Evaluation of Resin by XPS and TOF-SIMS

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XPS and TOF-SIMS analyses have been performed for heated POM and ABS resins. In the case of POM, elimination of oxygen and formation of hydrocarbon species were observed after heating treatment. In the case of heated ABS, oxidation of polybutadiene and polystyrene occurred at the surface, and oxidation of only polybutadiene is observed at ~0.1 mm depth from surface. Polyacrylonitrile showed no change by heating treatment.

1. Introduction

In recent years, resins have been widely used as the structural materials for various uses because of their light weight, low cost and ease of molding, compared with metal materials. In some cases, however, resin materials are deteriorated by light, heat and chemical reagents and their durability are not so good as that of metal materials in the particular environments. Accordingly, it is worth to evaluate the changes of resins when they are used in various environments. As the changes of materials are expected to proceed from their surface, we have investigated the evaluation methods sensitive to surface, X-ray photoelectron spectroscopy (XPS) and Time-of-flight secondary ion mass spectrometry (TOF-SIMS). XPS gives information about composition and chemical states of atoms, and TOF-SIMS gives information about the molecular structure. They have been applied to evaluation of interface of polymer and metal [1], and to evaluation of surface chemical state of surface-treated polymer [2-4]. In this work, polyoxymethylene (POM) and acryronitrile-butadiene-styrene (ABS) resins as the representatives of one-component system and multi-component system, respectively, have been examined on the effect of heat as an environmental factor.

2. Experimental

Molded resin samples, POM (Jyuracon M90-44 from Polyplastics Co., Ltd.) and ABS (Cycolac AM from Ube Cycon Co., Ltd.), were used in this report. Untreated and heated resins (POM heated at 383 K for 2000 h and ABS heated at 373 K for 2000 h) were measured at the surface of about 0.1 mm sliced samples by XPS and TOF-SIMS. In addition, measurements of TOF-SIMS were also done at the surfaces for ABS samples.

XPS data were obtained using PHI-5400 ESCA system. The used X-ray was Mg Kα line (400 W). The analyzed area was 1.1 mm ϕ. The charge corrections of binding energies were made by reference to the C 1s binding energies of O-CH_2-O (287.9 eV) for POM and of hydrocarbon species(285.0 eV) for ABS [5].

TOF-SIMS measurements were performed with PHI-TRIFT II system. Ga^+ ion (15 kV) was used as primary ion.

3. Results and Discussion

3.1 POM resin

C 1s XPS spectra for ~0.1 mm sliced POM surfaces are shown in Figure 1. The composition determined from peak area is tabulated in Table 1. The oxygen composition was decreased after heating treatment. The C 1s spectra in Figure 1 show two peaks with the energy difference of 3 eV, which is considered that the higher binding energy peak is assigned to O-CH_2-O and the lower binding energy peak is assigned to hydrocarbon (-CH_2-) species. The former intensity was decreased and the latter one was increased after heating treatment. These suggest that heating treatment leads to the elimination of oxygen and the formation of hydrocarbon species. The hydrocarbon species, which were observed even at the untreated sample, is considered to include the

contributions of additives and damage by X-ray irradiation. The influence of X-ray was presumed from the result that oxygen composition was 30% reduced after X-ray irradiation of 1 hour.

TOF-SIMS spectra in the mass range of 0-100 amu (atomic mass unit) for ~0.1 mm sliced POM resins are shown in Figure 2. Structures of typical fragment ions are also noted in Figure 2. Although the peak intensities of a heated sample were about one half of an untreated sample, no difference in relative intensity pattern was noticed between untreated and heated samples. However, a difference was observed comparing high-resolution mass spectra. Figure 3 and 4 show mass spectra in high mass resolution mode around 42 amu and 43 amu, respectively.

