

Original Paper

Oxidation Process of Phosphite Antioxidants Monitored by ToF-SIMS

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In order to demonstrate the advantages of time-of-flight secondary ion mass spectrometry (ToF-SIMS) as a tool for monitoring of chemical reactions, a typical phosphite antioxidant of bis(2,6-di-*tert*-butyl-4-methylphenyl) pentaerythritol diphosphite (trade name: Adekastab PEP-36, chemical formula: C₃₅H₅₄P₂O₆) was tested to monitor the oxidation process. It could be successfully observed that the PO₄-related ions such as C₂₀H₃₁P₂O₈⁻ and C₃₅H₅₄P₂O₈⁺ replaced the PO₃-related ions such as C₂₀H₃₁P₂O₆⁻ and C₃₅H₅₃P₂O₆⁺ with increasing air-exposure. XPS analysis complemented the quantitative information that almost half the phosphite molecules were oxidized after air-exposure of 48 h. Here we point out that the characteristic ions of PEP-36 are very sensitive to its oxidation state and their intensities have quite wide variation, which may cause the difficulty in quantitative analysis. Comparable studies with ToF-SIMS and XPS are helpful to realize not only qualitative but also quantitative analysis of interested organic molecules on the surface.

1. Introduction

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has a lot of capability for characterization of surface species through the analysis of mass spectra, which are full of qualitative information on the chemical structure of interested species. Changes in the molecular structure and/or the chemical state of key elements can be deduced from the variation in characteristic peak intensities [1]. Another unique advantage of ToF-SIMS is quick data collection, which enables us to monitor the chemical reaction with time resolution of ~1 s order [2]. In order to demonstrate the advantages of ToF-SIMS as a tool for monitoring of chemical reactions, the oxidation process of phosphite antioxidants is discussed.

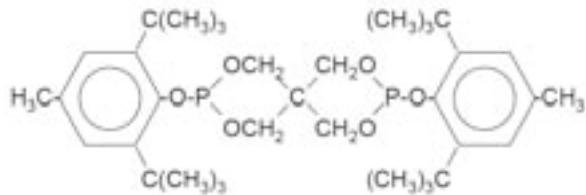


Fig. 1. Molecular structure of PEP-36.

2. Experimental

A typical phosphite antioxidant of bis (2,6-di-*tert*-butyl-4-methylphenyl) pentaerythritol diphosphite (trade name: Adekastab PEP-36, chemical formula: C₃₅H₅₄P₂O₆, supplier: ADEKA), which is often used for stabilization of polymer film [3], is characterized in order to monitor the surface oxidation. Its molecular structure is shown in Fig. 1. The white powder of PEP-36 was dissolved in acetone and cast on the clean Si wafer. It was expected to be easily oxidized from (RO)₃P to (RO)₃PO under atmosphere.

To investigate the changes in molecular structure with increasing air-exposure, ToF-SIMS measurements were performed at just, 0.25 h, 18.5 h and 48 h after the cast. Along with the ToF-SIMS measurements, comparable XPS measurements were performed at just and 48 h after the cast. The cast films of PEP-36 were not the same for each analysis, but they were similarly prepared.

An ION-TOF TOF-SIMS IV system was used for ToF-SIMS measurements. Pulsed Bi₃⁺⁺ ion gun operating at energy of 25 keV, current of 0.1 pA and pulse frequency of 5 kHz was randomly rastered in 200 μm × 200 μm on

the specimen surface. Positive or negative secondary ions were detected with reflectron-type mass spectrometer. The acquisition time to obtain a spectrum was typically 98 sec (30 scan). Under these conditions, total primary ion dose was 1.5×10^{11} ions/cm², which is well below the static limit.

A PHI Quantum 2000 system was used for XPS analysis. Photoelectrons were excited by monochromated Al K α and detected with CHA. The X-ray tube was operated at 34 W. The pass energy of CHA was 187.35 eV for wide-scan spectra and 23.50 eV for narrow-scan spectra. The analyzing area on the specimen surface was almost 200 μm^2 . The take-off angle was 45 degree. The binding energies of the spectra are calibrated by setting the C 1s peak maximum at 284.6 eV.

3. Results and discussion

3.1. XPS Analysis

XPS wide-scan spectra were acquired at just and 48 h after the cast. On both spectra, photoelectrons originating from C, O, P and Si core levels were observed and other lines of unexpected elements were not detected.

