Kinetics of PVDF film degradation under electron bombardment

L.A. Pesin [a], V.M. Morilova [a,*], D.A. Zherebtsov [b], S.E. Evsyukov [c]

[a] *Chelyabinsk State Pedagogical University, Chelyabinsk, Russia*
[b] *South Ural State University, Chelyabinsk, Russia*
[c] *Evonik Industries AG, Dossenheim, Germany*

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.

© 2012 Elsevier Ltd. All rights reserved.

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 polyyne 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 CF_2 (CH_2) or/and CF (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 Al K_α photons and

* Corresponding author. Chelyabinsk State Pedagogical University, 69, Lenin Avenue, Chelyabinsk, Russia. Tel.: +7 351 2630735; fax: +7 351 2647753.
E-mail address: vika_m@list.ru (V.M. Morilova).

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_α and F K_α 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 μm) produced via a blow extrusion technique (Atofina, France) and nearly amorphous film F2m (thickness 25–28 μm, 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 α-type of the chain conformation. The second film almost entirely consists of β-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 (5×5 mm^2) were fixed at their edges on an aluminum sample holder with a conductive double-sided, vacuum proof adhesive band (30 μm 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 μm^2 while a chemically investigating region was 25 times smaller and situated close to the center of the first one.
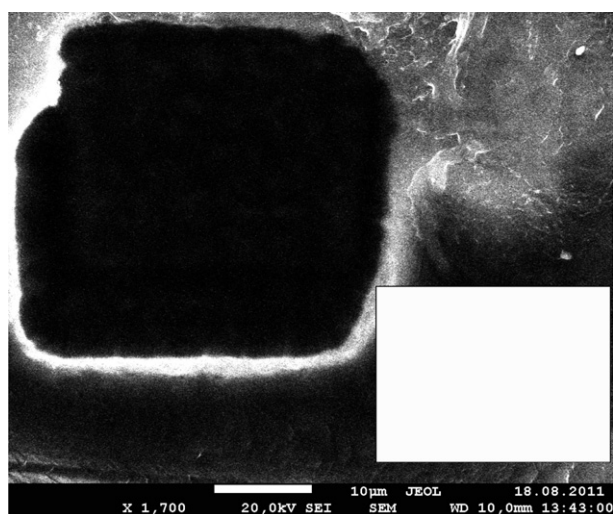

Fig. 1. SEM image of the film surface region subjected to electron bombardment at the end of a preliminary irradiation study made at magnification ×5000. A white rectangle in the right bottom corner shows a size of the area that might be irradiated if the sample did not move.

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_α 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 (interchain 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/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].
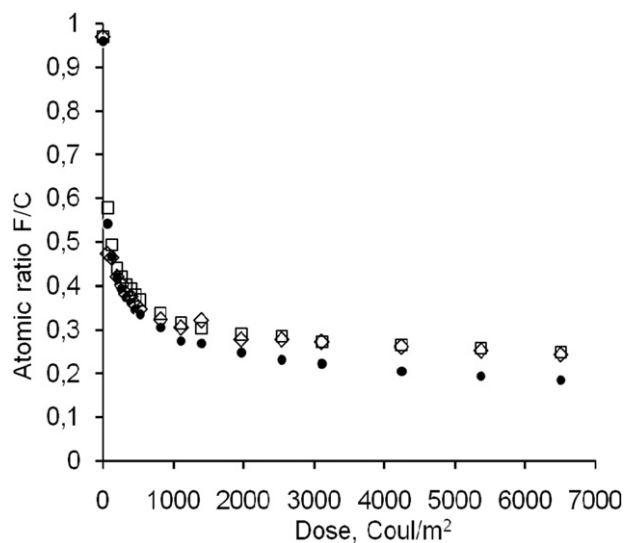
Fig. 2. Dose dependence of the relative atomic ratio F/C for three experimental series (Kynar ●, single layered F2m □, double folded F2m ◇).

Fig. 4. SEM image of the single layered F2m film surface region subjected to electron bombardment up to maximum dose.

Two rather narrow cracks of 30–40 μm long are visible in Fig. 3 for Kynar at the right lower and the left upper edges of the irradiated region. Besides one can see not far from the center of this region though not contrast but quite noticeable a regular small rectangle the corners of which are marked for better visibility with black arrows. This site has been subjected to additional irradiation during chemical composition measurements at minimum current.

