

Effects of Surface Cleaning and X-Ray Irradiation in XPS Study of Polymers

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Synopsis

We have examined effects of surface cleaning and X-ray irradiation in XPS study of polymers. Contamination-free surfaces of polymer samples for XPS study were successfully prepared by ultrasonic washing in organic solvents. Polymers were revealed to have lower surface chemical activity than metal and semiconductor crystals. The degradation behavior of polymers induced by X-ray irradiation was found to be different from thermal degradation processes. Polymers like PET, polyimide, and PAN have high stability against X-ray irradiation in XPS measurement. On the other hand, we must take degradation into consideration in XPS measurement for polymers such as PTFE and nylon because of their low stability against X-ray irradiation. For an extremely X-ray-sensitive polymer like nitrocellulose, a quantitative XPS study cannot be carried out.

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is one of the most effective tools to analyze polymer surfaces because of its capability for providing detailed chemical information concerning the outermost surface. Various difficulties, however, due to surface contamination and change of chemical composition by X-ray radiation and also ion sputtering, still exist.^{1,2}

In the present study, we have mainly discussed a method of surface cleaning and the effect of X-ray irradiation on the XPS measurement of polymers. A polymer sample frequently has organic contamination on the surface, which prevents detailed examination of the surface. Most polymers are not free from chemical degradation induced by Ar ion bombardment, which is usually used to clean surfaces of inorganic materials including metal, ceramic, and semiconductor. Ar ion bombardment is known to induce decarboxylation of poly(ethylene terephthalate) (PET) and to preferentially sputter fluorine atoms from poly(tetrafluoro ethylene) (PTFE).¹

Consequently we cannot use Ar ion bombardment for surface cleaning of a polymer because of its destructive effect to the surface chemical composition. Another surface cleaning procedure must be adopted for the quantitative XPS study of polymers. We have tried to remove organic contamination on the polymer surface by ultrasonic cleaning in organic solvents.

Compared with other surface analytical techniques like AES and SIMS, XPS is considered to be a relatively mild technique for radiation-induced damage in the examination of inorganic materials. However, we frequently encounter damage due to X-ray irradiation in the XPS measurement of polymers that makes quantification of the surface composition impossible. Wheeler found a

very strong effect of X-ray irradiation on the surface composition of PTFE.³ Chang studied the mechanism of dehydrochlorination of polyvinyl chloride (PVC) film due to the X-ray irradiation.⁴ We have performed a detailed study of the effect of X-ray irradiation on several industrially important polymers including PET, PTFE, and nylon.

EXPERIMENT

XPS Measurement

The AEI-Kokusai Denki model ES-200 was used for the XPS study with $\text{AlK}\alpha_{1,2}$ X-ray source ($h\nu = 1486.6$ eV) *in vacuo* of 3×10^{-8} torr. All spectra of XPS were collected and stored on 200 channels with a step of 0.1 eV using KRATOS model DS-300 data system based on PDP11 from Digital Equipment Corporation. Polymer film samples were attached to a double-sided adhesive tape on a copper slab holder and tightly bound with thin copper wires, which were also effective in keeping a constant charge-up level of a sample. The charging voltages of PET and PTFE were 4.5 and 7 eV, respectively. The larger value of PTFE is due to the large photoelectron yield of fluorine atoms.

Ultrasonic Washing

We used commercially available PET and PTFE films with surface organic contaminations, which had been kept in our laboratory with no care for a long time before being studied. The surface contamination probably came from an oil mist in the air. These films were washed twice in an ultrasonic cleaner with a fresh organic solvent such as methanol, acetone, or *n*-heptane for 15 min.

X-ray Irradiation

The X-ray source of ES-200, which was used to irradiate a polymer specimen and also to obtain XPS spectra, was operated at 10 kV and 20 mA. The normal of a specimen was about 80° to the direction of the incident X ray. All specimens were set at a distance of about 1 cm from the X-ray anode separated with a 13 μm thick Al foil *in vacuo* of 1×10^{-8} torr. The contamination-free PET, PTFE, polyacrylonitrile (PAN), nylon 6, polyimide (Kapton), and nitrocellulose films were used in the examination of an effect by X-ray irradiation.

