Nuclear Inst, and Methods in Physics Research B 430 (2018) 47–53

Contents lists available at ScienceDirect

Nuclear Inst. and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

The degradation behavior and mechanism of polytetrafluoroethylene under low energy proton irradiation

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ARTICLE INFO

Keywords:
Polytetrafluoroethylene
Low energy proton irradiation
Radicals evolution
Degradation mechanism

ABSTRACT

The degradation behavior and mechanism of polytetrafluoroethylene (PTFE) under low energy protons irradiation was investigated. Optical transmittance and Fourier transformed Infrared spectrometer (FTIR) indicate that there produce two kinds of specific defects during the proton irradiation, leading two optical absorption peaks at about 200 nm and 240–280 nm. The results of X-ray photoelectron spectroscopy (XPS) indicate that there include the processes of defluorination in the first stage and then carbonization in PTFE during proton irradiation. In addition, the results of electron paramagnetic resonant spectra (EPR) demonstrate the evolution of radicals that transform from peroxy radicals (g = 1.9907) to another pyrolytic carbon ones (g = 2.0025). The population evolutions of both kinds of the radicals are investigated and determined dependent on the fluence and also the degradation mechanisms.

1. Introduction

Polytetrafluoroethylene (PTFE) has many excellent properties, such as high chemical and thermal stability [1], very low coefficient of friction [2–5], thus it has wide applications in many industrial fields. However, PTFE is very sensitive to space radiation environments consisting of protons, electrons, and heavy ions. These energetic particles could penetrate into and interact with the materials, causing the degradation of polytetrafluoroethylene.

There have been a lot of researches on the mechanisms of degradation of PTFE exposed to electrons [6], γ-rays [7,8,9], or neutrons [10]. For example, Masakazu Furuta [11] et al. investigated the degradation process under γ-ray irradiation and indicated that the degradation is due to the cleavages of the C—C bonds. Akihiro Oshima [12] et al reported that the cross-linking among the molecular chains would be the main process when PTFE was irradiated by electrons at a temperature above its melting point. For light particles, such as photons and electrons, the degradation process maybe relatively simple. However, this is not true for protons or heavy ions irradiation. A recent study shows that the PTFE degradation mechanism changes with the absorbed dose of irradiated α-particle [13]. Wherein, the chain scission dominates at low absorbed dose; when the dose increases, the main damage mechanism turns to be the cross-linking. Zhang [14] et al. found the reversed phenomena in methyl silicone rubber irradiated by protons. Yang [15] shew that there exists competitive behavior between carbonization and substituting in the degradation process of PTFE irradiated by protons. However, there is lack of further research on the dynamic degradation behaviors and no mechanism related to fluences was found reported for the radical evolution in the irradiated PTFE. It is necessary to clarify the specific degradation process and characterize the damage quantitatively.

The degradation behaviors of PTFE under low energy proton irradiation were investigated. The degradation mechanism was also studied based on results of UV–Vis, FTIR, XPS, and EPR of the irradiated samples. This research would help us to understand the specific degradation process of PTFE irradiated by protons.

2. Experiment details

In this research, 25 μm-thick polytetrafluoroethylene films were irradiated by protons. The proton irradiation experiments were carried out in a ground-based space-radiation-environment simulator in Harbin Institute of Technology. The proton energy was set as 70,100 and 150 keV, respectively, and the flux was set as 5E11 $cm^{-2}s^{-1}$. The

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https://doi.org/10.1016/j.nimb.2018.06.005
Received 16 April 2018; Received in revised form 7 June 2018; Accepted 7 June 2018
Available online 14 June 2018
0168-583X/

maximal proton fluence was set up to 2E16 cm^{-2} in the tests. During the irradiation, the proton beam incidents perpendicularly into the samples. The tested chamber was kept in a vacuum better than 10^{-5} Pa, and the sample temperature was controlled at 30 °C.

The optical-transmittance spectra of the samples were measured in ambient using a Perkine-Elmer Lambda 950UV–VIS-NIR spectrophotometer, within the wavelength range from 200 to 800 nm.

EPR spectra were measured immediately on a Bruker A200 spectrometer (Bruker Instrument, Germany) just after the completion of proton irradiation. The spectrometer was operated at a microwave power of 19.05 mW, modulation of 1 Gauss, a time constant of 10 ms, and frequency of 9.857 GHz.

The X-ray photoelectron spectroscopy (XPS) was measured on a photoelectron spectrometer (PHI5300 system) with monochromatic Al Kα radiation and the take-off angle is 45°.

IR Magna 560 Fourier transformed Infrared spectrometer (FTIR Nicolet Comp.) was applied for the group-structural analyses and the test wave-number range is set in 400–4000 cm^{-1}. The instrument resolution was set on 4 cm^{-1}.

