

Surface Damage of Organic Materials during XPS Analysis (2)

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Various evaluation and standardization methods to analyze surface damages of organic materials during XPS measurements have been proposed using N1s peak intensity profile of nitrocellulose as a standard material. From the fitting of first order decomposition rate equation for nitro groups to the plots of normalized N1s intensity against measuring time and/or relative x-ray dose, three types of 'apparatus damaging factors' α , β and γ are confirmed to be useful for the evaluation of surface damage. We have also suggested the value of making a database of specific damaging factors for various materials and using 10% damaging and/or half-damaging relative x-ray doses as measures of damaging ability.

1. Introduction

The x-ray photoelectron spectroscopic (XPS) measurements of the organic materials have been widely carried out in many fields. However, it has been indicated that the intensity, configuration, etc. of some peaks may change during measurement because of the surface damage of samples including decomposition of components by x-ray irradiation[1-5]. Therefore, for the materials that are easy to decompose, one must measure XPS within a short time or after the examination of measuring conditions.

In this report, we propose a simple model for the decomposition of nitrocellulose and the evaluation methods for the surface damages of organic materials during XPS measurements.

2. Experiments

The sample used was a nitrocellulose membrane, abbreviated as NC, with a pore size of 0.1 μ m purchased from Advantec Toyo. Before the measurement of nitrocellulose, Ag3d_{5/2} peak of silver plate was measured after mild etching with argon ion for the calculation of relative x-ray dose. The conditions for NC and silver were exactly the same.

XPS measurements of NC were carried out using profile mode with 12 cycles to obtain O1s, N1s and C1s high-resolution peaks. During a set of measurements, the x-ray was continuously irradiated to the sample surface. The power of x-ray source P was varied from 100 to 400W at a constant voltage of 10kV and

the distance between the sample surface and the anode of x-ray source, L , was also varied to evaluate the various factors.

The apparatus used was Physical Electronics ESCA5600 with the conventional MgK α x-ray source. The electron take-off angle, ETOA, from the surface was 45°. The alternative apparatus, VG ESCALAB 220i-XL, with conventional MgK α and monochromatic AlK α x-ray sources at ETOA of 45° was also used for the confirmation of the validity of the method described in this report.

3. Results and Discussions

3.1 Relationship between N1s peak intensity and x-ray irradiation time

As we have pointed out[6], the N1s peak attributed to nitro group decreases with measuring cycle and then disappears more rapidly at higher P and shorter L . This indicates that nitro groups have decomposed during XPS measurement.

Figure 1 shows a few examples of the relationship between peak intensity I_N , represented by the area of the peak attributed to nitro groups, and the measuring time t . This time is defined using the measurement cycles, and each cycle time is defined as the interval between the start and the end of a measurement cycle. The peak intensity rapidly decreases in an early period in the cases of shorter L and higher P and finally the peak vanishes. The intensity of C1s, however, has been recognized to increase gradually by

small amounts with time. This may be attributed to the increase in the photoelectron attenuation length due to the surface structure change, especially decrease in atomic density by the elimination of nitro groups. Thus the decomposition process of nitrocellulose has been analyzed based on the N1s peak intensity.

Assuming that both the decomposition rate of nitro groups and the peak intensity I_N are proportional to the concentration of that group in surface layer at the time t , the following first order equation will be approximately derived,

$$I_N = I_N^0 \exp(-kt) \quad (1)$$

where I_N^0 is the initial value at time zero calculated by the extrapolation and k is the decomposition rate constant. By the fitting Eq.(1) to the relationship between $\ln I_N$ and t , one can obtain I_N^0 and k . However, in the case that the decomposition rate is very high the fitting is not so good. Therefore, the fitting has been done using data points until to half the value of I_N^0 or initial 3 or 4 points. This discrepancy will be due to changes in decomposition mechanism or surface structure.

Using fitting data, normalized intensity of N1s peak originated from nitro group, B_N , is calculated as follows:

$$B_N = I_N / I_N^0 = \exp(-kt) \quad (2)$$

Figure 2 shows the plots of $\ln B_N$ versus t , which give linearity down to the point at about $B_N = 0.5$. Thus the half-life of N1s peak of nitro group, $t_{1/2}$, will be calculated.

