ToF-SIMS and PCA Analysis of Oligomer Distribution within Glass Fiber Reinforced Plastic

Yasuko Kajiwara†
MGC Chemical Analysis Center, Mitsubishi Gas Chemical Company, INC.,
Niijuku 6-1-1, Katsushika, Tokyo 125-8601, Japan, and
Graduate School of Science and Technology, Seikei University,
Kichijoji-Kitamachi 3-3-1, Musashino, Tokyo 180-8633, Japan

Hiromitsu Nagashima
Engineering Plastics Division, Mitsubishi Gas Chemical Company,
INC., Marunouchi 2-5-2, Chiyoda, Tokyo 100-8324, Japan

Satoshi Nagai
Technical Center, Mitsubishi Engineering-Plastics Corporation,
Higashiyawata 5-6-2, Hiratsuka, Kanagawa 254-0016, Japan

Satoka Aoyagi
Graduate School of Science and Technology, Seikei University,
Kichijoji-Kitamachi 3-3-1, Musashino, Tokyo 180-8633, Japan
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Inorganic-organic composite materials are commercially utilized over a wide variety of industrial fields. The information on the distribution of inorganic and organic components on a nanometer scale is important for understanding the chemistry of the composite materials. In this study, the distribution of polycarbonate (PC) oligomer within a glass fiber reinforced PC was investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and principal component analysis (PCA). As a result, PCA indicated a component differentiating PC oligomer from PC polymer and revealed the homogeneous distribution of PC oligomer within the glass fiber reinforced PC. Therefore, a combination of ToF-SIMS and PCA is useful for identifying the detailed distribution of PC oligomer and evaluating the property of glass fiber reinforced PC. [DOI: 10.1380/ejssnt.2015.47]

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1. INTRODUCTION

Inorganic-organic composite materials have been widely developed owing to their high-performance functionality. Although understanding interactions between inorganic and organic components is essential for their further advancement, an evaluation method for such composite materials has not been fully established.

Glass fiber reinforced plastic (GFRP) has attracted much attention as a replacement for metal because it has high strength and toughness without sacrificing its lightweight. For instance, glass fiber reinforced polycarbonate (PC) (Fig. 1) has been generally used for machine parts of vehicles and frames of digital appliances. However, its surface appearance becomes rough because of the exposed glass fiber on the surface. To prevent such defect to the mold specimen surface, PC oligomer is deliberately added to glass fiber reinforced PC because PC oligomer is considered to block the exposure of glass fiber on the surface during injection molding [1]. On the other hand, mechanical behavior of GFRP is highly dependent on the interphase of glass fiber and polymer matrix [2-4]. Based on the atomic force microscope (AFM) investigation of glass fiber reinforced polypropylene (PP) composites, it is believed that the deformation of PP having low molecular weight occur in the interphase of glass fiber and polymer matrix whose thickness is from less than 100 nm to around 300 nm [4]. However, the distribution of the low molecular weight component in the interphase has not been directly investigated based on its chemical properties because of the limitation of analysis methods for acquiring chemical information on such a small scale.

ToF-SIMS is a powerful technique for studying surface and interphase chemistry because ToF-SIMS provides detailed chemical information with high spatial resolution down to a few hundred nanometers and high surface sensitivity at the ppm level. However, the complexity of mass spectra is one of the barriers for characterization using ToF-SIMS especially for organic materials. To interpret complex mass spectra, multivariate analysis (MVA) methods such as principal component analysis (PCA) have been applied to ToF-SIMS data [5-8]. PCA is generally used for differentiating the characteristic features within the ToF-SIMS spectra. On PCA, a vector space is rotated in the direction of the maximum variance and variables are converted into principal components, which reduce a dataset with hundreds of variables down to a few variables. Then, the data can be generally interpreted based on scores and loadings of the principal components. The scores describe the amount of each sample on the principal component axes and the loadings reveal variables which are responsible for the differences in scores plots. Detailed description can be found in references [5-8].

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† Corresponding author: yasuko-kajiwara@mgc.co.jp
FIG. 1. Negative ion ToF-SIMS spectra obtained from the cross section surfaces of the composites consisting of PC polymer, PC oligomer and glass fiber. (a) 0 wt% PC oligomer, (b) 10 wt% PC oligomer and (c) 30 wt% PC oligomer.

