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Study of poly(vinylidene fluoride) radiative modification using core level spectroscopy

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ABSTRACT

Modification of poly(vinylidene fluoride) (PVDF) directly during radiation exposure was investigated using core level spectroscopy. The strongly non-equilibrium condition of PVDF was studied. The high-resolved C K-edge NEXAFS spectra of poly(vinylidene fluoride) have been measured. The spectra modification due to the polymer degradation caused by monochromatic synchrotron radiation has been revealed. Residual fluorine content was monitored using x-ray photoelectron spectroscopy. The study has shown a significant modification of PVDF chemical content and electronic structure in the course of carbonization under synchrotron radiation. Gradual defluorination of the PVDF sample takes place during irradiation with enrichment of carbon skeleton with hydrogen. In the initial stages of radiative modification, defluorinated system is inhomogeneous and changes under the influence of two simultaneous processes: photochemical defluorination and diffusion of unbounded fluorine atoms to the sample surface.

1. Introduction

Poly(vinylidene fluoride) (PVDF) film is a promising raw material to produce a variety of carbonized derivatives on its surface using chemical treatment, ion and electron bombardment, and X-ray irradiation [1–5]. Dehydrofluorination occurs in all cases without scissions of the carbon backbone thus opening a possibility to create ‘naked’ carbon chains. However, one could expect the formation of not only nanoscaled one-dimensional sp^1-carbon, but also graphite- (sp^2) and diamond-like (sp^3) clusters due to probable cross-linking of the chains. The proportion of each of these phases can affect specific properties of the modified polymer surface depending on the chemical treatment duration, peculiarities of bombardment and radiation dose. One-dimensional carbon structures are expected to become promising materials for future applications in microelectronics, microwave and electrical technologies, medicine, etc [1,6]. In our earlier work, it has been shown that during deep carbonization of PVDF under X-ray radiation in ultrahigh vacuum the cross-linking effects are negligible [7]. Process of radiative release of fluorine and hydrogen is in general similar to photochemical reactions, namely to photodissociation reactions [8]. X-ray photon absorption by carbon atoms of PVDF chain results in transitions of electrons responsible for binding carbon and fluorine\hydrogen atoms to antibonding orbital in conduction band. In this case, these fluorine or hydrogen atoms can leave polymeric chain of PVDF [9,10]. Arisen metastable state of the chain is named carbyne-like structure [1]. Photon irradiation of PVDF could even result in chain disruption. The rate of such radiative conversion is proportional to the intensity of the electromagnetic radiation and the quantum yield of the reaction [8]. Synchrotron radiation (SR) has extremely high intensity, hence SR leads to significantly fast photodissociation that the removal of the reaction products from the sample volume is backward the generation of these products. As a result, constituents of radiative decomposition in form of hydrogen, fluorine and their compounds can accumulate in polymer (especially in near surface area) [11]. Elevated concentration of reagents in the bulk and on the surface furthers reverse process of hydrogen and fluorine bonding to the polymer chain with creation of new polymeric forms.

Near-edge absorption fine structure (NEXAFS) spectroscopy makes possible to investigate radiative degradation of PVDF directly during irradiation [12,13]. Though spectra showed in those

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articles had low resolution, nevertheless it has revealed a very important feature of the degradation process: creation of double carbon–carbon bonds into the backbone chain of PVDF due to the effective desorption of hydrogen and fluorine induced by the irradiation of photons corresponding to the transition between C 1 s core level and σ* unoccupied states in conduction band. New peak at photon energy of 285 eV appears in the C 1 s absorption spectrum of degraded PVDF sample, which is about 3 eV lower than that of the lowest peak in the C K-edge NEXAFS spectrum of the pristine PVDF film. The appearance of the new peak of irradiated PVDF film is assigned to the creation of π* orbitals. A similar effect was revealed also in Ref. [12]. On the other hand in Ref. [3] has been shown predominant elimination of H_2 as well as simultaneous release of hydrogen and fluorine as a molecular HF from the PVDF surface under synchrotron x-ray radiation in wide energy range ~0.5–2.0 keV centered at ~1.2 keV. This fact may testify to different mechanisms of PVDF radiative carbonization depending on photon energy and gives a wide and exciting field for research activities.

Besides there are no papers dealing with analysis of the C K edge spectrum modifications during degradation in connection with the residual fluorine content. The last parameter could be necessary to monitor a degree of the surface carbonization before and after each absorption spectrum recording. Therefore, the goal of the present study was to investigate the modification of poly(vinylidene fluoride) directly during radiation exposure using core level spectroscopy. The strongly non-equilibrium condition of PVDF was studied. One of the aim was to obtain high-resolved C K-edge NEXAFS spectra of PVDF and to reveal spectra modification due to the polymer degradation caused by monochromatic synchrotron radiation with monitoring of the current residual fluorine content using x-ray photoelectron spectroscopy (XPS).

2. Materials and methods

The PVDF samples studied were partially (~50%) crystalline Kynar films (Atofina, France).

