Quantitative analysis of organic additive content in a polymer by ToF-SIMS with PCA

Hidemi Ito*, Teiichiro Kono

Analysis and Simulation Center, Asahi Kasei Corporation, 2-1 Samejima, Fuji, Shizuoka 416-8501, Japan

1. Introduction

ToF-SIMS is a widely recognized technique for analysis of surfaces containing organic materials. For analysis of small surface areas, however, the primary ion dose must be relatively high and thus tends to cause decomposition of the organic materials, making it difficult to obtain accurate quantitative analysis of the composition. Matrix- or laser-based techniques of enhancing peak intensity to permit reduction of the primary ion dose have been reported [1,2], but have not been able to eliminate spectral degradation sufficiently for accurate quantitative analysis.

Principal component analysis (PCA) is a widely known technique for interpretation of ToF-SIMS spectra. A typical ToF-SIMS spectrum consists of hundreds of peaks, but a very small number of representative peaks are generally relevant and sufficient for the interpretation. With PCA, the whole set of ToF-SIMS data is reduced to several principal components and the differences among spectra are thus clearly revealed, enabling their classification into relevant groups. The principal components are described by loadings and scores. Each score represents the evaluation of a specific sample. Various applications for the classification of spectra have been reported by Pachuta [3] and Wagner and Castner [4]. In this study, we applied PCA as a means of compensating for spectral degradation caused by decomposition of organic materials under ion irradiation, to improve the accuracy of the quantitative analysis.

2. Experimental

Stearic acid and tris(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate (Irganox 3114) in polystyrene were used as two models for quantitative analysis of organic additive content in polymer by ToF-SIMS with PCA. It was expected that stearic acid would decompose rather rapidly under ion beam irradiation because of its long aliphatic hydrocarbon chain, and that Irganox 3114 would decompose more slowly because of its aromatic hydrocarbon structure. Samples with differing contents of each in polystyrene were carefully prepared by spin coating their solutions on Si wafers.

ToF-SIMS spectra were acquired on a Trift III (Physical Electronics Inc.) using 15 keV 69Ga+ as the primary ion. The samples with stearic acid were measured in the negative polarities and those with the Irganox 3114 in polystyrene were measured in the positive polarities. Each sample was irradiated for 60 min, resulting in a total primary ion dose of about 2.8 × 10^12 ions/cm². Spectra for each sample were extracted from the measured ToF-SIMS data at regular intervals as the irradiation proceeded, and thus at increasing primary ion doses.

Nearly all of the peaks, except for certain peaks related to contamination, were selected and their intensities were normalized to the total intensity within each spectrum. Normalized data...
was autoscaled, to make every peak equally significant in the spectrum.

3. Results and discussion

3.1. Stearic acid in polystyrene

Analysis using a 100% stearic acid sample showed that the intensity of its representative peak at $m/z = 283$ normalized to the total intensity is extremely sensitive to the amount of primary ion irradiation (Fig. 1), and thus verified that stearic acid is decomposed by ion irradiation in ToF-SIMS. As evident in Fig. 1, the change in the normalized intensity of the peak at $m/z = 283$ as the irradiation proceeded was greater for samples with high stearic acid content. This is in accord with our previous experience, which had shown that it is sometimes difficult to obtain quantitative analysis in cases where decomposition by ion irradiation occurs and the change in the normalized intensity varies with the content of the organic additive.

