-made X-ray photoelectron spectrometer ES IFM-4<sup>[10]</sup> equipped with a coaxial magnetic analyzer and a non-monochromatic  $\text{Al K}_{\alpha}$  (1486.6 eV) source. The apertures provided relative resolution of  $7 \times 10^{-3}$ , which gives an absolute value of approx. 3 eV for the most of the spectra obtained at 320 eV passing energy so as to gain sufficient statistical averaging of counts within a short period of measurement. Although the energy resolution in this case is relatively poor, the use of high passing energy allows one to speed up the spectra accumulation. This aspect proved to be crucial for reliable XPS and XAES monitoring of

anticipated changes in the unstable surface of PVDF. The residual gas pressure was approx.  $1.3 \times 10^{-6}$  Pa.

In order to detect the fine structure modification of C1s line the analyzer energy of 70 eV was used, which provides absolute resolution of approx. 2 eV as estimated from the half-height width (HHW) of the CF<sub>2</sub> C1s line.

The analyzer and filtering foil in the ES IFM-4 XPS spectrometer have ground potential, while positive retarding voltage is applied to the sample holder. Being retarding for photoelectrons, this electrostatic field accelerates secondary electrons born in the foil and in the chamber walls due to partial absorption of X-ray radiation, thus presumably enhancing their role in the degradation of PVDF. On the other hand, the application of negative voltage to the sample holder, which is for instance necessary for scanning C KVV spectra with passing energy of analyzer as high as 320 eV, prevents secondary electrons from attaining the sample. Hence, during the XPS measurements the sample is subjected to simultaneous combined irradiation by X-rays used for the photoelectron and Auger excitation and by a flux of secondary electrons, whose density and energy could depend on the binding energy range being scanned.

In the first series of this study the PVDF film was irradiated for 5400 min. The energy of secondary electrons varied in accordance with retarding or accelerating voltages necessary for scanning XPS and Auger spectra. Typical voltages and ranges of binding energy used in all carbonization series are given in TABLE 1.

TABLE 1 clearly shows that during the scanning of all types of the electron emission spectra, except those of the C KVV region, the secondary electrons should have energy sufficient for the ionization of the carbon core level. This effect can play an important role in the redistribution of electron density in the polymeric chain followed by the formation of HF molecules escaping from the irradiated surface<sup>[1]</sup>. On the contrary, while recording the C KVV spectra, the most of secondary electrons are unlikely to reach the sample surface at all.

Therefore, special efforts were undertaken in order to evaluate the influence of secondary electrons on the carbonization rate. For this purpose, the second series of experiments was carried out, in which a constant negative voltage of -50 V was applied to the

sample holder for sufficiently long periods of time. One can assume that this regime of the experiment does not allow interaction of secondary electrons with a sample, and the carbonization process occurs entirely due to the influence of Al K<sub>α</sub> photons. In order to monitor chemical and electronic states of the surface, the measurements of the electron emission spectra (analog to those recorded in the first experimental series) were carried out in the beginning of the second series and after 1, 2, and 4 hours of X-ray irradiation under -50 V applied.

Two independent series of the 600 eV Ar<sup>+</sup> bombardment of PVDF were carried out, wherein the dose was increased in a step-by-step manner (series 3 and 4). The maximum dose of  $4.5 \cdot 10^{15}$  ions/cm<sup>2</sup> was achieved in both cases. An additional series of the Ar<sup>+</sup> bombardment (series 5) was carried out with the use of 720 eV ion energy and a maximum dose of  $1.9 \cdot 10^{14}$  ions/cm<sup>2</sup>. Finally, the last series of measurements (6) was aimed at revealing the effect of lowest bombardment doses, when bombarding with 600 eV ions. In series 3–6, the XPS and XAES measurements were performed between the steps in order to monitor chemical composition and electronic structure of the irradiated surface. The features of all experimental series are summarized in TABLE 2.