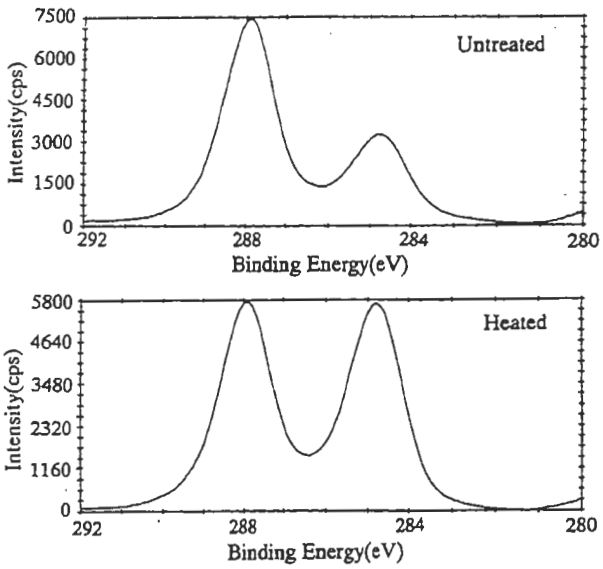

Figure 1. C 1s XPS spectra of untreated and heated POM resins at ~0.1 mm depth.

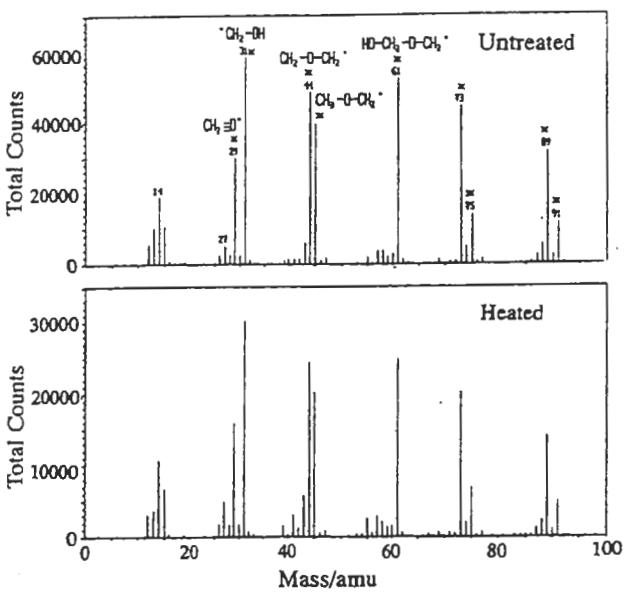

Figure 2. TOF-SIMS spectra in the mass range of 0-100 amu for untreated and heated POM resins.

Table 1 Compositions determined from C 1s and O 1s peak area intensities (atomic %)

Sample	C	O
Untreated	57.9	42.1
Heated	65.2	34.8

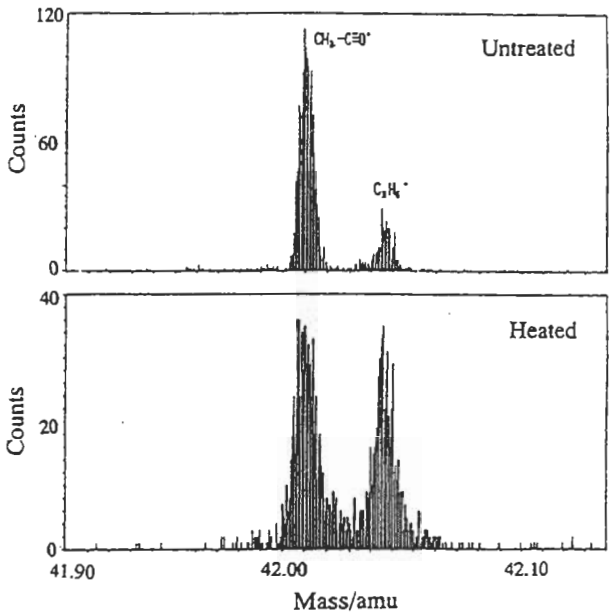

Figure 3. TOF-SIMS spectra around 42 amu for untreated and heated POM resins.