XPS narrow-scan spectra of C 1s, O 1s, P 2p and Si 2p are shown in Figs. 2a)-2d). Surface atomic composition was evaluated by relative sensitivity factors method via the instrument quantification software, which was given by manufacturer. Obtained results are tabulated in Table 1. After the air-exposure of 48 h, only C decreased. There was no sign of the changes in chemical state of C, as shown in Fig. 2a). Decrease of C is thought to be the fact that surface oxidation of the cast film leads to desorption of the hindered phenol units. Increase of O is also due to the surface oxidation.

The atomic ratio of O / P increased from 3.2 to 3.5. It means that almost half the phosphate molecules on the surface were oxidized to phosphate. Here we should note that the origins of oxygen are not only PEP-36 but also the native oxide on the Si wafer. If the oxygen content of the native oxide is estimated from the area proportion of Si oxide in Si 2p spectra on the assumption that the native oxide has a chemical formula of SiO₂, the corrected atomic ratio of O / P increased from 2.9 to 3.3.

Along with the increase of O / P atomic ratio, the line shapes of O 1s, P 2p and Si 2p were changed after the air-exposure, as shown in Fig.2. In O 1s spectrum a shoulder peak around 530.6 eV appeared. This new

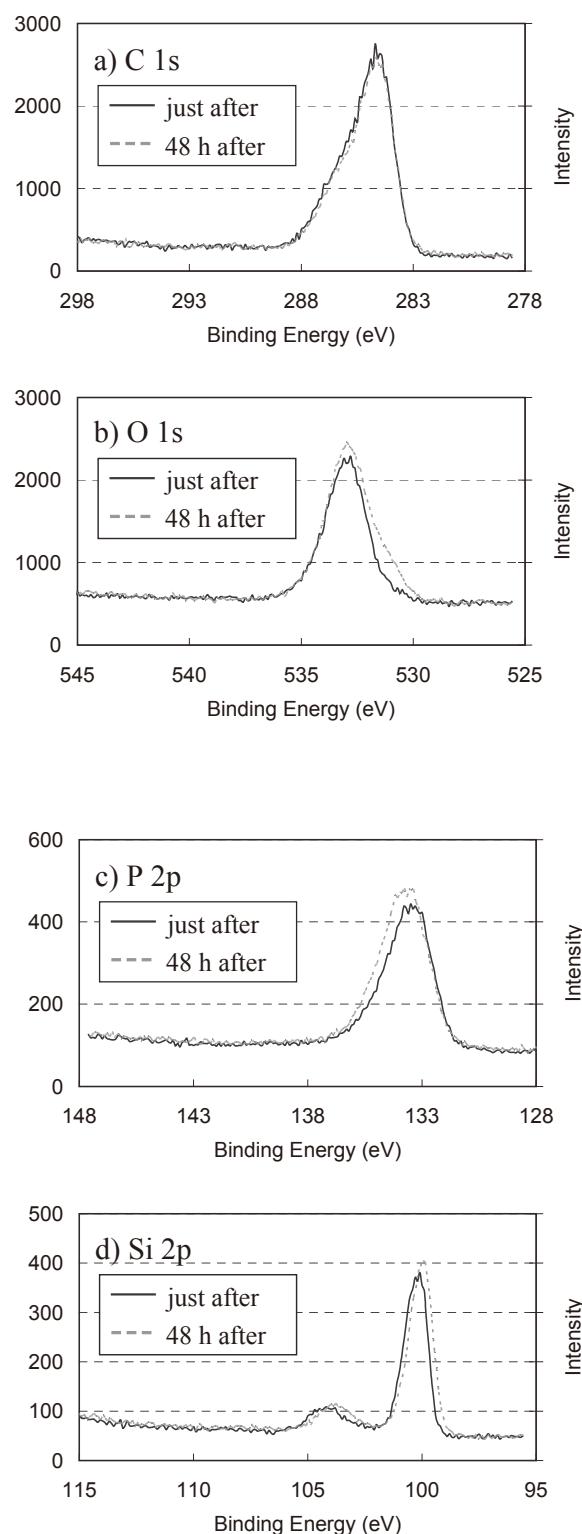


Fig. 2. XPS narrow-scan spectra of a) C 1s, b) O 1s, c) P 2p and d) Si 2p obtained from PEP-36 cast on the Si wafer at just and 48 h after the cast.

Table 1. Surface atomic composition (at%) of PEP-36 cast on the Si wafer obtained by XPS.

