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Fluoropolymer Studies for Radiation Dosymetry

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The polymers Tetrafluoroethylene- hexa- fluoropropylene (FEP) and Tetrafluoroethylene- per- fluoromethoxyethelene (PFA) are normally used as anti-adherent coatings and can also be applied for several applications in research. For example, they can be used as radiation dosimeters for X-ray and gamma photons, electrons, protons and other ionazing particles. In order to determine radiation induced damage, that can compromise applications in dosimetry, FEP and PFA films were bombarded with protons of 1 MeV at fluences from 1×10^{11} protons/cm^2 to 1×10^{16} protons/cm^2. During the bombardment, the chemical species emission was monitored with a Residual Gas Analyzer (RGA), and results show that the CF_3 radical is the specie preferentially emitted. The bombarded films were also analyzed with Optical Absorption Photospectrometry (OAP) which shows quantitative chemically specific evidence of the damage caused by the proton bombardment. Our results show that damage to polymers is detectable for all fluences used in this work, but damage that can compromise applications in dosimetry occurs only for fluences greater than 1×10^{14} protons/cm^2.

1 Introduction

Polymers are compounds formed by macro-molecules obtained with the arrangement of small molecules (monomers). They have chemical and physical properties that are different than those of the original monomers. Usually, they do not react with acids or alkalis, and present high mechanical and electrical resistance and have several applications[1, 2] which include clothes manufacturing, food and pharmaceutical packing, and medical supplies. Fluoropolymers can be used as radiation dosimeters [3, 4, 5] and can be applied as a spacecraft surface coating to avoid damage due to the high level of ionizing radiation met in its trajectory [6, 7]. These polymers can support high temperatures without damage.

During bombardment by ionizing radiation, the absorbed energy can break the polymeric chains with the releasing of fluorine, carbon and oxygen in amounts proportionally to the absorbed energy [8].

In this work we present experimental evidence of damage to Tetrafluoroethylene- hexa-fluoropropylene (FEP) and Tetrafluoroethylene-per-fluoromethoxyethylene (PFA) films after 1 MeV proton bombardment. The damage was determined through Residual Gas Analysis (RGA), and Optical Photospectrometry (OAP) techniques [9]. The OAP gave spectra which were shown to be dependent on the radiation dose absorbed in the polymeric films.

2 Material and Methods

PFA is a fluorinated polymer with oxygen cross links between chains expressed by the molecular formula $-\left[\left(CF_2CF_2\right)_n CF_2C\left(OR_F\right)F\right]_n-$. It melts at a temperature around 304^{o}C, has a density of 2.15 g/cm^3 and a molecular weight from 2×10^5 up to 4.5×10^5 dalton [10]. FEP is expressed by$-\left[\left(CF_2CF_2\right)_n CF_2C\left(CF_3\right)F\right]_n-$, has a density of 2.15 g/cm^3, a molecular weight from 2.5×10^5 up to 6×10^5 dalton [10], and melts at a temperature around 265^{o}C.

PFA and FEP films with 20×20 mm^2 and 25 μm thick were bombarded with 1 MeV protons from the Alabama A&M University Pelletron at fluences of 1×10^{11}, 1×10^{12}, 1×10^{13}, 1×10^{14}, 1×10^{15} and 1×10^{16} protons/cm^2 (one film for each fluence). The current was kept below 1 μA, to avoid sample heating. Residual Gas Analyses (Stanford Research Systems, Model 200) were conducted in real time during the bombardment.

In order to determine the polymer damage mechanisms, virgin and bombarded samples were analyzed with Optical Absorption Photospectrometry (OAP), in the UV-VIS region. The optical absorbance measured at a wavelength of 250 nm was determined for the absorbed radiation dose for each proton fluence value.

3 Results and Discussion

Fig. 1 and Fig. 2 present the RGA measurements that determine the gas emitted during bombardment of the films. There is clear evidence that proton bombardment breaks chemical bonds in the polymeric chains with attendant modifications of the polymer. The CF_3 radical accounts for a larger part of partial pressure detected during the bombardments, but $\cdot CF$, $\cdot CF_2$, $\cdot COF$ and CF_2CCF_3 and other species were also emitted from both films. PFA has the CF_3 as an original radical. A possible explanation that could justify the relative abundance of CF_3 radical emission from the FEP films, which has no CF_3 radical, is that a single fast proton breaks almost simultaneously neighboring C-F and C-C bonds and the active F would recombine with other liberated products, specially with CF_2 radical to form the observed CF_3 radical.

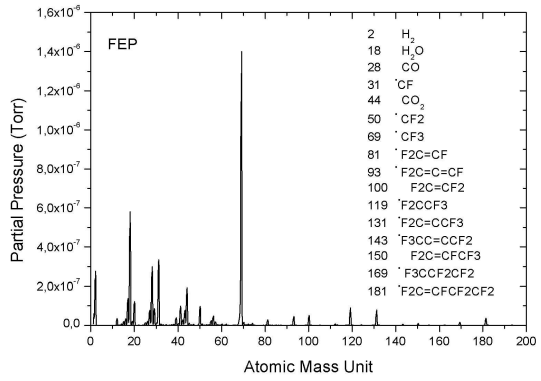

Figure 1. RGA spectrum obtained during 1 MeV proton bombardment of FEP polymer at a current of 0.5 μA.

