

## 7.7 Ion Beam Irradiation Effects on Aromatic Polymers

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**Abstract** We studied the optical and thermal properties of aromatic polymer films which had been irradiated with 1 MeV  $H^+$ ,  $H_2^+$  and  $He^+$  ions. The examined aromatic polymers were polyetherether ketone(PEEK), polyetherimide (PEI), polyether sulfon(PES), polysulfon(PSF), and polyphenylene sulfide(PPS). The optical densities at 300nm of PES and PSF greatly increased after the irradiation. The optical densities at 400nm of all the examined polymer lineally increased with the irradiation dose. The PEEK film which had been irradiated with 1 MeV  $H^+$  was not deformed above melting point. This demonstrates that cross-linking occurs in PEEK films by ion beam irradiation. As for the effects, depending on the mass of the irradiated ions, it was found that the ions with a high mass induced larger effects on the aromatic polymers for the same absorption energy.

### 1. Introduction

Ion beam applications for organic materials have not been put to practical use. One of the reasons is that the organic materials are less resistant than inorganic materials when irradiated with the ion beams. To reduce the damage caused by ion beams, we selected heat-resistant organic materials.

Aromatic Polymers, for example PEEK, PEI and PES are good heat-resistant materials. Therefore, we selected the aromatic polymers as the organic material to improve the performance using the ion beam irradiation.

### 2. Experimental

The aromatic polymer films were irradiated with 1MeV  $H^+$ ,  $H_2^+$  and  $He^+$  ions. The examined aromatic polymers were PEEK, PEI, PES, PSF, and PPS. We studied the optical and thermal properties of the irradiated polymer films.

### 3. Results and discussion

#### 3.1 Conversion of numbers of irradiated ions into absorption dose

In order to study the effect of ion beam species and ion beam energy, it is more convenient to express the quantity of implanted ions as the absorption energy rather than the number of ions. The number of irradiating ions could be converted into the absorption dose by calculating the stopping power for the implanted ions. The stopping powers for 1 MeV  $H^+$ ,  $H_2^+$ ,  $He^+$  ions in the aromatic polymers were calculated from the stopping powers corresponding to

C, H, N, O and S [1] based on the additivity rule. The stopping power for 1 MeV  $H_2^+$  is considered to be twice as high as that for 0.5 MeV  $H^+$ , as the molecular ion of 1 MeV  $H_2^+$  is broken into two atomic ions of 0.5 MeV  $H^+$  at the surface of a polymer film.

Using the stopping power, the absorption dose is calculated using the following equation [2]:

$$D = 1.6 \times 10^{-13} \times S \times N \quad (1)$$

where D is the absorption dose in MGy, S the stopping power in  $\text{MeV} \cdot \text{cm}^2 / \text{mg}$  and N the number of irradiated ions in  $\text{ions}/\text{cm}^2$ .

As the stopping power is a function of the implantation depth, the average stopping power,  $S_{av}$ , is used to calculate the absorption dose in this experiment.

When the ion beam range is longer than the film thickness,  $S_{av}$  is calculated using the following equation:

$$S_{av} = \frac{\int_0^T S(l) dl}{T} \quad (2)$$

where T is the thickness of the polymer film and l the ion implantation depth.

When the range is shorter than the film thickness,  $S_{av}$  is calculated using the following equation:

$$S_{av} = \frac{\int_0^R S(l) dl}{R} \quad (2)'$$

where R is the range of the ion beam.

The average stopping powers for the ions in the examined aromatic polymer films are listed in Table 1.

Table 1 The average stopping powers for 1 MeV ions  
in the examined aromatic polymer films

Polymer	Thickness [ $\mu\text{m}$ ]	Range of 1 MeV ions [ $\mu\text{m}$ ]			Average stopping power [ $\text{MeV cm}^2 / \text{mg}$ ]		
		$H^+$	$H_2^+$	$He^+$	$H^+$	$H_2^+$	$He^+$
PEEK	16	18.2	7.3	5.2	0.42	1.06	1.47
PEI	10	18.7	7.5	5.4	0.34	1.05	1.45
PES	8	18.6	7.5	5.4	0.30	0.98	1.36
PSF	9	19.2	7.7	5.5	0.33	1.05	1.46
PPS	8	18.0	7.3	5.3	0.32	1.03	1.41

### 3.2. UV and visible spectra

The aromatic polymer films that had been irradiated by the ion beams were all a brown color. The UV and visible spectra were measured. To examine the change in UV and visible spectra induced by the ion beam irradiation, a non-

irradiated film was used as reference. Therefore the obtained spectra are normalized with respect to the non-irradiated film. In this experiment, the optical density is obtained using the following equation:

$$OD = \log(I_n/I_i) \quad (3)$$

where OD is the optical density,  $I_n$  the intensity of the transmitted ray through the non-irradiated film and  $I_i$  the intensity of the transmitted ray through the irradiated film.