The electron emission spectra were obtained in the binding energy intervals including F2s, C1s, F1s, and C KVV regions. The C1s range (270–330 eV, passing energy 320 eV) was scanned before and after recording of any other spectrum. It was used to control the X-ray power, to monitor electrostatic charging of the sample, and to determine relative atomic contents of fluorine (F/C), using F1s/C1s and F2s/C1s intensity ratios<sup>[5]</sup>. Similarly to previous observations<sup>[6,7]</sup>, we have found these ratios to afford close F/C values just in the very beginning of measurements, thus indicating a depth gradient of the fluorine content emerging and increasing due to the radiative carbonization. The detailed analysis of F2s/C1s ratios will be published elsewhere.

Recently we developed a route for the evaluation of non-uniformities in the depth distribution of fluorine based on measurements of F1s spectra in the 670–730 eV range of binding energies<sup>[11]</sup>. Generally, the deeper is the PVDF molecule from the surface being irradiated, the slower is the rate of defluorination. This causes

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a more significant decrease of the main F1s peak compared to decrease of its inelastic satellite. This effect is shown in figure 1 for the PVDF film used in series 1 after 100, 1670 and 5220 min of Al K<sub>α</sub> exposure. All the spectra are normalized to the maximum height. It is quite evident that the maximum intensity in the satellite region ( $h_2$ ) rises in relation to that of the main peak ( $h_1$ ) during carbonization. Hence, the intensity ratio of these two spectral features provides a parameter  $h_2/h_1$  reflecting the fluorine depth gradient within the layer attainable by XPS analysis. A schematic for the determination of parameters  $h_1$  and  $h_2$  is shown in figure 1.

The main problem in elucidating the relationship between C KVV spectral parameters and fluorine content was that measurements of F1s, C1s, and C KVV spectra could not be performed simultaneously. As the carbonization proceeds, the real fluorine content monotonously decreases, being different when scanning each of these spectra separately, and thus preventing a direct comparison. But just monotonic character of the process gives an opportunity of calculating fluorine content at any time of the experiment. To measure F1s/C1s ratio and then relative fluorine content F/C we used average integral intensities of two C1s spectra obtained just before and after recording of each F1s spectrum. After that the dependence of F/C versus duration of X-ray exposure for series 1 (Figure 2) was interpolated with a 6th power polynomial equation, which very closely fits experimental data. The equation allows one to calculate average fluorine content when scanning each of C KVV or any other electron emission spectra (hereafter “calculated F/C values”). Special measurements have shown the validity of this equation for all the experimental series in this study. This fact suggests that if the X-ray source power is constant, the rate of carbonization induced by X-rays and secondary electrons does not depend on the preliminary treatment of the sample by a flux of Ar<sup>+</sup> ions or secondary electrons at a constant voltage applied to the sample holder.

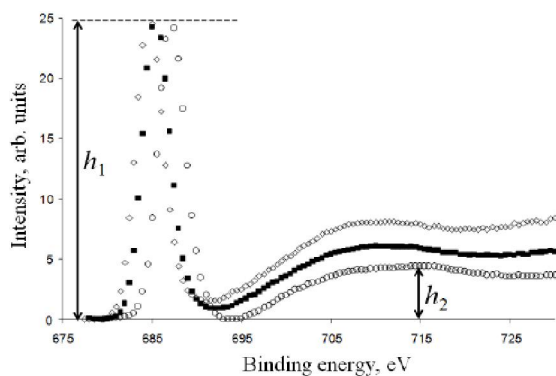
As it has been revealed previously in numerous studies, the shape of C KVV spectra is extremely sensitive to the mode of mutual arrangement of carbon atoms<sup>[12]</sup>. To avoid artifacts, which may be caused by insufficient statistical averaging of C KVV spectra, the latter have been smoothed heavily (100 iterations with a 5 eV filtering interval). First derivatives of C KVV spectra

obtained from the samples in the beginning and in the end of series 1 and after a maximum dose of the ion bombardment (series 3) are presented in figure 3. All of them contain 3 dominant features A, B, and C, whose energy positions and intensities noticeably differ in each of the three curves. In this study we used two parameters of the C KVV line-shape first derivative. The first of them ( $\Delta$ ) introduced by Galuska<sup>[13]</sup> is the energy difference between the positions of features A and B. The second one, being the intensity ratio of features C and A, is introduced here as a C KVV shape parameter for the first time ( $h_4/h_3$ , Figure 3). Both parameters significantly vary during radiative carbonization, thus demonstrating their sensitivity to the electron structure modification.

