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A model of radiation-induced degradation of the poly(vinylidene fluoride) surface during XPS measurements

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Abstract

Carbon core-level spectra of poly(vinylidene fluoride) (PVDF) have been studied by X-ray photoelectron spectroscopy (XPS) using a non-monochromatic (Al K_α) source. Surface degradation has been observed during prolonged measurements. Monotonic modification of the C1s-line satellite during dehydrofluorination of PVDF suggests the emergence of additional possibilities for inelastic energy losses, which may be due to the formation of some new peculiarities in the combined density of states (DOS) caused by the change in the hybridisation mode of carbon valence electrons. A simple mathematical model has been proposed to describe the radiation-induced carbonisation of PVDF. The calculated data nicely fit experimental results.

Keywords: Poly(vinylidene fluoride); XPS; Radiative degradation; Mathematical model

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1. Introduction

In 1998 Duca et al. reported on the effect of the surface degradation of poly(vinylidene fluoride) (PVDF) during XPS measurements [1]. It was shown that under X-ray irradiation the surface content of fluorine (and probably hydrogen) in PVDF decreased.

A decade before, Le Moel et al. studied dehydrofluorination of PVDF induced by irradiation with high energy ions (O, Kr, and Xe), X-rays, and electrons [2–5]. At early stages of irradiation the authors observed the appearance of two peaks in the C1s spectra at 284.6 and 285.1 eV, which were assigned to vinylene and methine carbon atoms, respectively. The energy and intensity of these peaks were found to depend on the irradiation dose. To explain their results, the authors proposed a reaction scheme involving simultaneous elimination of two HF molecules from three neighbouring carbon atoms with the formation of allenic fragments in the first stage [2]. The model was based on the lack of the peak of fluoromethine groups, which was expected to appear at 287–288 eV. According to this model, higher irradiation doses give rise to further elimination of hydrogen fluoride with the formation of longer cumulene sequences, i.e. carbynoid structures [6]. The formation of hydrogen fluoride was confirmed by mass-spectroscopic measurements [2]. Actually, the formation of HF during dehydrofluorination is beyond a doubt. However, the above-mentioned scheme appears

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to be rather unlikely, since it suggests selective excitement of exclusively difluoromethylene CF_2-groups by ions, electrons, and photons followed by simultaneous elimination of two HF molecules from two adjacent C–C-bonds. When studying chemical dehydrofluorination of PVDF, Ross et al. [7,8] noted that carbonyl C=O group does also contribute to the C1s-spectrum in the 287.7–288.0 eV range of binding energies. The authors pointed out that the spectral resolution of standard XPS does not suffice to unambiguously distinguish between some of the fluorine- and oxygen-containing groups in the elimination products [7], and the assignment of the peaks can include more than just one component [8]. Moreover, the signal (or signals) of fluorovinylene and fluoromethine groups might be hidden by a strong peak of CF_2-groups at 290.5–290.9 eV, as it was observed by Duca et al. [1], while vanishing at later stages due to their consumption caused by further elimination.

Later, Le Moel et al. proposed a four-centre mechanism for a single elimination act based on the assumed existence of hydrogen-like bonds between hydrogen and fluorine atoms in the polymer backbone in certain conformations [3]. According to that mechanism, the weakening of the C–H- and C–F-bonds due to their excitement upon irradiation can facilitate strengthening of the H···F-bond, resulting in the desorption of the HF molecule.

Despite extensive studies, the mechanism of the radiation-induced degradation of PVDF is still not clearly understood. Therefore, additional experimental data are needed to reveal fine features of the degradation process and to develop an appropriate model for its description.

Obviously, the elimination of fluorine modifies the hybrid state of carbon atoms, making it different from sp^3-type that is characteristic for pristine PVDF. On the other hand this alteration of the hybrid state was recently found to affect the XAES/XPS (CKVV/C1s) intensity ratio [9]. Most probably, the variation of carbon valence state modifies the probability of multiple effects leading to large energy losses by an Auger electron. This effect implies that certain changes in electronic structure of PVDF occur during prolonged XPS measurements. In this case one should expect modifications in the density of the valence and empty electronic states. As a result the spectrum of the band transitions, which are induced by emitted photoelectrons, must change. One of the reasons for the interband transition is the process of inelastic interactions of the core-level photoelectrons with valence electrons of the parent or neighbouring atom. Therefore, the shape of the energy loss spectra of the core photoelectrons is expected to reflect the changes in electronic structure due to defluorination.