RESULTS AND DISCUSSION

Surface Cleaning

XPS spectra of PET and PTFE before and after washing with methanol, acetone, and *n*-heptane are compared in Figures 1 and 2, respectively. The PET film before the cleaning has much contaminating hydrocarbon on the surface revealed by C1s spectrum with an intense hydrocarbon peak and relatively weak ester component, and also by an asymmetric shape of O1s spectrum. The C1s spectra of PET films cleaned in the organic solvents have well-separated peaks of the ester group and their O1s spectra have the symmetric double

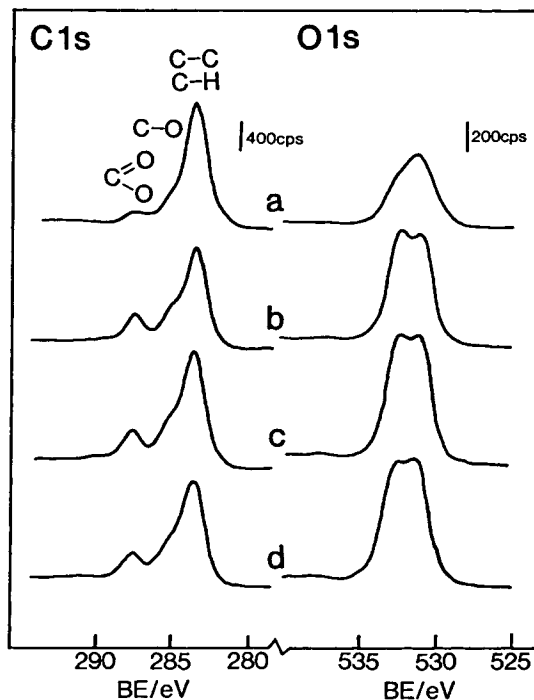


Fig. 1. XPS spectra of PET (a) before cleaning and after cleaning with an ultrasonic cleaner in (b) methanol, (c) acetone, and (d) *n*-heptane.

peaks corresponding to two oxygen atoms in the ester group. These XPS spectra agree with the chemical structure of PET⁵ and confirm successful removal of contamination from the surface by the cleaning procedure.

The PTFE film before the cleaning has a C1s spectrum with two components assigned to $-\text{CF}_2-$ and contaminating hydrocarbon, and a weak O1s peak. The PTFE films after the cleaning by acetone and *n*-heptane have C1s spectra with a single $-\text{CF}_2-$ component and the O1s spectra vanished. A weak O1s peak persisted in the PTFE film cleaned with methanol. The surface cleaning of PTFE film is also completely achieved by ultrasonic washing with these organic solvents except methanol.

These results suggest that a polymer sample with a contamination-free surface can be prepared easily by ultrasonic washing in an organic solvent without destruction of the surface chemical structure. The relatively easy removal of the surface contamination seems to come from the absence of surface dangling bonds, which could form stable chemisorbed structures with contamination molecules. Usually we cannot remove organic contaminants on metal and semiconductor surfaces completely by a washing procedure because of the presence of dangling bonds.

In XPS measurement of metals, we often encounter organic contaminants arising in the vacuum chamber. A change of the surface composition of a PET film was not observed after holding it in the XPS sample chamber under pressure of 1×10^{-8} torr for 24 h without X-ray irradiation. This indicates a lower

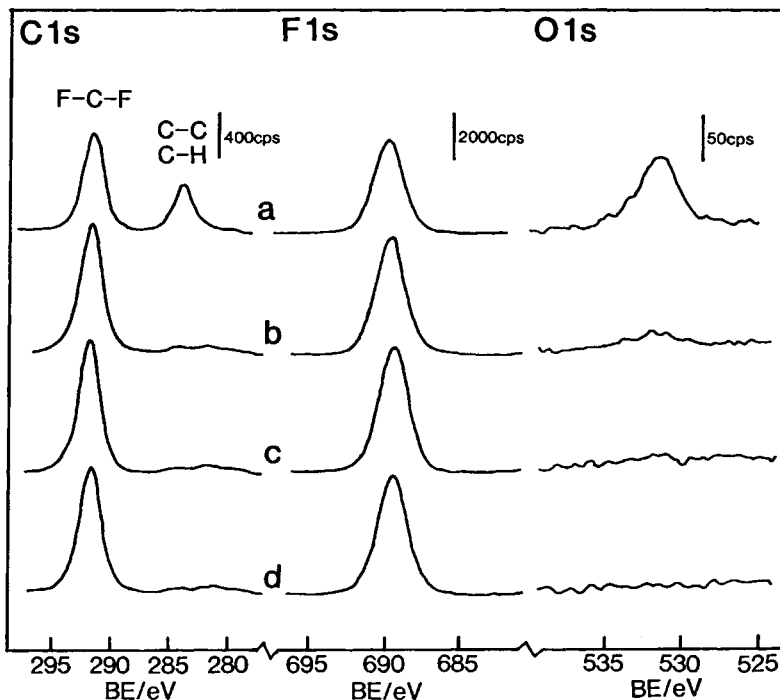


Fig. 2. XPS spectra of PTFE (a) before cleaning and after cleaning with ultrasonic cleaner in (b) methanol, (c) acetone, and (d) *n*-heptane.

sticking coefficient of organic contaminants to the polymer surface compared to metals. However, a fresh surface prepared by cleaving a thick polymer film under vacuum is quickly contaminated because of the creation of dangling bonds by breaking polymer chains in the cleaving process.

