Effect of X-rays on Poly(vinylidene fluoride) in X-ray Photoelectron Spectroscopy

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ABSTRACT: The polymer poly(vinylidene fluoride)(PVDF) was irradiated with X-rays produced by a nonmonochromatic (MgKα) source and the structural and electronic PVDF surface modifications were studied by X-ray photoelectron spectroscopy (XPS). Changes in the shape and intensity of the C_{1s} and F_{1s} lines show that a PVDF degradation consisting of the polymer defluorination takes place. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 67: 2125–2129, 1998

Key words: XPS; X-ray exposure; PVDF

INTRODUCTION

X-ray photoelectron spectroscopy (XPS), first known by the name ESCA (electron spectroscopy for chemical analysis),[1] is a powerful tool in material research, capable of providing information concerning the surface and immediate subsurface of the samples as well as the bulk properties. This particular feature of the technique is crucial for the understanding of the polymer surface modifications produced by different treatments such as oxidation, fluorination, ion bombardment, and plasma etching.[2]

A common problem during the XPS analysis is the X-ray-induced damage of the sample. Studies have been reported on X-ray-induced damage in XPS analysis on different polymers.[3–5] In the case of polytetrafluoroethylene (Teflon), Wheeler and Pepper,[4] using a nonmonochromatic MgKα X-ray source, showed that the polymer surface is defluorinated by X-rays rather than by electron bombardment used for the compensation of the sur-

face charging during XPS measurements. Chaney and Barth[5] published an XPS study on the X-ray-induced changes in Teflon and several other polymer materials (PMMA, PAN, PVC, PET) using an AlKα X-ray source. They found that nonmonochromatic X-rays cause more damage than do monochromatic X-rays on Teflon only.

We studied poly(vinylidene fluoride)(PVDF), which is a high molecular weight polymer of repeated units ($-CH_2-CF_2-$) and which has a large technological applicability. Because of the theoretical and practical interest, PVDF undergoing different treatments has been extensively studied by XPS,[6–9] but there have not been reported studies on the X-ray-induced damage by XPS on PVDF. It was the aim of this article to examine the effect of the X-rays in XPS on the constitution of the PVDF surface using a spectrometer with a nonmonochromatic MgKα X-ray source. We observed the time dependence of the shape, intensity, and binding energy of the C_{1s} and F_{1s} lines in the XPS spectrum, trying to understand the damage-responsible mechanism.

EXPERIMENTAL

Sample

PVDF (KYNAR) supplied by Goodfellow Cambridge Ltd. was used in a common form, without

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any piezoelectric or pyroelectric properties. The sample exposed to X-rays had a cylindrical disc shape (10-mm diameter × 0.8 mm). It was cleaned prior to the treatment in an ultrasonic bath of isopropanol for 30 min and then dried under a vacuum at room temperature.

Method

The X-ray irradiation and XPS measurements were performed using a Kratos XSAM 800 X-ray photoelectron spectrometer with the MgKα (1253.6 eV) anode of the quadric-anode X-ray source operating at 20 mA and 12 kV. The measurements were performed with a take-off angle of 90° (measured with respect to the sample surface). The energy analysis system consisted of a Kratos 127-mm radius hemispherical electrostatic electron energy analyzer fitted with a three-channel detector and an associated electron optical system between the sample and the analyzer entrance slit. The instrument was driven via a computer workstation which controlled all data acquisition, storage, and processing functions. The measurements were performed with a non-monochromatic resolution, at a pass energy of 20 eV, typically 1.0 eV. The base pressure was around 3.5×10^{-8} mbar or lower.

XPS spectra were taken in the fixed analyzer transmission (FAT) mode, with an energy range window of 1100 and 20 eV for survey scans and the C_{1s} and F_{1s} regions of interest, respectively. The sample was X-ray exposed for 800 min and the spectra were recorded from 100 to 100 min. The acquisition times ranged from a few minutes to 20 min. During data acquisition, the sample surface was flooded by low-energy (6 eV) electrons generated by the Kratos UV flood source. In this way, the energy shifts that arose from the charging were compensated in part. The charging of the samples not in electrical contact with the spectrometer has previously been shown to be a sensitive function of surface composition,[9] especially for fluoropolymers. A lesser degree of charging was found to be strongly correlated with decreasing of the fluorine content, both in model systems and in modified fluoropolymer surfaces.

