Investigation of the electronic state of poly-tetrafluoroethylene under bending stress using near-ambient pressure hard X-ray photoelectron spectroscopy

Polymer materials exhibit excellent chemical and physical properties, including formability, chemical stability, and electrical insulation, which are determined by differences in their molecular structure and crystallinity. Among these materials, polytetrafluoroethylene (PTFE, Fig. 1(a)) stands out owing to its remarkable chemical stability, heat resistance, and abrasion resistance. Consequently, it finds widespread applications in diverse fields such as medical engineering (including artificial joints), electrical engineering, and biology. Although PTFE is often subjected to external forces and stresses from multiple directions during use, the effects of these stresses on its surface interactions with the external environment have not been thoroughly investigated. Thus, it is essential to examine the surface states of PTFE under stress, including its electronic and chemical conditions.

X-ray photoelectron spectroscopy (XPS) is a powerful tool for elucidating surface states. However, investigating the electronic states of PTFE under multiple stresses has been challenging owing to its insulating nature, which causes charge-up and hinders accurate measurements.

In this study, the surface state of PTFE under multiple stresses, particularly changes in its electronic state and chemical composition induced by bending stress (multidirectional stress), was examined using near-ambient pressure hard X-ray photoelectron spectroscopy (NAP-HAXPES). The issue of charge-up during HAXPES measurements was resolved by introducing nitrogen gas and employing an efficient differential pumping system. This approach enabled the first successful HAXPES measurements of PTFE under applied stress. Notably, previously unreported changes in the chemical composition of PTFE were observed as tensile strain increased because of bending stress [1].

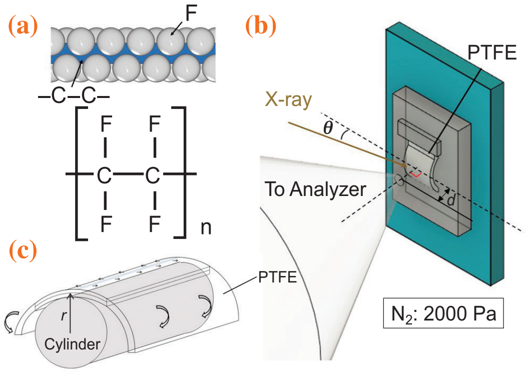

Fig.1. **(a)** Structural formula of PTFE. **(b)** Experimental setup for HAXPES measurement of PTFE under bending stress. **(c)** Schematic diagram of PTFE under bending stress.

HAXPES measurements were performed using SPring-8 **BL24XU** (Fig. 1(b)) [2]. The X-ray energy was set at 8 keV, with an incidence angle θ of 4°. Initial measurements in a vacuum failed to produce usable spectra due to charge-up effects from the insulating properties of PTFE. To address this issue, environmental change compensation was implemented by introducing inert nitrogen gas. In conventional setups, the distance *d* from the cone tip to the sample surface is 0.3 mm. However, at this distance, inert gas introduction does not effectively prevent charge-up or cone contamination from desorbed PTFE material [2]. Recent findings indicate that increasing *d* can achieve environmental charge compensation even at low pressures [2-5]. In this study, a distance of 1.8 mm was used, with nitrogen gas introduced at 2000 Pa, successfully eliminating charge-up effects. To investigate the dependence of PTFE surface states on bending strain, the strain was adjusted by varying the radius of curvature *r* applied to the material under stress (Fig. 1(c)).

Figure 2(a) shows the HAXPES spectra of C1*s* at different bending strains, obtained by adjusting the radius of curvature. Measurements were conducted on the outer surface (tensile stress surface) of the bent PTFE under bending stress. Curve fitting for each spectrum was performed using the Voigt function. In the spectrum of the unstressed PTFE in Fig. 2(a), peaks at binding energies around 295.1 and 293.2 eV correspond to CF_3 and CF_2, respectively. Additionally, peaks associated with C–C bonds in the main PTFE chain were scarcely observed. By contrast, the peak at 285.6 eV, corresponding to C–C bonds, became pronounced with an increase in the bending tensile strain. The F/C intensity ratio also decreases with increasing strain [1]. These results indicate that bending tensile stress induces the cleavage of C–F bonds in the side chains and fluorine desorption. Notably, this is the first report of a phenomenon where the C–C peak becomes pronounced under bending tensile stress.

