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Changes in the physical and chemical properties of PVDF irradiated by 4 MeV protons

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The behavior of poly-vinylidene fluoride (PVDF) under bombardment of different kinds of radiation is of interest due to the polymer's unique piezo-electric properties and various crystalline forms. In this work, PVDF film samples of 0.3 mm thickness and density 1.76 g/cm^3 were irradiated with 4 MeV protons from the Instituto de Física 9SDH-2 Pelletron Accelerator. Changes in the physical and chemical properties were investigated using Fourier Transform Infrared Spectroscopy (FTIR) with ATR, X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC) and gel fraction measurements. The gel percent increases with fluence to almost 60% for a fluence of 10^{13} cm^{-2}, and then more slowly up to 100% for a fluence of 3×10^{14} cm^{-2}. The DSC curve of the control sample shows a sharp band at 176 °C with a shoulder on the low temperature side. A well defined lower temperature peak, related to the relaxation of inter-crystalline regions appears at a fluence of 10^{13} cm^{-2}. At 3×10^{14} cm^{-2} there are no melting peaks, due to complete destruction of the crystalline structure. This was confirmed at this high fluence by the FTIR spectra, and by x-ray diffraction, where an amorphous structure was observed.

Keywords: Protons; irradiation; PVDF; physical properties; chemical properties.

El comportamiento del polifluoruro de vinilideno (PVDF) sometido a distintos tipos de irradiación es de interés por sus propiedades piezoeléctricas y sus distintas formas cristalinas. En este trabajo se irradiaron muestras de PVDF de 0.3 mm de grosor y densidad 1.76 g/cm^3 con protones de 4 MeV provenientes del acelerador Pelletron 9SDH-2 del Instituto de Física. Los cambios en las propiedades físicas y químicas se estudiaron por medio de espectroscopía infrarrojo con transformada de Fourier (FTIR) y reflexión total atenuada, difracción de rayos × (XRD), calorimetría diferencial de barrido (DSC), y medida de fracción de gel. El porciento de gel inicialmente aumenta con la afluencia hasta casi 60% para una afluencia de 10^{13} cm^{-2}, y luego lentamente hasta 100% a 3×10^{14} cm^{-2}. La curva de DSC de referencia muestra una banda angosta a 176 °C con un hombro del lado de baja temperatura. A una afluencia de 10^{13} cm^{-2} aparece un pico a más baja temperatura, relacionado con la relajación de regiones intercristalinas. A una afluencia de 3×10^{14} cm^{-2} no hay picos de fusión, debido a la destrucción completa de la estructura cristalina. Esto se confirmó para afluencias grandes con los espectros de FTIR y de XRD, donde se observa una estructura amorfa.

Descriptores: Protones; irradiación; PVDF; propiedades físicas; propiedades químicas.

PACS: 61.82.Pv; 81.40.Wx; 81.05.Lg

1. Introduction

Poly-vinylidene fluoride (PVDF) $(CH_2\text{-}CF_2)_n$ is a long chain, semi-crystalline (normally 50 to 55%), linear polymer. It has acquired importance due to the existence of two common stable crystalline forms with different piezo- and pyro-electric properties. There are four crystalline phases of PVDF: form I (β phase), form II (α phase), and two forms III (γ phase) with different parameters. The alpha and beta phases are the most commonly found; of these, the polar phase is associated with the piezoelectric properties of PVDF.

The modification of polymers with ionizing radiation is a field that has developed considerably and has produced numerous technological applications. PVDF, in particular, has been the focus of several studies, due to its applications as a biocompatible material with important applications in the pharmaceutical and food industries [1]. Various types of radiation have been used: alpha particles, gamma rays, x-rays, electrons, and positive ions of various energies. The behavior of PVDF under bombardment of different kinds of radiation [2-4], including ion beams of several different species in different energy regimes [5-12], has been studied before. The interaction of energetic heavy ions with the polymer induce the formation of chemically reactive species along the particle's trajectory in a complex manner. The production, recombination and migration of reactive species gives rise to physical and chemical changes in the polymer, including desorption of gases.

In the present work physical and chemical modifications of PVDF bombarded with 4 MeV protons were studied using Fourier Transform Infrared Spectroscopy (FTIR), x-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), and gel fraction determination. The evolution of these changes with proton fluence was observed up to a value where the material was totally modified. The gel fraction obtained by irradiating with different kinds of radiation has not been considered previously, with the exception of one case of irradiation with electrons and He beams [2].