As shown in Fig.3, the value of k increases in proportion to P and with the decrease in L . Thus, the surface degradation rate and its behavior of an apparatus and/or a set of conditions can be evaluated by using k or $t_{1/2}$. It is inefficient, however, to determine those values at many conditions by varying L and P . Therefore, considering that k is proportional to P , inverse L^n and $\cos\theta$, θ is the angle of x-ray incident from the surface normal, the characteristic constant of an apparatus α can be calculated from Eq.(3).

$$k = \alpha \frac{P \cos \theta}{L^n} \quad (3)$$

Here, α is defined as 'apparatus damaging factor, ADF'. The value of n has been obtained as 1.78 from other experiments, indicating that the x-ray source used is not a point source. If α is constant for an

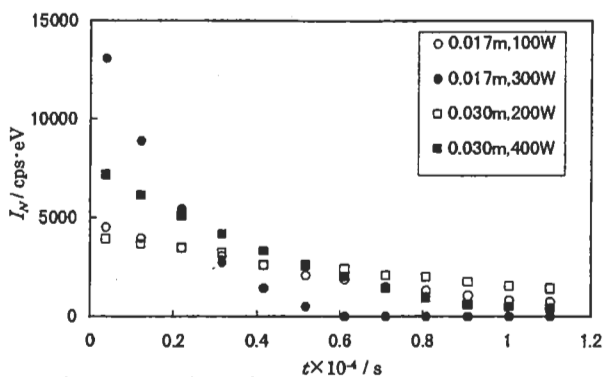


Fig.1 Reduction of N1s peak intensity I_N with x-ray irradiation time t .

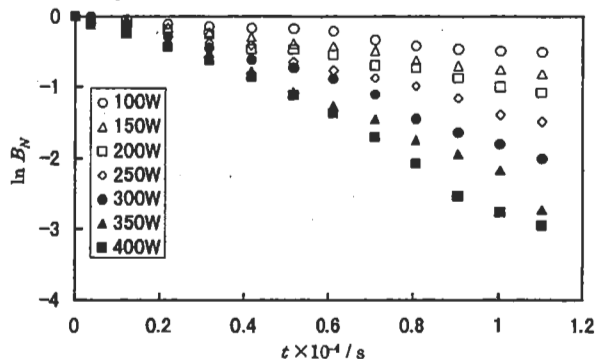


Fig.2 Relationship between $\ln B_N$ and t at $L=0.030m$.

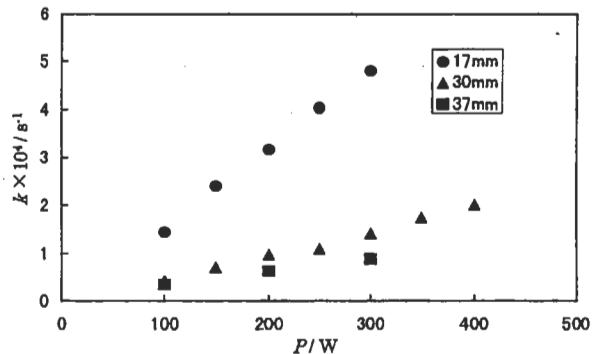


Fig.3 Relationship between k and P .

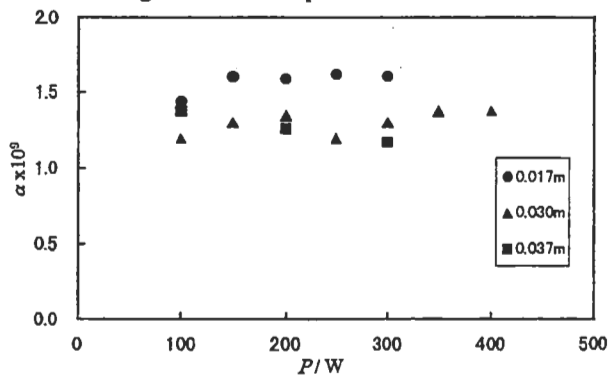


Fig.4 Relationship between α and P .

apparatus or an x-ray source, it is a useful factor to compare the degradation efficiencies of the apparatuses used and is very available because it can be obtained by measuring only one time of I_N under a suitable condition. Figure 4 is the plots of α against P , indicating

that α is about 1.3×10^{-9} at $L=0.030$ and 0.037m . However, the α at $L=0.017\text{m}$ has somewhat higher value than those for other conditions. At any rate, there is a disadvantage to use α value because it is difficult for some apparatuses to determine n and L precisely.

By the way, the extrapolation method using Eq.(1) or another equations from different damaging processes is very available and practicable to obtain XPS results of no damaged sample at the time zero.

