Modification of the Transmittance of Bulk Polytetrafluoroethylene via Synchrotron Radiation Irradiation

Masaya Takeuchi†, Akinobu Yamaguchi†, Toshiro Kobayashi‡, and Yuichi Utsumi†

† Laboratory and Advanced Science and Technology for Industry, University of Hyogo, 3-1-2 Koto, Kamigori, Ako, Hyogo 678-1205, Japan
‡ National Institute of Technology, Tsuyama College, 624-1 Numa, Tsuyama, Okayama 708-8509, Japan
*masaya@lasti.u-hyogo.ac.jp

We demonstrate the modification of transmittance of bulk polytetrafluoroethylene (PTFE) via synchrotron X-ray irradiation. X-ray irradiation of the PTFE substrate is conducted to mechanically suppress the photoevaporation of PTFE molecules. This method drastically increases the ultraviolet and visible transmittance of the irradiated areas of the substrates, with greater than 80% transmittance observed at the 350-nm wavelength. We observed the irradiated area via scanning electron microscopy and determined that this optical property modification is due to the homogenization of the bulk PTFE texture with nanometer to micron-sized pores. We expect that this modified PTFE will be employed as a construction material for various micro system devices such as Lab-on-a-chip and micro total analysis systems.

Keywords: Synchrotron radiation, Polytetrafluoroethylene, Modification, X-ray.

1. Introduction

Polytetrafluoroethylene (PTFE) has excellent material properties, such as high heat and chemical resistance, high mechanical strength, electrical insulation, a low dielectric constant, and low coefficient of friction. These ideal characteristics make PTFE an attractive material for microsystems such as micro-electro mechanical systems (MEMS), micro total analysis systems (µTAS), and Lab-on-a-chip (LOC). However, PTFE microfabrication and its bulk modification are difficult owing to the outstanding thermal and chemical stability of PTFE, with most PTFE research conducted using either x−/γ−, α, electron beam (EB), or neutron radiation to date [1–17].

The direct etching of PTFE induced by synchrotron radiation (SR) irradiation [1-3] and the precise process characteristics of PTFE etching using a high-energy (2–12 keV) X-ray and heat assistance have been studied extensively [4–7]. For example, tentative bubble-like structures were observed on the X-ray irradiated surface of PTFE substrates via scanning electron microscopy (SEM), and the results indicated that surface liquefaction occurred during the photolysis of bulk PTFE, with the desorption of photoproducts from the surface and subsequent degradation of the PTFE molecules [4–6]. Raman spectroscopy and X-ray diffraction measurements of the X-ray irradiated PTFE surfaces suggested that the chain scissions of PTFE were driven to completion [7], with confirmation that the melting temperature of the irradiated PTFE decreased because the molecular weight decreased owing to the chain scission of PTFE via X-ray irradiation, resulting in the evaporation of photoproducts from the surface. Furthermore, it has been reported that the modification of the optical properties of PTFE results in the transformation of the original opaque PTFE substrates into transparent PTFE substrates after several MeV of EB irradiation while in the molten state [9].

Here we report on the optical modification of bulk PTFE by suppressing the evaporation of the photoproducts generated via X-ray irradiation on
the PTFE substrate, which drastically increases its ultraviolet (UV) and visible transmittance.