2. Experiment

The PVDF samples were films of 0.3 mm thickness and density 1.76 g/cm^3 obtained from Goodfellow, Cambridge. All samples were cleaned in acetone in an ultrasonic bath prior to irradiation. A spectrum from an x-ray energy dispersive spectrometer showed only C and F peaks, indicating that impurities were negligible. Before irradiation the material was mainly α phase.

The samples were bombarded with 4 MeV protons from the Instituto de Física 9SDH-2 Pelletron Accelerator. The beam was rastered over an area considerably larger than the area of the samples, to ensure lateral homogeneity and to minimize errors in the beam current integration. The samples were tilted 8° from normal incidence.

The range of 4 MeV protons in this material, projected on the normal to the surface, is calculated using the code TRIM [13] to be slightly over 150 microns. The main energy deposit is due to the interaction of the protons with the atomic electrons of the polymer, giving rise to ionization and excitation, dissociation, formation of free radicals, cross-linking, etc. The distribution of ionization energy (Bragg curve) starts at about 15 eV/nm/proton at the surface and peaks above 70 eV/nm/proton near the end of the proton trajectory. Interactions with nuclei are rare at these proton energies, as compared with electronic interactions.

In order not to have undamaged regions, the samples were bombarded on both faces. In each case they were tightly pressed onto an aluminum backing in order to dissipate as much charge as possible, and also to allow measuring the beam current. As a result of bombarding both faces, the calculated ionization energy distribution is peaked near the middle of the film. Therefore the depth distribution is slowly varying over about 90% of the film thickness, with an average value close to 20 eV/nm/proton. The remaining 10% received about four times that amount. However, it must be stressed that due to the loss of material from heating and from radiation induced desorption, during bombardment the films change dimensions and density, therefore, the calculated distribution of ionization can only be considered as an approximation.

The beam flux density was kept at about 5×10^8 protons/mm^{2}s. At this flux density the film withstands the bombardment; at higher densities buckling is observed due to heating. The irradiations were always performed in a high vacuum of the order of 10^{-4} Pa.

To measure the gel fraction (cross-linking), the cross-linked (insoluble) fraction of the sample is extracted with high temperature dimethyl sulfoxide (DMSO) for 30 hours. The infra-red (IR) analysis was carried out in a Perkin-Elmer FTIR-1600 spectrometer, in the HATR (Horizontal Attenuated Total Reflectance) mode, equipped with a zinc selenide (ZnSe) crystal prism, and with 12 reflections at the crystal angle of 45°, with a penetration depth of the beam of the order of a few microns. This accessory allows the study of thick opaque solid samples.

For the calorimetric measurements a Model 2910 TA Instruments differential scanning calorimeter (DSC) was used, operated at a heating rate of 10° C/min in a nitrogen atmosphere; the calibration was made with a standard of In. The x-ray spectra were taken with a Philips Model Xpert diffractometer with a Cu source whose K$_{\alpha 1}$ line is at 0.154 nm. For these measurements spectra were taken in the interval from 10 to 70 degrees (2θ).

3. Results and discussion

The appearance before and after bombardment is shown in the scanning electron micrographs of Figs. 1a and 1b. Initially the surface is quite smooth, but after bombardment it becomes rough, due to the uneven loss of mass. The color changed gradually with exposure, from translucent white to dark brown.

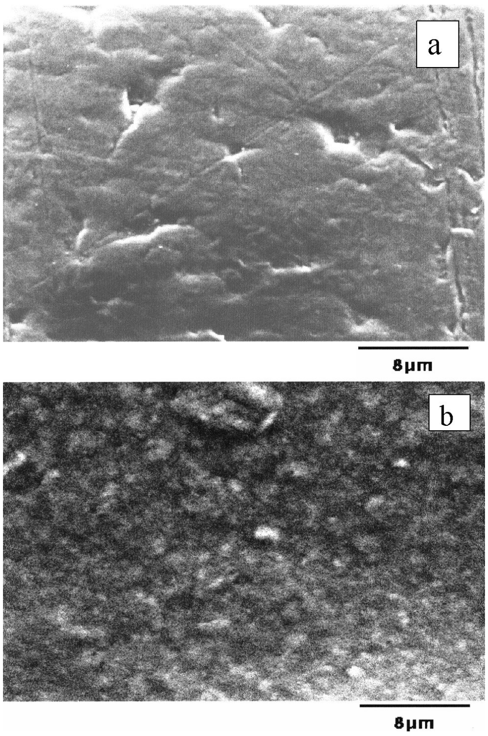

FIGURE 1. Scanning electron micrographs of the surface of PVDF samples. a) reference material, and b) after irradiation with 10^{14} protons/cm^2 at energy 4 MeV.

