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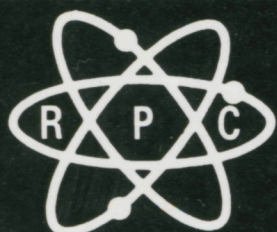
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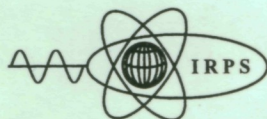
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Radiative defluorination of poly (vinylidene fluoride) under soft X-ray radiation

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Abstract

The rates of poly (vinylidene fluoride) (PVDF) degradation under synchrotron (SR) and conventional X-ray radiation have been measured and compared. NEXAFS spectra of fluorine show significant changes in their shape and intensity with elevation of radiation dose (or duration of SR exposure). Non-monochromatic AlK_α radiation and the flow of secondary electrons accompanying it also cause surface degradation of PVDF. XPS allows one to measure relative content of fluorine by three ways: via relative intensities of F2s/C1s, F1s/C1s, spectra and using the features arising due to of C1s peaks in CF₂ and CF groups.

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1. Introduction

The effect of surface degradation of poly (vinylidene fluoride) (PVDF) during X-ray exposure is quite well-known (Beamson and Briggs, 1992; Duca et al., 1998; Morikawa et al., 2000; Pesin et al., 2003; Voinkova et al., 2005), but the detailed mechanism of it is not fully understood. The result of this effect is dehydrofluorination of the sample surface with the formation of carbon atoms whose valence state is different from that characteristic for pristine PVDF. One can expect the

formation of nanoscaled chains, or graphite-like, or diamond-like clusters, or, most probably, a complicated combination of different carbon phases. Different proportions of each of them can be responsible for the unique properties of the modified polymer surface and must depend on dose and spectral composition of radiation. Thus, determination of modes of the valence state of carbon atoms and the possibility to vary their surface content by changing external conditions seems to be promising not only to study the degradation mechanism but in various practical aspects as well.

PVDF has been successfully utilized in a variety of industrial applications (Holmes-Siedle and Wilson, 1984). It exhibits pyroelectricity and ferroelectricity

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Moreover, it possesses good mechanical flexibility, high chemical inertness, high thermal stability, and excellent biocompatibility. These properties of PVDF have motivated further studies of its electronic structure and modifications.

Surface patterning in PVDF to generate microstructures has been achieved using synchrotron radiation (SR) (Morikawa et al., 2000). Quadrupole mass spectrometry and ultraviolet photoemission spectroscopy were employed to investigate the mechanism of direct photomicromachining. The mass spectrometry identified H_2 , F, and HF as the etched products, with no carbon containing species being detected. The authors concluded that the mechanism of direct photomicromachining is ascribable to the shrinking of the irradiated polymer region due to defluorination and conjugation of the polymer backbone.

The analysis of desorption ions by inner shell excitation is one of the useful methods for clarification of the relationship between the photodegradation mechanism and the electronic configuration of excited states. Ion time-of-flight mass spectra of poly (tetrafluoroethylene) and PVDF near fluorine and carbon K-edges were observed recently (Okudaira et al., 2002). Peaks corresponding to F^+ and H^+ indicate that the bond scission occurs mainly at the C–F and C–H bond for PVDF. Partial ion yields (PIY) of these ions show strong photon energy dependencies near fluorine and carbon K-edges, which are different from the near-edge X-ray absorption fine structure spectra. The yield of F^+ increase strongly at the transition from $F1s$ to $\sigma(C-F)^*$ by irradiation of photons with $h\nu = 690$ eV. It is noted that the PIY intensity of F^+ at the transition from $F1s$ to $\sigma(C-C)^*$ ($h\nu = 692$ eV) is four times as small as that of CF transition.

Recently, total photoabsorption spectra of CF_3COCH_3 were measured in the C, F and O K-shell regions and the peak assignments were tentatively given (Ibuki et al., 2005). In contrast with (Okudaira et al., 2002) the authors assign peaks 691.4 and 693.4 eV in the F K-shell region to the transition from $F1s$ to $\sigma(C-C)^*$ and $\sigma(C-F)^*$, respectively.

Our preliminary photodegradation experiments were aimed to use PVDF as a precursor to forming a one-dimensional carbon structure on its surface. We used a conventional non-monochromatic AlK_{α} X-ray source during ca. 1000 min (Pesin et al., 2003; Voinkova et al., 2005). Defluorination of PVDF surface was evident from the decrease in relative intensities of $F1s/C1s$ and $F2s/C1s$ peaks. The variation of fluorine content vs. exposure time has been found from these two ratios. The electron effective attenuation lengths (EEAL) for each group of photoelectrons have been estimated. They have appeared to be proportional to their kinetic energies and did not vary during the measurements (Pesin et al., 2003).