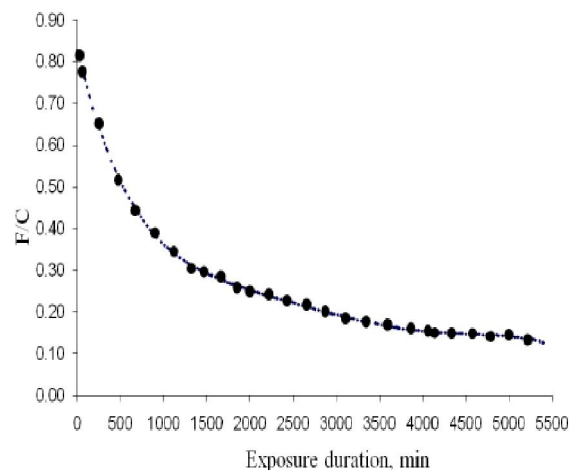
## RESULTS & DISCUSSION

Our study reveals two noticeable effects clearly showing the presence of secondary electrons and their influence on the electron emission spectra. Both of them concern energy positions of C1s and F1s peaks maxima. These positions, measured for dielectric samples differ from the commonly adopted values<sup>[14]</sup> due to electrostatic charging. The photoemission causes positive charging of the sample surface, thus shifting peaks towards higher binding energies. Naturally, secondary electrons impinging the surface shift the peaks to the opposite side. In our case the positions of C1s and F1s peaks are considerably lower as compared to reported values<sup>[14]</sup>, thus suggesting overcompensation of the effect of positive charging and indicating the presence of secondary electrons in considerable amount.

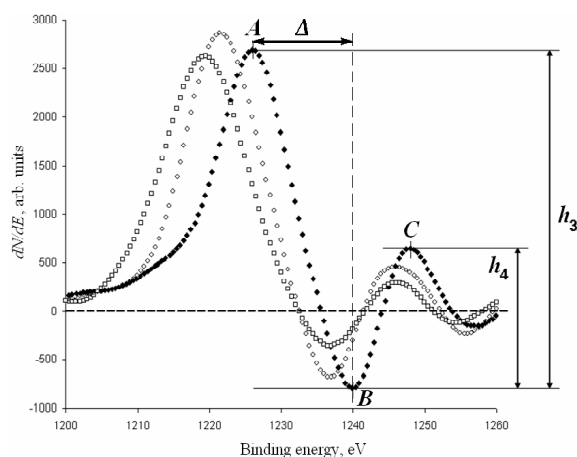
The second effect is a reliably observed shift of C1s peak towards higher binding energy in the spectra recorded immediately after each C KVV measurement (Figure 5). This is due to certain inertness of charging: as negative voltage is applied to the sample holder (TABLE 1) when scanning C KVV spectra, secondary electrons are rejected by the surface, thus eliminating the compensation effect of positive charging. Fast scanning of C1s spectrum (for ca. 2 min) just after recording C KVV (ca. 70 min) does not give enough time for accumulation of secondary electrons on the sample surface in sufficient quantity to return C1s peak in its position in case of “usual” overcompensation.



**Figure 1 :** Determination of parameters  $h_1$  and  $h_2$ , which are heights of F1s peak and its inelastic satellite, respectively : The normalization to the height of F1s peak is necessary to make the effect better visible : Spectra 1–3 were scanned 100, 1670, and 5220 min after the start of Al  $K_{\alpha}$  irradiation (series 1)



