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UPS study of VUV-photodegradation of polytetrafluoroethylene (PTFE) ultrathin film by using synchrotron radiation

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Abstract

The VUV-photodegradation of polytetrafluoroethylene (PTFE) ultra-thin film was studied by ultraviolet photoelectron spectroscopy and quadrupole mass spectrometry. These results were compared with the previous photodegradation studies of the polyvinylidenefluoride (PVDF) and polyethylene (PE). Generation of new peak, π-band originated from the C=C bond, was observed in the low binding energy region of the UPS spectra in both PVDF and PE during the photodegradation. In contrast, no new peak generation was observed in the UPS of the photodegraded PTFE. Mass spectrometry analysis also suggested that the C=C bond generation is not a major mechanism in the VUV photodegradation of PTFE.

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1. Introduction

It is no doubt that polytetrafluoroethylene (PTFE), popularly known as the DuPont tradename Teflon®, is one of the most technologically

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important polymers in modern industries. Its superb chemical resistance, wide temperature range thermal stability, high electrical resistivity, excellent optical properties, and low surface adhesion are unique material properties suitable for producing wide variety of commercial applications ranging from non-stick coatings on frying pans to medical components.

Katoh et al. showed fabrication of the high aspect-ratio PTFE microstructures with synchrotron radiation exposure [1]. Since there is no solvent to process PTFE and heating over its melting point does not result in enough fluidity for molding, photo-machining capability of PTFE is very attractive. Polyvinylidenefluoride (PVDF) is another fluoropolymers also possessing unique material properties similar to PTFE. Our group reported photo-machining possibility (photodegradation) in PVDF by using ultraviolet photoelectron spectroscopy (UPS) and mass spectrometry [2]. The study concluded that fluorine and hydrogen atoms are eliminated from the polymer upon the photodegradation, and conjugated double bonds are generated in the polymer backbone and the neighboring cross-linked chains. Similar photodegradation mechanism was observed in our recent studies of polyethylene (PE) [3] and polystyrene (PS) thin films [4]. In this paper we have studied the photodegradation of PTFE thin films also by using UPS and mass spectrometry. Results are discussed by comparing with the degradation mechanism observed in PVDF and PE.

2. Experimental

2.1. UPS measurements

The UPS experiments were performed at the synchrotron facility UVSOR at the Institute for Molecular Science. The beamline 8B2 with the SR-ARUPS endstation [5] was used. The 75 eV photon beam was utilized for both the photodegradation of PTFE film and measurements of ultraviolet photoelectron spectra. The photon intensity was intentionally lowered by using gold meshes to avoid extensive radiation damage to the films. This allowed measuring a series of photoelectron spectra for the degradation process. The energy resolution of the electron analyzer was 240 meV estimated from the Fermi-edge of poly-crystalline gold. The temperature during the measurements was 299 K. The incident angle of the synchrotron light was 45°, and the detection angle of the photoelectrons was normal to the surface. The spot size of the photon beam at the sample position was $1 \times 1\ \text{mm}^2$ estimated by the focused image of the zero-order light. Since the VUV photon irradiation was performed under ultrahigh-vacuum condition (5×10^{-8} Pa), any chemical reaction with ambient gases is not involved in the observed photodegradation process. The irradiation intensity was estimated from photoelectron current of the gold mesh (photon beam intensity monitor).

The PTFE thin films for UPS measurements were prepared by vacuum deposition on poly-crystalline gold at the deposition rate of 0.15 Å/s under the pressure of 4×10^{-7} Pa. Thickness of the PTFE films was 250 Å. The PTFE powder (average molecular weight of ~8000) was obtained from Central Glass Co., Ltd. and used without further purification.

2.2. Mass analysis

Mass analysis of photodesorption fragments from the PTFE thin films were performed at the plane grating monochromator beamline of the CAMD synchrotron source at Louisiana State University. The fragments from the PTFE thin films irradiated by the zero-order light (20–200 eV) from the beamline were analyzed by a quadrupole mass spectrometer (INFICON, H200M). The thin films were prepared also by vacuum deposition (thickness = 150 Å). Mass spectra were recorded under ultrahigh vacuum condition (3×10^{-6} Pa).

3. Results and discussion

3.1. Mass spectra

Fig. 1 shows a typical mass fragment pattern for the PTFE thin films irradiated with the zero-order light from the beamline. Molecular emissions of