Unfortunately, it appears to be impossible to reveal a purely photonic radiative effect due to simultaneous influence of secondary electrons generated in the filtering window and the chamber walls. This influence might be significant in our case as a self-made spectrometer was used in which a retarding positive voltage was applied to the sample. The high degradation rate does not allow accurate monitoring of the electron structure modification using low analyzer pass energy. Besides only a fixed photon energy value (1486.6 eV) was available. The use of SR can help to avoid the problems mentioned above and opens up some additional opportunities in studying electronic structure of materials.

This paper reports on the comparative analysis of the data obtained using conventional XPS technique and NEXAFS spectra of fluorine excited with SR at the Russian–German beamline of Berlin electronic storage ring in the single bunch mode (current 10–20 mA).

2. Experimental

A starting sample for all the degradation experiments was a PVDF film (KYNAR, type 720, thickness 50 μ m). The experiment is analogous to that described in (Pesin et al., 2003; Voinkova et al., 2005) but the XPS data reported in this paper have been obtained for much more prolonged measurements (ca. 7000 min of X-rays exposure).

The radiation-induced modification of fluorine empty states in the surface of PVDF was studied using monochromatic SR (700 eV). The vacuum level was $(5-7) 10^{-10}$ Torr. The sample and the chamber were kept at a temperature of ca. 130 °C for 24 h before measurements. An Echelette grating (1200 lines/mm and $Cff = 2.25$) was used to obtain monochromatic SR. The aperture width was set to 200 μ m. NEXAFS spectra were measured using secondary electron multiplier KEITHLEY@14. The energy resolution in the energy range of 680–700 eV was 0.6 eV. All the measured spectra were normalized to the current in the storage ring.

3. Results and discussion

The conventional XPS data confirms the previous results (Duca et al., 1998; Pesin et al., 2003; Voinkova et al., 2005) indicating fluorine elimination from the PVDF surface. The dependencies of fluorine content vs. time of exposure are shown in Fig. 1. Two of them have been revealed using the same spectra treatment as in Pesin et al. (2003) separately for the data obtained from $F2s/C1s$ (\square) and $F1s/C1s$ (\blacktriangle) ratios.

A different technique to measure the fluorine content has been used based on the evaluation of the yields of

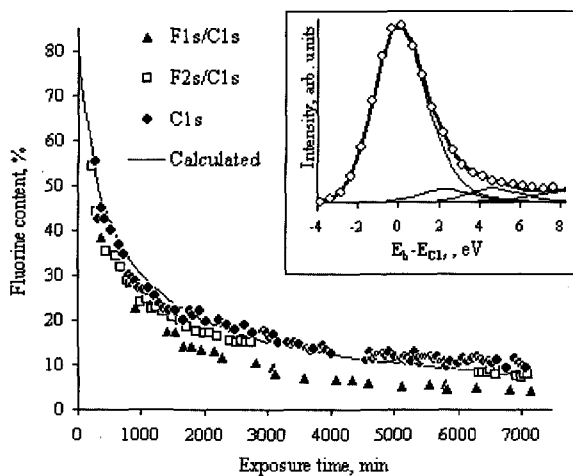


Fig. 1. Variation of fluorine content in the PVDF surface vs. duration of X-ray and secondary electrons exposure measured by treatment of XPS spectra for different groups of electrons. An example of the C1s peak (○-experimental data) fitting (bold line) with four components (normal lines) is shown in the inset.

CF₂ and CF groups in the C1s spectra. A preliminary treatment of C1s spectra has been made in two steps. At first, the yield of the photoelectrons excited by AlK_{α,3,4} radiation and then the constant value corresponding to the intensity of the low-energy edge of C1s peak were subtracted. Secondly, the dominant peak position for each C1s spectrum has been assumed as a zero point for binding energy. In fact the binding energy position of the C1s peak for CF₂ groups is shifted to 4.4–4.6 eV relative to the photoemission from carbon atoms having no chemical bonds with fluorine (Beamsom and Briggs, 1992; Duca et al., 1998; Voinkova et al., 2005). The yield from CF groups is not directly observable (Voinkova et al., 2005). It is reasonable to assume that a chemical shift is an additive factor and their C1s peak position suffers a shift close to 2.2–2.3 eV as these groups contain only one fluorine atom. Hence, the experimental C1s spectra have been calculated as a sum of three model functions, approximating these C1s lines with maximum positions at 4.6, 2.3, and 0 eV, and a symmetrical and broad Gauss function centered at 9.4 eV to fit a background level from the side of higher binding energies. The shapes of C1s peak of poly (ethylene) and F1s peak of PVDF proved to be identical at 320 eV pass energy and have been used to plot the model peaks. An example of the fitting is shown in the inset of Fig. 1. During this fitting, only heights of all peaks could vary, while the positions and widths were fixed. This technique allows one to measure a relative content of CF₂ (X₁) and CF (X₂) groups independently as a ratio of the area of the corresponding model peak to the total area of three model peaks (the latter is assumed to be proportional to