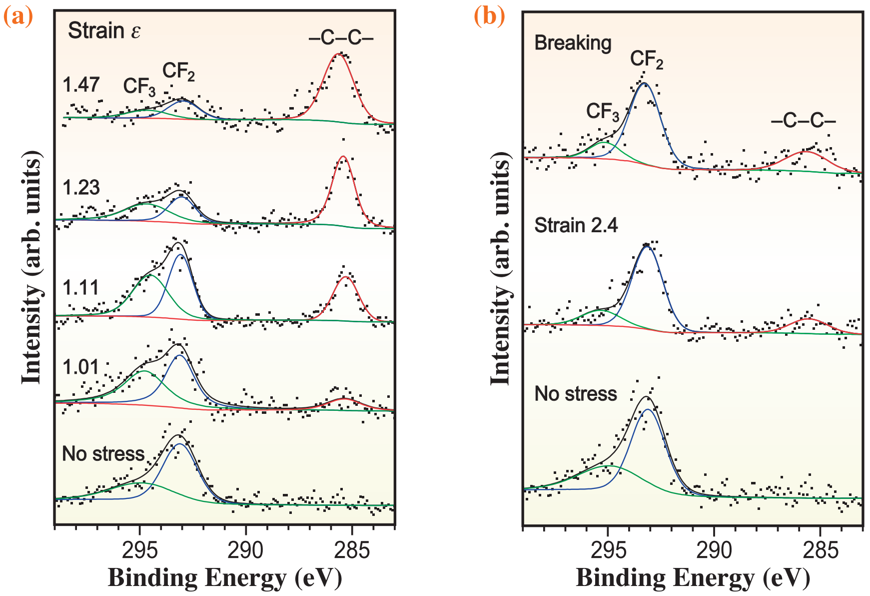

Fig. 2. Narrow scan analysis of C1*s* of PTFE with changing strain by applying **(a)** flexural tensile stress and **(b)** uniaxial tensile stress.

Based on these results, it was hypothesized that the C–F bond scission and desorption of F might also occur under uniaxial tensile stress. Figure 2(b) shows the C1*s* HAXPES spectrum of PTFE subjected to uniaxial tensile stress (tensile strain: 2.4). CF_3, CF_2, and C–C peaks were observed in the spectrum of the non-stressed PTFE, but the C–C intensity was significantly lower than that under flexural tensile stress, as shown in Fig. 2(b). Measurements of PTFE fractured by uniaxial tensile stress showed even low C–C peak intensities. These findings demonstrate that C–F bond scission occurs minimally under uniaxial tensile stress but progresses significantly with flexural tensile stress. However, measurements of the inner surface (compression stress surface) of bent PTFE revealed almost no C–C peak [1]. These results indicate that tensile stress due to bending, rather than compressive or uniaxial tensile stress, leads to significant side-chain scission on the PTFE surface (Fig. 3).

These findings reveal that using NAP-HAXPES will lead to a better understanding of the microscopic surface of PTFE when bending stress is applied, which is expected to contribute to further applications in microelectric mechanical systems (MEMS) and medical engineering.

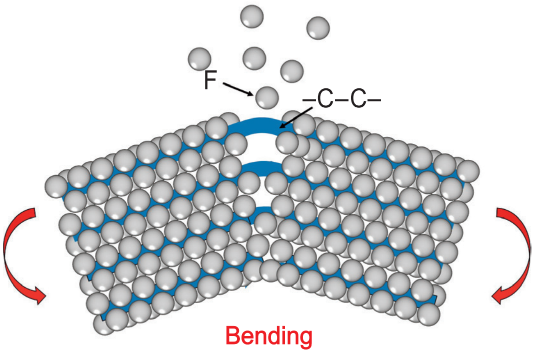

Fig. 3. Schematic of the surface of PTFE under bending stress.

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