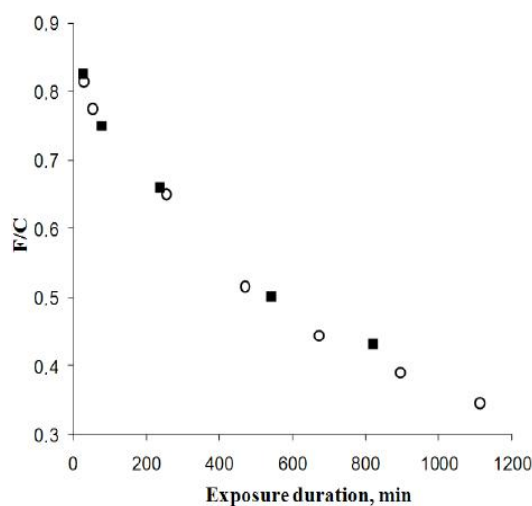
**Figure 2 :** Comparison of experimental (filled circles) and calculated (dots) F/C values for series 1



**Figure 3 :** First derivatives of C KVV spectra of a starting film ( $\blacklozenge$ ), after maximum X-ray exposition ( $\diamond$ ), and after maximum  $\text{Ar}^+$  dose ( $\square$ ) : The determination of spectral parameters  $\Delta$  and  $h_4/h_3$  is also shown

Two additional questions arise in this connection: i) can secondary electrons influence the rate of defluorination and ii) can their energy affect the position of spectral features?

The F/C variations over time of exposure in series 1 and 2 are presented in figure 5. Both sets of data demonstrate very similar behavior. This fact suggests that secondary electrons, although definitely exist, do not noticeably affect the rate of defluorination. Hence, the interaction of PVDF with Al  $K_{\alpha}$  photons plays a dominant role in the carbonization process. This also means that total duration of exposure, provided the power of the X-ray source being constant, is a crucial parameter in the defluorination kinetics<sup>[12]</sup>, regardless energy variations of secondary electrons that occur while

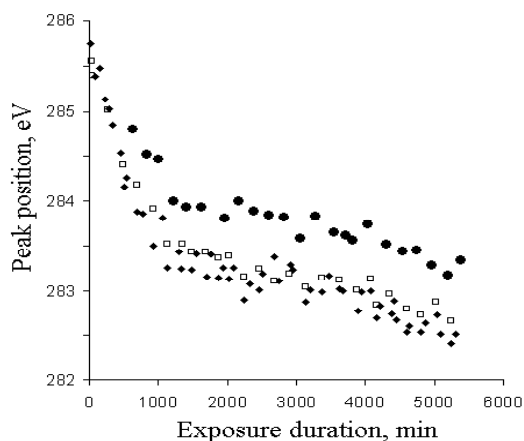


**Figure 4 :** F/C variations measured from F1s/C1s ratio versus duration of exposure in comparable periods of time for series 1 ( $\circ$ ) and 2 ( $\blacksquare$ )

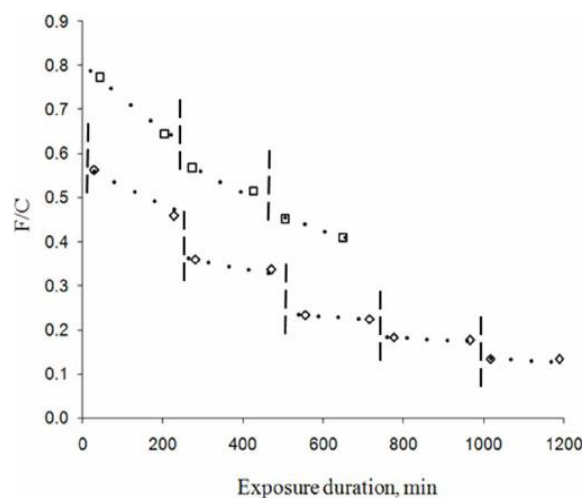
scanning different ranges of binding energy.