In this study, PCA was applied to ToF-SIMS spectrum image data in order to separate PC oligomer from PC polymer and investigate the distribution of PC oligomer within a glass fiber reinforced PC.

II. EXPERIMENTAL

A. Sample preparation

Three types of composites consisting of PC polymer (Mw 21,000, Tg 149 C-deg: Mitsubishi Engineering-Plastics Co., Tokyo, Japan), PC oligomer (Mw 5,100, Tg 104 C-deg: Mitsubishi Engineering-Plastics Co., Tokyo, Japan) and glass fiber (Nippon Electric Glass Co., Ltd., Otsu, Japan) in weight ratios of 90:0:10, 80:10:10 and 60:30:10 were prepared by injection molding. The mixtures of PC flakes and fibers were kneaded by a plastic mill at 533 K and then pelletized by a grinder mill. After dried for 5 h at 393 K, the pellets were injected into a mold at 1050 bar. The temperatures of pellet and mold were 593 K and 373 K, respectively. The composites were processed as plates with a size of 50mm × 30mm × 1mm. The cross-section surfaces were prepared with an ultramicrotome (Leica Microsystems K. K., Wien, Austria). All samples were rinsed with ethanol by an ultrasonic cleaner for 5 minutes twice.

B. ToF-SIMS measurement

Negative ion ToF-SIMS spectra were obtained using TRIFT II (Physical Electronics Inc., Chigasaki, Japan) with a Ga+ primary ion beam accelerated at 15 kV (1.4 nA) in bunched mode. A primary ion beam was rastered over an area of 100 um by 100 um with a pulsed low-energy electron flood gun. Mass calibration was performed using CH−, OH−, C2H− and C3H− peaks. The typical mass resolution was m/Δm 2300 for C10H13O−. An ion dose for each measurement was 1.2×1012 ions/cm² to ensure the static limit, 1012 ions/cm².
TABLE I. The intensity ratios of fragment ions originating from repeat units (C\textsubscript{14}H\textsubscript{11}O\textsubscript{2}: m/z 211) and end groups (C\textsubscript{10}H\textsubscript{13}O\textsubscript{2}: m/z 149) of PC obtained from the cross section surfaces of the composites consisting of PC polymer, PC oligomer and glass fiber.

| PC oligomer (wt%) | Intensity (counts/sec) | I\textsubscript{211}/I\textsubscript{149} | Average (wt%) |
|-------------------|------------------------|-----------------|----------------|
| 0                 | 431                    | 2118            | 4.9            |
|                   | 434                    | 1999            | 4.6            |
| 10                | 486                    | 1858            | 3.8            |
|                   | 393                    | 1775            | 4.5            |
| 30                | 6279                   | 2723            | 0.4            |
|                   | 2377                   | 1799            | 0.8            |

C. Multivariate analysis

PCA was performed using PLS_Toolbox with MIA Toolbox (Eigenvector Research, Inc., Wenatchee, WA) for Matlab (The MathWorks, Inc., Natick, MA). Intensities of secondary ions in the mass ranges from 0 to 300 u were compiled manually to create peak list (165 peaks). Each spectrum was exported as a binary image file (BIF) and then binary image files were imported into Matlab.

III. RESULTS AND DISCUSSIONS

In negative ion ToF-SIMS spectra, the intensity ratio of fragment ions from repeat units and end groups of PC shows a linear dependence on the average number of repeat units [9]. The lower the intensity ratio, the lower the average molecular weight of PC. Therefore, the intensities of these two fragment ions can be used as indicators of PC oligomer.

In the spectra from the cross-section surfaces of the composites with 0 wt%, 10 wt% and 30 wt% PC oligomer (Fig. 1), the intensity ratio of the two fragment ions on the composite decreased as the content of PC oligomer increased. The intensity ratio on the composite with 30 wt% PC oligomer was the lowest at 0.6 whereas those on the composites with 0 wt% and 10 wt% PC oligomer were almost the same at 4.8 and 4.2, respectively (Table I). The low intensity ratio represents the low average molecular weight of PC. Therefore, it is confirmed that the average molecular weight is the lowest in the composite with 30 wt% PC oligomer because of the existence of PC oligomer.