the total number of carbon atoms, involved in photoemission). The fluorine content was found as $2X_1 + X_2$. Its variation under AlK_α X-rays exposure is also shown in Fig. 1 (●). It reflects the process of defluorination in the surface layer at intermediate depth. The fluorine content measured using this technique demonstrates the highest values at any time of X-ray exposition as compared to those determined via standard treatment in which F1s/C1s and F2s/C1s ratios are used. The reason for this contradiction is the fluorine concentration profile increasing with depth having a typical dimension lower than the order of the magnitude of the maximum XPS analysis depth (ca. 100 Å (Ferraria et al., 2003)). This effect originates most probably from the secondary electrons interaction with the outmost layer of the irradiated sample than due to X-ray absorption. Hence, the rate of defluorination is the highest in the layer responsible for the emission of F1s photoelectrons and the lowest in the layer emitting F2s photoelectrons.

This effect also causes non-monotonic decrease in density, which in turn elevates the EEAL. This increase varies for different groups of photoelectrons and is greater in the sequence F1s, C1s, and F2s. This effect leads to overestimation for the value of the fluorine content measured from F1s/C1s ratio and underestimation for that determined from F2s/C1s ratio. These deviations increase with the time of exposure. Nevertheless, the model of radiative carbonization (Voinkova et al., 2005) satisfactorily fits experimental data (Fig. 1, solid line) and allows to estimate factors $K_1 = 6.96 \times 10^{-3}$ and $K_2 = 2.08 \times 10^{-3} \text{ atom}^{-1} \text{ s}^{-1}$ characteristic for CF₂→CF and CF→C transformation rates, correspondingly.

The NEXAFS spectra of fluorine show significant changes in their shape and intensity with elevation of radiation dose (or duration of SR exposure). Monotonic increase in intensity of the spectra along with their background with the dose elevation has been observed in a striking contrast with Morikawa et al. (2000): it has been shown previously that fluorine content on the surface of PVDF exposed to soft X-rays decreases with time. This contradiction has led us to the idea that the decrease of the ring current in the single bunch mode can presumably slightly enlarge the beam brightness due to lowering the repulsion of electrons forming it. This effect makes the monochromatic beam intensity vary not strictly proportionally to current in the ring. This additional effect is expected to be monotonic. Additional normalization of the spectra intensity by alignment of background levels from the side of lower energies (Fig. 2) was obtained by multiplying each spectrum by the empirical coefficient. This decreases smoothly as current decreases. There exists a practically linear relationship between this coefficient and current which can be considered as an indirect confirmation for

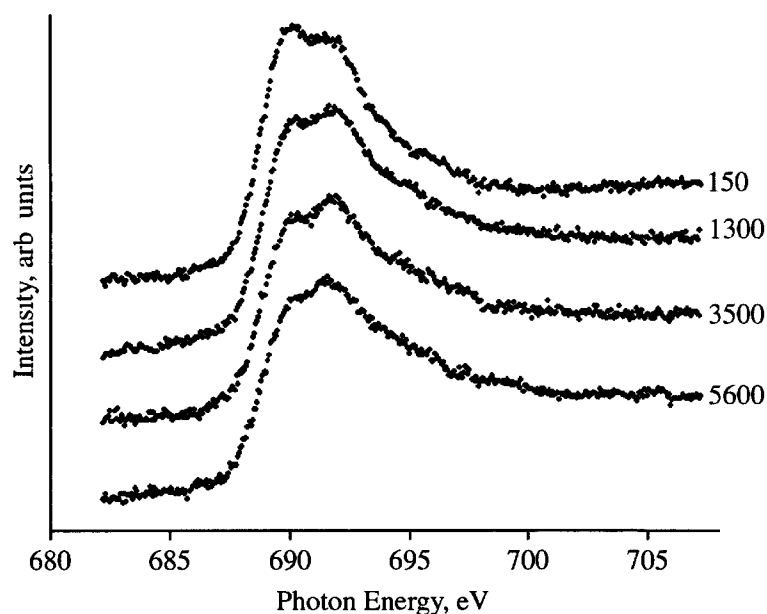


Fig 2 NEXAFS spectra of fluorine of the irradiated PVDF film and its derivatives obtained under monochromatic SR (700 eV). Duration of exposure is denoted in seconds for each curve.