All the measurements have been done in Helmholtz Zentrum Berlin fuer Materialien und Energie at the Russian-German beamline of the electron storage ring BESSY II (Berlin, Germany) [14]. The samples for x-ray absorption and photoelectron measurements were prepared in air. The PVDF samples were 50 μm thick and $10 \times 10\ \mathrm{mm}^2$ in size. The films were fixed on cupper sample holders to prevent the charging effect.

The NEXAFS spectra were obtained by recording the TEY of the x-ray photoemission in the mode of measurement of the drain current of the sample by varying the energy of incident photons. All x-ray absorption and photoelectron spectra were measured under ultrahigh vacuum $\sim 2 \times 10^{-9}$ Torr. The sample was adjusted to the synchrotron-radiation beam with the use of visible light reflected from the diffraction grating of the monochromator in the 0th diffraction order. The samples were located at an angle of ~45° with respect to the incident beam of monochromatic radiation. The size of the focused spot on the sample was $\sim 0.2 \times 0.1\ \mathrm{mm}^2$.

The energy resolutions ΔE of the monochromator in the range of the C 1s x-ray absorption edge ($h\nu \sim 285$ eV) was equal to 70 meV. The x-ray absorption spectra were normalized with respect to the incident photon flux, which was monitored by recording the TEY from the clean surface of a gold crystal mounted on the manipulator holder. The $h\nu$ in the range of the fine structure of the C x-ray absorption spectra was calibrated against the energy position of the C 1s x-ray absorption spectrum of HOPG (285.45 eV) [15].

In recording x-ray photoelectron spectra, $h\nu$ was fixed at 1030 eV. Energy resolution ΔE of the monochromator with the 200 μm exit slit was 680 meV. Photoelectron spectra of the samples were measured in the normal photoemission registration mode by using the Phoibos 150 spherical analyzer from Specs whose resolution in recording the spectra remained equal to 200 meV. The analyzer was calibrated against energy based on photoelectron spectra of Au atom $4f_{7/2,5/2}$ electrons. The monochromator was calibrated by recording the basic photoelectron lines of C 1s spectra excited by radiation reflected from the diffraction grating in the first and second diffraction orders.

To control compositions of the samples, survey photoelectron spectra at $h\nu = 1030$ eV within the binding energy (BE) range of $BE = 0$–900 eV were measured for all of them. They did not show the presence of the different chemical contaminations in the samples. Several samples of each type were prepared; spectra of each sample were measured with good statistics at several different points of a sample. In repeating the measurements, we observed good reproducibility of measurements and high homogeneity of the samples.

XPS spectra necessary for residual fluorine content measurements were scanned before and after each NEXAFS spectrum registration. Relative fluorine atomic content F/(C + F) has been measured from a ratio of integral XPS F 1s and C 1s intensities taking into account ionization cross sections, the analyzer transmission function and different mean escape depths of these two groups of photoelectrons:

$$\frac{F}{C+F} = \frac{\frac{I_{F1s}\cdot f_{F1s}}{\sigma_{F1s}}}{\frac{I_{C1s}\cdot f_{C1s}}{\sigma_{C1s}} + \frac{I_{F1s}\cdot f_{F1s}}{\sigma_{F1s}}} = \frac{I_{F1s}\cdot f_{F1s}\cdot \sigma_{C1s}}{I_{C1s}\cdot f_{C1s}\cdot \sigma_{F1s} + I_{F1s}\cdot f_{F1s}\cdot \sigma_{C1s}} \tag{1}$$

where I is integrated intensity, f is transmission function and σ is ionization cross section. In our case, it was taken:

$$\frac{f_{F1s}}{f_{C1s}} = \frac{5.1845}{3.3839} \approx 1.53 \qquad \frac{\sigma_{F1s}}{\sigma_{C1s}} = \frac{0.1525}{0.037} \approx 4.12$$

Investigation of electron structure modifications of PVDF surface under photon radiation was made by continuous x-ray photoelectron spectra recording ($h\nu = 1030$ eV) during 50 min. It was possible to record 19 spectra with interval 2.5 min. One scan for each spectrum was taken.

3. Results and discussion

C 1s NEXAFS spectra for several doses of irradiation are shown in Fig. 1. Corresponding F/(C + F) values are inserted into the figure space. For comparison, total DOS in PVDF conduction band according the calculations is shown at the bottom of the figure [16].

The NEXAFS shape of the sample after its x-ray exposition differs from those of HOPG, polyethylene and diamond known from various sources [see, for example [17–21],]. Nevertheless the NEXAFS spectra are qualitatively consistent with the lower-resolved data from Refs. [12,13].

According calculations [16], it is possible to attribute the main features in the C 1 s absorption spectra as following (see Fig. 1). Peak A corresponds to electron transitions from 1 s states to π states near Fermi level. Features B and C reflect the transitions C 1 s electrons to C–H hybridized states in conduction band of hydrogenated carbon chain [22]. Besides, peaks D and E characterize electron transitions from 1 s states to C–F hybridized states in conduction band.

The comparison of x-ray absorption spectra on Fig. 1 allows making several conclusions. First, the contribution of π states in the spectra (peak A) increases significantly with decreasing of concentration of fluorine atoms connected to carbon atoms in chain. Second, intensity increasing and broadening of peak C corresponding to C–H bonds takes place during the sample irradiation.