2. Experimental

The SR irradiation experiment on the PTFE substrates was conducted at beam line BL-11 [18] of the NewSUBARU SR facility at the University of Hyogo, Japan. The X-ray beam obtained from the bending magnet source was inserted into a toroidal mirror, where it was collimated by the mirror and passed through two Be filters to exclude any photon energy below 2 keV from reaching the exposure apparatus. The storage ring electron kinetic energy was set at 1.5 GeV, with a storage ring current of 160–320 mA. Figure 1 (a) illustrates the experimental apparatus for improving the PTFE substrates. Each PTFE substrate (500-µm thickness) was enclosed in a 12-µm-thick Al film barrier layer. The sample heating was adjusted to maintain an incident SR beam that was perpendicular to the PTFE surface in the reaction chamber, and the PTFE surface was vertically scanned to ensure a homogeneous intensity distribution, which was performed by moving the exposure stage. The SR irradiation dose was controlled by changing the number of scans. The X-ray irradiation was conducted with heating in a vacuum. The dashed line of Fig. 1 (b) shows the calculated spectrum considering the reflection of the Pt coated Si mirror and transmission of the Be filters. The line is obtained by the 1.5 GeV operation with a storage ring current of 300 mA. The solid line of Fig. 1 (b) shows the spectrum of the beam adding the transmission of the Al film barrier layer of PTFE substrate to the above spectrum. The photon energy of the X-ray irradiated PTFE substrates spans the 3–8 keV range. Additionally, the UV and visible transmittance of the irradiated area of the substrates were measured using a spectrophotometer, which comprised a spectrometer (Ocean Optics, Inc., HR4000), deuterium-halogen light sources (Ocean Optics, Inc., DH-2000), and spectroscopy software (Ocean Optics, Inc., OceanView). A deuterium lamp (250–450 nm wavelength) and halogen lamp (450–900 nm wavelength) were used as the light sources.

3. Results and discussion

We performed X-ray irradiation of the PTFE substrates under 4 ± 2 Pa pressure and a heating temperature of 200 °C. The SR doses were 0, 13, 20, 23, 25, 26, 30, and 33 J/cm² with the 1.5 GeV operation in BL-11. Photographs of the irradiated PTFE substrates at various SR doses are shown in Fig. 2.

![Diagram](image-url)
Fig. 2, where it is observed that the irradiated area of the substrates gradually becomes transparent as the SR dose is increased. Furthermore, the transmittance increases with higher SR doses, as shown in Fig. 3, with more than 80% transmittance at the 350-nm wavelength and SR dose of 33 J/mm².

Our results demonstrate that the drastic change in the transmittance of bulk PTFE via SR irradiation is attributed to the homogenization of the bulk PTFE substrate. Commercialized PTFE substrates generally possess a low UV and visible transmittance owing to light scattering because they are produced via sintering as-polymerized powder, and their bulk morphology comprises a porous texture with nanometer to micron-sized pores [19]. However, it is confirmed that the PTFE melting point decreases via SR irradiation and allows the material from the irradiated area to infiltrate the pores in the non-irradiated area as the melting liquid; this leads the homogenization of the bulk PTFE texture. Figure 4 (a) shows a SEM image of a PTFE substrate cross section that was dry-etched using the 1.5 GeV operation of beam line BL-2 [20, 21] at NewSUBARU. The sidewall of the irradiated area is smooth compared with that of the non-irradiated area. Figure 4 (b) shows a SEM image of an SR-irradiated PTFE surface that suppressed the evaporation of photochemical products in BL-11, with an SR dose of 33 J/mm². Similar to Fig. 4 (a), the SR irradiated surface is smooth. As mentioned above, we confirmed that this optical property modification arose with the homogenization of bulk PTFE. Further, we assume that the degradation in the crystallinity of the PTFE bulk texture owing to SR irradiation is another contributing factor.

Fig. 3. Transmittance of the X-ray irradiated PTFE in the visible light region: (a) 0 J/mm², (b) 13 J/mm², (c) 20 J/mm², (d) 23 J/mm², (e) 25 J/mm², (f) 26 J/mm², (g) 30 J/mm², and (h) 33 J/mm². (i) Transmittance of a 0.5-mm-thick quartz.

4. Conclusion

In this paper, we demonstrate that X-ray irradiation modifies bulk PTFE by mechanically suppressing photoevaporation of the PTFE molecules and drastically increases the UV and visible transmittance of the PTFE molecules. We suggest that the modification of the transmittance of bulk PTFE is caused by the homogenization of bulk
PTFE. It is expected that this modified PTFE will be employed as a construction material in various micro system devices, such as LOC and µTAS, for the observation of cells and chemiluminescent immunoassays to detect target substances in microliquids.

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