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Latent track radius of PTFE irradiated with high energy ion beam

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ABSTRACT

PTFE foils were irradiated with different ion beams (Xe, Au and U) with energies up to 1.5 GeV and fluences between 1×10^8 and 1×10^{13} ions/cm^2 at room temperature. The induced modifications in the polymer were analyzed by FTIR, UV–Vis spectroscopy, and XRD. In the FTIR spectra, the CF_2 degradation accompanied by the formation of CF_3 terminal and side groups were observed. In the UV–Vis spectra, the observed increase in the absorption at UV wavelengths is an indication of polymer carbonization. From XRD, the amorphization of the material was evidenced by the decrease in the intensity of the main diffraction peak. An exponential fit of the intensity of the IR absorption peaks resulted in the following values: 2.9 ± 0.8; 4.5 ± 0.9 and 5.6 ± 0.8 nm for the latent track radius after irradiation with Xe, Au and U beams, respectively.

1. Introduction

Polytetrafluoroethylene (PTFE) shows an outstanding combination of chemical and physical properties such as excellent chemical and electric resistance, thermal stability, and low friction coefficient. It belongs to a class of fluorine containing polymers that encloses a combination of interesting properties, making them very useful materials for hi-tech and biological applications [1,2]. PTFE is semi-crystalline in nature, with its linear chains adopting complicated helical configurations [3], where the F atoms cover the backbone chain and ensure the chemical stability of the polymer. However due to this high stability, it is not possible to determine the ion track radius in irradiated PTFE using the standard technique of chemical etching. Since it is well-known as an extremely sensitive polymer for high energy radiation undergoing scission of the main chain [4], the incidence of swift heavy ions should create latent tracks in the material. Hence the aim of this work is to estimate the radius of these latent tracks, created after irradiation with different ion beams, through the analysis of the induced chemical and structural modifications in the irradiated PTFE.

2. Experimental

PTFE films with 25, 50 and 100 μm thick (Enflo Canada Ltd.) were irradiated under normal beam incidence at room temperature with Xe, Au and U ions with energies from 0.9 to 1.5 GeV and fluences between 1×10^8 and 1×10^{13} ions/cm^2 at the accelerator UNILAC at the GSI in Darmstadt, Germany. The fluence was measured by monitoring the signal from a secondary-electron emitting Al-foil detector placed in front of the samples and calibrated via a Faraday cup (precision ~20%).

The sample analysis was performed during and after the irradiation period. A novel setup at M3 beam line, at GSI [5], allowed in situ infrared spectroscopy (FTIR) used for the analysis of one sample irradiated with different ion fluences. In the FTIR measurements a NICOLET 6700 FT-IR spectrometer of ThermoFisher Scientific was used in the range 400–4000 cm^{-1}, with a resolution of 2 cm^{-1}. After irradiation, a set of samples irradiated with different fluences were analyzed with UV–Vis absorption spectroscopy and X-ray diffraction (XRD). The UV–Vis spectroscopy was performed at the GSI, with a UV4 spectrometer of Unican, in the range of 190–900 nm with resolution of 2 nm. For the XRD analysis an X-ray Diffractometer Ultima+ of Rigaku was used in the mode θ–θ, at the LCr, IFUSP in São Paulo, Brazil.

3. Results and discussion

3.1. FTIR

The FTIR analysis of pristine and irradiated PTFE foils, Fig. 1, points out the formation of new chemical groups which were induced by the ion irradiation. The formation of CF_3 terminal and side group, with IR absorption peaks at 740 and 985 cm^{-1}, respectively, is accompanied by the decrease in the intensity of absorption of the bands assigned to the CF_2 bonds (at 2360 cm^{-1}). This indicates that the dynamics of CF_3 formation starts with the scission of the main polymer producing a pending CF_2 group, which