Because of the different energy shifts during the XPS measurements, the binding energies of the XPS peaks were referenced by setting the $\underline{CF}_2$ peak in the C_{1s} spectra to 290.90 eV.[10] Routine quantitative XPS analysis, using the peak area that was calculated after the linear background had been removed, yielded the "surface" atomic percentage of element (functional group) i, C_i, as given by

$$C_i = \frac{X_i/q_i}{\sum\limits_{j} X_j/q_j}$$

where X_i and X_j are the areas under peaks i and j, respectively, and q_i and q_j are the quantification factors of the elements (functional groups) i and j, respectively.

The summation is performed over all detected elements (functional groups). The empirical values of the quantification factors in our case were $q_{F1s} = 1.00$ and $q_{C1s} = 0.19$. The C_{1s} spectra were curve-fitted with a routine using a 80% Gaussian/ 20% Lorentzian line-shape function.

To eliminate the contribution in the XPS spectra of adventitious contamination generally caused by pump oil vapors in the sample chamber of the spectrometer,[11] a virgin PVDF was kept in the spectrometer at about 5×10^{-8} mbar for 14 h. The XPS spectra recorded before and after this period showed no changes.

Another experiment was carried out to differentiate between an X-ray versus electron-induced effect. A virgin PVDF was flooded by an electron flux from the Kratos UV flood source for a period of 14 h. The kinetic energy of the electrons was adjusted to 6 eV. No spectral changes were observed after this time period.

RESULTS AND DISCUSSION

The initial C_{1s} core-level spectrum consists of two main component peaks, at 290.90 eV attributable to the $\underline{CF}_2$ species and at 286.50 eV attributable to the $\underline{CH}_2$ species,[10] respectively. A minor component peak was also evident at 285.20 eV. Its relative intensity was about 12.03% of the total intensity of the C_{1s} core-level spectrum. A very small peak also appeared at 288.30 eV. These minor peaks can be attributable to the contamination of the polymer prior to loading it into the spectrometer.

The evolution of the C_{1s} and F_{1s} core-level spectra of exposed PVDF versus X-ray exposure times is shown in Figure 1. It can be seen from this figure that the F_{1s} peaks show a gradual decrease in relative intensity compared to the C_{1s} peaks with increasing exposure time. This defluorination is also provided by the shape of the curve plotted in Figure 2 that shows a linear decrease of the ratio X_t/X_{100} with the X-ray exposure time
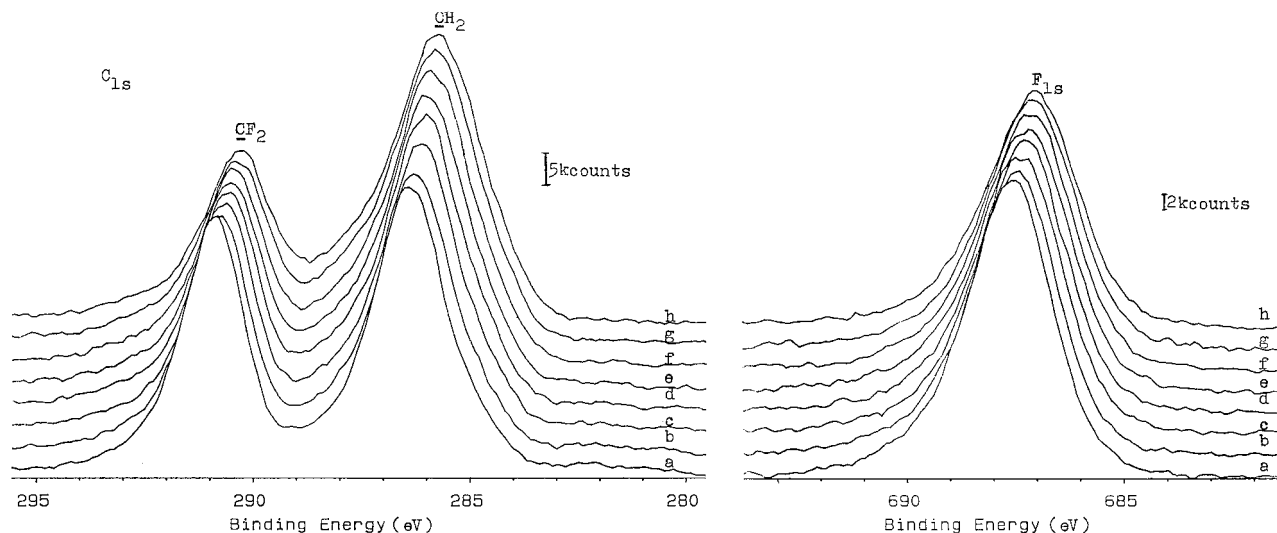
Figure 1   Evolution of the C_{1s} and F_{1s} core-level spectra of PVDF versus X-ray exposure time: (a) 100 min; (b) 200 min; (c) 300 min; (d) 400 min; (e) 500 min; (f) 600 min; (g) 700 min; (h) 800 min.