The measured gel percent as a function of fluence is shown in Fig. 2; the numerical values are in Table I. From zero for a pristine sample, it rises quickly to almost 60% for a fluence of 10^{13} cm^{-2}, and then more slowly until it reaches essentially 100% for a fluence of 3×10^{14} cm^{-2}. This indicates that cross-linking is the predominant effect in this interval of fluence.

The IR results are shown in Fig. 3 for several values of proton fluence, showing the chemical changes due to the irradiation .

The characteristic absorption bands of the symmetric and asymmetric stretching vibration of the CH_2 group are assigned in the literature to the region of 2840 to 2975 cm^{-1}. Fluorine atoms attached to carbon double bonds have the effect of shifting the C=C stretching vibration to higher frequencies near 3000 cm^{-1} [14]; we observed these bands at 2920 and 2850 cm^{-1}, in addition to a very small band near 3025 cm^{-1}.

As the FTIR determinations were made in ATR mode, the intensity of the bands can be influenced by the roughness of the sample surface and the pressure on the sample during the measurement. At the highest fluence studied, 3×10^{14} cm^{-2}, where the polymer destruction occurs simultaneously with amorphization, we found the increase of many wide bands in the range of 2400 to 3700 cm^{-1}. This could be an indication of the existence of a post-irradiation oxidation processes.

TABLE I. Measured values of gel percent for a 4 MeV proton fluence.

Fluence [cm^{-2}]	Gel %
0.0	0.0
1×10^{12}	45.2
3×10^{12}	38.6
1×10^{13}	57.2
3×10^{13}	82.0
1×10^{14}	92.6
3×10^{14}	100.0

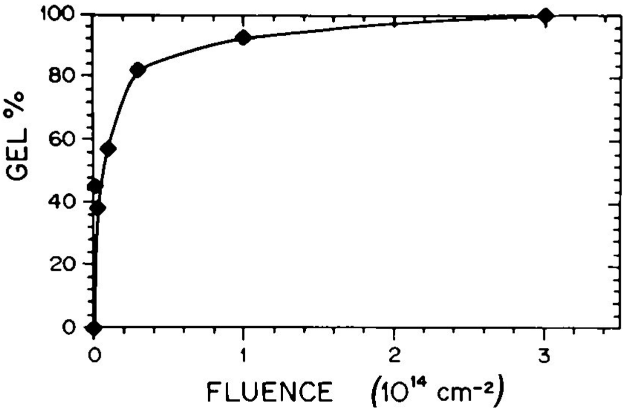

FIGURE 2. Behavior of measured gel percent with fluence of 4 MeV protons. The points are experimental; the lines are only to guide the eye.

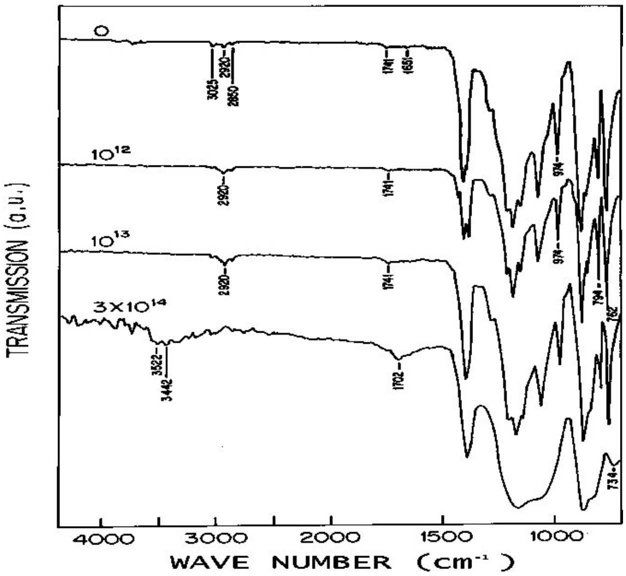

FIGURE 3. FTIR spectra of PVDF samples bombarded with 4 MeV protons at different values of fluence: zero (pristine), 10^{12}, 10^{13}, and 3×10^{14} cm^{-2}.