The present paper reports on a study of the carbon core-level spectra in PVDF during prolonged XPS measurements. To describe the process of the radiation-induced carbonisation, a simple mathematical model has been proposed.

2. Experimental

The partially crystalline PVDF film (KYNAR, type 720, thickness 50 μm) was kindly donated by ATOFINA.

The XPS/XAES spectra were measured using a home-made ES IFM-4 spectrometer developed and assembled at the Institute of Metal Physics, Ekaterinburg, Russia [10]. The starting PVDF film was fixed on edges of a sample holder by means of thin elastic tungsten strings and exposed for ca. 970 min to non-monochromatic Al K_α radiation filtered with an aluminium foil in the spectrometer. The Al $K_{\alpha1,2}$ photons ($\hbar\nu = 1486.6$ eV) predominate in Al K_α radiation, and hence they excite the most of photoelectrons. However, the yield of photoemission due to the Al$K_{\alpha1,2}$ photons comes to about 10% of the total intensity. The single (Al) anode (power ca. 300 W) was permanently and effectively cooled with a flow of distilled water. This prevents the heating of the sample: its temperature was maintained at 25–27 °C. The distance between the anode and the sample was 35 mm. The electron optics of the spectrometer includes a retarding system consisting of two plane parallel grids and a Siegbahn's type magnetic analyser [11] based on two pairs of coaxial coils providing double focusing in the optical axis within a radius of 30 cm. Apertures provide the relative resolution value of 7×10^{-3} which gives absolute value of ca. 2.2 eV for our spectra obtained with constant passing energy of 320 eV. Though 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/XAES monitoring of anticipated changes in the unstable surface of PVDF. The retarding voltage was applied to the sample, while the potential of a chamber of the energy analyser was zero. The pressure of residual gases did not exceed 10^{-9} Torr. Two survey spectra were measured at the beginning and the end of the experiment (Fig. 1). The survey spectra demonstrate the presence of fluorine and carbon as dominant elements. Small amounts of oxygen (ca. 4%) in the polymer can probably be explained by oxygen-containing auxiliary substances (like stabilizers, antistatic agents, etc.) in the commercial PVDF film. The F1s/C1s and F2s/C1s ratios show a similar decrease with time of exposure. No variations of O1s/C1s ratio have been observed throughout the duration of the experiment. The fluorine content was determined using the reference values of the photoemission cross-section [12] and taking into consideration the transmission function of the spectrometer [10]. The C1s-, F1s-, C KVV and valence band spectra

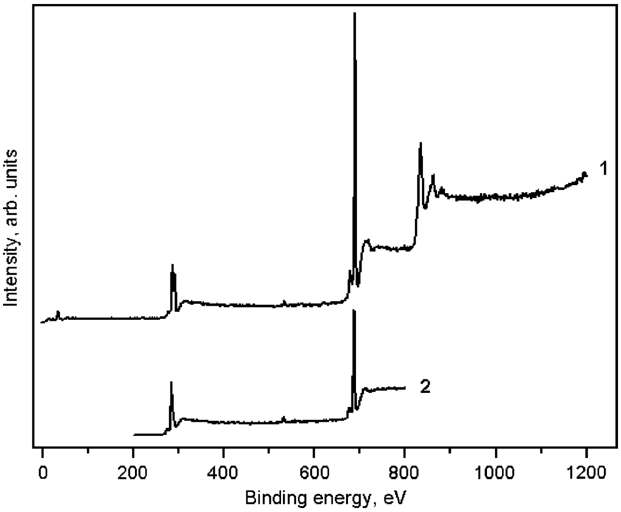

Fig. 1. Survey spectra measured in the beginning (46 min, spectrum 1) and in the end (970 min, spectrum 2) of the experiment.

along with F2s-line were scanned continuously during the entire period of exposure. The integral intensity of C1s-spectra was chosen as a natural internal normalizing factor [13]. Thus, these spectra were scanned before and after registration of every other spectrum to control the stability of the exciting X-ray flux.

