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Study on depth profile of heavy ion irradiation effects in poly(tetrafluoroethylene-co-ethylene)

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ABSTRACT

High linear energy transfer (LET) heavy ion beams were used to irradiate poly(tetrafluoroethylene-co-ethylene) (ETFE) under vacuum and in air. The irradiation effects in ETFE as a function of the depth were precisely evaluated by analyzing each of the films of the irradiated samples, which were made of stacked ETFE films. It was indicated that conjugated double bonds were generated by heavy ion beam irradiation, and their amounts showed the Bragg-curve-like distributions. Also, it was suggested that higher LET beams would induce radical formation in high density and longer conjugated C=C double bonds could be generated by the second-order reactions. Moreover, for samples irradiated in air, C=O was produced correlating to the yield of oxygen molecules diffusing from the sample surface.

1. Introduction

Poly(tetrafluoroethylene-co-ethylene) (ETFE) is a thermoplastic type fluoropolymer, which is a copolymer of ethylene and tetrafluoroethylene (TFE), $-(CF_2-CF_2)_n-(CH_2-CH_2)_m-$. Because of this combination of fluorocarbon and hydrocarbon resins, ETFE has more balanced properties than other typical fluoropolymers such as PTFE. ETFE is used in various fields including the aerospace environment and nuclear facilities, because of its excellent mechanical toughness, chemical, radiation resistance, and so on.

It is known that ETFE is partially crosslinked by low linear energy transfer (LET) beam irradiation such as γ-rays or an electron beam at room temperature under oxygen-free conditions (Oshima et al., 1997). On the other hand, it has been suggested that high LET beams, such as heavy ion beams, should produce conjugated double bonds in the track structure (Oshima and Washio, 2003).

In this study, heavy ion beams were used to irradiate ETFE under vacuum and in air. The heavy ion beams lose their energy increasingly from the sample surface (Bragg curve) and deposit the maximum energy at the end of their penetration ranges (Bragg peak). It has been reported that this distribution of the energy deposition would induce irradiation effects in a localized area (Hama et al., 2003; Hama and Oka, 2005). To investigate the depth distribution of the heavy ion beam irradiation induced phenomena, the irradiated samples were made of stacked ETFE films. The irradiation effects on the molecular structures of ETFE as a function of the sample depth were precisely evaluated by analyzing each one of the films with ultraviolet–visible spectroscopy (UV–vis) and Fourier transform infrared spectroscopy (FT-IR).

2. Experimental procedure

2.1. Heavy ion irradiation

ETFE (Flon Industry Co., LTD.) selected in this experiment was a 1:1 copolymer of ethylene and TFE with a density of 1.74 g/cm^3. 25 μm thick ETFE films were stacked on a carbon plate and irradiated under vacuum and in air by 6 MeV/u accelerated C^{6+}, Ne^{10+}, Si^{14+} and Ar^{18+} beams from a Medium Energy Experimental Port (MEXP) at the Heavy Ion Medical Accelerator in Chiba (HIMAC) in the NIRS.

The irradiation was performed at ambient temperature for both irradiation conditions. In the case of irradiation under vacuum, the base pressure of the irradiation chamber was below 5E−4 Pa and the irradiated samples were annealed at 100 °C for 5 min in the vacuum chamber to avoid post-irradiation effects caused by the ambient condition outside the chamber.

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For irradiation in air, ion beams lose their energies after passing through a 6 μm thick Havar foil (ρ: 8.2, Nilaco Co.) and 15 mm air space before the sample position. The ion beam energies at the sample position and their penetration ranges in ETFE (Table 1) were evaluated using the SRIM-2008 code (Ziegler, 2008). The fluence (ions/cm^2) was estimated by the ion flux, which was detected by a Faraday cup set in the vacuum beam line.

2.2. Measurements

The absorbance of each film was measured by UV–vis spectroscopy (V-630, JASCO Co.) and FT-IR spectroscopy (JIR6000, JEOL) at room temperature in dry air. The range of the wavelengths for the UV–vis spectroscopy was 190–1100 nm and the scan speed was 100 nm/min. The irradiation induced effects were evaluated from the optical density (OD), which was calculated as $OD=A_i-A_0$ where A_i is the absorbance of irradiated ETFE and A_0 is that before irradiation. The FT-IR spectra were taken from 400 to 4000 cm^{-1} with a spectral resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Irradiation effects

After the heavy ion beam irradiation, the ETFE films were colored yellow or brown. This was an indication that significant change was induced in the UV–vis photo-absorption. Fig. 1 shows the UV–vis spectra of each of the ETFE films after C^{6+} ion beam irradiation at room temperature under vacuum (left) and in air (right). The fluences were about 9.8E+11 and 2.6E+11 ions/cm^2 for irradiation in vacuum and air, respectively, and the calculated ion energies at the samples were 72 and about 60 MeV, respectively. In the case of irradiation in air, the actual irradiation fluence on the ETFE should be smaller because of the absorption at the Havar foil and the air space before the samples.