(t) (X_t = F/C atomic concentration ratio after "t" X-ray exposure time).

The changes in the C_{1s} spectra also point to fluorine loss. Upon X-ray exposure, the C_{1s} recorded spectra exhibit a decrease of the $\underline{C}F_2$ peak while the components due to carbon $\underline{C}$ not directly attached to fluorine ($-CH_2-$, $-\underline{C}H-$, $=CH-$) do not show a significant variation. The ($-CH-$, $=CH-$) groups are supposed to appear during the X-ray irradiation.

The peak localized at 288.30 eV shows an in-

crease that can be attributable to the $\underline{C}F$ functionalities.[13,14] The results of the component analysis of the C_{1s} spectra and grouping together of the carbonaceous components are shown in Figure 3.

For the description of the X-ray-PVDF surface interaction, we must take into account the results reported in some previous XPS studies on PVDF under electron and ion irradiation.[6,13] These studies show that PVDF is a polymer in which scissions occur primarily between the chain backbone carbons and the side substitutes, leading to the formation of double bonds in the main chain and
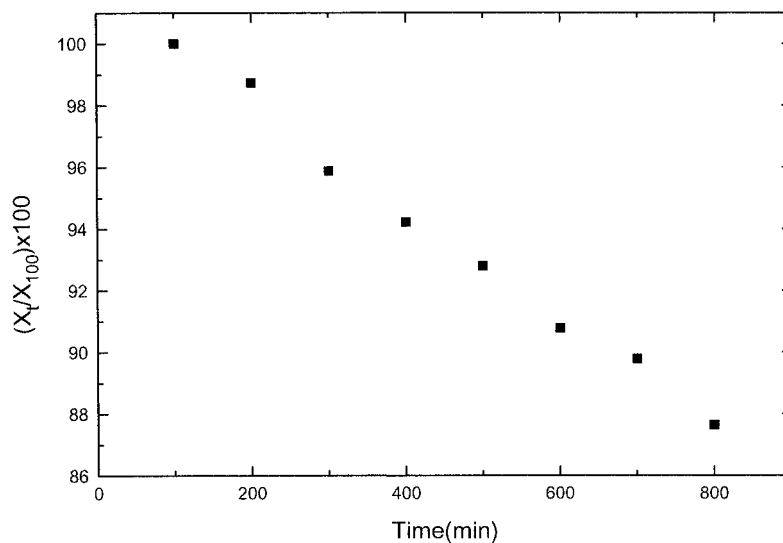

Figure 2   Plot of $(X_t/X_{100}) \times 100$ versus X-ray exposure time for PVDF. X = F/C atom concentration ratio.
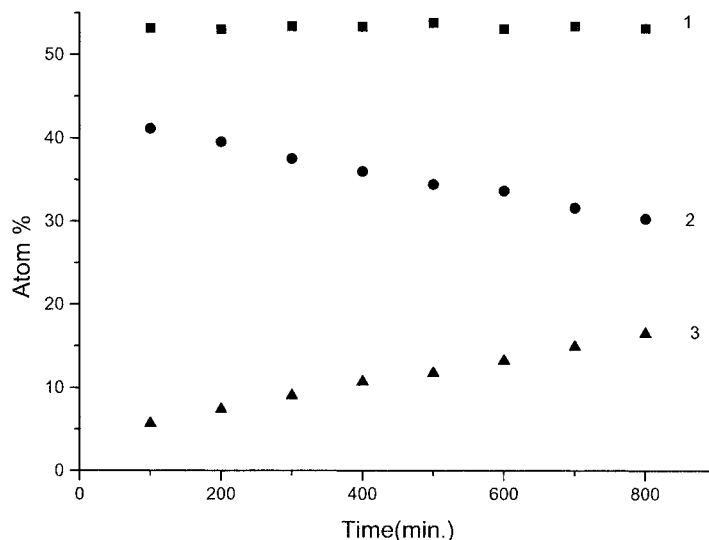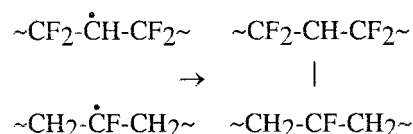
Figure 3 Variation of the C_{1s} components with X-ray exposure time: (1) $\underline{C}$; (2) $\underline{C}F_2$; (3) $\underline{C}F$.