SEM images of upper sides of a single layered and a double folded F2m films are shown in Figs. 4 and 5. There are clearly seen much deeper and more extended cracks than it has been observed for Kynar. This difference is most probably caused by different thickness of the films studied.

3.2. Theory

To discuss the experimental data let us consider a model proposed by Le Moël et al. [1] just for the case of PVDF degradation under electron bombardment and based on XPS analysis. It predicts cleavage of the covalen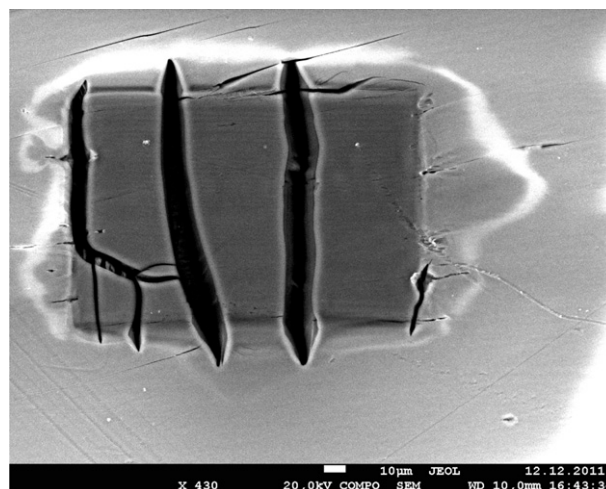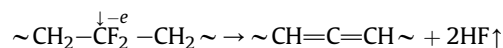t CF and CH bonds initiated by an electron bombardment at low dose rate with simultaneous elimination of both fluorine atoms bonded to a carbon atom and two hydrogen atoms from the two neighboring carbon atoms resulting in the formation of two allenic double bonds in a polymeric chain.

$$\sim CH_2 - \overset{\downarrow -e}{CF_2} - CH_2 \sim \rightarrow \sim CH{=}C{=}CH \sim + 2HF\uparrow$$

In this case a compound of general formula $-(CF_2-CH{=}C{=}CH)_n-$, where F/C = 0.5, is produced with elimination of $2n$ HF.

Kinetics of this process can be described by an equation:

$$-dN = \lambda N^\alpha dt,$$

where N is number of CF_2 groups at the given moment of time, dN is its decrement within a small period of time dt proportional in our case to the dose increment, λ is a kinetic constant which characterizes a process rate, α is a constant corresponding to the reaction order [6,11].

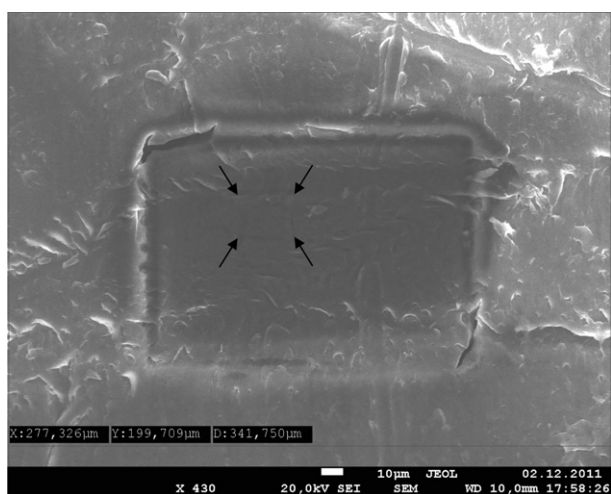Solution of this equation after simple transformations gives in a general case:

Fig. 3. SEM image of the Kynar film surface region subjected to electron bombardment up to maximum dose.
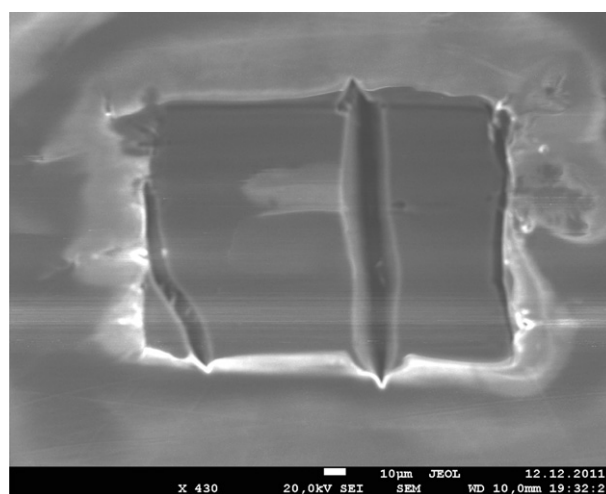