Sample	C	O	P	Si	O / P
just	71.3	18.6	5.8	4.4	3.2
48 h	66.2	22.6	6.4	4.8	3.5

component is believed to originate from the P=O bonding in $(RO_3)_3P=O$. Its area proportion is estimated at 12.5% from the difference spectrum. This indicates that the proportion of O is supposed to be $(RO_3)_3P : (RO_3)_3PO : (RO_3)_3PO = 50\% : 37.5\% : 12.5\%$, which is in agreement with the above estimation based on the O / P ratio. Almost half the phosphite molecules on the surface might be oxidized to phosphate. In P 2p spectrum, only a slight energy shift of 0.3 eV towards the higher binding energy was observed as a result of oxidation of almost half the phosphite molecules. On the contrary, the lower energy shift of 0.2 eV is observed in Si 2p spectrum, which may be the sign of differential charging between the cast film and the substrate.

3.2. ToF-SIMS analysis

Positive and negative ion ToF-SIMS spectra were acquired at just, 0.25 h, 18.5 h and 48 h after the cast. Obtained negative ion mass spectra are shown in Fig. 3. Variations in relative intensities of characteristic peaks are summarized in Table 2, where the intensities are normalized to those for just after the cast.

(1) PO_x^- : In contrast with the decrease of PO_4^{+} and PO_2^- peak intensities, those of PO_3^- and $H_2PO_4^-$ rapidly increased with increasing air-exposure. These variations are unambiguously believed to indicate the progress in surface oxidation of P, which is not remarkable in the XPS spectra (Fig. 2c)). Change in intensity is consistent with the lattice valency model, which was proposed for oxidized metal surfaces by Plog *et al.* [4].

(2) *tert*-Butyl: The intensity of $C_9H_{19}^+$ peak originating from *tert*-butyl in the hindered phenol units exceptionally kept constant. If there are no other compounds that have *tert*-butyl units, it can be used for the quantification index of PEP-36.

(3) Hindered phenol: Whereas the intensity of $C_{15}H_{23}O^-$ peak originating from the hindered phenol units monotonously decreased, $C_{15}H_{23}O^+$ peak had maximum intensity at 0.25 h after the cast. In the initial oxidation stage, the ionization probability is supposed to be

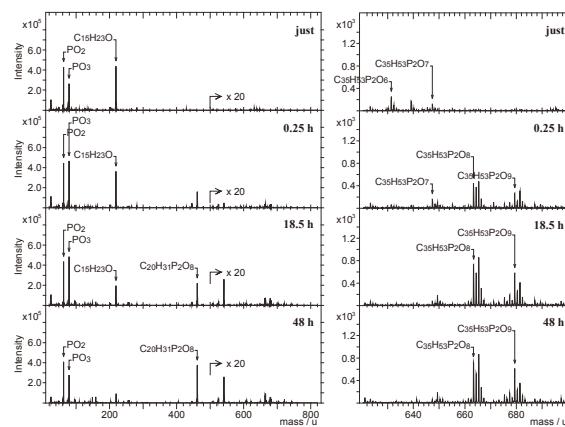


Fig. 3. Negative ion ToF-SIMS spectra obtained from PEP-36 cast on the Si wafer at just, 0.25 h, 18.5 h and 48 h after the cast.

changed and the hindered phenol units tend to be cationized. After the initial oxidation stage, desorption of the hindered phenol units and consequent signal decrease occurs as a result of the surface oxidation. Fortunately, the intensity of $C_{15}H_{23}O^+$ at just and 48 h after the cast is nearly equal. It may be used for the quantification index of PEP-36.

(4) Pentaerythritol: The intensity of $C_5H_7O^+$ peak originating from the pentaerythritol unit monotonously decreased. It may be caused by the difference in the fragmentation probability between PEP-36 and oxidized PEP-36.

(5) Molecular and Δ hindered phenol: At just after the cast, PO_3^- -related ions such as $C_{20}H_{31}P_2O_6^-$ and $C_{35}H_{53}P_2O_6^+$ were clearly observed as expected from the original molecular structure. Exposing of the specimen to air led to decrease these ions and highly oxidized ions such as $C_{20}H_{31}P_2O_8^-$ and $C_{35}H_{53}P_2O_8^+$ came to appear. The prolonged exposure time accelerated these changes. As demonstrated here, we can obtain the qualitative information on the molecular structure of oxidizing PEP-36 through the analysis of characteristic peak intensities. Because the intensities of these characteristic ions that have more molecular information tended to vary in quite wide range of 10^3 orders depending on the oxidation state, there are many difficulties in quantitative analysis, which should be overcome in near future.

