Molecular Structure Evaluation of Bulk Polytetrafluoroethylene Modified by X-ray Irradiation

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Bulk polytetrafluoroethylene (PTFE) can be modified via X-ray irradiation. The X-rays, which have a continuous spectrum from 3 to 8 keV, penetrate deep into the PTFE substrate and induce a scission in the polymer main chain, -C-C-. In previous research, the optical properties of a PTFE sample were successfully modified; UV and visible transmittance drastically increased in the irradiated area of the substrates. In this study, the characterization of the chemical structure of the samples was carried out using Raman and FTIR spectroscopies. The results suggest the formation of CF₃ branches, which are not intrinsic to PTFE. In previous works, it has been reported that a similar modification was achieved using electron beam irradiation of several-MeV in molten PTFE, or by α-irradiation onto a PTFE substrate, where the modification depth was of tens of micrometers. On the contrary, we have succeeded the similar modification by using the X-rays.

Keywords: Polytetrafluoroethylene, X-ray, Synchrotron radiation, Photochemical reaction

1. Introduction

Polytetrafluoroethylene (PTFE) is a material with excellent properties, such as high heat and chemical resistance, low friction coefficient, and good electrical insulation. Due to its outstanding characteristics, it is used in various applications, e.g., as medical piping tube, for packing in chemical plants, and as coating for cables. To further expand its use, PTFE modification has been conducted using X-, γ-, α- or electron (EB) beams, or neutron radiation [1-16]. When PTFE is irradiated by γ-rays, EB, or neutron radiation, its mechanical properties deteriorate due to the scission of the polymer main chain, -C-C- [1-5]. However, it has been reported that EB irradiation of PTFE in the molten state at around 340 °C induces recombination of the radicals generated within the polymer and the deteriorated tensile strength improves [1]. This is because the mobility of radicals is much higher in the molten polymer than in its solid form, and the recombination reaction is thus promoted [8]. Also, it is known that the process of recombination suppresses the crystallization, turning the white pristine PTFE into a transparent substrate [2,8]. It has also reported that the recombination occurs when PTFE substrates are irradiated with α-radiation at room temperature. Compared to other radiation types, α-radiation have a much-higher linear energy transfer (LET) to PTFE substrate, inducing a high-density reaction site within the polymer. This enables the recombination of the radicals without the need of high mobility [10]. Nevertheless, the high LET of α-radiation results in a small penetration depth into the PTFE substrate; the reported modification depth is below 30 µm.

On the other hand, we have carried out research regarding the photochemical reaction between X-ray of several keV and PTFE [12-17]. The X-rays can penetrate PTFE surface to a depth of around 300 µm and induce interaction with PTFE molecular. In previous research, we confirmed that UV and visible transmittance drastically increased by the X-rays irradiation [16]. In this paper, we analyzed their chemical structure of the sample
using Raman and FTIR spectroscopy.

2. Experimental

PTFE irradiation with X-ray was conducted in beamline BL-11 [18] of the NewSUBARU synchrotron radiation (SR) facilities at the University of Hyogo, Japan. The kinetic energy of the electrons in the storage ring was set to 1.5 GeV. A schematic experimental setup is shown in Fig. 1 of Ref. 8. PTFE substrate was enclosed in a 12-µm-thick Al film barrier layer. The PTFE substrates used in this work were commercially available samples (UNIVERSAIL Co., Ltd., 001-251-02) with a thickness of 300 µm. The PTFE substrates were ultrasonically cleaned using acetone, then 2-propanol, and finally pure water. The clean samples were placed perpendicular to the incident X-ray beam in the exposure chamber and heated up to 200 ºC and vertically scanned at 5 mm/s. The X-ray irradiation dose was controlled by changing the number of scans. Helium gas (10 kPa) was introduced to the exposure chamber to suppress any temperature increase of the PTFE substrate due to X-ray irradiation. Figure 1 (a) shows the calculated spectrum of the X-ray irradiated to the surface of the PTFE substrate. In addition, Fig. 1 (b) shows the transmittance through PTFE substrates as a function of photon energy for films with thickness ranging from 10 to 300 µm. The penetration depth, calculated from the surface of the substrate, increases with the energy of the photons.