3. Results and discussion

During the prolonged measurements the shape of the carbon core-level spectrum was changing (Fig. 2). The C1s-peak consists of two components. The intensity of the dominant peak, being formed by the core-level photoelectrons emitted from carbon atoms C* that have no chemical bonds to fluorine, was found to increase. This group of fluorine-free carbon atoms C* includes both methylene carbons (CH_2) in original PVDF and those formed during degradation (methine CH or "naked" carbons in various hybridisation modes). The intensity of the second peak caused by the photoemission from carbon atoms of CF_2-groups decreased. During the experiments the effect of electrostatic charging became weaker probably owing to increasing conductivity of the exposed film due to the elimination of fluorine. To take this effect into account the binding energy scale (E_b) should be renormalized. It was done by taking the binding energy position of the dominant peak (E_{C1s}) as a unique zero value for each spectrum. All the raw spectra were first identically treated to remove the yield of Al $K_{\alpha3,4}$ radiation. Then the C1s-spectra, which were measured for ca. 21–22 min at the end and at the beginning of the experiment, were summed. Both spectra accumulated in this way were normalized to the equal area before subtraction. The difference spectrum thus obtained is shown in Fig. 3.

It has some meaningful features. Positive ones are caused by an increase in the proportion of carbon atoms chemically bonded to only carbon (a) and of CF-groups (b) on the surface of the film during measurements. A high-intensity negative feature near 5 eV (c) reflects a decrease in the surface content of CF_2-groups. Further analysis of the difference spectrum reveals a small but clear increase of intensity in a rather broad binding energy range (ca. 7–18 eV from the position of the dominant peak) with a maximum (d) at 9 eV.

The last feature is most probably associated with the emergence of additional possibilities for inelastic energy losses, which may be due to the formation of some new peculiarities in the combined density of states (DOS) caused by the change in the hybridisation mode of carbon valence electrons.

The presence of feature (d) near 9 eV in the difference spectrum is also noticeable even in the raw spectra (Fig. 2). The analysis shows that the growth of its intensity with increased time of exposure (or decreased content of fluorine) occurs not abruptly but gradually.

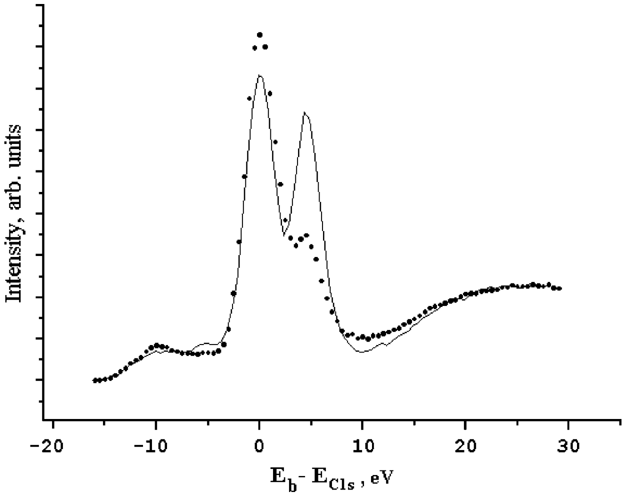

Fig. 2. Line shapes of C1s-spectra in the beginning (solid line) and in the end (dotted line) of measurements after renormalization.

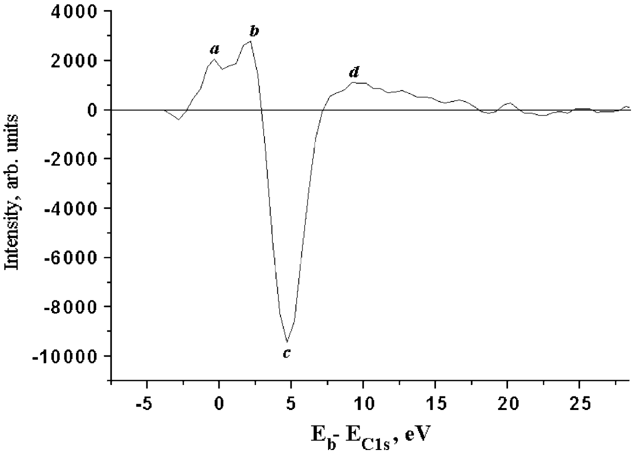

Fig. 3. Difference spectrum of C1s-spectra obtained in the end and in the beginning of XPS measurements.

Apparently this rise is caused by the increase in abundance of carbon atoms whose state of hybridisation of the valence electrons differs from sp^3. To evaluate this effect at first absolute intensity at binding energy of 9 eV was measured in each core-level spectrum. The obtained value was then normalized to the integral intensity of the same spectrum. The dependence of normalized intensity of the energy loss spectrum at 9 eV on the content of fluorine is plotted in Fig. 4. Its almost linear character clearly demonstrates that the increase in the number of modified carbon atoms results from the decrease in the fluorine content.