the validity of this additional normalization. The spectra treatment as described above allows elucidating the effect of SR on the empty states of fluorine. Obviously, the integral intensity of the spectra must be proportional to the fluorine surface content. This parameter has been calculated as an area of each spectrum in the 685–700 eV interval after the subtraction of linear background. Fig 3 demonstrates a general tendency of the spectra intensity to decrease with the photon dose elevation in accord with the previously observed lowering of fluorine content under soft X-radiation (Duca et al., 1998; Pesin et al., 2003) and model calculations (solid line, (Voinkova et al., 2005)). The latter gives 7.83×10^{-5} and $2.34 \times 10^{-5} \text{ atom}^{-1} \text{ s}^{-1}$ for the rate factors K_1 and K_2 , correspondingly. The initial fluorine content has been assumed ca. 82% as measured in the previous study of the same PVDF film (Pesin et al., 2003). Indeed, this value is somewhat lower than one could expect from the chemical formulae of PVDF. The most probable reason for this contradiction is an extremely high rate of dehydrofluorination at the very beginning of the experiment: even very short exposition of the sample surface is able to decrease fluorine (and hydrogen) content considerably.

The changes in the spectra shape caused by SR are clearly seen from Fig 2 and mainly concern the relative intensity of two dominant maxima (at ca. 690 and 692 eV). The first of them dominates in the spectrum of pristine polymer. With the increase of the radiation dose, the redistribution of intensity between these features occurs and the second maximum dominates at longer exposure times. Taking into account an obvious elimination of fluorine under SR, it is reasonable to assume that both features originate from two F1s→

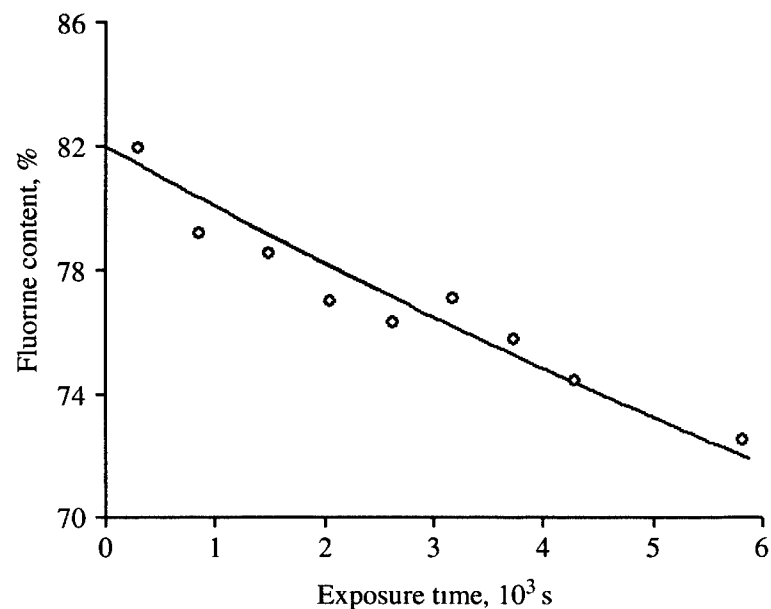


Fig 3 Integral intensity of fluorine NEXAFS in 685–700 eV range vs duration of SR exposure (open circles) and a calculated curve (solid line).

$\sigma(\text{C-F})^*$ transitions which final states are formed by the different number of fluorine atoms (correspondingly 2 or 1) bonded with the carbon atom in the main chain. Existence of the second feature in the “initial” spectrum once more suggests that, at first stage of degradation, the rate of $\text{CF}_2 \rightarrow \text{CF}$ transformation is very high.

A preliminary interpretation of the results obtained is based on the assumption of two-step process of dehydrohalogenation under both conventional and SR. At first, the photon hits any of the carbon atoms producing a photoelectron leaving a positively charged ionic complex. The latter decays with the elimination of HF and formation of $\text{CF}=\text{CH}$ fragment in the polymeric chain. The reason for the noticeably lower rate of the second step ($\text{CF} \rightarrow \text{C}$) is presumably due to its higher activation energy owing to conformations of a polymeric chain after elimination of the first HF molecule from a monomeric unit of PVDF.

4. Conclusions

The most important feature of the reported data is the possibility of their description using the same K_1/K_2 ratio, regardless of the nature of beams used for radiative carbonization of PVDF in our two independent experiments. No energy and dose dependence of the K_1/K_2 ratio is revealed. Individual values of these factors seem to be governed just by the different intensities of radiation. This suggests the validity of the identical mechanism of dehydrofluorination (Voinkova et al., 2005) in both cases.

Acknowledgments

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