

Surface Damage of Organic Materials during XPS Analysis(3)

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It is known that organic materials exhibit a wide range of damage rates. We examined surface damage for nitrocellulose (NC) and teflon (PTFE) samples after 120 minutes at an X-ray Al K α source power in a range of 100-300 W. NC decomposed considerably rapid due to the X-ray irradiation, while PTFE didn't almost degrade. In order to analyze the decomposition process of nitrocellulose due to X-ray induced surface damage, we estimated where the cleavage of the NC occurs from the bond order and two-center bond energy by AM1 MO calculations using the dimer model, C₁₂H₁₈N₄O₁₉. The valence X-ray photoelectron spectra at the initial time and after 120 minutes were analyzed by the HAM/3 MO and deMon density functional theory (DFT) calculations using model monomer molecules, C₆H₁₀N₂O₁₁ and C₆H₆O₆, respectively. The simulated results afforded us that NO₂ groups of the nitrocellulose cleave mainly due to the X-ray radiation. The scission of NO₂ group was confirmed from the TOF-SIMS measurements of NC.

Introduction

X-ray induced sample damage is a common problem during the XPS analysis of materials in any marker XPS instruments, and can cause the spectrum to change with exposure time. It is known that organic materials exhibit a wide range of damage rates. Teflon (PTFE) degrades almost imperceptibly slowly, while nitrocellulose (NC) and chlorine-containing polymers degrade quickly. The first guide to the damage rates of polymer was performed by Beamson and Briggs[1]. They indicated the degradation indices of aliphatic ether, fluorine-and chlorine-containing polymers for the percentage damage after 500 minutes at an X-ray source power of 1.4 kW.

In the connection with the sequel works of "Surface Damage of Organic Materials during XPS Analysis (1) and (2)", we, here, examine surface damage for nitrocellulose and teflon samples after 120 minutes at an X-ray Al K α source power in a range of 100-300W. We analyze the decomposition process of nitrocellulose due to X-ray induced surface damage from the X-ray photoelectron spectra at the initial time and after 120 minutes by the HAM/3 MO[2] and deMon density functional theory(DFT) [3] calculations using model monomer molecules.

Practical Details of Calculation

1) MO calculations for XPS analysis

For the comparison between calculations for a single molecule of the oligomer or monomer model and experiments on a solid polymer, we must shift each computed vertical ionization potentials (VIPs), I_k by a quantity WD as $I_k(\text{EF}) = I_k - \text{WD}$, to convert to ionization energy $I_k(\text{EF})$ relative to the Fermi level. This quantity WD denotes the sum of the work function of the sample and other energy effects, as stated in our previous studies [4-8].

For ionization of an electron from molecular orbital (MO) ϕ_k , for example, we can apply the Janak theorem[9]. For the VIPs of the valence regions, we use the so-called diffuse ionization (DI) model which Asbrink et al. [2] proposed in the HAM/3 method. In the rDI model, half of an electron is removed evenly from the valence MOs and the negative of the resulting orbital energies correspond to calculated VIPs. This allows us to obtain all the valence VIPs in a single calculation. The molecules [C₆H₁₀N₂O₁₁, C₆H₆O₆, and F-(CF₂-CF₂)₃-F] were calculated by HAM/3 MO and deMon DFT programs [2, 3]. For the geometry of the molecules, we used the optimized cartesian coordinates from the semiempirical AM1 (version 6.0) method [10].

The deMon calculations were performed with the exchange-correlation potential labeled as B88/P86, made from Becke's 1988 exchange functional [11] and Perdew's 1986 correlation functional [12].

In the program, we used a nonrandom grid and a polarized valence double-zeta (DZVP) basis (621/41/1*) for C, N, O and F, and (41) for H with auxiliary fitting functions labeled (4,4;4,4) for C, N, O and F, and (3,1;3,1) for H.

In order to simulate the valence XPS of polymers theoretically, we constructed from a superposition of peaks centered on the VIPs, I_k . As was done in previous works [4-8], each peak was represented by a Gaussian curve. The intensity was estimated from the relative photoionization cross section for Al $K\alpha$ radiation using the Gelius intensity model [13]. For the relative atomic photoionization cross-section, we used the theoretical values from Yeh [14]. In the case of the linewidth (WH(k)), we used $WH(k) = 0.10 I_k$ for the models, as adopted in previous works [4-8].

2) MO calculations for a prediction of cleavage of polymer-bond

The electronic structure of model molecules [C₁₂H₁₈N₄O₁₉, and F-(CF₂-CF₂)₅-F] were calculated using a semiempirical AM1 program (version 6.0). Bond-orders and two-center bond energies of the model molecules were obtained from the optimized results by the energy gradient method, as indicated in the previous works [15, 16].