Fig. 5. SEM image of the double folded F2m film surface region subjected to electron bombardment up to maximum dose.

$$n(t) = \sqrt[\alpha-1]{\frac{n_0^{\alpha-1}}{1 + (\alpha - 1)n_0^{\alpha-1}\lambda t}},$$

where n_0 and $n(t)$ are consequently relative atomic ratios F/C at $t = 0$ and any moment of time or any dose.

Then one must take into consideration that polymer defects prevent exhaustive elimination of fluorine. So it is necessary to modify the latter formula: n_0 must correspond not to the total relative fluorine content in the very beginning of irradiation (F/C = n_0 = 1) but just to those of CF$_2$ groups surrounded with CH$_2$ ones in the polymeric chains and thus able for defluorination according to the scheme above. If at $t = \infty$ residual content F/C = b one can easily obtain:

$$n(t) = \sqrt[\alpha-1]{\frac{(n_0 - b)^{\alpha-1}}{1 + (\alpha - 1)(n_0 - b)^{\alpha-1}\lambda t}} + b,$$

or equally

$$n(t) = \sqrt[\alpha-1]{\frac{(1 - b)^{\alpha-1}}{1 + (\alpha - 1)(1 - b)^{\alpha-1}\lambda t}} + b$$

Comparison of the calculations based on the latter equation with experimental data gives best fitting at $\alpha = 3$ and is displayed for Kynar and single layered F2m films in Fig. 6 in semi-logarithmic scale to improve visualization. The third order of the reaction can be interpreted in terms of three possibility factors need to release fluorine. Simultaneous coincidence of three factors is necessary, i.e. exact electron impact in the chain unit with CF$_2$ group and presence of two neighboring hydrogen-containing groups. Thus a probability of a complex event (fluorine cleavage) is a product of equal probabilities for three individual events, each of which is proportional to the current residual content of CF$_2$ groups.

At high dose rate the authors [1] assume an important additional role of thermal effects in the course of further dehydrofluorination of PVDF towards a longer cumulene backbone with loss of HF molecules as follows:
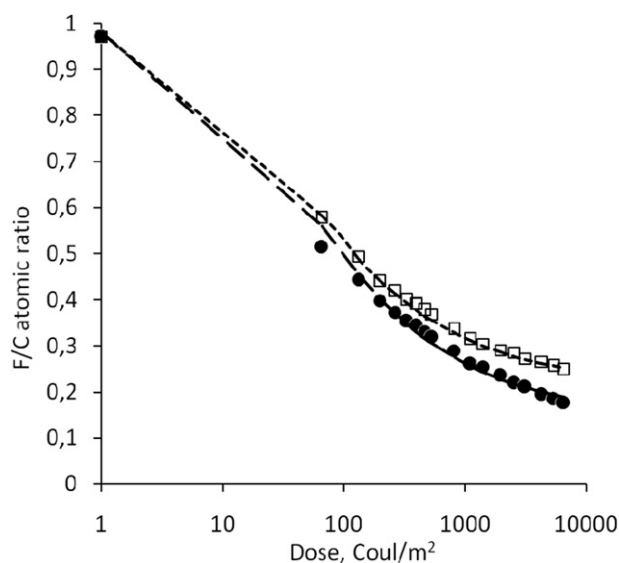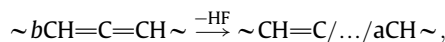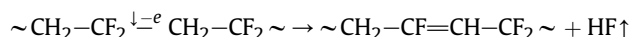

Fig. 6. Comparison of the experimental data (markers) and fitting results (dashed curves) for Kynar (●, $\lambda = 0.033$, $b = 0.14$) and single layered F2m (□, $\lambda = 0.043$, $b = 0.21$) films.
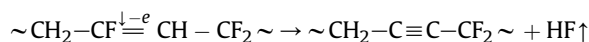
$$\sim b\text{CH}{=}\text{C}{=}\text{CH} \sim \xrightarrow{-\text{HF}} \sim \text{CH}{=}\text{C}/.../a\text{CH} \sim,$$

(F/C = 0), which is evidently not our case.