The absorbance in the range of 1500 to 2000 cm^{-1} is important because it shows the changes produced by the irradiation corresponding to the formation of double bonds. Betz [15] mentions a band at 1711 cm^{-1} that can be ascribed to a double bond due to the loss of HF. This band is not observed in our irradiated samples. It is known that double bonds vibrate from 1655 to 1690 cm^{-1} approximately, and can be displaced to higher frequencies by the presence of fluorine. Socrates [14] gives values from 1735 to 1755 cm^{-1} for end $C=CF_2$. In our case we observe two well defined bands at 1651 and 1741 cm^{-1}. In the case of electron irradiation in vacuum [2], these bands were also observed at 1648 and 1741 cm^{-1}. As the proton fluence increases, the intensity of these bands increases. Neither of these bands correspond to those found by Betz [15] at 1752, 1730 and 1620 cm^{-1}, corresponding to the C=C bonds of $RR'C=CF_2$ when irradiated with Kr ions, but the band we found at 1651 cm^{-1} can be due to the end double bond, formed because of the degradation of the polymer. The range of these bands must be between 1650 and 1655 cm^{-1} [14]. The band at 1741 cm^{-1} exists prior to irradiation, but it increases with increase in fluence.

At the fluence of 3×10^{14} cm^{-2}, where amorphization was found, the bands of 1741 and 1651 disappear and a new broad band appears at 1702 cm^{-1}; this band has no assignment in the PVDF literature. It could be due to the carbonyl group of aldehydes formed in the process of oxidative degradation. Aldehydes near to unsaturated C=C groups absorb in the region of 1710-1685, accompanied by a medium intense absorption near 2720 [16], as it is shown in Fig. 3.

In the region up to 1000 cm^{-1} some bands which are characteristic of the crystalline phase exist, located at 974, 795 and 766 cm^{-1} [17]. We can observe these bands in pristine and irradiated samples up to a fluence of 1014 cm^{-2} at about 974, 794 and 762 cm^{-1}. At a fluence of 3×10^{14} cm^{-2}, the disappearance of the first two bands was observed, due to amorphization of the irradiated sample. Betz [5] found the bands characteristic of the crystalline α phase at 796, 763 and 532 cm^{-1}.

There exists some difference of these results with irradiation with Kr and electron beams studied by Betz *et al.* [5], under different atmospheres, mainly in the range of double bonds.

The DSC plots for different fluences are shown in Fig. 4 and in Table II.

DSC curves of pristine and irradiated PVDF samples with different proton fluences are reported in Fig. 4. The control sample shows a sharp band at 176 °C with a shoulder on the low temperature side (172 °C) corresponding to the melting point of PVDF. A well defined lower temperature peak, related to the relaxation of inter-crystalline regions [12] appears at a fluence of 1013 cm^{-2}. The size of these two peaks, which were also observed in the electron irradiation of PVDF at a dose of 50 kGy [2], decreases when the radiation dose increases.

TABLE II. Parameters obtained from the thermograms of Fig. 4, corresponding to different values of fluence.

Fluence [cm^{-2}]	**T$_m$ upper peak, °C**	**T$_m$ lower peak,°C**	**Heat of fusion, J/g**
0.0	176.2	171.6	35.1
10^{12}	168.0	shoulder	52.6
10^{13}	165.7	156.3	50.8
10^{14}	——	142.8	27.5

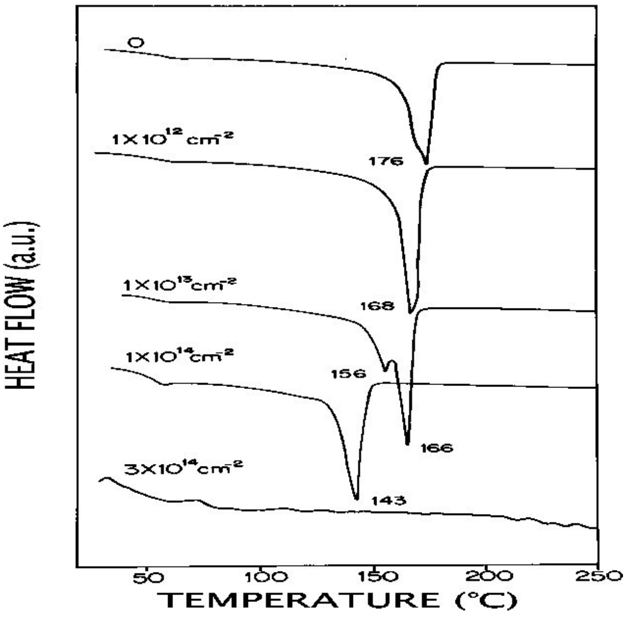

FIGURE 4. DSC thermograms of PVDF samples irradiated with different proton fluences.