To describe in general terms the degradation process that can be referred to as radiative dehydrofluorination, a simplified mathematical model can be proposed. We assume that any fluorine atom may leave the sample only being coupled with a hydrogen atom, thus generating an HF molecule. This assumption is supported by the data of mass-spectroscopic measurements [2]. Our suggestion, however, does not take into account the possibility of random elimination of neutral fluorine and hydrogen atoms as free radicals $F^{\cdot}$ and $H^{\cdot}$, which can recombine in the gas phase to form HF as a major product or F_2 and H_2 (minor products), though the probability of this process is much lower than that of splitting off "coupled" HF [2,3].

We next assume that the elimination of the HF molecule only occurs when CF_2 (or CF)-group is located next to CH_2 (or CH)-group. This assumption does make sense inasmuch as C–X bonds (X = H or F) in vinylene groups are stronger than those in saturated CX_2-groups and much stronger than those in allylic C=C–CX-groups.[1] Therefore, when an allylic group gets excited by a photon, the counter-ion will be split off from the next saturated group, just because the neighbouring =C–X bond is stronger. Once several first double bonds have been formed, further elimination becomes easier due to the effect of allylic activation, and the polyene sequences can start growing similarly to the well known chain-like zip-process of thermal dehydrochlorination of PVC [15].

A decline in the proportion of CF_2-groups in this case can be described by Eq. (1):

$$-\mathrm{d}N_1 = k_1 N_1^2\,\mathrm{d}t, \tag{1}$$

where k_1 is a coefficient, characterizing the probability of transformation CF_2–CH_2 → CF=CH and N_1 is the proportion of CF_2-groups at any moment of X-ray exposure.

The exponent 2 appears in this equation inasmuch as the numbers of CF_2- and CH_2-groups are assumed to be the same at any moment of XPS measurements. In reality, however, the ratio of these numbers can slightly deviate from 1 due to the presence of intrinsic defects in the polymer chains. The polymers produced by common polymerisation technologies always contain a certain proportion of defect structures such as "head-to-head" and "tail-to-tail" links [16,17] as well as branching sites [18,19]. In particular, PVDF was shown to contain up to 6 mol.% [16,17] of abnormal links.

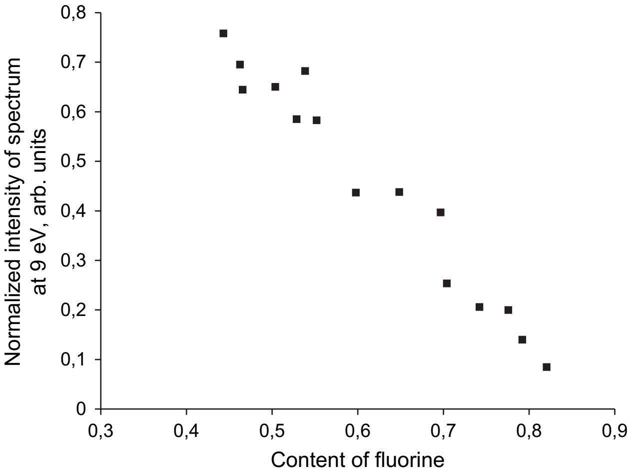

Fig. 4. Dependence of normalized intensity of the energy loss spectra at 9 eV on the fluorine content.

The solution of Eq. (1) gives:

$$N_1 = \frac{N_{1(0)}}{\tau}, \tag{2}$$

where $N_{1(0)}$ is original proportion of CF_2-groups, and

$$\tau = 1 + k_1 N_{1(0)} t. \tag{3}$$

The change in the proportion of CF-groups (N_2) during the measurements may be written as:

$$\mathrm{d}N_2 = -k_2 N_2^2\,\mathrm{d}t + k_1 N_1^2\,\mathrm{d}t, \tag{4}$$

The integration of Eq. (4) gives:

$$N_2(\tau) = \frac{\frac{N_{1(0)}}{\gamma}(\tau^{\gamma} - 1)}{(a_2\tau^{\gamma} + a_1)\tau}, \tag{5}$$

where

$$\gamma = \frac{k_2}{N_{1(0)}k_1};$$

and

$$a_1 = \frac{1}{2\gamma} + \sqrt{\frac{1}{4\gamma^2} + \frac{N_{1(0)}}{\gamma}} > 0;\quad a_2 = -\frac{1}{2\gamma} + \sqrt{\frac{1}{4\gamma^2} + \frac{N_{1(0)}}{\gamma}} > 0.$$

