

Study of surface chemical changes in PVDF irradiated by 1.3 MeV electrons.

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Summary

The chemical changes that occur on the surface of poly(vinylidene fluoride) (PVDF) irradiated with 1.3 MeV electrons at doses up to 30 MGy, were studied by X-ray photoelectron spectroscopy (XPS) and by infrared spectroscopy (FTIR) in the horizontal attenuated total reflectance mode (HATR) and in the transmission mode. The wettability of the surface before and after irradiation was measured by dynamic contact angle measurements.

The *C 1s* structure in XPS reveals that as a result of irradiation, the $-\text{CF}_2-$ related peak practically disappears. The remaining *C 1s* peak is mainly associated with C=C bonds in the heavily cross-linked carbon structure produced as a result of irradiation. FTIR spectra are consistent with the XPS observations. The irradiated films showed improvement in the oxidation and wettability of the surface.

Introduction

Irradiation of polymers has been widely applied for the modification of surfaces that render them useful for technological applications. PVDF, in particular, has been the focus of several studies, due to its applications as a biocompatible material [1] with important applications in the pharmaceutical and food industries. Several reports have been published that describe the effects on PVDF of ionizing radiations such as ions [2-6], photons [7] and electrons [8]. Our group has been systematically studying the irradiation induced modification of polymeric surfaces, in order to understand the chemical and structural changes that may allow new applications [9,10]. In particular, we are interested in the deposition of metallic thin films on polymeric surfaces. Reports indicate that the adhesion of metallic thin films has been significantly improved when the polymeric substrate has been irradiated [11-14].

Experimental

The PVDF samples were 0.3mm thick films purchased from Goodfellow Cambridge. They were put in sealed polyethylene bags, previously purged with nitrogen, and irradiated with a 2 MeV Van de Graaff accelerator with a beam energy of 1.3 MeV and a beam current of 5 μA , at a dose rate of 25 kGy/min. The total dose was

determined by FWT-60 radiochromic film dosimetry. Additional data and experimental conditions have been previously described [8]. The chemical changes produced on the surface of the samples, were studied by applying X-ray Photoelectron Spectroscopy (XPS), with a CAMECA-MAC-3 spectrometer. The X-ray source uses the $Al K_{\alpha}$ line (1486.6 eV) to excite the sample. The energy scale of the spectrometer was previously calibrated using the reference binding energy of $Cu 2p_{3/2}$ at 932.7 eV and $Ag 3d_{5/2}$ at 368.3 eV. The maximum resolution obtained under these conditions is 1.0 eV, measured from the $C 1s$ transition in a pyrolytic graphite target. In addition, changes in peak energies associated with surface electron charging were monitored following the $O KLL$ Auger transition at 978 eV. All chemical shifts were measured by fixing the value of the $C 1s$ binding energy of graphite (284.5 eV) and the $O KLL$ Auger transition. The control and irradiated samples were measured by transmission FTIR-spectroscopy, and in the horizontal attenuated total reflectance mode (HATR), with a zinc selenide (ZnSe) crystal prism and with 12 reflections at the crystal angle of 45° , using a Perkin-Elmer FTIR-1600 spectrometer in both cases. Under these conditions, the penetration depth of the IR-beam is of the order of a few microns. This device allows the study of thick opaque solid samples.

The wettability of the surface before and after irradiation was studied by dynamic contact angle measurements. The equipment used was Sigma 70, Model T100F. The hydrophilic or hydrophobic behavior of the control and irradiated samples was determined using tridistilled and deionized water at room temperature ($25^{\circ}C$). All contact angle values were estimated from the mean value of quintupled measurements of each sample.