3.2 Introduction of relative x-ray dose and definition of ADF β

To evaluate x-ray flux to the sample surface we have introduced the concept of 'relative x-ray dose, D ' [6] to the following analysis.

The relative x-ray dose D is defined as

$$D = I_{Ag} t = f_{Ag/N} I_N^0 t \quad (4)$$

where I_{Ag} is the peak intensity of $\text{Ag}3d_{5/2}$ under the same condition as nitrocellulose and will be constant for a set of measurements, and $f_{Ag/N}$ is a factor defined as $f_{Ag/N}/I_N^0$. Substitution of Eqs.(3) and (4) into Eq.(2) gives

$$B_N = \exp\left(-\frac{\alpha P \cos\theta}{L^n} \frac{D}{I_{Ag}}\right) \quad (5)$$

Furthermore, I_{Ag} is also considered to be in proportion to P , $\cos\theta$, and $1/L^n$ as

$$I_{Ag} = K_{Ag} \frac{P \cos\theta}{L^n} \quad (6)$$

where K_{Ag} is a parameter for $\text{Ag}3d_{5/2}$ under specific condition. Substituting this equation into Eq.(5) gives

$$B_N = \exp\left(-\frac{\alpha}{K} D\right) = \exp(-\beta D) \quad (7)$$

Here, β is another apparatus damaging factor. If these equations hold true, all experimental data must be on one line even if the L and P parameters are varied. Figure 5(a) shows the relationship between $\ln B_N$ versus D , indicating that the data points at $L=0.030$ and 0.037m are approximately on one line. The deviation of the data at $L=0.017\text{m}$ cannot be described with a proper reason. As shown in Fig.5(b), the data points for non-monochromatic x-ray source are also on one line and do not agree with those for monochromated x-ray mainly due to the difference of measuring conditions. Anyhow

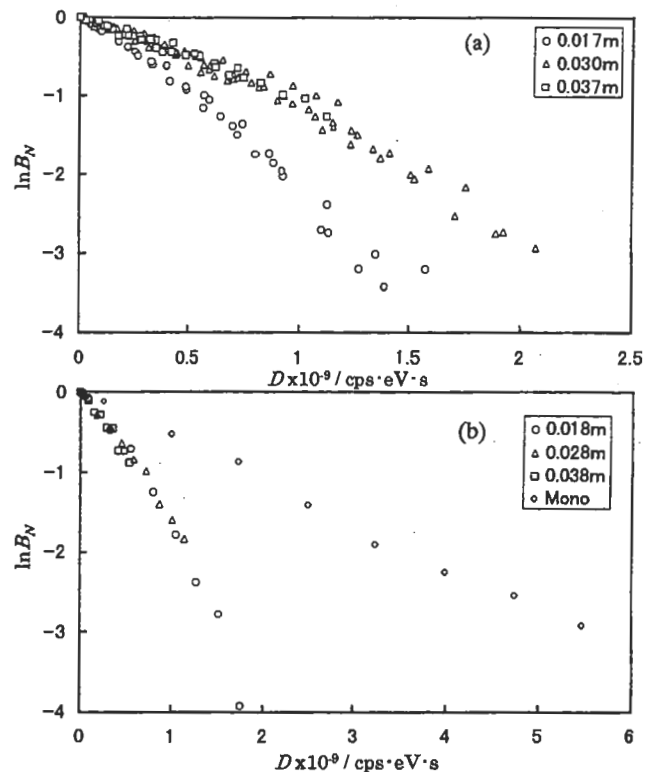


Fig.5 Plots of $\ln B_N$ against D by Physical Electronics ESCA5600(a) and VG ESCALAB 220i-XL(b).

all data in Fig.5 are on straight lines at the B_N range from 1 to 0.5, giving β value as $9.8 \times 10^{-10} (\text{cps} \cdot \text{eV})^{-1} \cdot \text{s}^{-1}$ for $L=0.030$ and 0.037m in Fig.5(a) and $1.7 \times 10^{-9} (\text{cps} \cdot \text{eV})^{-1} \cdot \text{s}^{-1}$ for conventional x-ray source in Fig.5(b). Thus, the β can be obtained by a measurement under a set of conditions within a range where all data points are on one line. Then the β is a valuable parameter to compare the measuring conditions of each apparatus and gives the direction in order to get a good spectrum close to the true one for degradable materials. Besides, the relative x-ray dose D at a characteristic point of surface damage of nitrocellulose will be a measure to evaluate the damage of another degradable materials, especially organic materials, and nitrocellulose will be a candidate for the reference material.