to a crosslinked structure. It is also possible that chain scissions occur but this is not a main characteristic.[13] Another study on PVDF irradiated by oxygen energetic ions ($E \geq 1$ MeV amu)[14] revealed that upon irradiation a polyenic network $\left(\begin{array}{c}\diagdown\\\diagup\end{array}C{=}C\begin{array}{c}\diagup\\\diagdown\end{array}, {=}C{=}\right)$ is obtained and HF elimination is the dominant mode of fluorine loss. An ESR study on γ-ray-irradiated PVDF[15] also revealed a polyenic network. In the above-mentioned studies on PVDF, the polyenic features $\left(\begin{array}{c}\diagdown\\\diagup\end{array}C{=}C\begin{array}{c}\diagup\\\diagdown\end{array}, {=}C{=}\right)$ appear at -1.5 or -1.7 eV from the $\underline{C}H_2$ peak.

Our XPS spectra for X-ray-exposed PVDF do not reveal a peak that could be attributed to a polyenic structure. This could be explained if we take into consideration that X-rays are soft ones. The evolution of $\underline{C}F_2$, $\underline{C}F$, and $\underline{C}$ in the C_{1s} spectra (Fig. 3) indicates that the loss of $\underline{C}F_2$ groups from a chain occurs via $\underline{C}F_2 \rightarrow \underline{C}F$ processes.

It is therefore quite plausible to assume that the initial reaction involves a breaking of the C—H, C—F, or C—C bond, leading to a radical or ionic intermediate. We should specify that the breaking of the C—C bond could take place in PVDF, but it is less probable than the breaking of the C—H or C—F bond as shown by the previously mentioned studies on PVDF. A radical intermediate could react with an adjacent radical intermediate under crosslinking,[13] for example:

$$\begin{array}{ccc}
\sim CF_2\text{-}\overset{\bullet}{C}H\text{-}CF_2\sim & & \sim CF_2\text{-}CH\text{-}CF_2\sim \\
\rightarrow & & | \\
\sim CH_2\text{-}\overset{\bullet}{C}F\text{-}CH_2\sim & & \sim CH_2\text{-}CF\text{-}CH_2\sim
\end{array}$$

The above crosslinking could be indicated by the increase of the peak localized at 288.30 eV in the C_{1s} spectra *versus* the X-ray exposure time, attributable to $\underline{C}F$ features that are predominantly in a nonfluorinated environment.[13]

Since HF has a high bond strength,[16] the H and F atoms generated in the initial reactions may abstract another F or H atom, leading to the HF molecule elimination and generating other radicals in the chain. The H and F atoms may also abstract another F or H atom from a CF_2 or CH_2 group next to a radical center, leading to a HF molecule elimination and the formation of double bonds ($\sim CF_2{-}CH{=}CF{-}CH_2 \sim$) in the main chain. The free H atoms may abstract another H atom, propagating the generation of radicals in the chain. The abstraction of F atoms by free F atoms is not envisaged to be favorable.[13]

In our study, we did not consider the thermal effect that could decrease the rigidity of the polymeric backbone, allowing a new configuration, which, in turn, can produce further damage.[16] Wheeler and Pepper[4] showed that thermal degradation was negligible and could be ruled out as a cause of the changes in the PTFE during X-ray exposure and a similar situation is expected for PVDF.

CONCLUSION

The results revealed here show that soft X-rays introduce compositional changes on the fluoropolymer PVDF after prolonged exposure. The polymer surface is found to be depleted of fluorine. The decrease of the $\underline{C}F_2$ (290.90 eV) group percentages and the increase of the $\underline{C}F$ (288.30 eV) group percentages with no significant variation of the components due to carbon not directly attached to fluorine prove that a crosslinking and double-bond formation follow the polymer defluorination. In spite of this, XPS can be considered a nondestructive surface analytical technique for PVDF in typical analysis times because the X-ray induced damage is not very noticeable for these short time periods.

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