Experimental

We used a commercially-available nitrocellulose (NC) membrane with a pore size of 0.1 μ m purchased from Advantec Toyo, and poly(tetrafluoroethylene) (PTFE) (Scientific Polymer Products, Inc.). For PTFE, we used the pressed disc.

XPS measurement

Experimental photoelectron spectra of the samples due to the X-ray irradiation were obtained on a PHI 5400 MC ESCA spectrometer as one of normal XPS instruments, using unmonochromated Al $K\alpha$ radiation. The spectrometer was operated at an X-ray Al $K\alpha$ source power in a range of 100-300 W, at a constant voltage of 15 kV, and at a constant current of 40 mA. The photon energy was 1486.6 eV. A pass energy of 35.75 eV was employed for high-resolution scans in a valence-band analysis (50 eV of range). The angle between the X-ray source and the analyzer was fixed at 45°. The spot size in the measurement was 3 X 1 mm².

During a set of measurements, the X-rays were continuously irradiated to the sample surface. The use of dispersion compensation yielded an instrumental re-

solution of 0.5 eV with the full width at half-maximum on the Ag 3d line of silver. Multiple-scan averaging on a multichannel analyzer was used for the valence-band region, although a very low photoelectron emission cross section was observed in this range.

Gold of 20 Å thick was deposited on the membrane (or disc) of the samples using an ion sputter unit (Hitachi E 1030) for scanning electron microscope.

A low-energy electron flood gun was used in order to avoid any charging effect on the surface of the sample. We used the Au 4f core level of the gold decoration membrane (or disc) as a calibration reference. The C1s line positions of CH₂ and CF₂ groups in the samples could be fixed at 285.0 and 292.5 eV for NC and PTFE, respectively.

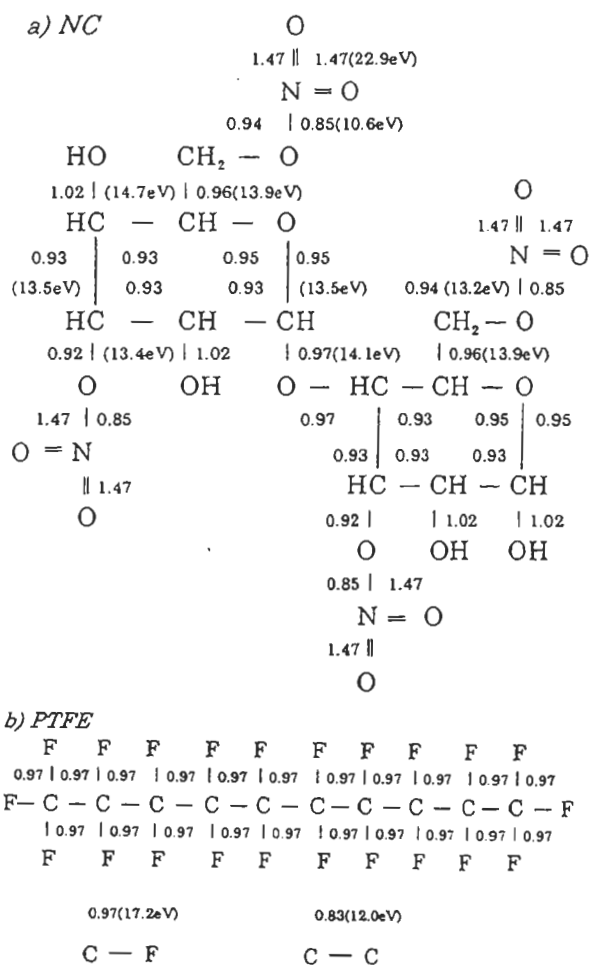


Fig. 1. Bond-order and two-center bond energies (in eV) of the model molecules by the semi-empirical AM1 MO calculations a) nitrocellulose(NC) b) teflon(PTFE)

Results and Discussion

(1) A prediction of cleavage of polymer-bond for NC and PTFE

With an unmonochromated X-ray source the sam-

ple is much closer to the X-ray anode, and thermal effects may be more important. We will, thus, predict where the cleavage of the polymer-bond occurs on X-ray irradiation, although the decomposition process of surface damage due to the irradiation may be very complicated. When we consider the dissociation of the molecule species on the surface as the thermal effects, we can estimate the cleavage of polymer-bonds from the bond-orders and two-center bond energies of the model molecules by MO calculations using AM1 program, as indicated in our previous works[15,16].

