Surface Damage of Organic Materials during XPS Analysis (1)

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Organic Materials Group of Surface Analysis Society of Japan is investigating the surface damage of the organic materials during X-ray photoelectron spectroscopy (XPS) analysis. Round-robin tests are being conducted to evaluate the criteria for assessing sample damage and to select standard samples for use in testing [1]. In this study, XPS data on nitrocellulose obtained from three organizations were analyzed. The results suggest that dissociation of the NO_2 group depends on the measurement time and that the power of a the X-ray source and its distance from the samples affect the dissociation. In addition, the measurement time multiplying by the area of the Ag3d5 peak was used as a parameter to estimate sample damage. The results show that the attenuation curves have almost the same features regardless of the different measurement conditions used at the same organization. This parameter could be used to control sample surface damage during XPS analysis.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is known to be a low-destructive method as compared with other surface analysis techniques. However, surface damage during XPS analysis should be taken into account in the case of organic materials [2-4]. XPS analysis of organic materials causes such effects as polymerization,reduction, evaporation of volatile components, bleeding out of additives and speeding up of chemical reaction processes. The causes of surface damage include various factors,such as photo degradation by X-ray irradiation, heat radiation from the X-ray source, emission of secondary electrons from an X-ray filter and photo-electrons from the samples, oxidation and contamination.

Organic Materials Group of Surface Analysis Society of Japan is investigating the surface damage done to organic materials during XPS analysis. Round-robin tests are being conducted to estimate the damage qualitatively and quantitatively. The nitro-cellulose membrane and the PTFE membrane have been selected as standard samples. XPS data were collected from eleven participating organizations.

This paper concerns an analysis that was made of the XPS data on nitro-cellulose obtained from three organizations.

2. Experimental procedure

Nitrocellulose membranes were used as the samples for evaluating surface damage during XPS analysis. A sputtered silver plate was used for reference to compare the X-ray density. Damage was compared for the apparatus of three participating organizations: NISSAN ARC, LTD. (BE), S.B. TECHNO-RESEARCH CO., LTD. (DH), Fuji Xerox Co., Ltd. (BK). The apparatus used for XPS measurements were the PHI ESCA-5600 (BE) and the VG ESCA LAB-220i-XL (DH and BK), both of which were equipped with a conventional Mg-Kα X-ray source. The XPS measurement conditions were as follows. At BE, the power of the X-ray source was varied from 100 to 300 W, while keeping the distance between the X-ray source and the sample at about 5 mm. At DH and BK, the distance was varied from 15 to 35 mm, while keeping the power constant at 200 W. XPS measurements were performed for the C1s, O1s and N1s peaks

in the profile mode under continuous X-ray irradiation for approximately 2 hours. The surface damage was compared by using the Xt/Xo values (X = N1s/C1s or O1s/C1s) [5]. Xt is its value at time t and Xo is its value at the first cycle. Time t is irradiation time at the intermediate point of the cycle. The area of each N1s peak was estimated only for a high-binding energy component of the two N1s peaks attributed to the NO2 group of the nitrocellulose samples.

3. Results and Discussion

3.1 Time, power and distance dependence

Figure 1 shows XPS spectra of nitrocellulose measured at BE. The N1s peak clearly decreases in intensity with increasing measurement time. Figure 2-4 plot the Xt/Xo values observed at each organization. The areas of the N1s and the O1s peaks decrease as the measurement time increases. Under the harshest condition at all three organizations, almost all of the NO2 group decomposed from the measured surface of nitrocellulose within 120 min. The attenuation curves were obtained approximately by an exponential function, because of the decrease in the N1s/C1s ratio due to the dissociation of the NO2 group.

In the measurement mode at BE by varying the power of the X-ray, damage process proceeded more quickly as the power was increased. In the measurements mode at DH and BK by varying the distance, damage process proceeded more rapidly as the distance was shortened. These results reveal that the damage rate during XPS analysis depends on the power of the X-ray source, its distance from the samples and elapsed measurement time.