Effect of X-ray Irradiation

XPS spectra of PET and PTFE irradiated by X ray are shown in Figures 3 and 4, respectively. There is no remarkable change in the C1s and the O1s spectra of PET by X-ray irradiation for several hours. The intensities of the ester component of C1s and O1s of PET slightly decrease by X-ray irradiation for 24 h. But there is no change of the O1s doublet peaks shape. The ester group in PET seems to be degraded with decarboxylation by X-ray irradiation. The $-\text{CF}_2-$ component of C1s of PTFE decreases remarkably along with increase of other components by X-ray irradiation. The spectral change suggests rapid elimination of fluorine atoms from the polymer.¹

The changes of O1s/C1s of PET and F1s/C1s of PTFE by the X-ray irradiation are shown in Fig. 5. By X-ray irradiation for 24 h, the surface concentration of oxygen on PET and that of fluorine on PTFE decrease to 90 and 50% of that before X-ray irradiation, respectively. Cooling of the sample to 5°C reduces the rate of the degradation of PTFE induced by X-ray irradiation down to 70% of that at 20°C. It is considered one of the more effective methods

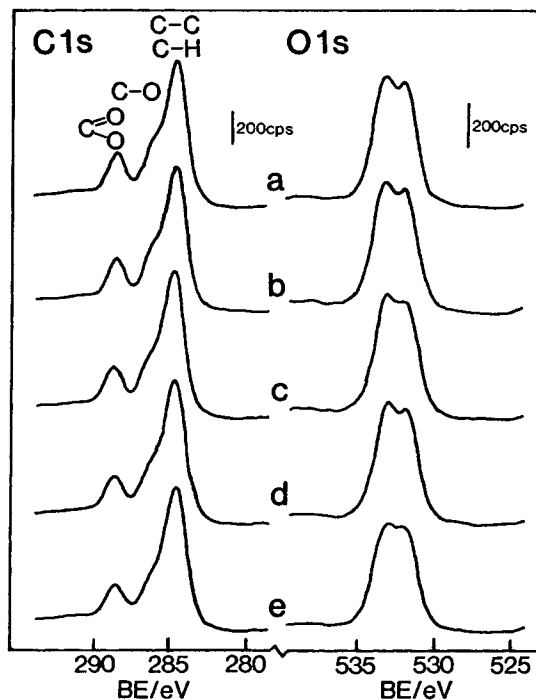


Fig. 3. XPS spectra of PET irradiated by X ray with power of 10 kV and 20 mA at 20°C. Times of irradiation are (a) 0 h, (b) 2 h, (c) 5 h, (d) 9 h, and (e) 24 h.

to reduce the X-ray damage. The rate of degradation of PTFE by X-ray irradiation is observed to be directly proportional to the X-ray power. Decrease of the X-ray power also reduces the rate of degradation but necessitates longer measurement time to obtain spectra with sufficiently low noise level.

The degradation behavior of several industrially important polymers by X-ray irradiation are compared in Fig. 5. Polyimide and PAN have relatively high stability against X-ray irradiation close to PET. Nylon 6 has low stability close to PTFE. Nitrocellulose has extremely low stability, and 50% of the nitroester groups are decomposed in only an hour. As an example of the XPS measurement of a sample containing nitrocellulose, N1s spectra of a magnetic tape are shown in Fig. 6. N1s spectrum in the beginning has two components assigned to nitroester and urethane with almost equal intensities. Intensity of the nitroester component rapidly decreases and almost disappears within 120 min of XPS measurement. We probably underestimate the amount of the nitroester component in a magnetic tape in an XPS measurement that typically takes about an hour.

PET, polyimide, and PAN are quite stable in typical XPS measurement conditions. For PTFE and nylon we need to take degradation induced by X-ray irradiation into consideration in XPS measurements that take over an hour. It is extremely difficult to estimate the real composition on surfaces containing nitrocellulose under typical XPS measurement conditions. Nitrocellulose, with high sensitivity to thermal or mechanical energy, also rapidly loses

