



## Kinetics of PVDF film degradation under electron bombardment

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### ARTICLE INFO

#### Article history:

Received 22 July 2012

Received in revised form

11 October 2012

Accepted 14 November 2012

Available online 29 November 2012

#### Keywords:

Poly(vinylidene fluoride) (PVDF)

Scanning electron microscopy (SEM)

Defluorination

Kinetics

### ABSTRACT

A dose effect of high-energy (20 keV) electron irradiation on the chemical composition of PVDF films has been revealed using a scanning electron microscope Jeol JSM-7001F equipped with an X-ray fluorescence spectrometer Oxford INCA X-max 80. All the experimental series have demonstrated similar decreasing dependence of relative atomic fluorine content (F/C) upon the electron irradiation dose. The final non-zero F/C ratio can be explained in terms of primary defects in the original PVDF and secondary ones arising during irradiation. In general a defluorination process is consistent to a Le Moël model of PVDF degradation and can be satisfactorily described with a third-order kinetic equation, parameters of which depend on the type of a PVDF film.

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### 1. 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 [1–7]. 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 [4]. These facts confirm the formation of a surface layer enriched with carbon, and this kind of degradation was coined a “radiative carbonization” [6].

Radiative modification of PVDF surface is prospective in a lot of aspects. 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 [1,8]. This opens up opportunity for creation of conducting and/or semiconducting nanofilms on elastic and transparent dielectric substrates for micro and nanoelectronic and photonic devices. Secondly, equal amounts of hydrogen and fluorine in pristine 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  $\text{CF}_2$  ( $\text{CH}_2$ ) or/and  $\text{CF}$  ( $\text{CH}$ ) species remaining due to incomplete dehydrofluorination or intrinsic defects existing in the polymer macromolecules (ca. 7–15% of residual fluorine [6,7]). 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 predicts 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 [9].

Although numerous studies involving X-ray [4,5,10], electron [1,6,7] or ion [1] irradiation of PVDF have been carried out since mid 1980s, a microscopic mechanism of fluorine elimination is not fully understood so far. Kinetic studies can provide valuable information concerning this issue. For example, based on the data of a long-term XPS study, a simple model of the simultaneous elimination of fluorine and hydrogen from PVDF surface has been proposed [11]. Unfortunately, in the number of previous studies [1,5–7,10,11] the PVDF sample was irradiated simultaneously with  $\text{Al K}\alpha$  photons and

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a flux of secondary electrons from a filtering foil. This fact prevents elucidation of two different radiolysis mechanisms.

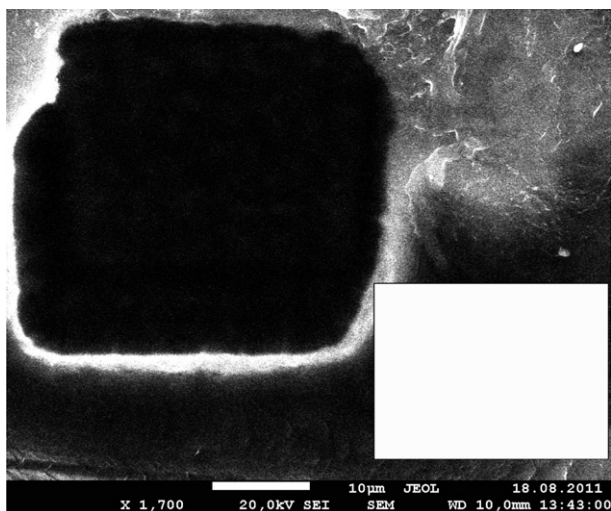
The aim of the present study is to reveal the dose effect of purely high-energy (20 keV) electron irradiation on the chemical composition of a PVDF surface. Electron beam has been used for simultaneous surface modification and excitation of C  $K_{\alpha}$  and F  $K_{\alpha}$  photons, whose intensities are proportional to the atomic content of carbon and fluorine within the analysis depth.

## 2. Samples and experimental technique

Partially crystalline film of PVDF Kynar (type 720, thickness 50  $\mu\text{m}$ ) produced via a blow extrusion technique (Atofina, France) and nearly amorphous film F2m (thickness 25–28  $\mu\text{m}$ , Plastpolymer, Russia) were used in this study as starting materials. The first one contains almost equal proportions of crystalline and amorphous phases, both having predominantly non-polar  $\alpha$ -type of the chain conformation. The second film almost entirely consists of  $\beta$ -phase.