The content of fluorine at the beginning of experiment was found in the following way. The peak intensities h_1

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[1] The energy of the C–X bond in allylic compounds, H_2C=CH–CH_2X, is known to be 50–105 kJ/mol less than that in saturated analogues [14].

and h_2 of two components of C1s-doublet (fluorine-free C^* and fluoromethylene CF_2, respectively) were measured. We assumed that there are no CF-groups present at the beginning of the experiment (exposure time $t = 0$). However, one should remember that the real polymer may contain tertiary CF- and CH-groups at branching sites whose amounts can be different. Nevertheless in our model the sum $h_1 + h_2$ is attributable to the total yield of carbon atoms. The ratio $h_2/(h_1 + h_2) = 0.41$ at $t = 0$ is proportional to the relative content of CF_2-groups. Therefore the relative fluorine content can be obtained by doubling this value. Thus the F1s/C1s ratio and the relative fluorine content of 0.82 are known for the beginning of the experiment. This allows one to calculate the factor of proportionality between these two values. As the F1s/C1s ratio is proportional to the fluorine content, the relative content of fluorine at any time of exposure can be calculated by multiplying F1s/C1s by this factor. Experimental results and calculated data are compared in Fig. 5. The empirical dependence of relative fluorine content on time of exposure is represented by the series of black circles (1). The dotted line running very close to the experimental series (1) shows the relative content of fluorine vs. time of exposure calculated from the equation:

$$N_F = 2N_1 + N_2. \quad (6)$$

Here N_1 and N_2 are obtained from Eqs. (2) and (5). Coefficients k_1 and k_2 are the only fitting parameters in this study. They have been found using the least-square technique to be 0.004346 and 0.001366, respectively, from comparison of the calculated curve (6) with the experimental one. These very values were then used for all the calculations presented below.

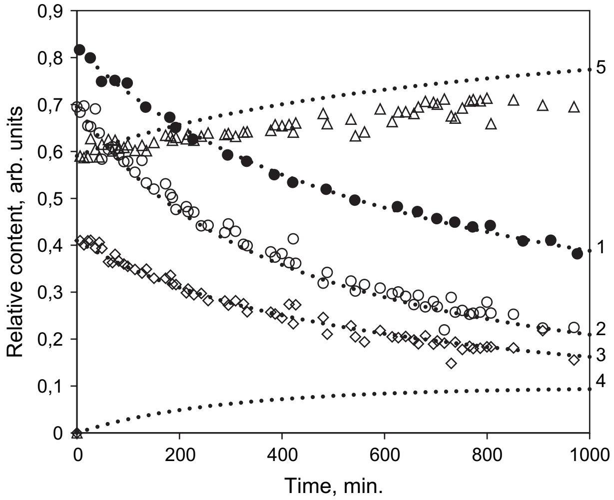

Fig. 5. Comparison of the observed and calculated data. 1 – Relative fluorine content vs. exposure time (● – experiment; dots – calculated); 2 – intensity ratio h_2/h_1 of $C1s^{CF2}$- and $C1s^{C*}$-components, respectively, vs. exposure time (○ – experiment; dots – calculated); 3 – intensity h_2 of $C1s^{CF2}$-component vs. exposure time (◇ – experiment; dots – calculated); 4 – calculated relative content of fluoromethine (CF)-groups vs. exposure time; 5 – intensity h_1 of $C1s^{C*}$-component vs. exposure time (△ – experiment; dots – calculated).

The series of open circles (2) shows the intensity ratio h_2/h_1 found from the experimental data vs. the exposure time. The adjoining dotted line shows a calculated dependence. The latter was found using the following consideration. The number of CF-groups must first increase due to defluorination, and therefore the intensity of C1s-peak which should be located strictly between the dominant peak and the CF_2-one [20] rises too. This peak is not noticeable experimentally because the spectra were scanned using high passing energy that allows one to speed up the spectral accumulation for monitoring their modification. This "virtual" peak equally increases the intensity of both observed peaks. We assumed that all C1s-peaks in this energy region are practically symmetrical and have the same shape. The ratio m of the main peak intensity at binding energy of 2.3 eV from the maximum towards the lower energies to its maximum intensity was measured and appeared to be 0.16±0.03. So one should expect the same yield from the CF-peak in the regions of localization of the peak maxima created by photoelectrons emitted from carbon atoms of both C^* and CF_2-groups. Therefore the calculated ratio of the observed peaks h_2/h_1 may be written as:

$$\frac{h_2}{h_1} = \frac{N_1 + mN_2}{N_3 + mN_2}. \quad (7)$$

Here N_3 is a content of carbon atoms, which has no chemical bonds to fluorine and may be calculated as:

$$N_3 = 1 - N_1 - N_2. \quad (8)$$

The series of rhombs (3) shows the experimental dependence of the h_2 height on exposure time. The normalization of h_2 was done while taking into account that the initial content of CF_2-groups was 0.41. The calculated dependence (black dots) was found as $N_1 + mN_2$.