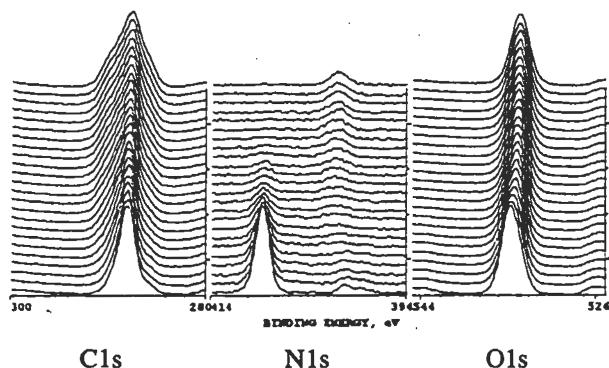

Fig.1 XPS spectra of nitrocellulose measured at BE (300 W)

3.2 Relative X-ray dose

In order to more easily compare XPS data obtained from each organization, an attempt was mode to select more quantitative parameter than the measurement time. The parameter defined in this study was the area of the Ag3d5 XPS peak multiplied by the measurement time which is referred to here as the relative X-ray dose. Figures 5-7 plot the Xt/Xo ratio in relation to this parameter. Compared with the evaluation based on measurement time, the attenuation curves plotted in relation to the relative X-ray dose show the same features regardless of the different conditions used at each organization. In this case as well, the area of the N1s peak was approximated by an exponential function, because the decline stemmed from the dissociation of the NO2 group. The results indicate that plotting the attenuation in relation to the relative X-ray dose makes it possible to estimate the sample damage independent from the measurement conditions, such as the power of the X-ray source and its distance from the sample. Using the resultant curves makes it possible to compare the sample damage caused by each apparatus.

3.3 Comparison among three organizations

Figure 8 shows the typical N1s/C1s curves obtained at the three organizations. The curves are observed to have different features. Figure 9 shows the areas of the Ag3d5 peak plotted against the half-life of the Xt/Xo ratios. At the same organization, the half-life decreased as the area of the Ag3d5 peak increased indicating that sample damage proceeded more quickly. This result indicates that the half-life is influenced by the X-ray density, which is given by the area of the Ag3d5 peak. Figure 10 plots the areas of the Ag3d5 peak in relation to the relative X-ray dose that should the half-life of the Xt/Xo ratios. The plots indicate that regardless of the X-ray density, the relative

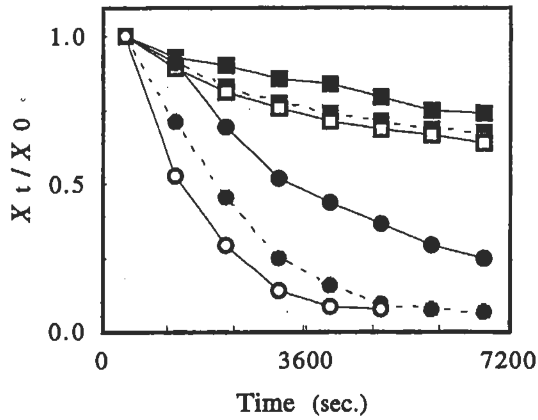

Fig. 2 Plots of Xt/X_0 vs. measurement time at BE
●: N1s/C1s (100 W) ■: O1s/C1s (100 W)
●: N1s/C1s (200 W) ■: O1s/C1s (200 W)
○: N1s/C1s (300 W) □: O1s/C1s (300 W)

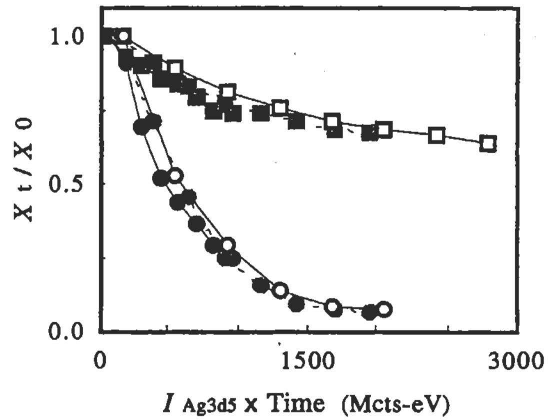

Fig. 5 Plots of Xt/X_0 vs. relative X-ray dose at BE
●: N1s/C1s (100 W) ■: O1s/C1s (100 W)
●: N1s/C1s (200 W) ■: O1s/C1s (200 W)
○: N1s/C1s (300 W) □: O1s/C1s (300 W)