Figure 5 gives an answer to the second question. It shows variations of C1s and F1s energy positions over time of measurements in series 1. The virtual lowering of binding energy is most probably caused by the increase of conductivity in the carbonized surface, which diminishes effects of positive charging. One can notice very similar behavior in the case of scanning C1s and F1s spectra, thus suggesting the same overcompensation, i.e. the same currents of secondary electrons towards the sample, notwithstanding the fact that energies of secondary electrons are quite different (a saturation regime). The variation of C1s peak measured directly after scanning C KVV spectra and plotted as a series of filled circles evidently illustrates the inertness

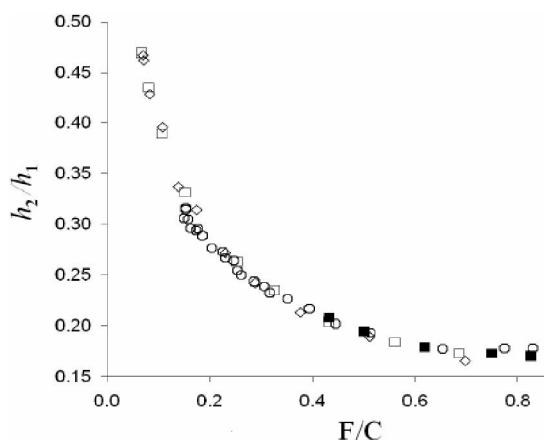
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**Figure 5 :** Variation of C1s (◆ and ●) and F1s (□) energy positions vs : duration of measurements in series 1 : In order to get visually comparable dependencies in the same plot the data of F1s measurements were shifted 402 eV towards lower binding energies : The upper series of measurements (●) corresponds to C1s spectra obtained immediately after C KVV scans



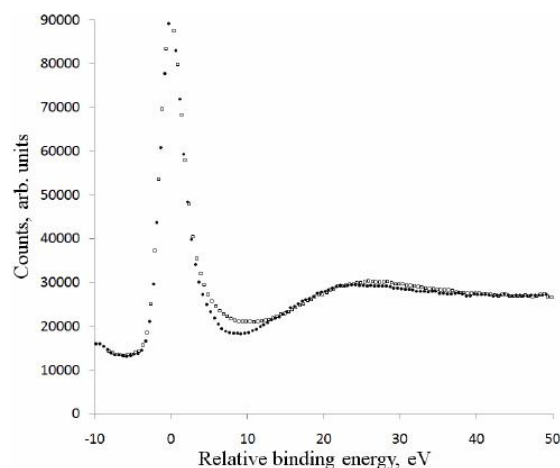
**Figure 6 :** Time variation of relative atomic fluorine content (F/C) in experimental series 5 (◇) and 6 (□) in comparison with values calculated from the polynomial equation fitting the data from series 1 in comparable ranges of residual fluorine content (dots)



**Figure 7 :** The intensity ratio of F1s satellite to F1s peak plotted vs : F/C measured from F1s/C1s ratio for series 1 (○), 2 (■), 3 (□), and 4 (◇)

of charging discussed above.

The rate of defluorination of PVDF induced by Ar<sup>+</sup> ions (series 3–6) is higher in comparison with data from series 1. Therefore, in order to superimpose the defluorination rates under interaction of the sample with photons and ions special additional measurements were carried out (series 5 and 6). After each step of bombardment with Ar<sup>+</sup> ions (720 eV and 600 eV in series 5 and 6, correspondingly) the F1s/C1s ratios were registered twice in the beginning and in the end of Al K<sub>α</sub> irradiation during XPS and C KVV measurements within 200–260 min. The results are presented in figure 6. The intervals in which ion bombardment occurred



**Figure 8 :** C1s spectra of carbonized PVDF derivatives obtained in the end of series 1 (●) and 3 (□)

(marked with vertical broken lines) varied from 15 s to 3 min and are negligibly small as compared to the duration of photon irradiation. However, the results of each step of ion bombardment are clearly visible in figure 6 as step-like drops in F/C ratio. These drops are smaller in case of series 6 due to much smaller a dose increment and, possibly, due to lower energy of ions. On the other hand, a careful analysis has revealed that the defluorination rates in the intervals of time, when only Al K<sub>α</sub> photons and secondary electrons affect the sample surface, are almost identical to those observed in series 1 in comparable F/C ranges. This means that the polynomial equation used to fit the F/C variation in

**TABLE 1 : Binding energy ranges and voltage regimes used during XPS measurements**

Spectrum	Binding energy range, eV	Voltage range, V	Analyzer passing energy, eV
C1s	278 ÷ 294	1130 ÷ 1114	70
C1s	270 ÷ 330	891 ÷ 831	320
Valence band, F2s	-5 ÷ 45	1166 ÷ 1116	320
F1s	670 ÷ 730	491 ÷ 431	320
C KVV	1170 ÷ 1270	-9 ÷ -109	320