FIG. 2. ToF-SIMS images from cross section surfaces of the composites. (a) Total ion image of the composite with 0 wt% PC oligomer, (b) total ion image of the composite with 30 wt% PC oligomer and (c) the combined image of the composite with 0 wt% and 30 wt% PC oligomer in the mass range of 50 u - 250u.

Prior to PCA, the binary image files from the composites with 0 wt% and 30 wt% PC oligomer were halved and left side of each spectrum image data (Fig. 2 (a) and (b)) was combined on Matlab. Then, the combined data (Fig. 2 (c)) was treated as one spectrum image data in order to apply the same PCA model to the two types of data simultaneously. Poisson scaling was carried out to leave only the true variance originating from chemical concentration [8]. To prevent undiagnostic peaks lower than m/z 50 from dominating PCA results, the mass peaks between m/z 50 and 250 (135 peaks), where Ga ion peak was omitted, were used for PCA. The first three components were chosen because the scores of the following components showed almost uniform distributions throughout the whole pixels. The low contributions of the three PCs (3.76 %, 3.07 % and 1.82 %) were mainly due to the lack of large differences in the data. The variations among PC polymer, PC oligomer and glass fiber were small in the mass range from m/z 50 to 250 where the high intensity peaks lower than m/z 50 were left out.

FIG. 3. ToF-SIMS images from cross section surfaces of the composites. (a) Total ion imagPC1 scores (3.76 %) , (b) PC2 scores (3.07 %) and (c) PC3 scores (1.82 %).

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FIG. 3. ToF-SIMS images from cross section surfaces of the composites. (a) Total ion imagPC1-3 scores explained the overall characteristic features on the composites (Figs. 3 and 4). PC1 loadings were similar to the average spectrum of the two spectrum image data because the variation of each peak from the origin was larger than the difference between pixels. PC1 from mean-centered data captured characteristic differences within the data more effectively than that from non-centered data. Therefore, PC1 obtained from mean-
FIG. 4. PCA loadings for the combined spectrum image data of the composite with 0 wt% and 30 wt% PC oligomer. (a) PC1 (3.76%), (b) PC2 (3.07%) and (c) PC3 (1.82%).

centered data. PC2 revealed the differences between glass fiber and PC. On the positive loadings of PC2, the secondary ions originating from glass fiber such as SiO$_2$ and HSiO$_3$ were the dominant peaks whereas those from PC such as C$_6$H$_5$O, C$_6$H$_5$O, C$_6$H$_5$O, C$_{10}$H$_{13}$O and C$_{14}$H$_{11}$O$_2$ were strongly shown on the negative loadings. Finally, PC3 differentiated the characteristic structures within PC. C$_{10}$H$_{13}$O, the end groups of PC was the major peak on the positive loadings of PC3 while the other secondary ions from PC including the repeat units (C$_{14}$H$_{11}$O$_2$) were shown on the negative loadings. Therefore, it is suggested that PC3 revealed the differences between PC oligomer and PC polymer and positive scores on PC3 (Fig. 3) indicated the distribution of PC oligomer. Since the peaks from glass fiber, HSiO$_3$ and HSiO$_3$ were also contained on the positive loadings of PC3, the bright areas on the left half reflect the remaining differences between PC and glass fiber.

PC3 scores on the right half clarified that PC oligomers distribute homogeneously among the composite although the localization of PC oligomer in the interphase of glass fiber and polymer matrix were not confirmed. It may be possible to obtain the same result as PC3 scores by using the intensity distribution of I$_{2111}$/I$_{149}$. However, the intensities of I$_{2111}$/I$_{149}$ were from 0 to 2 and not strong enough to make a clear contrast between the composites with 0 wt% and 30 wt%. Thus, PCA is useful for providing clearer contrast between PC polymer and PC oligomer than the intensity ratio of the specific secondary ions. And this direct chemical information on the PC oligomer distribution is valuable for evaluating mechanical behavior of the composite.

IV. CONCLUSION

The distribution of PC oligomer was clarified by applying PCA to the combined ToF-SIMS spectrum image data. And based on PCA results, PC oligomer is distributed homogeneously in the composites with 30 wt% PC oligomer. This method can be a powerful approach to evaluating the property of glass fiber reinforced PC and understanding the chemistry of inorganic and organic composite materials.

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