Fig. 1(a) shows the absorption spectra of the aromatic polymer films which had been irradiated with  $1 \text{ MeV } 1 \times 10^{15} \text{ H}^+/\text{cm}^2$  (about 50MGy). The spectra of only PES and PSF have large absorption peaks near 300nm. These absorption peaks are possibly related to the  $-\text{SO}_2-$  group, because only PES and PSF contain the  $-\text{SO}_2-$  group. The peaks near 300nm seemed to appear because of the decomposition of the  $-\text{SO}_2-$  group.

The optical density of the irradiated films linearly increase with the numbers of implanted ions. The optical density at 400nm of the films was plotted as a function of absorption dose calculated by equation (1) in Fig.1(b). This figure shows that  $1 \text{ MeV He}^+$  colored the films more efficiently than  $1 \text{ MeV H}^+$ .

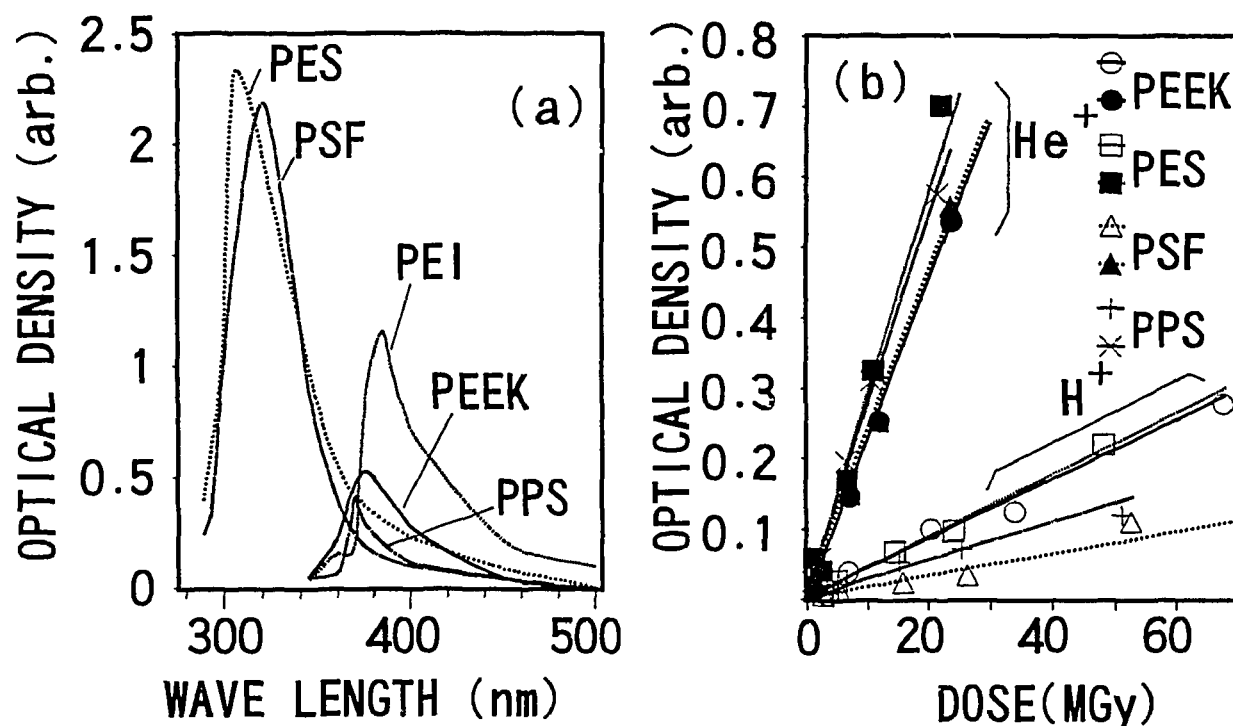


Fig. 1 (a)UV and visible absorption spectra of the aromatic polymer films which had been irradiated with  $1 \text{ MeV } 1 \times 10^{15} \text{ H}^+/\text{cm}^2$ . (b)Optical Density at 400nm of the colored aromatic polymer films irradiated with a  $1 \text{ MeV}$  ion beam.

### 3.3. Gel fraction

The gel fraction, the insoluble part of the polymer, of the irradiated PEI film was measured. The films were immersed for 24 hours in Dimethylformamide at 120°C. Afterwards they were dried for 24 hours at 80°C.

Fig. 2 shows the gel fraction of the PEI as a function of absorption dose. As for the gel fraction, 1 MeV  $\text{He}^+$  most efficiently formed the gel, in a similar way to UV and visible spectra. In other words, 1 MeV  $\text{He}^+$  most efficiently crosslinked the PEI.

As listed in Table 1, the stopping power for 1 MeV  $\text{He}^+$  is about four times higher than for 1 MeV  $\text{H}^+$ . As for the effects, depending on the stopping power, it was found that the ion whose stopping power is high efficiently crosslinks the polymer in same absorption dose. This effect is called the LET (Linear Energy Transfer) effect in radiation chemistry. A similar effect has been found in Polystyrene [2],[3] and some aromatic polymers [4],[5].