**TABLE 2 : Main experimental parameters employed in different series of radiative carbonization of the PVDF film**

Series No :	Dominant carbonizing agents	Voltage applied, V	Maximum exposure, min (Al K <sub>α</sub> / Ar <sup>+</sup> )	Maximum dose, 10 <sup>13</sup> ions/cm <sup>2</sup>
1	Al K <sub>α</sub> photons and secondary electrons	Various	5400 / 0	0
2	Al K <sub>α</sub> photons	-50	820 / 0	0
3	Ar <sup>+</sup>	600	1800 / 120	450
4	Ar <sup>+</sup>	600	1800 / 120	450
5	Ar <sup>+</sup>	720	1230 / 5	19
6	Ar <sup>+</sup>	600	670 / 1.5	1.1*

\*The Ar<sup>+</sup> ion current was 5 times weaker than in series 3-5

series 1 can be applied to calculate relative fluorine content at any moment during the X-ray irradiation and that the rate of defluorination induced by Al K<sub>α</sub> photons does not depend on preliminary treatment of the sample with ions. This fact is illustrated in Fig. 6. Hence, just a single F/C measurement between two series of ion bombardment is enough to obtain a current F/C value, provided the power of X-ray source is stable. Thus, the parameters of any XPS and C KVV spectra can be plotted as a function of F/C so as to compare effects of Al K<sub>α</sub> irradiation and ion bombardment upon the spectral lineshape, which is sensitive to electronic structure of carbonized species being created in the polymer surface during its radiative carbonization.

The intensity ratio of the F1s satellite and F1s peak ( $h_2/h_1$ ) was determined for all F1s spectra obtained in series 1-4 and plotted in figure 7 versus F/C measured from the F1s/C1s ratio.

All the data show a very close resemblance, no matter photons or ions irradiate the surface. This fact appears to be the most surprising in this study. It means that both photons and ions produce the same depth gradient of fluorine, if the fluorine content in the surface layer attainable for XPS analysis is the same. In fact, one could hardly predict such a result, bearing in mind

a huge difference in momenta of these two sorts of particles.

At passing energy of 320 eV the resolution is rather poor and it does not allow a detailed compositional analysis of C1s lineshape similar to that we have performed previously<sup>[7]</sup>. Nevertheless, there are two features that depend on the kind of radiative treatment of the sample and become most obvious in the stages of profound carbonization. Figure 8 shows C1s spectra of carbonized PVDF obtained in the end of series 1 and 3.

The spectra are aligned by the energy position of their main peaks adopted as zero to remove charging effects and normalized by their total area within the same energy intervals.

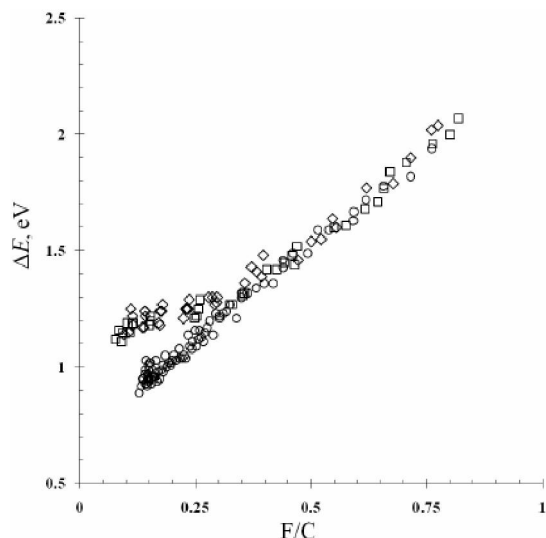
The main distinction is observed within the 4-12 eV binding energy range: the spectrum intensity is higher in series 3. This feature is consistent with inelastic scattering inherent in sp<sup>2</sup> hybridized carbons and known as so-called “π plasmon”. A weak but quite obvious shift of the main satellite feature (“σ+π plasmon”) towards higher binding energy in series 3 provides further confirmation to the idea that sp<sup>2</sup> hybridized carbon species emerge in the sample surface due to the ion bombardment. This modification of C1s lineshape was exactly reproduced in the end of series 4, when the same irradiation dose was achieved. On the contrary, after maximum duration of Al K<sub>α</sub> exposure in series 1, some carbon structures with hybridization mode different from sp<sup>2</sup> predominate in the carbonized polymer surface. An additional experiment has shown that these structures are unstable under ion bombardment, which gives rise to their gradual transformation into sp<sup>2</sup> structures with increasing dose.