In Fig.1a, the bond-order (and two-center bond energies) of O-NO₂ bonds for the model NC showed 0.85(10.6 eV) less than 0.93-0.96(13.4-13.9 eV) and 0.94-1.0(13.2-14.7 eV) for C-C and C-O bonds of NC, respectively. Thus, the cleavage of O-NO₂ bonds occurs first in NC.

For PTFE(Fig. 1b), the two center bond energies of the main chain C-C bonds were evaluated as 12.0 eV, thus much less than 17.2 eV of C-F bonds. We can assume that the cleavage of the PTFE polymer occurs at any bonds of main chain with side chain groups. The prediction corresponds to the positive-ion fragment spectra [16].

In these organic materials(NC and PTFE), O-NO₂ bonds will cleave first to the utmost, since the two-center bond energies is the least value as 10.6 eV. The estimation can result in the scission of O-NO₂ bonds for NC due to the X-ray radiation.

(2) Decomposition process of NC

The decomposition process of NC due to X-ray induced surface damage was observed from the X-ray photoelectron N1s and valence spectra at the initial time and after 120 minutes. The N1s spectra at the initial time disappeared absolutely after 120 minutes at an X-ray Al Kα source power of 300 W. The result corresponds well to the prediction of the scission of NO₂ bonds using MO calculations.

Then, let's consider the decomposition process of NC by analyzing the valence electron spectra which constitute the unique fingerprint. We can see the process from the valence spectra(in Fig. 2a-c) at the initial time and after 60 and 120 minutes due to X-ray irradiation. The mechanism of the cleavage for the model dimer of NC can be written in Fig. 3, by considering the scission of NO₂ bonds as the thermal effect:



In order to analyze the valence spectra in Fig. 2 a and c, we used the model monomers, C₆H₁₀N₂O₁₀ and C₆H₆O₆, respectively, due to the limit of total

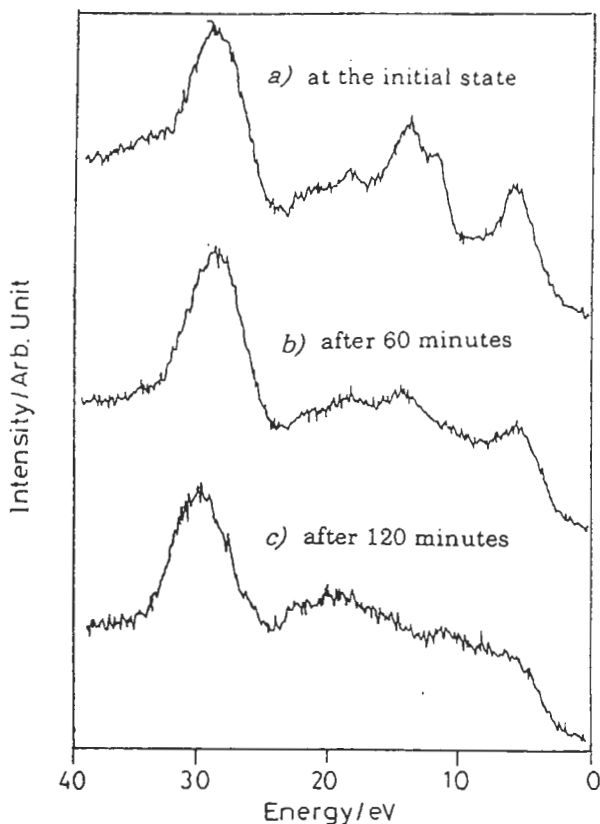


Fig. 2. Valence X-ray photoelectron spectra of NC due to X-ray irradiation
a) at the initial state b) after 120 minutes
c) after 120 minutes

atom numbers of our computer using ab initio de-Mon program(We confirmed that simulated results using model monomers are similar to those of the dimers in Eq. (1) using semiempirical HAM/3 calculations). Fig. 4a and b shows observed valence spectra of nitrocellulose at the initial time and after 120 minutes with the simulated spectra using the monomer models. The good accordance of the simulations with the observed spectra afforded us that NO₂ groups of nitrocellulose cleave mainly due to the X-ray radiation. The result was also confirmed from the TOF-SIMS measurements of the samples.

In the negative-ion mode, the NO₂⁻ and NO₃⁻ fragments can be only seen at the initial time. The fragments after the 120 minutes absolutely disappeared due to the scission of NO₂ groups. The positive-ion fragment spectra at the initial state are considerably similar to those of polyvinyl methyl ether (PVME) in our previous work[16]. This implies that remainder molecular chains consist of carbon, hydrogen, and oxygen atoms, since the NO₂ groups change stable NO₂'s after the NO₂ cleaves first.