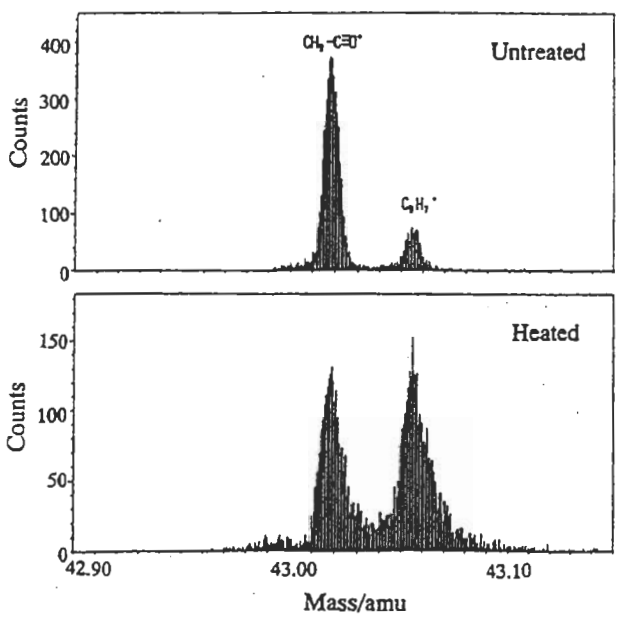

Figure 4. TOF-SIMS spectra around 43 amu for untreated and heated POM resins.

The intensity ratio of non-oxygen-containing fragment ion ($C_3H_6^+$, $C_3H_7^+$) to oxygen-containing fragment ion (CH_2CO^+, CH_3CO^+) was increased after heating treatment. This is consistent with XPS result.

3.2 ABS resin

XPS survey spectra of ~0.1 mm sliced ABS samples are shown in Figure 5. In the spectrum of the heated ABS, O 1s peak was appeared. The composition determined from peak area is tabulated in Table 2.

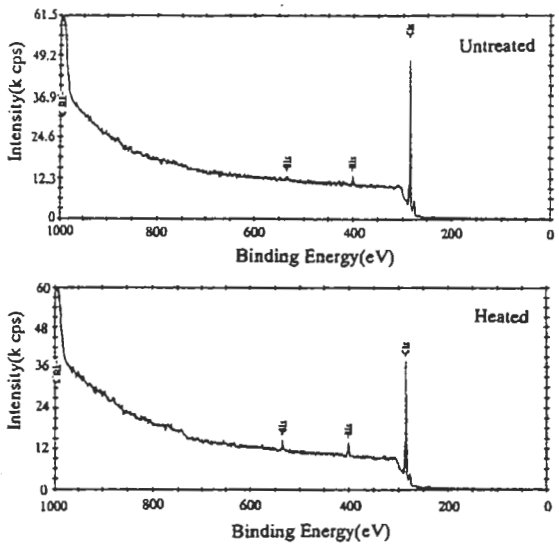

Figure 5. XPS survey spectra of untreated and heated ABS resins.

Table 2 Compositions determined from peak area intensities (atomic %)

Sample	C	N	O
Untreated	96.2	3.8	----
Heated	91.4	5.3	3.3

The carbon composition was decreased and the nitrogen and oxygen compositions were increased, after heating treatment. In C 1s spectra, the peak intensity around 286.5 eV, which thought to be bonded to oxygen, was increased after heating. These results indicate oxidation of ABS surface occurred by heating treatment. As there was no difference in N 1s peak shape between untreated and heated ABS samples, it was presumed that polyacrylonitrile did not change. The spectral change by X-ray irradiation was not observed in the case of ABS.

TOF-SIMS spectra in the mass range of 10-60 amu for ~0.1 mm sliced ABS resins are shown in Figure 6. The intensity of a fragment ion of 41 amu attributed to polybutadiene [6] was decreased after heating. Figure 7 shows mass spectra in high mass resolution mode around 55 amu. The peak intensity of $C_2H_3CO^+$ formed by oxidation of polybutadiene was increased after heating treatment. These results suggest that oxidation of polybutadiene occurs at inner portion near surface (0-0.1 mm region) after heating. On the other hand, at the surface of ABS, $C_2H_3CO^+$ ions were observed before and after heating treatment.