In any way, there are some precautions and problems to use D as follows:

- (1) The conditions of detection side assembly should be same for all samples.
- (2) The value ADF β should be obtained again when the x-ray source and its assembly have been exchanged.
- (3) When using monochromated x-ray, the value of β should also be obtained again, and must care for the effects of electrostatic charge

and the electron flux from neutralizer.

3.3 Specific damaging factor F_X

Considering that nitrocellulose film will be a standard material for the evaluation of surface damage as described above, we define, here, 'specific damaging factor, F_X ' as the ratio of β_X for a material X using Eq.(7) to that for nitrocellulose as follows:

$$F_X = \beta_X / \beta_{NC} \quad (8)$$

It is valuable to prepare its database that gives directions for determining conditions of degradable materials. However, the concept of F_X has an approximation that the effects of x-ray, secondary electron, photoelectron, heat irradiation and others on the surface damage are almost equal for each instrument. And also, there is still a problem how to determine the damaging mechanism and the evaluation parameter of a specific material. These will be investigated in near future.

3.4 Introduction of a concept of $D_{0.1NC}$

As described in section 3.2, the D value at a characteristic point will be one of useful parameters. Thus, we propose $D_{0.1NC}$ as the maximum permissible dose at which the surface damage has proceeded up to 10% of the final damage, i.e. $B_N=0.9$, as follows:

$$D_{0.1NC} = -\frac{1}{\beta_{NC}} \ln(0.9) = \frac{0.105}{\beta_{NC}} \quad (9)$$

From the value of $D_{0.1NC}$, the permissible time is also obtained for a set of measuring conditions. As the β_N for nitrocellulose is $9.8 \times 10^{-10}(\text{cps} \cdot \text{eV})^{-1} \cdot \text{s}^{-1}$ under the conditions used here, $D_{0.1NC}$ is obtained as $1.1 \times 10^8 \text{ cps} \cdot \text{eV} \cdot \text{s}$. Therefore at $L=0.030\text{m}$ and $P=200\text{W}$, to measure within about 1000s is recommended for nitrocellulose.

Besides, it can be practically valuable to use $D_{0.1NC}$ as a measure of surface damage of other materials. Examples of its expressions are:

(1) XPS of this material has been measured within $D_{0.1NC}$.

(2) As this sample is not so degradable, XPS has been measured within $5D_{0.1NC}$.

If the F_X of a specific material X has been known, the maximum permissible dose $D_{0.1X}$ will be also obtained by Eq.(10)

$$D_{0.1X} = -\frac{1}{\beta_X} \ln(0.9) = \frac{0.105}{F_X \beta_{NC}} \quad (10)$$

3.5 Half-damaging relative x-ray dose $D_{1/2}$

For the evaluation of surface damage and to

determine the measuring conditions, the half-damaging relative x-ray dose $D_{1/2}$, is also a useful parameter as we have pointed out elsewhere [6], and can be used in the same way of $D_{0.1X}$. The $D_{1/2}$ can be determined by fitting Eq.(7) to the data points or by interpolation. The latter method is simpler than the former, and the values determined by both methods are approximately equal with each other. In these methods, the calculated initial intensity at time zero I_N^0 is not needed for the normalization because the half-life of I_N does not depend on the initial value.

Furthermore, the reciprocal value of $D_{1/2}$ is considered to be proportional to decomposition rate constant, we can define one more ADF γ as follows:

$$\gamma = \frac{1}{D_{1/2}} = -\frac{\beta}{\ln(1/2)} = \frac{\beta}{\ln(2)} = 1.44\beta \quad (11)$$

4. Conclusion

To evaluate the surface damage of organic materials and to establish its method, we have measured XPS of nitrocellulose as a standard material. Applying the first order decomposition rate equations to the reduction feature of N1s peak intensity originated from nitro groups with the duration of x-ray irradiation, we have proposed three types of 'apparatus damaging factors' α , β and γ . These are valuable and useful to compare and determine measuring conditions and to evaluate surface damage of nitrocellulose. It has been also suggested that the specific damaging factor should be summarized as a database and that 10% damaging and half-damaging relative x-ray doses, $D_{0.1NC}$ and $D_{1/2}$, are also considered to be measures of the surface damage of degradable materials.

5. References

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