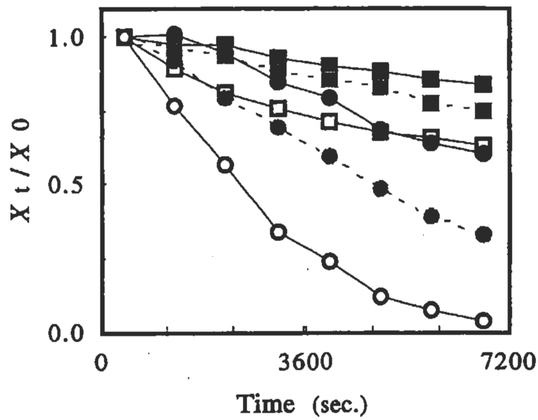

Fig. 3 Plots of Xt/X_0 vs. measurement time at DH
●: N1s/C1s (35 mm) ■: O1s/C1s (35 mm)
●: N1s/C1s (25 mm) ■: O1s/C1s (25 mm)
○: N1s/C1s (15 mm) □: O1s/C1s (15 mm)

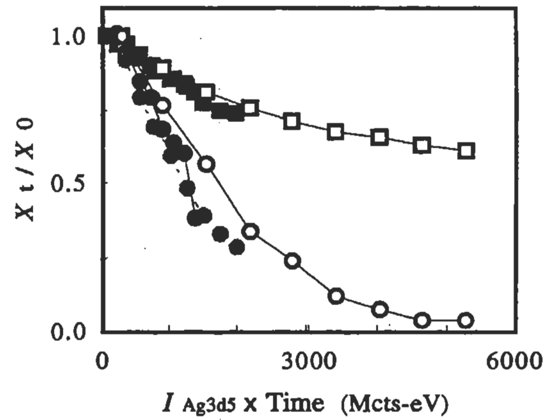

Fig. 6 Plots of Xt/X_0 vs. relative X-ray dose at DH
●: N1s/C1s (35 mm) ■: O1s/C1s (35 mm)
●: N1s/C1s (25 mm) ■: O1s/C1s (25 mm)
○: N1s/C1s (15 mm) □: O1s/C1s (15 mm)

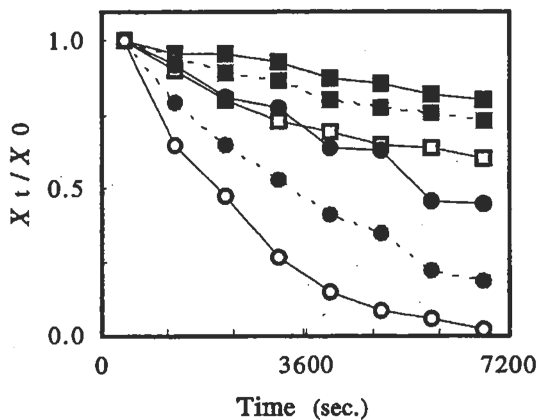

Fig. 4 Plots of Xt/X_0 vs. measurement time at BK
●: N1s/C1s (35 mm), ■: O1s/C1s (35 mm)
●: N1s/C1s (25 mm), ■: O1s/C1s (25 mm)
○: N1s/C1s (15 mm), □: O1s/C1s (15 mm)

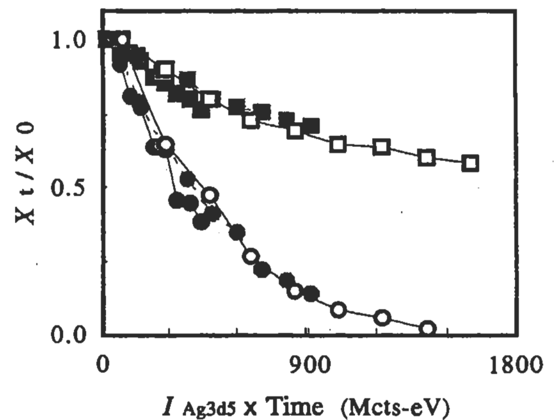

Fig. 7 Plots of Xt/X_0 vs. relative X-ray dose at BK
●: N1s/C1s (35 mm) ■: O1s/C1s (35 mm)
●: N1s/C1s (25 mm) ■: O1s/C1s (25 mm)
○: N1s/C1s (15 mm) □: O1s/C1s (15 mm)