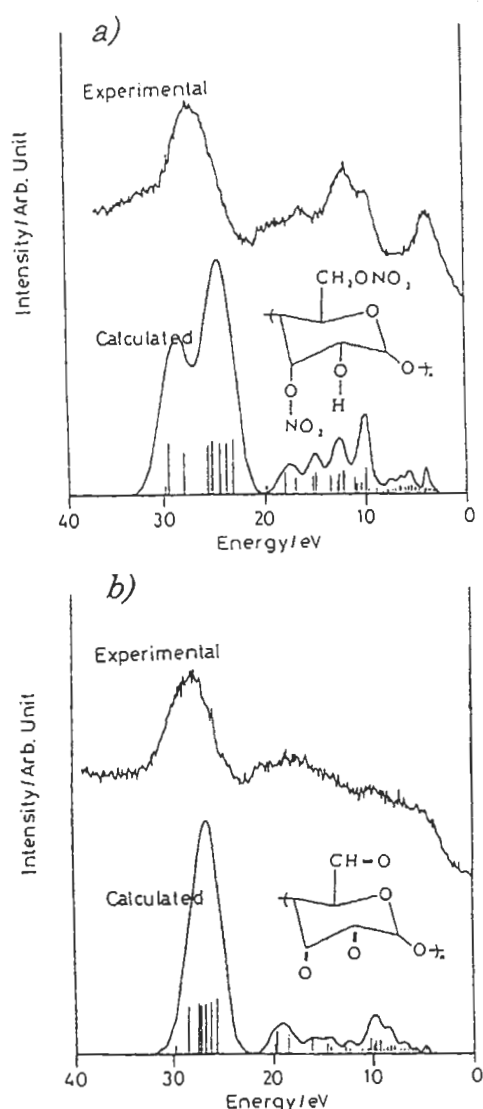


Fig. 3. Valence X-ray photoelectron spectra of NC with the simulated spectra of the model monomer molecule using deMon program due to X-ray irradiation a) at the initial state b) after 120 minutes

(3) Surface damage of PTFE

Although Beamson and Briggs[1] indicated ten percentage damage of PTFE after 500 minutes at an X-ray source power of 1.4 kW, we didn't observe such damage after 120 minutes at an X-ray power of 300 W. The valence spectrum after 120 minutes due to the X-ray irradiation showed considerably good agreement with that at the initial state.

Conclusions

We examined surface damage for NC and PTFE samples after 120 minutes at an X-ray Al K α source power in a range of 100-300 W. The results were analyzed by MO calculations using the model molecules.

- (1) The surface of NC degrades very quickly due to the X-ray irradiation, while PTFE doesn't almost degrade.
- (2) We can predict where the cleavage of NC and PTFE occurs due to thermal decomposition, by considering the bond-order and two-center of bond energies by semiempirical AM1 calculations using model oligomers.
- (3) Observed X-ray photoelectron spectra of NC and PTFE at the initial time and after 120 minutes due to X-ray irradiation can be simulated by the HAM/3 MO and deMon density functional theory(DFT) calculations using the model monomers or oligomers, respectively.
- (4) The decomposition process of NC due to X-ray induced surface damage is written as the following chemical reaction:



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Referee's comments and Authors' answers

Comments: Dr. J. Kawai(kyoto University)

- (1) Judging from the title "*Surface Damage of Organic Materials during XPS Analysis (3)*", this manuscript is the 3rd for the series of the studies. In the Introduction, the relationships to the previous manuscripts "*(1) and (2)*" should be described.
- (2) The thermal effect due to X-ray irradiation of the PHI XPS instrument should be compared with other maker's. I hear X-ray anode of JEOL XPS instruments was designed in order that the thermal damage of samples does not affect. I think PHI apparatus may be good for such units. In this manuscript, authors should indicate that X-ray induced sample damage is a common problem in each maker XPS instrument. I think the thermal effects using monochromated source should be compared with ones with the unmonochromated.

Answers to the comments

- (1) We described in Introduction that this manuscript is the sequel work of manuscripts titled in "*Surface Damage of Organic Materials during XPS Analysis (1) and (2)*".
- (2) As we wrote in the head of the sentence in Introduction, we think thermal damage of the samples due to X-ray irradiation is a common problem in each maker XPS instrument. We cited Beamsom and Brigg's book [1], in order especially to examine the thermal damage of samples due to unmonochromated X-ray irradiation.

Lastly, we acknowledge the referee Prof. J. Kawai very much for his comments.