The dotted line (4) represents a content of CF-groups (N_2) calculated from Eq. (2). The series of triangles (5) shows the experimental dependence of the normalized h_1 height vs. time of exposure. The content of carbon atoms (N_3) that have no chemical bonds to fluorine was determined from Eq. (8). The theoretical dependence (dotted curve slightly above) was found as $N_3 + mN_2$.

From Fig. 5 one can see that experimental data are in very good agreement with the calculations based on this model. This is a strong formal support to the proposed mathematical model of radiative carbonisation of PVDF during XPS measurements. It also means that our assumption that the contribution of intrinsic methine (CH)- and fluoromethine (CF)-groups which are present in the original PVDF as branching sites in overall degradation process does not much matter and can be neglected.

Two discrepancies with data reported by Duca et al. [1] are noticeable: (1) in our case the decrease is not linear, it shows a weak but quite clear tendency towards saturation; (2) the elimination degree of fluorine with respect to its content at 100 min in the 100–800 min-range is much higher in our case (44 and 12.4% [1], correspondingly). It should be noted that Beamson and Briggs have found a degradation index of 15% after 500 min irradiation based on F1s/C1s intensities measured using monochromatic Al K_α radiation [21].

One can suggest several plausible explanations of these contradictions. First, Duca et al. employed non-monochromatic Mg K_α radiation [1], in which the dominant photon energy is lower ($\hbar\nu = 1253.6$ eV) than that in our experiments ($\hbar\nu = 1486.6$ eV). Secondly, we have no information to compare X-ray intensity; it is quite probable that our X-ray source might be more powerful. Finally, since in our case the retarding positive voltage was applied to the sample the secondary electrons generated in the filtering foil or in the chamber walls could bombard the sample surface thus facilitating the elimination of fluorine. The latter effect explains as well the contradiction with the degradation index given by Beamson and Briggs [21]. Therefore, during our experiments the surface content of fluorine could become low enough to make the saturation tendency visible. Both mechanisms (degradation under X-rays and secondary electrons) are involved and proceed with different kinetics. If we could separate individual contributions due to each of them and find partial rates of defluorination, we should have obtained different values. But in our case they act simultaneously and continuously throughout the whole time of the experiment. Thus the sum of individual rates is simply the effective rate that we did measure, and we can consider our probabilities of CF_2, CH_2 and CF, CH dissipation, i.e. k_1 and k_2, to be the sums of relevant probabilities due to each of the individual mechanisms.

4. Conclusions

The shape of the C1s satellite spectra of PVDF has been found to alter during prolonged XPS measurements using a non-monochromatic (Al K_α) source. Owing to radiation-induced dehydrofluorination of PVDF, this monotonic modification corresponds to the emergence of additional channels for inelastic energy losses, which may be due to the formation of some new peculiarities in the combined density of states caused by the change in the hybridisation mode of carbon valence electrons. A simple mathematical model proposed to describe the process of the radiation-induced carbonisation is in very good agreement with experimental results. It should be admitted, however, that our model can describe the dehydrofluorination process in quite a general manner, while the detailed mechanism still remains unclear, yet leaving several questions to be dealt with. How does the fine mechanism of a single elimination act look? Whether elimination of both atoms (halogen and hydrogen) occurs simultaneously or in a stepwise manner with a very short delay in the femtosecond region? Are there any differences in the energy dissipation pattern and, consequently, the elimination mechanism, if a photon hits directly fluorine or hydrogen atoms, methylene CH_2 or difluoromethylene CF_2-groups? What is the role of photoionisation in principle? Is there any difference in probability of coupling if the photon hits a CF_2- or a CH_2-group? In our model the probabilities k_1 and k_2 may be considered as products of individual probabilities of independent events reflecting interaction of a photon with CF_2- and CH_2-groups or with CF- and CH-groups. The knowledge of these individual probabilities is important for more detailed understanding of radiative degradation of the PVDF surface. To answer these questions further experiments are necessary.

Acknowledgments

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