The heat of fusion increases from 35.1 J/g in a pristine sample to 52.6 J/g for a sample irradiated at a fluence of 10^{12} cm^{-2}, and then decrease at higher fluences to 27.5 J/g at 1014 cm^{-2}, indicating a transition to a more disordered material due to the cross-linking effect. One explanation [3] for the disappearance of the higher temperature melting peak at high fluence could be the annealing effects during the thermal scanning itself. For instance, it is quite conceivable that for the pristine and low-dose samples the DSC scan itself could cause either lamellar thickening or an enhanced ordering of the lower-melting crystallites, which then melt at the higher temperature. It is also possible that the cross-linking caused by the irradiation could hinder the lamellar thickening and ordering, preventing them at fluences of 10^{14} cm^{-2}. At 3×10^{14} cm^{-2} there are no melting peaks, due to complete destruction of the crystalline structure. This was confirmed at the high fluence by the IR spectra, and by x-ray diffraction, where an amorphous structure was observed.

The x-ray diffractograms are shown in Fig. 5 for different values of fluence. The pristine sample exhibits a group of lines in the region of 2θ from 17° to 21°, which are identified as the 100, 020 and 110 reflections of the phase. The line in the vicinity of 26.5° corresponds to the 021 reflection of the β phase. There is very little change in the shape of the peaks from pristine to 10^{14} cm^{-2}, but for 3×10^{14} cm^{-2} the diffraction peaks are lost, indicating that the crystalline structure is heavily modified. The percent of crystalline content is indicated in the figure and it goes from 46% crystallinity for the pristine sample, to 0% crystallinity for the most irradiated sample.

According to Zhao [4], the defects in the crystal structure of PVDF produced by radiation destroy the perfection of the crystalline regions; cross-linking does not reduce crystallinity if it takes place in the amorphous region. The change

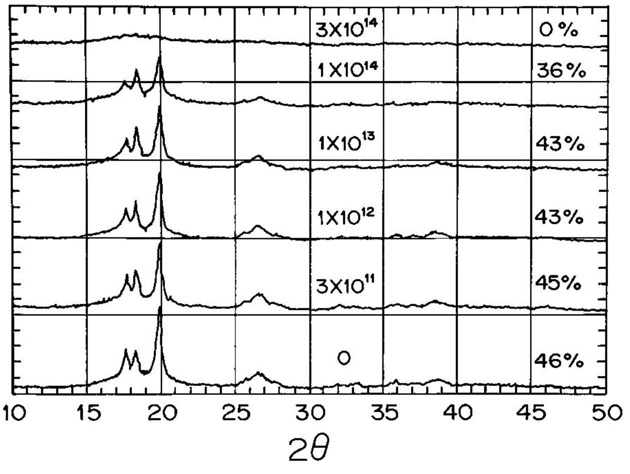

FIGURE 5. X-ray diffractograms for different values of fluence (in cm^{-2}). The percent amount indicates the crystalline content in each sample as a function of fluence.

in crystallinity is also observed as a reduction of the melting point and the reduction of the enthalpy observed in the DSC curves.

Table II shows the behavior of the melting point and heat of fusion for different proton fluences. At the lower fluences there is a 45% gel formation, the melting point decreases, and the heat of fusion increases with respect to the pristine sample. However, at 10^{14} cm^{-2} the heat of fusion diminishes due to a greater loss of crystallinity, and at a greater fluence the crystallinity is almost totally lost, so no melting point is observed.

4. Conclusions

PVDF irradiated with 4 MeV protons exhibits fluence-dependent changes in physical and chemical properties. The gel percent measurements show a quick rise with fluence to almost 60% for 10^{13} cm^{-2}, and then a slow rise up to 100% for 3×10^{14} cm^{-2}, indicating that cross-linking is the predominant effect in this interval of fluence. The X-ray diffractograms show little change in the shape of the peaks from the control sample to 10^{14} cm^{-2}, but at 3×10^{14} cm^{-2} the crystalline structure is heavily modified. This modification is also evident in IR spectra and heat of fusion measurements.

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