Table 1
Ion beam energies and their penetration ranges.

		C^{6+}	Ne^{10+}	Si^{14+}	Ar^{18+}
Under vacuum	Energy (MeV)	72	120	168	240
	Penetration (μm)	120	86	75	75
In air	Energy (MeV)	60	88	114	158
	Penetration (μm)	90	56	45	45

For the samples irradiated under vacuum, the absorption change appeared from the 1st to the 5th films (i.e., surface to 125 μm depth), but no change was observed in the 6th film (i.e., 125–150 μm depth). On the other hand, in the case of irradiation in air, the absorption changed only from the 1st through the 4th films (i.e., surface to 100 μm depth). These results well describe the penetration ranges simulated by SRIM-2008: 120 μm for irradiation under vacuum and 90 μm for irradiation in air. As 72 MeV ions (under vacuum) did not reach the 6th film and 60 MeV ions (in air) did not reach the 5th and 6th films, irradiation effects should not appear in these films.

For both irradiation conditions, an absorption change appeared around 190–400 nm. This was due to the formation of conjugated double bonds in ETFE. Especially, for the samples irradiated under vacuum, the peaks around 195, 217, 258, 296 and 335 nm could be assigned to alkenes (–C=C–), dienes (–C=C–C=C–), trienes (–C=C–C=C–C=C–), tetraenes (–C=C–C=C–C=C–C=C–) and pentaenes (–C=C–C=C–C=C–C=C–C=C–), respectively (Izumi et al., 1997; Oshima and Washio, 2003). On the other hand, it was found that ODs of the peaks for the irradiated samples in air were not clearly separated compared with those of the samples irradiated under vacuum. It is considered that the spectra of the samples irradiated in air contain other species that would be formed by the reaction of radicals with oxygen, especially to form C=O bonds that absorb around 200–300 nm.

The ODs of the irradiated samples under vacuum increase from the 1st through the 5th film in that order, and reach a maximum at the 5th film. In the case of irradiation in air, the ODs increase from the 1st to the 4th film, and the 4th film shows the maximum value. These results could be described by the energy deposition, which was calculated for the Bragg curves shown in Fig. 2. The energy deposition of the C^{6+} ions shows a rapid rise from the sample surface and an increase to a maximum before the end of the penetration range. It would be considered that larger energy deposition induces formation of a higher concentration of free radicals and hence produces conjugated double bonds or crosslinking sites. For the other ion beams, Ne^{10+}, Si^{14+} and Ar^{18+}, similar results were obtained, which would indicate the generation of conjugated double bonds, and their amounts should show Bragg-curve-like distributions.

The depth profiles of the ODs of several kinds of conjugated double bonds generated by C^{6+} beam irradiation (left) and Ar^{18+} irradiation (right) are shown in Fig. 3. Here, only samples irradiated under vacuum are discussed because the samples irradiated in air would contain oxidation effects as mentioned above. From the obtained results, the molar concentrations of each fluorocarbon conjugated double bond sequence were calculated. The molar absorption coefficients were estimated as

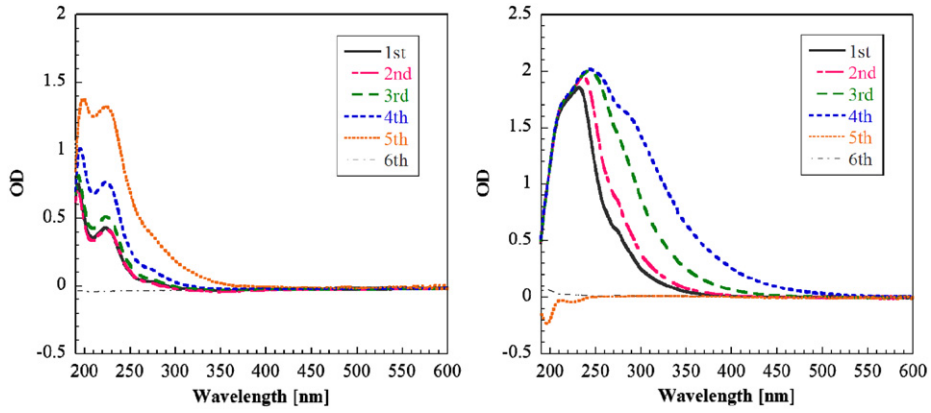

Fig. 1. UV–vis spectra of ETFE films after C^{6+} beam irradiation under vacuum (left) and in air (right).