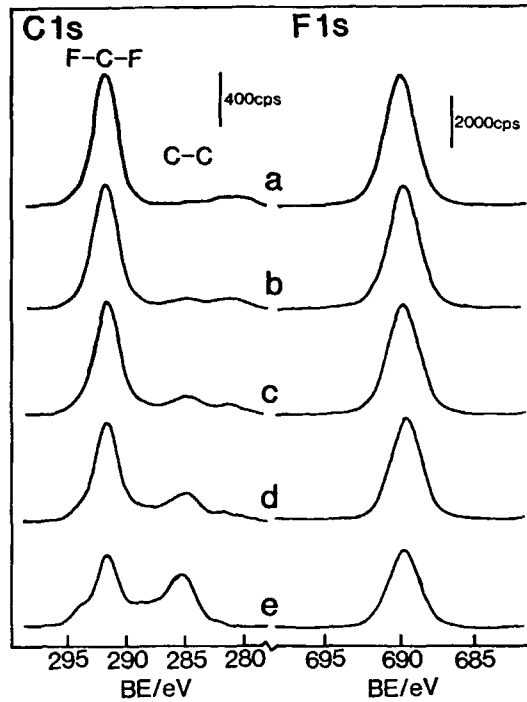


Fig. 4. XPS spectra of PTFE irradiated by X ray with power of 10 kV and 20 mA at 20°C. Times of irradiation are (a) 0 h, (b) 2 h, (c) 5 h, (d) 9 h, and (e) 24 h.

the nitroester group by X-ray irradiation. Nylon 6 and polyimide are considered to be decomposed with elimination of amide and imide groups, respectively, from the main chains by X-ray irradiation. PTFE is known to have high thermal

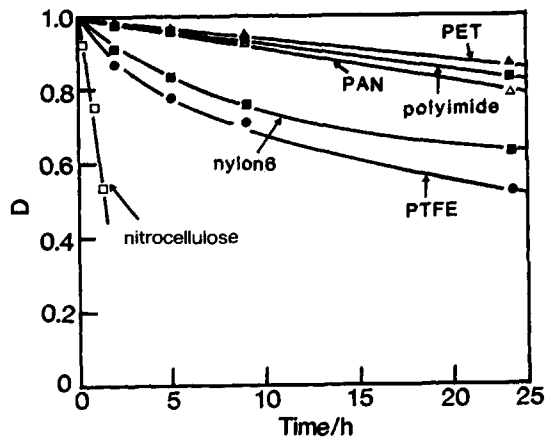


Fig. 5. Surface compositions of polymers by irradiation of X ray with power of 10 kV and 20 mA *in vacuo* of 3×10^{-8} torr at 20°C. Degradation parameters (D) are O1s/C1s for PET, F1s/C1s for PTFE, and N1s/C1s for nylon 6, polyimide, PAN, and nitrocellulose. These values are normalized to each sample without irradiation.

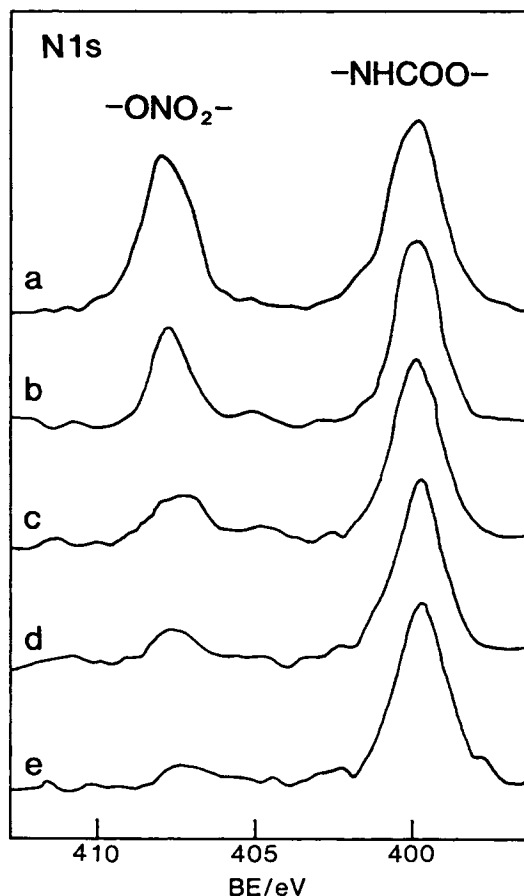


Fig. 6. Change of a N1s spectrum of a magnetic tape containing nitrocellulose in the XPS measurement. Times of irradiation by X ray with power of 10 kV and 20 mA *in vacuo* of 3×10^{-8} torr at 20°C are (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min, and (e) 120 min.

stability, but fluorine atoms are quickly eliminated from polymer chains by X-ray irradiation leaving carbon atoms behind.

PAN is presumed to lose cyano groups from the main chain by X-ray irradiation because of a decrease of N1s intensity with no change in peak position and also a decrease of the component assigned to the cyano group in the C1s spectrum. The degradation behavior of PAN induced by X-ray irradiation is very different from that by thermal treatment. PAN forms a conjugated aromatic ladder structure by the cyclization reaction of cyano groups by thermal treatment in air.^{6,7} The difference between the degradation behavior induced by X-ray irradiation and that by thermal treatment is considered to come from differences in activation energies of the two processes. Activation with high energy by X-ray irradiation may be able to initiate reactions that cannot occur in a thermal process.

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