A satisfactorily fitting shown above cannot be enough to consider a Le Moël model as a unique undeniable interpretation and does not exclude some other explanations. Indeed many studies [see, for example [5–7,9–11]] consider an idea that the dehydrofluorination could occur in two stages, the rates of which were different. The first stage brings about to creation of fluorine-substituted polyene fragments in PVDF chains and dominates at low doses:

$$\sim \text{CH}_2{-}\text{CF}_2 \overset{\downarrow = e}{} \text{CH}_2{-}\text{CF}_2 \sim \rightarrow \sim \text{CH}_2{-}\text{CF}{=}\text{CH}{-}\text{CF}_2 \sim + \text{HF}\uparrow$$

The second stage is an exhaustive dehydrofluorination of these fragments.

$$\sim \text{CH}_2{-}\text{CF} \overset{\downarrow = e}{} \text{CH} - \text{CF}_2 \sim \rightarrow \sim \text{CH}_2{-}\text{C}{\equiv}\text{C}{-}\text{CF}_2 \sim + \text{HF}\uparrow$$

These stages are not temporary separated. As soon as just the first chain link undergoes transformation consistent to the first stage in the very beginning of electron bombardment both reactions may occur simultaneously. In this case these processes can be described by a system of two kinetic equations:
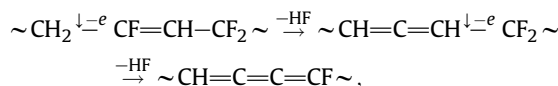
$$-\text{d}n = \lambda n^\alpha \text{d}t$$

and

$$\text{d}n_1 = -\lambda_1 n_1^{\alpha_1} \text{d}t + \text{d}n$$

where $-\text{d}n$ is a decrement in the content of CF$_2$ and CH$_2$ groups within a small interval of time dt, proportional to the dose increment, λ is a unique probability constant for the decay of CF$_2$ and CH$_2$ groups, n is concentration of CF$_2$ (and CH$_2$) groups at a given time, α is a reaction order. Analogously, dn_1, λ_1, n_1, α_1 mean the same for CF and CH groups. The parameter α (α_1) is expected to be 1 if CF$_2$ and CH$_2$ (CF and CH) groups decay independently from each other, and 2 in the opposite case [7,11].
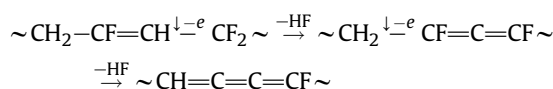
If $\alpha = \alpha_1 = 1$, integration and following transformation to relative atomic fluorine content give:

$$\frac{\text{F}}{\text{C}} = \frac{1}{2}\left[\left(2 + \frac{\lambda}{\lambda_1 - \lambda}\right)e^{-\lambda t} - \frac{\lambda}{\lambda_1 - \lambda}e^{-\lambda_1 t}\right]$$

We have found that this equation does not fit our experimental data at any values of λ and λ_1. Moreover, for very long times ($t \to \infty$), the F/C ratio asymptotically tends to zero. The only second stage reaction which can explain the discussed saturation may be written as follows:

$$\sim \text{CH}_2 \overset{\downarrow = e}{} \text{CF}{=}\text{CH}{-}\text{CF}_2 \sim \xrightarrow{-\text{HF}} \sim \text{CH}{=}\text{C}{=}\text{CH} \overset{\downarrow = e}{} \text{CF}_2 \sim$$
$$\xrightarrow{-\text{HF}} \sim \text{CH}{=}\text{C}{=}\text{C}{=}\text{CF} \sim,$$

or equally

$$\sim \text{CH}_2{-}\text{CF}{=}\text{CH} \overset{\downarrow = e}{} \text{CF}_2 \sim \xrightarrow{-\text{HF}} \sim \text{CH}_2 \overset{\downarrow = e}{} \text{CF}{=}\text{C}{=}\text{CF} \sim$$
$$\xrightarrow{-\text{HF}} \sim \text{CH}{=}\text{C}{=}\text{C}{=}\text{CF} \sim$$

Nevertheless, such quite special transformations are unlikely to occur via this specific and unique manner in any four-atom

fragment due to a random character of electron impacts that cleave covalent bonds in the PVDF chains. Moreover one must keep in mind that in the case of profound degradation (high doses) the double bonds are not isolated as shown in the scheme above, but conjugated (polyene fragments), and a single electron impact is enough to create a sequence of three cumulated double bonds (butatriene).