Results and discussion

An XPS survey of the control sample is shown in Fig.1. The main contributions to the spectrum are the $C 1s$ transition, $F 1s$ and $O 1s$ transitions. Given the surface sensitivity of XPS, the O contribution observed in the survey may be associated to O adsorbed on adventitious carbon on the surface of the test sample. Also shown are the $O KVV$, $F KLL$ and $C KVV$ Auger electron emissions. On close examination, one can see the typical $C 1s$ peak with its well-known chemical shifted structure associated with fluoropolymers. Peak contributions and the type of bond associated with each component have been assigned from an extensive review of the literature associated with this type of materials. Fig.2 (a) shows a wide peak centered at 285.6 eV in the binding energy scale (B.E.) and a peak centered at 290.5 eV associated with $-CF_2-$ bonds in PVDF (peak 4) [3,5,6,11,19]. The first peak is further analyzed by a gaussian fit of the experimental XPS spectrum and several components may be fitted. The first corresponds to a contribution at 284.6 eV (peak 1), which is generally associated with $C=C$ bonds related to adventitious surface carbon [2,3,5,6,11]. The second and main contribution is centered at 285.7 eV (peak 2) and is attributed to the $-CH_2-$ bonds of PVDF [2,3,5,6,11,19]. In addition, one can include a third contribution, centered at 287.2 eV (peak 3) which may be associated with surface related $C-O$ bonds [14-18] and these may play a role in the surface properties of PVDF after irradiation, as will be shown later.

Fig. 2 (b), (c) and (d), show the same portion of the XPS spectrum for three increasing radiation doses: 3, 10 and 30 MGy, respectively. As may be observed, the main effect of the radiation is a drastic reduction of the F-related peak (peak 4). As previously reported [2-6,11], radiation induces the generation of HF, F_2 and other volatile species

as a result of bond breaking by the ionizing radiation. In addition, one can observe a change in relative contributions to the $C 1s$ peak. An increase in the contribution associated with $C=C$ bonds, which constitutes the main residual carbon material in the heavily irradiated samples. The $-CH_2-$ component (peak 2) decreases as expected. Also present in the irradiated samples is the peak associated with surface related $C-O$ bonds (peak 3). In the irradiated samples, an additional contribution at 288.5 eV (peak 5) is observed, attributed to carboxylate groups ($R-COOH$) [16, 17], considering that irradiated samples were exposed to the ambient and that in heavily irradiated polymer, extensive cross-linking, structural damage and F-gas desorption may generate oxygen absorption and adsorption on the irradiation induced roughness of the surface.

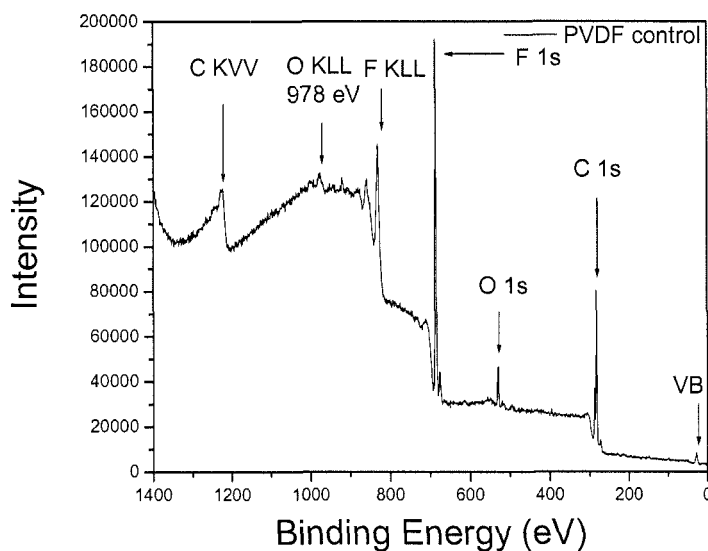
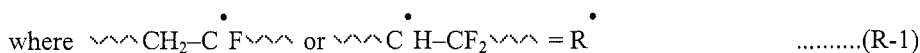
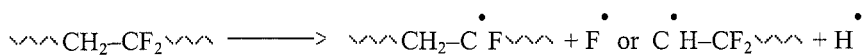


Figure 1. XPS survey of the control sample.

Both the control and irradiated samples were studied by FTIR in the transmission and HATR mode. The corresponding spectra in the HATR mode are shown in Fig. 3. Two small bands located at 1381 cm^{-1} and 1400 cm^{-1} are observed in the control sample, and are attributed to the symmetrical and asymmetrical bending vibration of CH_3 terminations in the $CH_2-CF_2-CH_3$ polymer chain. As the irradiation dose increases the bands become narrower towards 1400 cm^{-1} , which is the more stable band when the methyl group is attached to carbon, consistent with the following reaction:



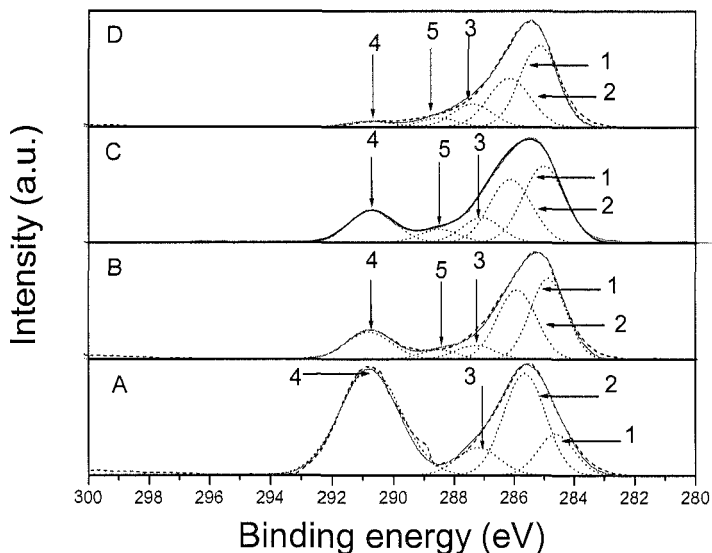
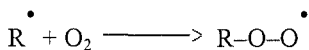


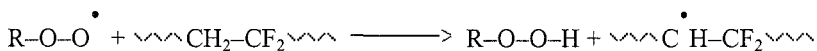
Figure 2. XPS corresponding to the *C 1s* core level for: A) control sample and irradiated samples at increasing radiation dose: B) 3 MGy, C) 10 MGy, D) 30 MGy.

The next observable feature, which changes as a function of irradiation dose, is located at 1175 cm^{-1} . It shows two shoulders that generate a broadening of the peak overlapping a peak at 1178 cm^{-1} . This feature may be associated with C–O–C bonds related to ether groups on the surface of the irradiated polymer. This interpretation is consistent with the more hydrophilic behavior of the irradiated polymer. The contact angle measurements, which will be described later, are consistent with this observation.

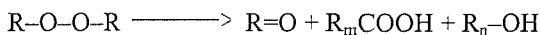
Oxygen adsorption gives rise to peroxides which in turn break-up to produce polar groups on the surface, which may be attached to macro-radicals to form ether groups. The reaction steps may be summarized as follows:



Followed by hydrogen extraction from other chains,



And formation of radiolytic products from the hydroperoxide,



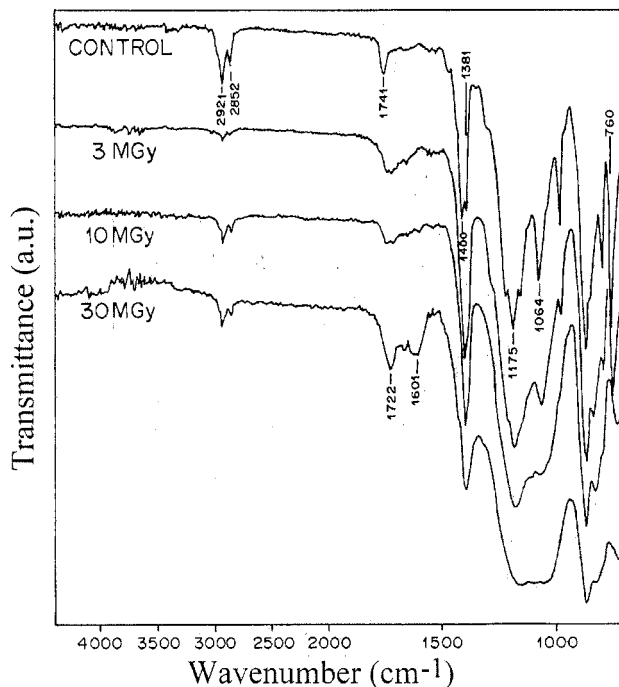


Figure 3. FTIR in the HATR mode of control and irradiated samples.

The feature at about 1061 cm^{-1} is clearly modified by the irradiation dose and is associated with $\text{CH}_2\text{-CH}_3$ terminations on the surface. These are the source of the above mentioned polar groups formed by irradiation. The band at 760 cm^{-1} decreases as a function of irradiation since it is associated with $\text{-CF}_2\text{-}$ bonds, which are dissociated by the irradiation process. The bands near to 3000 cm^{-1} , corresponding to $\text{-CH}_2\text{-}$ groups, show an irregular behavior that may be associated to the increased surface sensitivity of the HATR mode and the roughness of the surface, resulting from the irradiation process. The band at 1741 cm^{-1} , corresponding to C-F, almost disappears as the irradiation dose increases. New bands appear at a lower wave numbers (1722 and 1601 cm^{-1}) due to the formation of C=O and C=C groups respectively.