Further analysis confirmed that surface modification occurs not in a sudden way but gradually. Figure 9 shows variation of ΔE parameter characterizing asymmetry of C1s line, depending on calculated F/C ratio in experimental series 1, 3, and 4.

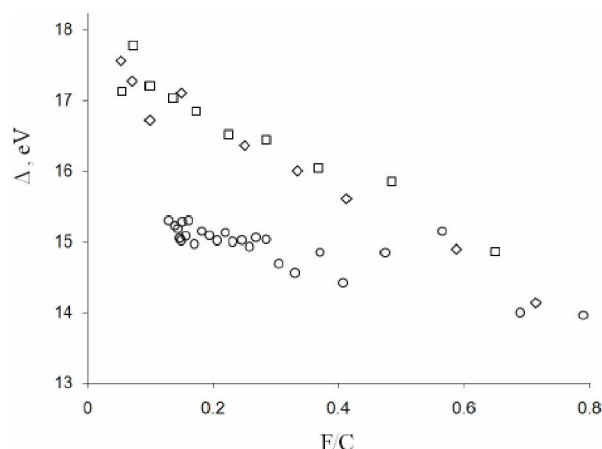
The ΔE parameter was measured as an energy difference between the position E<sub>0</sub> of the lower binding energy peak of C1s doublet and a “mass center” of the C1s spectrum within the binding energy range between E<sub>0</sub>-5 and E<sub>0</sub>+9 eV after subtraction of the constant background component.

Defluorination should decrease the intensity of core

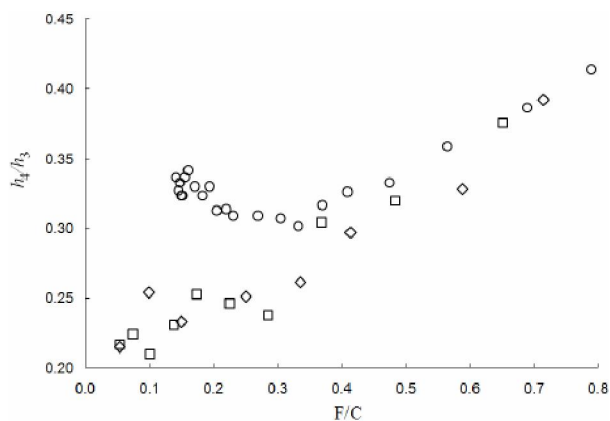
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**Figure 9 :** Variation of the C1s line asymmetry parameter ( $\Delta E$ ) vs : calculated F/C ratio in experimental series 1 (O), 3 ( $\square$ ), and 4 ( $\diamond$ )



**Figure 10 :** Modification of  $\Delta$  parameter vs : calculated F/C values in series 1 (O), 3 ( $\square$ ), and 4 ( $\diamond$ )



**Figure 11 :** Modification of  $h_4/h_3$  parameter vs : calculated F/C values in series 1 (O), 3 ( $\square$ ), and 4 ( $\diamond$ )

photoelectrons emitted from fluorine-bonded carbon atoms. This makes C1s line more symmetrical. On the contrary, the increase of the feature caused by interband transitions in the empty  $\pi$ -states (“ $\pi$ -plasmon”) should make it more asymmetrical. As one can see from Fig. 9, when going from original F/C values down to ca. 0.5, the dependence of  $\Delta E$  vs. F/C is linear and almost the same in series 1, 3 and 4 regardless the nature of irradiating particles (either Al  $K_{\alpha}$  photons or  $Ar^+$ ). At lower F/C values the decrease in  $\Delta E$  became less pronounced in experiments with ion bombardment, thus providing additional evidence for the gradual formation of  $sp^2$  hybridized carbon species in the stages of profound carbonization.