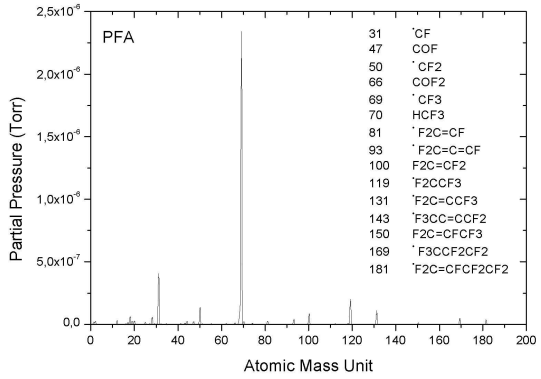

Figure 2. RGA spectrum obtained during 1 MeV proton bombardment of PFA polymer at a current of 0.5 μA.

The results measured with Optical Absorption Photospectrometry are shown in the Fig. 3 and Fig. 4. In these figures we compare the spectra obtained from films bombarded at fluences of 1×10^{11}, 1×10^{12}, 1×10^{13}, 1×10^{14}, 1×10^{15} and 1×10^{16} protons/cm^2. With increasing fluence, the spectra reveal increasing absorbance at longer wavelengths to the increased formation of carbon double bounds.

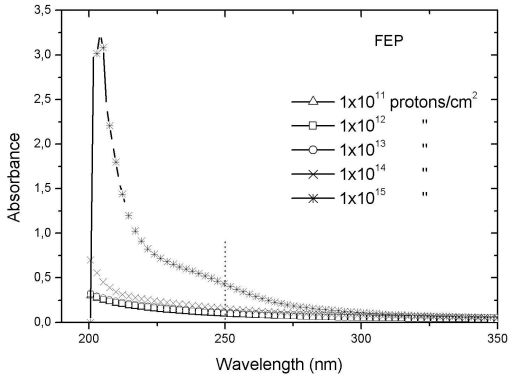

Figure 3. U.V. spectra from FEP films bombarded with 1 MeV protons for fluence from 1×10^{11} up to 1×10^{15} protons/cm^2.

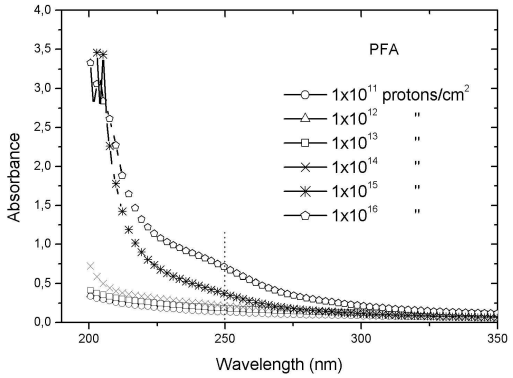

Figure 4. U.V. spectra from PFA films bombarded with 1 MeV protons for fluence from 1×10^{11} up to 1×10^{16} protons/cm^2.

In the Fig. 5 and Fig. 6 are shown the optical absorbance versus estimated absorbed dose for the PFA films bombarded at fluences 1×10^{11}, 1×10^{12}, 1×10^{13}, 1×10^{14}, 1×10^{15} and 1×10^{16} protons/cm^2 and for FEP bombarded at fluences 1×10^{11}, 1×10^{12}, 1×10^{13}, 1×10^{14} and 1×10^{15} protons/cm^2. The OAP spectrum for FEP could not be obtained at the 1×10^{16} protons/cm^2 owing to excessive damage of the bombarded film. OAP results show that the absorbance is directly proportional to dose in the range of 10^3 - 10^5 Gy, for both polymers. For 10^6 - 10^7 Gy for FEP and 10^6 - 10^8 for PFA, one can notice that the absorbance is not directly proportional to the dose, indicating that the damage mechanism is more efficient for the fluences lower than 1×10^{15} and 1×10^{16} protons/cm^2.

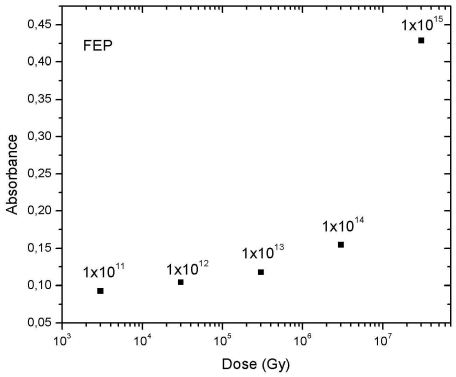

Figure 5. Absorbance *versus* dose from FEP films bombarded by 1 MeV protons.

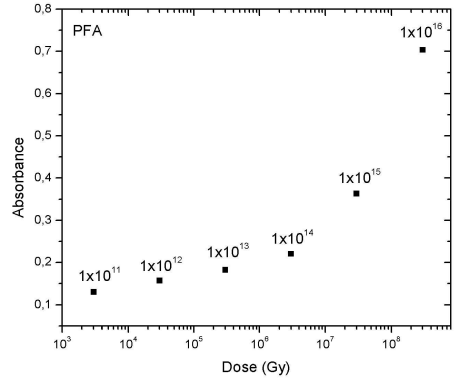

Figure 6. Absorbance *versus* dose from PFA films bombarded by 1 MeV protons.

These films become fragile after bombardment at fluences greather than 10^{14} protons/cm^2 such that their use as proton dosimeters, and for many other applications, may be compromised.

4 Conclusions

Residual Gas Analysis and Optical Photospectrometry are effective to evaluate charged particle bombardment damage in thin polymer films. Optical absorption spectra can be used to determine the absorbed dose in fluoropolymer films after exposure to ionizing radiation. The optical absorbance is dose dependent in the region from 10^3 up to 10^5 Gy.

RGA measurements during proton bombardment show that $\cdot CF_3$ is the preferentially emitted specie, probably because $\cdot CF_3$ is a radical in the PFA polymeric chain. $\cdot CF_3$ observed to be emitted also from bombarded FEP, which has no CF_3 radical, is produced by another mechanism.

Acknowledgments

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