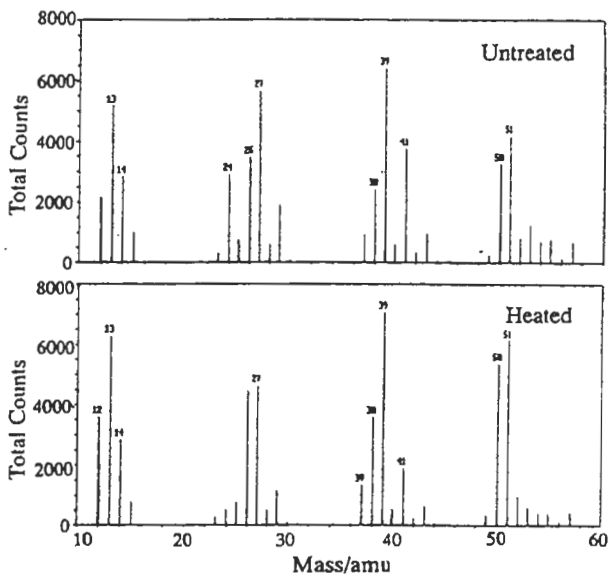

Figure 6. TOF-SIMS spectra in the mass range of 10-60 amu for ~0.1 mm sliced samples of untreated and heated ABS.

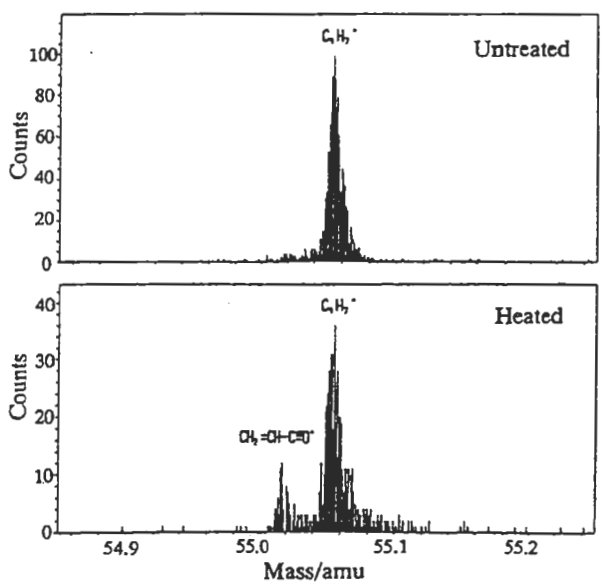

Figure 7. TOF-SIMS spectra around 55 amu for ~0.1 mm sliced samples of untreated and heated ABS.

This means that oxidation of polybutadiene occurs even at the room temperature.

TOF-SIMS spectra in the mass range of 80-120 amu at the surface are shown in Figure 8. The intensities of fragment ions of 91 amu ($C_7H_7^+$) and 115 amu ($C_9H_7^+$) attributed to polystyrene [6] were decreased after heating. Figure 9 shows TOF-SIMS spectra around 105 amu. The peak intensity of $C_6H_5CO^+$ ion was increased after heating. For ~0.1 mm sliced sample, however, the peak intensities were scarcely changed after heating. These results suggest that oxidation of polystyrene occurs only at the surface.