Variations of parameters  $\Delta$  and  $h_4/h_3$  versus calculated F/C values in series 1, 3, and 4 are shown in Figures 10 and 11, respectively. In series 3 and 4 (ion bombardment) the  $\Delta$  parameter rises almost linearly, when decreasing F/C, and approaches the value characteristic of graphite (ca. 20 eV<sup>[13]</sup>).

In series 1 (Al  $K_{\alpha}$  irradiation) this parameter appears to vary in a more complicated way: initial increase in the beginning of carbonization is almost the same as under ion bombardment. In the F/C range between 0.6 and 0.4 the  $\Delta$  decreases and, with further decreasing fluorine content it rises again, showing a tendency for saturation. The dispersion of experimental data in this F/C region is most probably due to an error of measurements. Variations of the  $h_4/h_3$  parameter of C KVV lineshape during radiative carbonization (Figure 11) are also different in cases of Al  $K_{\alpha}$  irradiation and  $Ar^+$  bombardment only if F/C becomes less than 0.4.

## CONCLUSIONS

All the data obtained show that both kinds of radiative treatment of partially crystalline PVDF applied in this study (i.e. soft X-ray Al  $K_{\alpha}$  irradiation and  $Ar^+$  bombardment) lead to carbonization of the sample surface. Secondary electrons formed in the filtering foil and in the walls of the chamber play an important role in electrostatic charging of the surface, but their contribution to the rate of defluorination process is quite small if any. In the case of Al  $K_{\alpha}$  irradiation the relative fluorine content, F/C, decreases, although not linearly as it was previously found by Duca et. al.<sup>[2]</sup> but monotonously. If



the power of X-ray source is constant, the rate of this monotonic variation depends only on F/C, but not on the nature of preliminary radiative treatment. This allows one to calculate F/C at any moment of measurements, thus providing an opportunity for comparison of spectral features inherent in PVDF samples carbonized to the same extent either by Al K $\alpha$  irradiation or by Ar $^{+}$  bombardment.

In this study we have introduced new lineshape parameters sensitive to the valence state of carbon in addition to those already known hitherto. Analysis of C1s and C KVV lineshape has revealed obviously different electronic structure of carbonized layers derived from PVDF via two kinds of radiative treatment. In case of Ar $^{+}$  bombardment the sp $^2$ -bonds predominate. The Al K $\alpha$  irradiation leads to some other form(s) of carbon, but additional ion bombardment transforms them into species with predominating sp $^2$ -bonding. Two stages of carbonization caused by defluorination of CF $_2$  and CF groups are confirmed. The first one can only lead to fluorine-substituted polyenes regardless the nature of irradiation. Hence, the lineshape parameters vary in the same way, when F/C is larger than 0.5. During the next stage, "naked" carbon atoms appear in the chains, while their mutual arrangement is governed by the nature of carbonizing radiation. Ions possess high momentum and, therefore, they most probably can produce distortions large enough to effect cross-linking with the formation of sp $^2$ -bonds. In the case of Al K $\alpha$  photons the formation of one-dimensional carbon is quite possible. Although the CF $_2$   $\rightarrow$  CF and CF  $\rightarrow$  C reactions may occur simultaneously in different polymeric chains or in different parts of the same chain, the rate of the former is considerably higher than that of the latter<sup>[12]</sup>.

Finally, the most puzzling result of this study is that both photons and ions produce the same depth gradient of fluorine, provided the fluorine content is the same in the layers of carbonized surface accessible for XPS analysis. This fact is confirmed in numerous independent experiments and is unlikely to be a fortunate coincidence. Nevertheless, its nature is not clear and has yet to be dealt with.

#### ACKNOWLEDGEMENT

The authors gratefully acknowledge the Russian

Foundation for Basic Research for financial support of this study (grant No. 7-02-96008) and Prof. Vitaly Latyushin for his permanent interest and kind assistance.

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