DEPTH DISTRIBUTION OF FLUORINE DURING RADIATIVE CARBONIZATION OF PVDF

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Introduction

Carbon containing polymers of low dimensionality (carbynoids) are prospective materials to use in electronics, medicine, optics, synthesis of diamonds and other important fields [1]. One of the well known techniques to study electron structure is X-ray photoelectron spectroscopy (XPS). Surface degradation of poly(vinylidene fluoride) (PVDF) is observed during XPS measurements [2]. Fluorine content decreases under X-rays i.e. the radiative carbonization of surface occurs. It is naturally to assume that surface defluorination of PVDF is not uniform. X-rays are absorbed by the solid, hence the quantity of photons reaching the deeper layers decreases. This should lead to appearance of fluorine content gradient directed from the surface into the bulk of the sample.

Results and Discussion

A partially crystalline PVDF film (KYNAR, type 720, thickness 50 μm) was kindly granted by ATOFINA. The XPS data were measured with a home-made ES IFM-4 spectrometer using Al $K\alpha_{1,2}$ radiation (photons energy $\hbar\omega$ = 1486.6 eV). The experimental technique has been described in details in [3]. The total time of X-ray exposure comes to ca. 9000 min. The fluorine content during exposition was measured as in [3].

The quantity of core photoelectrons of fluorine excited within a near-surface layer of some depth is proportional to the total integral intensity of the F1s-spectrum. The quantity of those ones suffering inelastic losses is proportional to the integral intensity of F1s satellite. Consequently, the probability of inelastic scattering may be characterized by the ratio of integral intensity of scattered beam (area of satellite) to the area of F1s- peak. The increase of this ratio has been observed [3] presumably. This effect takes place due to increase inelastic processes with F1s- photoelectrons participation. One of the most probable reasons of this phenomenon is the increase of the relative yield of photoelectrons outgoing from the deeper layers. Let us suppose that core photoelectrons of fluorine can outgo from the maximum depth L. Their quantity is proportional to the content of fluorine which varies with the depth x in the following way:

$$n_F(x) = n_0 + (n_1 - n_0)\cdot e^{-\chi x}, \qquad (1)$$

where n_1 is the linear content of fluorine on the PVDF surface (x=0); n_0 is the content of fluorine in the non-treated film of PVDF; χ is a coefficient of absorption of X-rays by the solid.

Number of photoelectrons escaping from a layer of infinitesimal thickness dx can be found as:

$$dN(x) = n_F dx. \qquad (2)$$

Integration of this equation within the thickness of the layer L gives the total quantity of electrons escaping from this layer:

$$N = n_0 L + (n_0 - n_1)\cdot\frac{1}{\chi}\left(e^{-\chi L} - 1\right). \qquad (3)$$

The quantity of photoelectrons escaping from the same layer dx and experiencing a single energy loss is proportional to the depth x of layer dx:

$$dN' = \alpha\cdot n_F\cdot x\cdot dx, \qquad (4)$$

where α is a coefficient which equals to the probability of a photoelectron energy loss during its movement through the layer of unit thickness. Integration of this equation from L to zero gives the number of photoelectrons escaping with a single inelastic interaction:

$$N' = \alpha\left[L^2\frac{n_0}{2} - \frac{(n_1 - n_0)}{\chi}\cdot\left(Le^{-\chi L} + \frac{1}{\chi}\left(e^{-\chi L} - 1\right)\right)\right]$$

Similarly, one can take into account the quantity of photoelectrons experienced double inelastic scattering during emission. Experimental values of ratio S_{sat}/S were found as in [4] and compared with the calculated values.

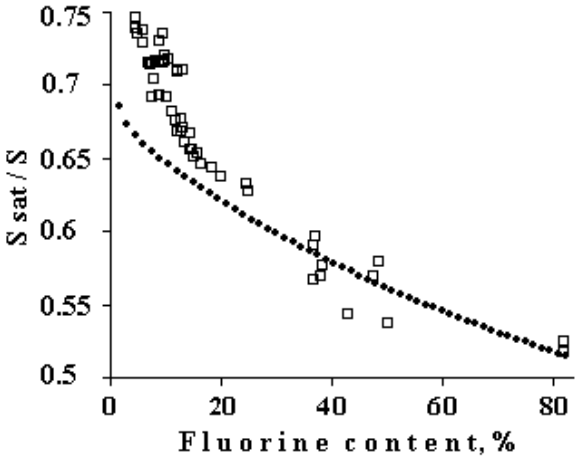

Fig. 1. □- Experimental dependence of the ratio S_{sat}/S on the content of fluorine;
• - dependence obtained as a result of simulation.

With the certain values of α=8.7*10^7 m^{-1} calculated by fitting and χ=2.2*10^5 m^{-1} estimated from [5] our simplified model describes qualitatively the experimental curve S_{sat}/S (Fig. 1).

Estimation of attenuation length L was carried out using equation (5.9) from [6, p. 210, 221] and gave 0.8 nm. One can assume that L is inversely proportional to the linear density of a solid. The latter consists of two components. The first one comes from the yield of carbon atoms and is constant [7]. The second corresponds to the yield of fluorine atoms and decreases with increase of duration of exposure. The yield of hydrogen atoms is neglected. The volume density of a solid is proportional to the total content of C and F. Thus the dependence of attenuation depth of photoelectrons on the average fluorine content (n_a) may be written as:

$$L = \frac{K}{\sqrt[3]{1+n_a}},$$

where K=9.9*10^{-9} is the empirical factor. The unity in the denominator characterizes the constant content of carbon atoms.

Conclusions

The depth gradient of fluorine atoms arising during radiative carbonization of PVDF, attenuation length of photoelectron, probabilities of energy losses by a photoelectron during its movement from the bulk were estimated. Simulation agrees only qualitatively with the S_{sat}/S intensity ratio.

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