Both *in situ* degradation and chemical analysis of the film have been performed using a scanning electron microscope Jeol JSM-7001F equipped with an X-ray fluorescence spectrometer Oxford INCA X-max 80. Pieces of PVDF films ( $5 \times 5 \text{ mm}^2$ ) were fixed at their edges on an aluminum sample holder with a conductive double-sided, vacuum proof adhesive band (30  $\mu\text{m}$  thick). Thus there was only aluminum under the probing zones of the films. The residual gases pressure in the sample chamber did not exceed  $10^{-4}$  Pa.

Preliminary prolonged measurements have shown that carbon increment in the sample surface brought about by oil from the vacuum system is negligible. Besides we have noticed not uniform and chaotic sample displacements due to thermal extension of the Al holder. This creep leads to unpredictable changes in the irradiated region shape. It has been visually observed in the course of the experiment and is confirmed by the final SEM image (Fig. 1). A white rectangle in the right bottom corner of Fig. 1 shows the area that might be irradiated if the sample did not move at all. So as to avoid this effect on the relative fluorine content determination during the main experiments the irradiated area was 15,000  $\mu\text{m}^2$  while a chemically investigating region was 25 times smaller and situated close to the center of the first one.



**Fig. 1.** SEM image of the film surface region subjected to electron bombardment at the end of a preliminary irradiation study made at magnification  $\times 5000$ . A white rectangle in the right bottom corner shows a size of the area that might be irradiated if the sample did not move.

Working distance between the objective lens and the PVDF film surface was 10 mm. The acceleration voltage of 20 kV was used in all experiments. Electron beam current has been maintained at 14 nA when the films are irradiated. Between irradiation sessions residual fluorine content has been measured at a significantly less current (300–310 pA). Duration of each operation has been monitored to calculate a total irradiation dose.

Three series of irradiation experiments have been made using Kynar, F2m films and the latter one folded in two so as to check whether a film thickness could effect on degradation rate. Step-by-step irradiation and measurement sessions have been made in turn in the unique manner for all the samples studied. The efficiency of electron bombardment was evaluated from relative atomic F/C-ratio plotted versus a current dose. Besides of carbon and fluorine some 0.03–0.2 atomic% of Cl was detected. A minor yield of Al  $K_{\alpha}$  radiation shows that the electron penetration depth exceeds the films thickness.

## 3. Results and discussion

### 3.1. Experiment

Preliminary experiments have shown no relaxation effects when electron bombardment is interrupted for some time. One might expect these effects from the following reasons. High electron energy leads to their significant mean free path in the PVDF target. So polymer defluorination (most probably dehydrofluorination) as well as C1s and F1s core levels ionization occurs not only within a near-surface layer but also in the bulk of the PVDF film. HF molecules leave polymer chains and move towards the surface due to diffusion for some period of time yielding to the total fluorine content in the investigated film. When electrons do not influence on the sample for some time new HF molecules are not cleaved from polymeric chains but those ones created before can escape from the sample. As a result fluorine content measured just after new switching the electron gun on must be noticeably lower than just before switching it off. But experimental data do not correspond to this expectation as no content variation has been found in this case. This fact testifies to a very fast fluorine-containing moieties escape from PVDF under electron irradiation.

Three series of degradation experiments have shown a significant decrease in fluorine content. All the series have demonstrated similar dependence of relative atomic fluorine content (F/C) upon the electron irradiation dose (Fig. 2). This similarity most probably testifies to the unique mechanism of the surface degradation in the studied films. At low doses F/C falls in extremely rapid way, then more and more slowly with dose elevation thus demonstrating an evident tendency for saturation. The final non-zero F/C ratio can be explained in terms of primary (intrinsic) defects in the original PVDF (branching and head-to-head links) and secondary defects (inter-chain cross-links) arising during irradiation. These defects cause the F/H ratio to deviate from 1, which makes exhaustive elimination impossible. Thus, according to Fig. 2 data F2m film is more defective in comparison with Kynar. F/C ratio for a single layered and a double folded F2m samples varies practically in identical manner.

Figs. 3–5 demonstrate SEM images of the degraded regions of all studied PVDF samples after maximum irradiation up to 6500 Coul/ $\text{m}^2$ . Dark rectangles correspond to the area irradiated with maximum current and have regular shape. The latter fact shows that the thermal creep of the samples can be neglected. Irradiation of all the samples produces cracks which most probably have created due to changes in interatomic distances induced by degradation. This effect qualitatively resembles a film twisting and cracking which we usually observed in our earlier studies of prolonged PVDF degradation under X-rays [6,11].

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