3. Results

3.1. Optical property after irradiation

Figs. 1–3 show the spectral transmittance (T) and its change (ΔT) after irradiation with various fluences of 70 keV, 100 keV and 150 keV protons respectively. It can be seen that after proton irradiations, the samples are darkened with the increase of the influences. There show the optical absorption peaks appearing at different wavelengths after proton irradiation as presented in Figs. 1 (b), 2(b) and 3(b), respectively. Hence, there appear two absorption peaks at about 200 nm and 240 nm respectively. It should be noted that, the peak at about 200 nm was detected in the early stage of proton irradiation regardless of proton energy, then its intensity increases with the proton fluences up to about 5E14 cm^{-2}, but then this peak seems disappearing. On the other hand, the peak at about 240 nm could be seen obviously only as the proton fluences is larger than 5E13 cm^{-2}. Its intensity would increase with the proton fluences up to that it becomes the main absorption peak as the fluences is larger than 2E15 cm^{-2}. Furthermore, one could also find that this peak shows red shift as the peak intensity increases with the proton fluences. The results imply that there produce two kinds of specific defects during the proton irradiation up to a fluence of 2E16 cm^{-2}. As referring to some published literatures, the defects produced at a wavelength of about 240 nm can be attributed to $\pi \rightarrow \pi^*$ transition [16–18]. The reasons for the appearance of two absorption peaks would be discussed in the following parts.

3.2. FTIR analysis of the irradiated PTFE

The FTIR spectra of the proton-irradiated samples are shown in Fig. 4(a), (b) and –(c)–. It was found that the irradiated samples show a similar spectrum to the as-received one regardless of the proton energy. The main absorption peaks were detected at wavenumbers of 1205 cm^{-1} and 1147 cm^{-1}, corresponding to the asymmetric and

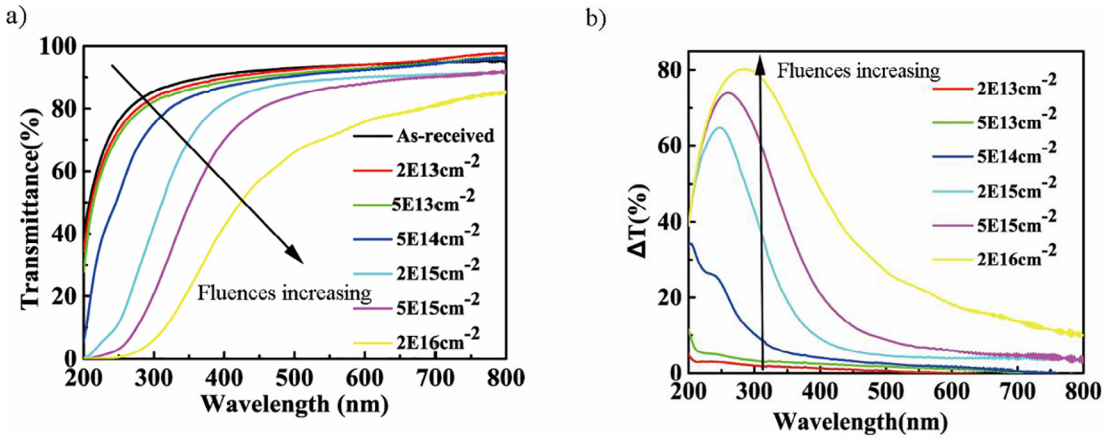

Fig. 1. Spectral transmittance and absorption spectrum of PTFE after 70 keV proton radiation with various fluences: a) spectral transmittance; b) absorption spectrum.

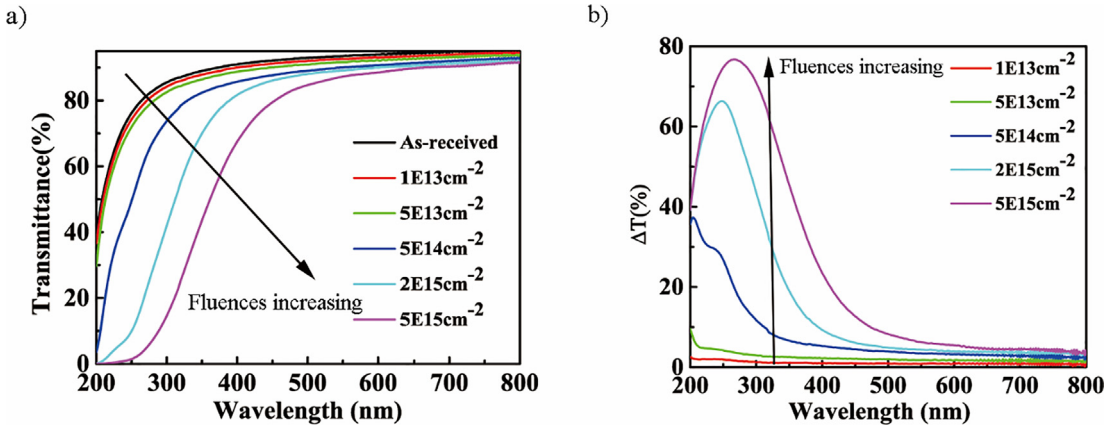

Fig. 2. Spectral transmittance and absorption spectrum of PTFE after 100 keV proton radiation with various fluences: a) spectral transmittance; b) absorption spectrum.