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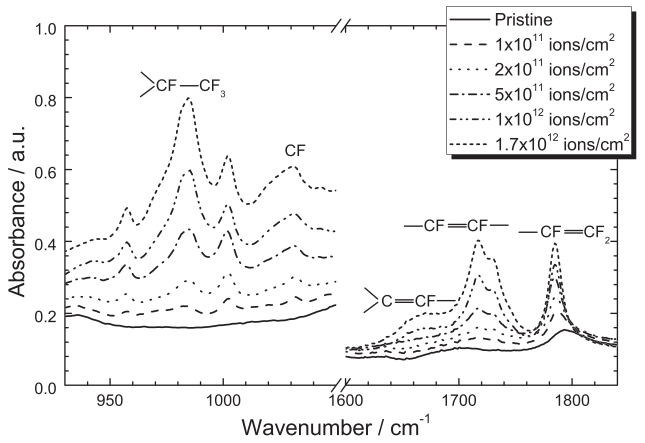

Fig. 1. FTIR spectra of pristine and irradiated PTFE films with different fluences of 0.9 GeV Au beam. Some new IR absorption bands observed after foil irradiation are indicated.

recombines with an ionized F atom, which was initially split of the chain.

In addition, double bond formation and cross-linked structures are also observed in the range of 1650–1800 cm^{-1}. The formation of internal double bonds is an indication of C–F bond scission. Normally, this scission is unlikely due to the higher stability of the C–F bonds, but the observed increase in the intensity of the respective absorption peaks reveals that this process plays a significant role in the degradation induced by swift heavy ions (SHI). After the C–F scission of neighboring atoms, the pending bonds can create a double bond structure inside the polymer chain. If the C ionization is followed by a C–C scission in the neighborhood, the pending bonds can reorganize themselves forming double bonds or even cross linking the polymer chains. Some routes for this chemical processes, proposed by Lunkwitz et al. [6,7] and Oshima et al. [8,9], in the case of electron beam irradiation seems to be also applicable in the case of SHI irradiation, since the observed modifications are similar although with higher intensity.

3.2. UV–Vis spectroscopy and XRD

The UV spectroscopy, Fig. 2, shows a decrease in the intensity of the light absorption at wavelengths in the visible range of the spectra, with maximal diminution at about 400 nm, that denotes more transparency of the PTFE foils after irradiation.

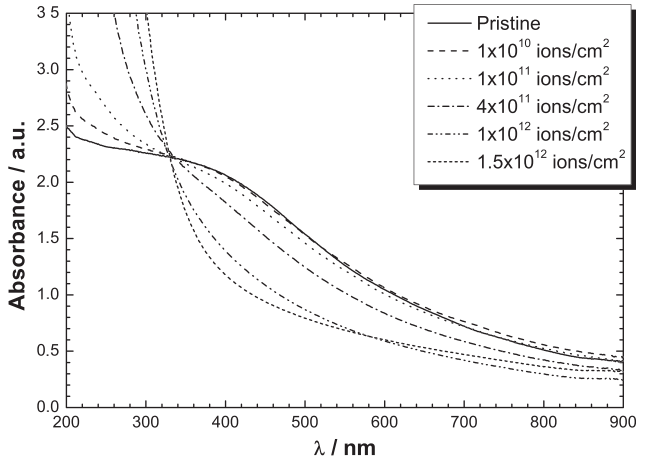

Fig. 2. UV–Vis spectra of pristine and irradiated PTFE films with different fluences of 1.3 GeV U beam.

In opposition, a large increase in the absorption at wavelengths in UV region of the spectra is observed. The absorption edge becomes more pronounced, which means that a great number of new chemical structures are absorbing at this wavelength range and can be a sign of polymer carbonization. The PTFE carbonization is plausible since a great number of F atoms are ionized in the material during the ion irradiation, permitting the rearrangements of the C backbones atoms. When compared with degradation processes of other common polymers, as PI [10] and PC [11], the PTFE carbonization occurs at a relatively reduced rate and becomes really evident just above the irradiation fluence of 4×10^{11} ions/cm^2, in the case of irradiation with U ions.

From the XRD analysis, Fig. 3, a decrease in the polymer crystallinity is observed, even for lower irradiation fluences ($\sim 1 \times 10^9$ ions/cm^2). The diffraction peak at about 18° is attributed to the (1 0 0) direction, where the PTFE chains are parallel to the polymer surface. The decrease in the intensity of the diffraction peak signifies reduction in the number of repeat units (polymer chains) of the same length, which is a strong evidence of polymer chain scission. The amorphization is a related effect to the increase in the transparency of the PTFE, since the smaller the partial crystallinity, smaller is the opacity of the polymer.