The case of α (α_1) $\neq$ 1 is of special interest. The decay probabilities of methylene (CF_2 or CH_2) and methine (CF or CH) groups could be different [10,11]. If the probability in the latter case is less, this could qualitatively explain the observed decrease in the variation rate of atomic F/C ratio. This interpretation requires a more detailed and bulky analysis similar to that employed previously [7,11], which currently is in progress and will be published elsewhere.

Actually all the discussed above phenomena may take place simultaneously thus making the detailed analysis of the experimental data even more complicated.

4. Conclusions

A dose effect of high-energy (20 keV) electron irradiation on the chemical composition of two types 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 (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. 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 and simplified accounting only intrinsic PVDF defects. The parameters of the equation depend on the PVDF defectiveness and a dominant mode of the polymer chains conformation. SEM images of the heavily irradiated samples have demonstrated creation of cracks the size of which depends on the film thickness. Most possibly this effect is caused by a decrease in specific volume of polymer molecules initiated by the polymer degradation.

Acknowledgments

References

[1] Le Moël A, Duraud JP, Balanzat E. Modifications of poly(vinylidene fluoride) (PVDF) under high energy heavy ion, X-ray and electron irradiation studied by X-ray photoelectron spectroscopy. Nucl Instrum Methods Phys Res 1986; 18(1):59–63.

[2] Duca MD, Plosceanu TL, Pop T. Effect of X-rays on poly(vinylidene fluoride) in X-ray photoelectron spectroscopy. J Appl Polym Sci 1998;67(13):2125–9.

[3] Okudaira KK, Yamane H, Ito K, Imamura M, Hasegawa S, Ueno N. Photodegradation of poly(tetrafluoroerthylene) and poly(vinylidene fluoride) thin films by inner shell excitation. Surf Rev Lett 2002;9(1):335–40.

[4] Morikawa E, Choi J, Manohara HM, Ishii H, Seki K, Okudaira KK, et al. Photoemission study of direct photomicromachining in poly(vinylidene fluoride). J Appl Phys 2000;87(8):4010–6.

[5] Pesin LA, Gribov IV, Kuznetsov VL, Evsyukov SE, Moskvina NA, Margamov IG. In situ observation of the modification of carbon hybridization in poly(-vinylidene fluoride) during XPS/XAES measurements. Chem Phys Lett 2003; 372(5–6):825–30.

[6] Chebotarev SS, Volegov AA, Pesin LA, Evsyukov SE, Moskvina NA, Gribov IV, et al. Modification of X-ray excited photoelectron and C KVV Auger spectra during radiative carbonization of poly(vinylidene fluoride). Phys E Low-Dimensional Syst Nanostructures 2007;36(2):184–9.

[7] Kuvshinov A, Pesin L, Chebotaryov S, Kuznetsov M, Evsyukov S, Sapozhnikova T, et al. Kinetics of radiation-induced carbonization of poly(-vinylidene fluoride) film surface. Polym Degrad Stab 2008;93(10):1952–5.

[8] Ferraria AM, Lopes da Silva JD, Botelho do Rego AM. XPS studies of directly fluorinated HDPE: problems and solutions. Polymer 2003;44(23):7241–9.

[9] Heimann RB, Evsyukov SE, Kavan L, editors. Carbyne and carbynoid structures. Dordrecht: Kluwer Academic Publishers; 1999.

[10] Pesin LA, Voinkova IV, Evsyukov SE, Gribov IV, Kuznetsov VL, Moskvina NA. Simplified method for measuring fluorine concentration on the surface of poly(vinylidene fluoride) and products of its partial carbonization. Izv Chelyabinsk Nauchn Tsentra 2004;4(26):21–5 [in Russian].

[11] Voinkova IV, Ginchitskii NN, Gribov IV, Klebanov II, Kuznetsov VL, Moskvina NA, et al. A model of radiation-induced degradation of the poly(-vinylidene fluoride) surface during XPS measurements. Polym Degrad Stab 2005;89(3):471–7.