We attempted to compensate for the degradation of these ToF-SIMS spectra by this decomposition, by applying PCA. Fig. 2 shows (a) the loadings of the first principal component (PC1), (b) the ToF-SIMS spectrum of the stearic acid, and (c) the ToF-SIMS spectrum of the polystyrene. We obtained several principal components and found that the PC1 loadings are similar to the pure spectra; i.e., that the PC1 positive loadings are similar to the ToF-SIMS spectrum of the stearic acid and PC1 negative loadings are similar to that of the polystyrene. Moreover, we observed that the PC2 positive loadings weighted peaks which tended to decrease with ion irradiation and that the PC2 negative loadings showed several small masses such as $\text{H}_x\text{CH}_y\text{O}_z$ (Fig. 3), and furthermore that among them $\text{O}_z$ was most clearly increasing with ion irradiation. This indicates that the PC2 loadings clearly indicate the degree of decomposition for stearic acid, but also include the degree of decomposition of polystyrene. The ToF-SIMS spectrum of polystyrene represents hydrocarbon ions that also exist in the fragments of stearic acid. Because the spectral degradation of stearic acid is larger than that of polystyrene, the change in intensity of hydrocarbon ions from stearic acid tends to cover that of the polystyrene.

From this analysis it was concluded that PC1 mainly shows stearic acid content and PC2 mainly shows the degree of decomposition of both stearic acid and polystyrene by ion irradiation. In a plot of the PC1 scores versus the PC2 scores, as shown in Fig. 4, the sample of a given stearic acid content is clearly represented by a single straight line showing its stearic acid and polystyrene decomposition. Since the PC2 is predominated by the decomposition of stearic acid than polystyrene, all the lines in Fig. 4 show almost identical slope except pure polystyrene (stearic acid 0%). Also only the pure polystyrene’s line shows a different trend in terms of PC1 score. By rotating the coordinate system so that the axis for the PC1 scores (the upward-pointing arrow in
Fig. 4) is perpendicular to these lines, the plot of rotated PC1 scores versus stearic acid content was obtained (Fig. 5).

Although there observed the deviation for the pure poly-
styrene (stearic acid 0%), it seems to be reasonable to draw a calibration curve from 10% to 100% stearic acid content shown in Fig. 5. By using this calibration curve, it becomes possible to obtain the stearic acid content above 10%, compensating for the spectral degradation effect of its decomposition. The deviation for the pure polystyrene from the calibration curve is considered to be due to the different trend in the PC1 score for pure polystyrene from that of other samples with stearic acid content above 10% in Fig. 4.

Though a further study is necessary for the samples with stearic acid content below 10%, this calibration curve could be effective for quantitative analysis on samples with stearic acid content above 10%.

3.2. Irganox 3114 in polystyrene

In the analysis using 100% Irganox 3114, the normalized intensity of its representative peak at \( m/z = 219 \) to the total intensity decreased only slightly with the primary ion dose. The degree of change was too small to affect qualitative analysis, but in quantitative analysis the calibration curve made for the normalized intensity of this peak to the total intensity showed about a 5% error attributable to decomposition (Fig. 6). The error is sufficient to make accurate quantitative analysis for this organic additive difficult, despite its relatively low rate of decomposition under ion irradiation.

For high accuracy, PCA was applied to the ToF-SIMS spectra of the samples having different Irganox 3114 contents, in the same manner as for the stearic acid. The loadings of PC1 were similar to the pure spectra of the Irganox 3114 and the polystyrene. The degree of decomposition by ion irradiation can be observed as PC6. PC6 loadings showed peaks which tended to decrease with ion irradiation especially related to Irganox 3114. Plotting the PC1 scores versus the PC6 scores indicates that the samples with Irganox 3114, like those with stearic acid, can be separated into different lines depending on the Irganox 3114 content (Fig. 7). By plotting the PC1 scores versus the Irganox 3114 content, it was possible to obtain a more accurate calibration curve, showing just 0.6% error (Fig. 8). The application of PCA on this basis enabled
effective compensation for the spectral degradation effect and thus made it possible to perform accurate quantitative analysis for the Irganox 3114 content.

4. Conclusions

Quantitative analysis for organic additives using ToF-SIMS data is intrinsically difficult, because of their tendency to decompose under ion irradiation. By applying PCA to the ToF-SIMS spectra, we found it possible to extract a principal component related to the organic additive content that was independent of the decomposition, and to perform quantitative analysis for the content of two quite different organic additives in polystyrene without loss in accuracy due to spectral degradation.

References