The samples were also studied by transmission FTIR in the 400 to 4000 cm^{-1} range (Fig 4). The main feature is a double peak at 3024 and 2980 cm^{-1} in the control sample, associated with $\text{-CH}_2\text{-}$ groups in the polymer. As a result of irradiation, the band becomes broader, as cross-linking progresses and C=C bonds are formed as the dose increases. Also, the peaks at 3424 , 3522 and 3606 cm^{-1} , could be attributable to O-H stretching modes, related to organic peroxides, carboxilates and alcohols, respectively [20]. The presence of these peaks, are in good agreement with the proposed mechanism of PVDF degradation due to the irradiation process. Another distinctive feature is observed around the 1700 cm^{-1} region, which drastically changes as a result of irradiation, due to the de-hydro-fluorination of the polymer sample. New bands appear at 1732 and 1682 cm^{-1} associated with the C=O and C=C bonds

respectively.

Contact angle measurements were performed on both the control and irradiated samples in order to verify if an enhanced oxidation of the surface, suggested by both XPS and IR spectroscopies, would affect the wettability of the samples.

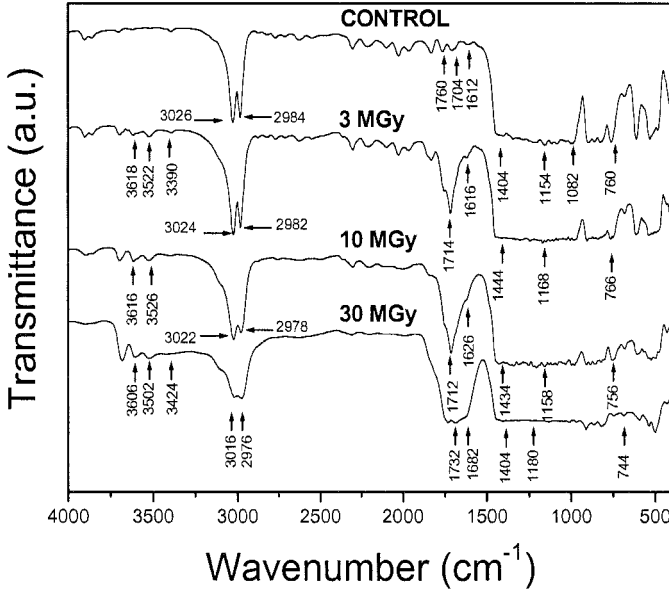


Figure 4. FTIR in the transmission mode for: control and irradiated samples at 3, 10 and 30 MGy.

Table 1 shows the results obtained from contact angle measurements of tri-distilled and de-ionized water on PVDF. Results are given for the control and samples irradiated at 3, 10 and 30 MGy. The observed increase in the differences between the advance and receding contact angles in the irradiated sample is consistent [21] with an increased wettability related to the radiation-induced roughness on the surface of PVDF.

	Irradiation Dose (MGy)							
	Control		3		10		30	
Contact Angle	Adv	Ret	Adv	Ret	Adv	Ret	Adv	Ret
θ	98	72	92	37	93	33	84	24
$\text{Cos } \theta$	-0.14	0.31	-0.03	0.8	-0.05	0.84	0.1	0.91

Table 1. Contact angle measurements in the control and irradiated PVDF samples

Conclusions

The chemical changes that take place in electron irradiated PVDF at doses up to 30 MGy were studied by XPS, FTIR and contact angle measurements. The C 1s structure in the XPS spectrum reveals that as a result of irradiation, the -CF₂- related peak practically disappears, in accordance with previously reported desorption of HF, F₂, H₂ and other related volatile species. The remaining C 1s peak is mainly associated with C=C bonds in the heavily cross-linked carbon material produced as a result of irradiation. FTIR spectra in both the reflectance (ATR) and transmission modes are consistent with the XPS observations. In addition, as a result of irradiation, evidence is provided about oxygen adsorption and peroxide formation on the surface leading to the formation of polar groups on the surface.

Contact angle measurements clearly show that radiation improves the oxidation, and the wettability of the surface.

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