3. Results and discussion

The X-ray irradiation of the PTFE substrate induces the evaporation of the fragment, decreasing the film thickness and the mass of the sample. These were measured after X-ray irradiation with different doses. To determine the thickness, the cross sectional images of the sample were observed using a digital microscope. As shown in Fig. 2, the thickness decreases and the mass loss increases with X-ray irradiation. This indicates that the fragments produced during the X-rays irradiation evaporated from the surface of the PTFE substrate. We investigated the molecular bonding states of the irradiated samples via Raman spectroscopy (JASCO Co., NRS-5100) at an excitation laser wavelength of 532 nm. Dashed line in Fig. 3 (a) shows the Raman spectrum of the non-irradiated 0.1-mm-thick PTFE substrate. Molecular structure of PTFE is shown in Fig. 4 (a). The peaks in the spectrum are very similar to previously reported values [19]. The intensity of the Raman peaks

![Fig. 1](image1.png)

![Fig. 2](image2.png)
changed according to the transmittance of the samples with different SR irradiation doses, shown in Fig. 3 (b). The fluorinated ethylene propylene copolymer (FEP, Fig. 4 (b)) shows an additional small peak at 753 cm⁻¹ (dotted line in Fig. 3 (b)), which has been previously observed [20]. It is reasonable to assume that the peak is attributed to CF₃ branches due to being observed only with FEP. This small peak at 753 cm⁻¹ is also observed in the Raman spectra of the irradiated samples (solid lines in Fig. 3 (b)), indicating that the concentration of CF₃ branches in the irradiated samples is greater than in non-irradiated PTFE. Additionally, the peak at 734 cm⁻¹ is slightly shifted to lower

Fig. 3. (a) Raman spectrum of pristine PTFE. (b) Raman spectra samples with different X-ray doses (A) 1731, (B) 866, and (C) 433 J/mm²; (D) 0.1 mm thick PTFE substrate, and (E) 0.1 mm thick FEP substrate. Peaks at (i) 753 and (ii) 734 cm⁻¹ are respectively assigned to CF₃ branches and CF₂ bonds.

Fig. 4. Molecular structures of (a) PTFE and (b) FEP.

Fig. 5. FTIR spectra of samples with different X-ray doses (A) 1731, (B) 866, and (C) 433 J/mm²; (D) non-irradiated 0.1 mm thick PTFE, and (E) 0.1-mm thick FEP substrates in the region of (a) 1020–940 cm⁻¹ and (b) 1900–1600 cm⁻¹.
wavenumbers as the X-ray irradiation dose increases. This suggests that tensile stress arises within the irradiated samples, as also reported in other studies [21].

The molecular structure of the samples was also evaluated via transmission Fourier transform infrared spectroscopy (FTIR) with a FT/IR-6100 spectrometer (JASCO INTERNATIONAL Co., LTD.). The optical path length was calibrated to 100 µm because the thickness of the samples differ depending on the X-ray does, as shown in Fig. 2. Figure 5 (a) shows the FTIR spectra of the irradiated samples and of the 0.1-mm-thick PTFE and FEP substrate. The band at 985 cm⁻¹ can be assigned to CF₃ branches [8,10], as they are only observed in the PTFE substrate transparency by the X-rays. The band at 985 cm⁻¹ can be assigned to -COF group [8,10,23] which is presumed as one of the factors that made the PTFE substrate transparency by the X-rays.

Figure 5 (b) shows the FTIR spectra in the region from 1900 to 1600 cm⁻¹. For the irradiated samples, new peaks were observed at 1884, 1785, 1729, 1716, 1670 cm⁻¹. Those at 1670 and 1785 cm⁻¹ correspond to -CF=CF₂ and -CF=CF₂ groups [9,10]. The bands at 1716 and 1729 cm⁻¹ are assigned to -CF=CF₂, and that at 1785 cm⁻¹ to the terminal -CF=CF₂ group [9,10,22]. Finally, the band at 1884 cm⁻¹ was assigned to a -COF group [8,10,23] which is assumed to be formed by residual oxygen in the exposure chamber or due to the exposure of the samples to the atmosphere. These peaks are similar to those reported for PTFE modified by EB or α-radiation [9,10].