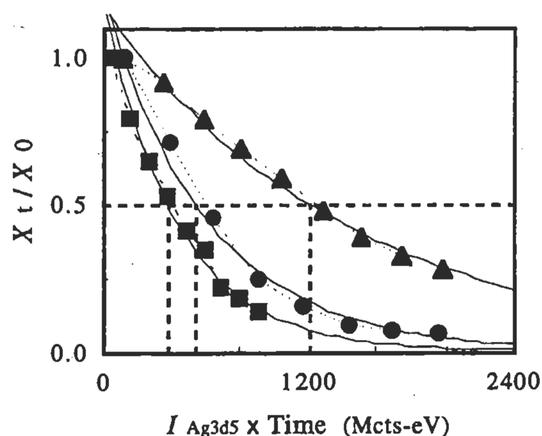

Fig. 8 Plots of Xt/Xo vs. measurement time
● : N1s/C1s (200 W, 5 mm) at BE
▲ : N1s/C1s (200 W, 25 mm) at DH
■ : N1s/C1s (200 W, 25 mm) at BK

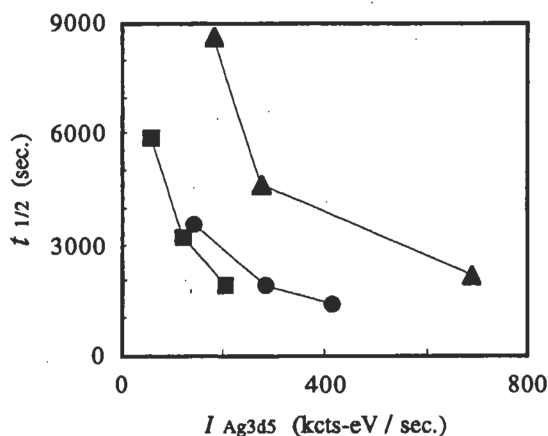

Fig. 9 Plots of half life vs. I_{Ag3d5}
● : BE ▲ : DH ■ : BK

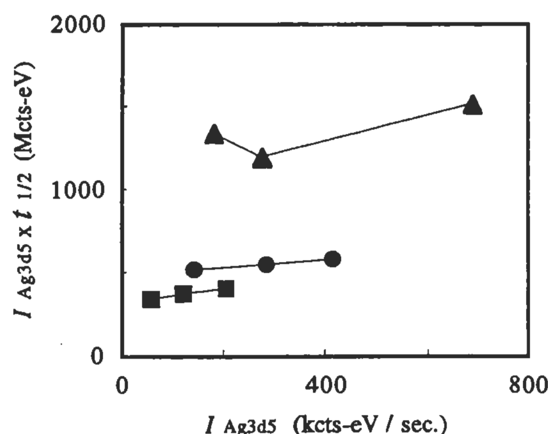

Fig. 10 Plots of $D_{1/2}$ vs. I_{Ag3d5}
● : BE ▲ : DH ■ : BK

X-ray dose has almost the same value at the Xt/Xo ratio of 0.5. Therefore, the $D_{1/2}$ value, defined by the relative X-ray dose at the half-life of the Xt/Xo ratio, can be utilized to control the degree of sample damage.

4. Conclusions

The surface damage done to samples is a serious issue in XPS analysis, and some evaluations of sample damage resulting from XPS analysis have been carried out. However, it has been not so easy to normalize sample damage and to make comparisons among different apparatus. The results of this study show that the $D_{1/2}$ value is not useful in estimating the damage that the apparatus causes to samples. This is because the intensity of the Ag3d5 peak is more affected by the detection conditions of the apparatus, such as the measurement area and Detector efficiency, whereas sample damage reflects the conditions of the X-ray source. The $D_{1/2}$ value is useful in standardizing the degree of sample damage that occurs during XPS analysis. For example, when we want to obtain the standard XPS spectra at the same level of sample damage, the power, distance and the measurement time of an X-ray source can be determinate by applying the $D_{1/2}$ value of nitrocellulose to the samples. In the future, an attempt will be made to propose more suitable parameters of the surface damage during XPS analysis.

5. References

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