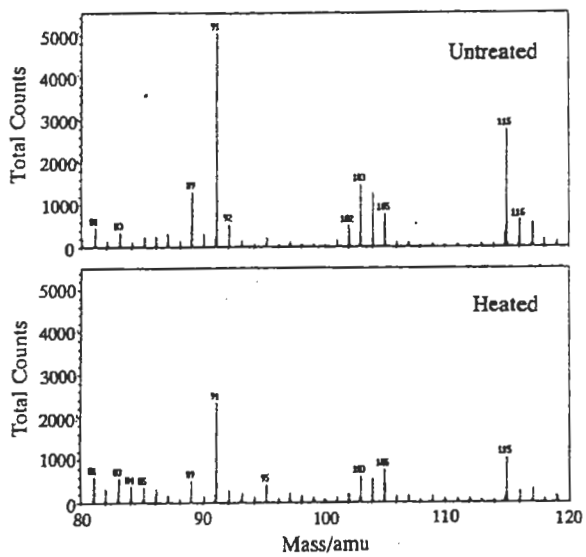

Figure 8. TOF-SIMS spectra in the mass range of 80-120 amu at the surface of untreated and heated ABS resins.

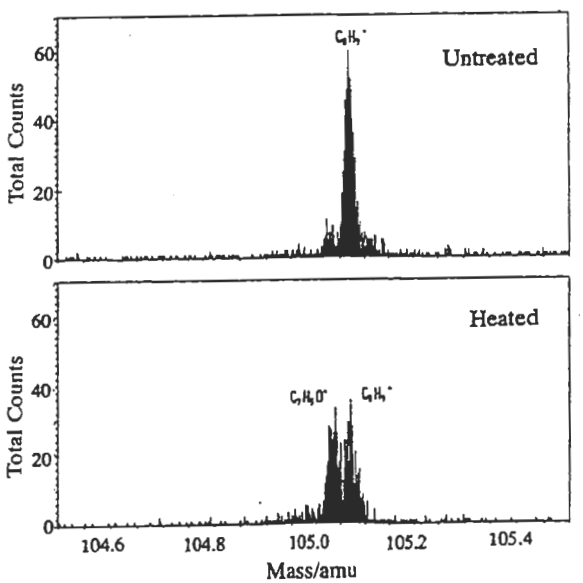

Figure 9. TOF-SIMS spectra around 105 amu at the surface of untreated and heated ABS resins.

4. Conclusion

From the results of XPS and TOF-SIMS analyses for POM, the elimination of oxygen and the formation of hydrocarbon species were observed by heating treatment.

In the case of heated ABS, the oxidation of polybutadiene and polystyrene occurred at the surface, and the oxidation of only polybutadiene was observed at ~0.1 mm sliced sample. Polyacrylonitrile did not change by heating treatment.

By using XPS, besides the elemental determination, the evaluation of chemical state is possible in one-component systems such as POM, while only understanding of the general tendency of change is possible and the detail analysis of the chemical state of each component is difficult in multi-component systems such as ABS. On the other hand, it is confirmed that the evaluation of chemical state is possible about not only one-component systems but also multi-component systems by TOF-SIMS and that it is useful for the evaluation of the deterioration of resins. As TOF-SIMS is poor in quantification, the valuable evaluation is expected to be possible by combining XPS and TOF-SIMS methods.

5. References

[1] Y. M. Tsai, F. J. Boerio, W. J. van Ooij, D. K. Kim, and T. Rau, Surf. Interface Anal., 23, 261(1995).

[2] M. Morra, E. Occhiello, and F. Garbassi, Surf. Interface Anal., 16, 412(1990).

[3] F. M. Petrat, D. Wolany, B. C. Schwede, and L. Wiedmann, A. Benninghoven, Surf. Interface Anal., 21, 274(1994).

[4] F. M. Petrat, D. Wolany, B. C. Schwede, and L. Wiedmann, A. Benninghoven, Surf. Interface Anal., 21, 402(1994).

[5] G. Beamson and D. Briggs, "High Resolution XPS of Organic Polymers. The Scienta ESCA 300 Database", John Wiley & Sons (1992).

[6] J. G. Newman, B. A. Carlson, R. S. Michael, and J. F. Moulder, "Static SIMS Handbook of Polymer Analysis", editted by T. A. Hoklt, Physical Electronics Inc. (1991).