4. Conclusion
This paper examine the molecular structure of PTFE substrates to EB or α-radiation. The formation induces a decrease in crystallinity and PTFE substrate becomes transparent. In the case of EB, the modification was performed by irradiation of molten PTFE. When using α-radiation, the depth of PTFE substrate modification was several tens of µm from the surface. In this work, we have succeeded the similar modification for PTFE substrate with a thickness of 300 µm by using the X-rays.

References
1. A. Oshima, Y. Tabata, H. Kudoh, and T. Seguchi, Radiat. Phys. Chem., 45 (1995) 269.
2. A. Oshima, S. Ikeda, T. Seguchi, and Y. Tabata, Radiat. Phys. Chem., 49 (1997) 279.
3. A. Oshima, S. Ikeda, H. Kudoh, T. Seguchi, and Y. Tabata, Radiat. Phys. Chem., 50 (1997) 611.
4. O. K. Harling, G. E. Kohse, and K. J. Riley, J. Nucl. Mater., 304 (2002) 83.
5. Y. Tabata, H. Suzuki, and S. Ikeda, Radiat. Phys. Chem., 84 (2013) 14.
6. U. Lappan, U. Geißler, and K. Lunkwitz, Radiat. Phys. Chem., 59 (2000) 317.
7. K. Lunkwitz, U. Lappan, and D. Lehmann, Radiat. Phys. Chem., 57 (2000) 373.
8. U. Lappan, U. Geißler, and K. Lunkwitz, J. Appl. Polym. Sci., 74 (1999) 1571.
9. U. Lappan, U. Geißler, L. Haußler, D. Jehnichen, G. Pompe, and K. Lunkwitz, Nucl. Instr. Meth. Phys. Res. B, 185 (2001) 178.
10. D. L. Pugmire, C. J. Wetteland, W. S. Duncan, R. E. Lakis, and D. S. Schwartz, Polym. Degrad. Stab., 94 (2009) 1533.
11. G. L. Fisher, R. E. Lakis, C. C. Davis, C. Szakal, J. G. Swadener, C. J. Wetteland, and N. Winograd, Appl. Surf. Sci., 253 (2006) 1330.
12. Y. Ukità, M. Kishihara, K. Kanda, S. Matsui, K. Mochiji, and Y. Utsumi, Jpn. J. Appl. Phys., 47 (2008) 337.
13. H. Kido, T. Kuroki, M. Okubo, and Y. Utsumi, Microsyst. Technol., 19 (2013) 301.
14. A. Yamaguchi, H. Kido, and Y. Utsumi, J. Photopolym. Sci. Technol., 29 (2016) 403.
15. A. Yamaguchi, H. Kido, Y. Ukità, M. Kishihara, and Y. Utsumi, Appl. Phys. Lett., 108 (2016) 051610.
16. M. Takeuchi, A. Yamaguchi, T. Kobayashi, and Y. Utsumi, J. Photopolym. Sci. Technol., 32 (2019) 253.
17. M. Takeuchi, H. Izumi, M. Ishihara, T. Kobayashi, A. Yamaguchi, and Y. Utsumi, J. Photopolym. Sci. Technol., 32 (2019) 249.
18. M. Takeuchi, A. Yamaguchi, and Y. Utsumi, J.
19. J. L. Koenig and F. J. Boerio, *J. Chem. Phys.*, 50 (1969) 2823.
20. P. I. Okagbare and M. D. Morris, *Analyst*, 137 (2012) 77.
21. I. D. Wolf, H. E. Maes, and S. K. Jones, *J. Appl. Phys.*, 79 (1996) 7148.
22. M. I. Bro and C. A. Sperati, *J. Polym. Sci.*, 38 (1959) 289.
23. M. Hagiwara, T. Tagawa, H. Amemiya, K. Araki, I. Shinohara, and T. Kagiya, *J. Polym. Sci.*, 14 (1976) 2167.