3.3. Radius of latent ion tracks

The atom ionizations and chain scissions observed in the PTFE analysis are due to the process of latent track creation along the way of the passage of ions during the polymer irradiation. The intensity of damaged and created chemical groups is directly related to the volume of the disturbed region, and can be fit using an exponential function with the ion fluence [12]. Thus fitting the intensity of the IR absorption peaks and assuming the model of cylindrical ion tracks, the radius of the latent ion tracks created in PTFE can be estimated.

Obtained values for the average ion track radius after irradiation with Xe, Au and U ions, in Table 1, show a systematic increase with atomic number of the incident ion. This tendency suggests that the radial range of the damage area is directly related to the stopping power of the incident ion, which increases with the projectile atomic number.

Furthermore the good data agreement with the exponential fit, in Fig. 4, leads us to the conclusion that the creation of double bonds and the cross-linked structures in the ion tracks probably follow the so-called one hit process. Although it depends on more

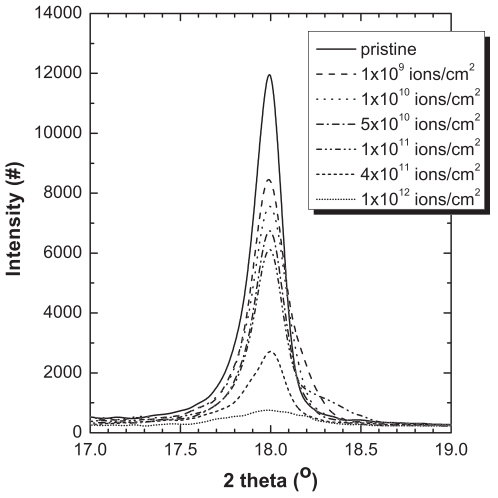

Fig. 3. XRD spectra of pristine and irradiated PTFE films with different fluences of 1.3 GeV U beam.

Table 1
Values of maximal stopping power S_{max} (calculated with the code SRIM 2006) and estimated radius R_{track} of the latent tracks for different incident ions in PTFE with initial energy between 0.9 and 1.5 GeV.

Ion/energy (GeV)	Xe/1.5	Au/0.9	U/1.3
S_{max} (keV/nm)	14	22	27
R_{track} (μm)	2.9 ± 0.8	4.5 ± 0.9	5.6 ± 0.8

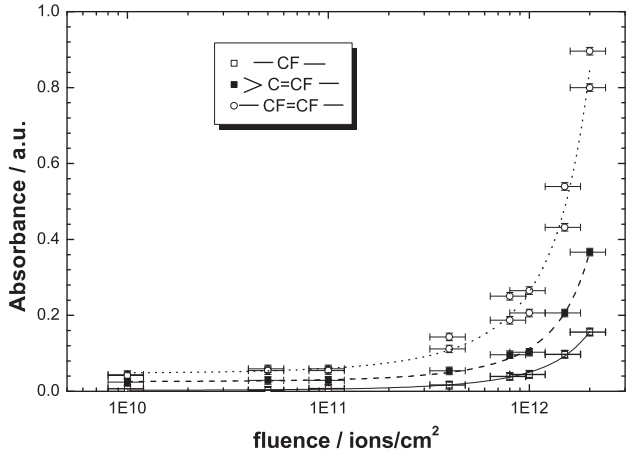

Fig. 4. Exponential fit (lines) to the IR absorption intensity of some new chemical groups in PTFE as a function of irradiation fluence for films irradiated with 1.3 GeV U beam.

than one chemical step, as discussed before, this creation is possible since the energy of the projectile is so high, that the electronic energy loss of this single ion is high enough to create a great number of different phenomena along its path and in the neighborhood of the chain scission point.

4. Conclusion

Although being a very chemical resistant polymer, PTFE undergoes great damage under SHI irradiation. The damage process can be described as essentially scission of the backbone chain accompanied by the split of F atoms that cover the main chain. The mobility of the ionized F atoms, associated with the great number of produced pending bonds, evolutes to different new structures such as double bonds and cross-linked chains. Furthermore the damage process involves the decrease in the polymer crystallinity and increase in its transparency. The analysis of the new structures, as a function of the ion fluence, leads to values between 2.9 ± 0.8 and 5.6 ± 0.8 nm for the latent track radius, increasing with the atomic number of the incident ion.

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