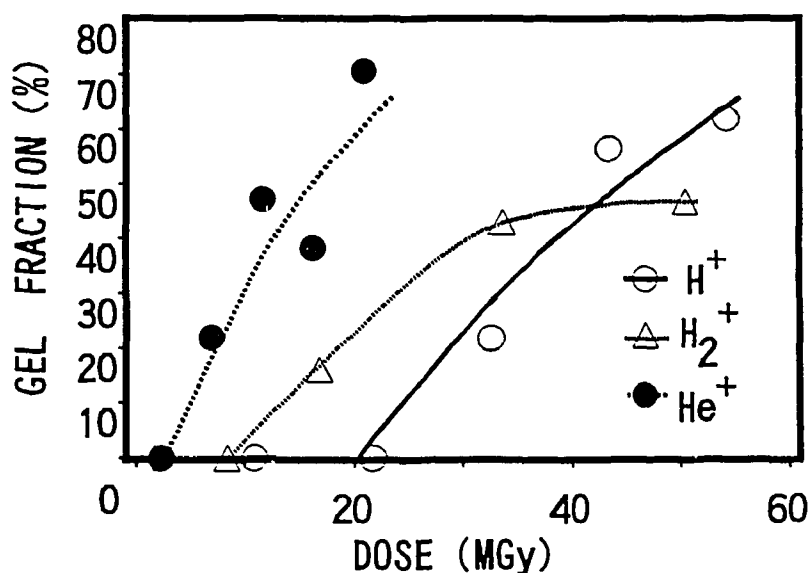


Fig. 2 Gel fraction of the PEI films irradiated with 1 MeV  $\text{H}^+$ ,  $\text{H}_2^+$  and  $\text{He}^+$ .

### 3.4 Deformation

Deformation of the irradiated PEEK film up to 500°C under a load of 4.6 kg/cm<sup>2</sup> was measured by Thermo Mechanical Analysis (TMA). The film was irradiated with 1 MeV  $\text{H}^+$ . The original thickness of the film was 25 μm. The sample film was placed under a crystal rod with a flat face of 1 mm in diameter. The temperature of the sample was raised up to 500°C at 20°C per minute. The deformation was obtained by measuring the film thickness during the test. The test results are shown in Fig. 3.

PEEK is a crystalline polymer and its melting point is 334°C. The crystal melts and the polymer flows above the melting point. Therefore the non-

irradiated PEEK film has deformed rapidly above the melting point. However, the irradiated film did not deform as much as the non-irradiated one above the melting point. This suggests that crosslinking occurred in the PEEK by ion beam irradiation.

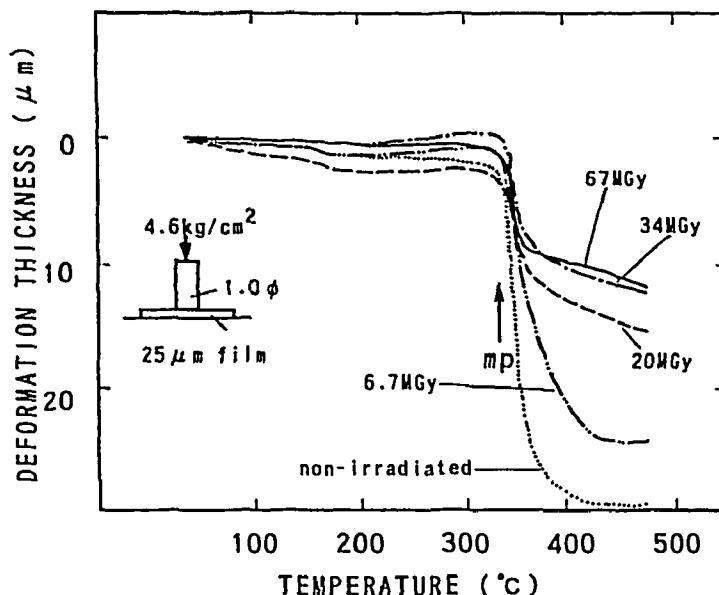


Fig. 3 Deformation of the 25  $\mu\text{m}$  PEEK films irradiated with 1 MeV  $\text{H}^+$ , measured by TMA.

#### 4. Conclusion

Various aromatic polymer films were irradiated with 1 MeV  $\text{H}^+$ ,  $\text{H}_2^+$ ,  $\text{He}^+$  ions. It was found that the ion whose stopping power is high significantly changes the property of the aromatic polymers by the LET effect, this is also the case for coloration and gel formation. The absorbance at 300nm of both PES and PSF were greatly increased after irradiation.

The PEEK film which had been irradiated with 1 MeV  $\text{H}^+$  was hardly deformed above the melting point. This demonstrates that crosslinking occurred in the PEEK film by ion beam irradiation.

#### References

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