Table 2. Relative intensities of characteristic peaks on ToF-SIMS spectra obtained from PEP-36 thin films at just, 0.25 h, 18.5 h and 48 h after the cast, normalized to the just after the cast.

Unit	Estimated ion	Observed mass	Intensity	Relative intensity			
				just	just	0.25 h	18.5 h
PO _x	PO ⁺	46.970	19698	1.00	0.74	0.40	0.29
	PO ₂ ⁻	62.967	1600344	1.00	0.94	0.67	0.53
	PO ₃ ⁻	78.960	367979	1.00	3.72	5.36	5.71
	H ₂ PO ₄ ⁻	96.971	4193	1.00	5.94	11.1	13.4
<i>tert</i> -butyl hindered phenol	C ₄ H ₉ ⁺	57.076	945989	1.00	1.11	1.14	1.13
	C ₁₅ H ₂₃ O ⁺	219.182	3627	1.00	3.39	1.87	1.19
pentaerythritol	C ₁₅ H ₂₃ O ⁻	219.180	1115054	1.00	0.61	0.23	0.12
	C ₅ H ₇ O ⁺	83.059	140828	1.00	0.82	0.52	0.33
Δ hindered phenol	C ₂₀ H ₃₁ P ₂ O ₅ ⁺	413.180	4747	1.00	0.67	0.19	0.07
	C ₂₀ H ₃₁ P ₂ O ₆ ⁺	429.166	2363	1.00	1.03	0.46	0.22
	C ₂₀ H ₃₁ P ₂ O ₇ ⁺	445.153	168	1.00	18.2	15.3	8.96
	C ₂₀ H ₃₁ P ₂ O ₈ ⁺	461.171	115	1.00	6.67	18.6	17.8
	C ₂₀ H ₃₁ P ₂ O ₅ ⁻	413.166	1889	1.00	0.58	0.30	0.23
	C ₂₀ H ₃₁ P ₂ O ₆ ⁻	429.157	21674	1.00	0.69	0.23	0.10
	C ₂₀ H ₃₁ P ₂ O ₇ ⁻	445.142	3996	1.00	22.8	11.6	9.18
	C ₂₀ H ₃₁ P ₂ O ₈ ⁻	461.142	809	1.00	509	866	883
	C ₂₀ H ₃₁ P ₂ O ₉ ⁻	477.151	1097	1.00	7.26	6.53	4.53
	C ₃₅ H ₅₃ P ₂ O ₆ ⁺	631.386	13162	1.00	0.57	0.09	0.02
	C ₃₅ H ₅₃ P ₂ O ₇ ⁺	647.361	623	1.00	3.86	2.10	0.86
	C ₃₅ H ₅₃ P ₂ O ₈ ⁺	663.371	159	1.00	8.37	18.5	15.6
	C ₃₅ H ₅₃ P ₂ O ₆ ⁻	631.313	1901	1.00	0.29	0.07	0.05
	C ₃₅ H ₅₃ P ₂ O ₇ ⁻	647.309	1052	1.00	1.09	0.53	0.40
	C ₃₅ H ₅₃ P ₂ O ₈ ⁻	663.314	152	1.00	20.4	33.8	32.3
	C ₃₅ H ₅₃ P ₂ O ₉ ⁻	679.305	185	1.00	10.2	21.7	22.1

4. Summary

The oxidation process of PEP-36 was discussed by ToF-SIMS and XPS. On ToF-SIMS mass spectra obtained at just after the cast, C₁₅H₂₃O⁻ originating from the hindered phenol units, C₅H₇O⁺ originating from the pentaerythritol units and PO₃-related ions such as C₂₀H₃₁P₂O₆⁻ and C₃₅H₅₃P₂O₆⁺ were clearly observed as expected from the original molecular structure. Exposing of the specimen to air led to decrease these ions and highly oxidized ions such as C₂₀H₃₁P₂O₈⁻ and C₃₅H₅₄P₂O₈⁺ came to appear. These changes were accelerated by the prolonged exposure time. A comparable analysis by XPS revealed the quantitative information on atomic composition that almost half the phosphite molecules on the surface were oxidized after air-exposure of 48 h. Here we point out that the characteristic peaks of PEP-36 are very

sensitive to the oxidation state and their intensities have quite wide variation, which may cause the difficulty in quantitative analysis. A lot of help with conventional techniques such as XPS are continually needed to realize the quantitative characterization of organic molecules by ToF-SIMS.

5. References

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