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Microscopic Chemical-state Analysis of Carbon Fiber Reinforced Plastic by Synchrotron X-radiation

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Abstract

Scanning transmission X-ray microscopy (STXM) is a microscopic analysis technique of the chemical state using synchrotron X-radiation. It is suitable for the analysis of 2-dimensional distributions of the chemical state such as valence of atoms, functional groups and molecular orbital orientation. We performed STXM measurements of carbon fiber reinforced plastic (CFRP) in order to obtain guidelines to enhance the tensile strength and the elastic modulus of CFRP. The results of the C K-edge XANES imaging suggest the presence of another phase at the interface between resin and carbon fiber, which may be a coating layer. In addition, the preferred orientation of the stack of graphene sheets to the fiber axis direction was observed by using linear polarized X-ray beams.

1. Introduction

In composite materials, the characteristics at the interfaces between different types of materials are important factors for the expression of macroscopic physical properties such as strength (e.g., tensile strength and elastic modulus) and heat conduction. For example, regarding carbon-fiber-reinforced plastic (CFRP), a composite material of epoxy resin and carbon fiber (CF), the adhesiveness between the resin and CF is a controlling factor of the strength properties. In order to analyze the adhesiveness between resin and CF, it is important to study the spatial distribution of chemical states such as chemical bonds, functional groups, and molecular orbital orientation.

For such chemical state analysis, X-ray photoemission spectroscopy (XPS), infrared spectroscopy (IR), and X-ray absorption spectroscopy (XAS) are conventional techniques. However, their spatial resolutions are in the order of μ m to mm. Analyzing the interfaces in detail is insufficient. On the other hand, spectroscopy using electron beams (e.g., electron energy-loss spectroscopy [EELS] with the spatial resolution of less than 1 nm) significantly damages organic matter by the radiation of electron beams, so the use of such spectroscopy is not suitable for CFRP. Therefore, we focused on the scanning transmission X-ray microscopy (STXM) using synchrotron radiation X-rays as a method for microscopic chemical state analysis of organic composite materials.

Due to the advancement of the lithography techniques in recent

years, Fresnel zone plates (FZPs) that can focus X rays to 10–100 nm have been developed. Scanning transmission X-ray microscopy (STXM) is a very powerful method for chemical imaging around the interface of composite materials in the spatial resolution of 10–100 nm. X-ray beams are much softer than electron beams.

X-ray absorption near edge structure (XANES) spectra provides information about chemical states such as element-specific valences and functional groups. In addition, by using linear polarized synchrotron radiation X-rays, it is possible to evaluate the relative orientation degree between a specific molecular orbital and the vibration direction of the electric field vectors, so the distribution of the molecular orbital orientation in the materials can be analyzed, which is difficult by electron beams.¹⁾ This paper reports the results of the analysis of the interface between the resin and CF in CFRP and the distribution of chemical states in the CF.²⁾

2. Experimental

2.1 Measurement method

The principle of STXM is explained below.³⁾ **Figure 1** is a schematic illustration of STXM. First, synchrotron radiation X-rays are gathered with a FZP. A FZP is a device with concentrically micro-fabricated multiple grooves. The intervals between the grooves become narrower as it gets closer to the periphery. The zero-order and high-order diffracted light beams passed through the FZP are removed by an order sorting aperture (OSA) and only the first-order

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diffracted light beams are gathered. The final diameter of the gathered beams is roughly the width of the groove at the most outer side of the FZP. Synchrotron radiation X-rays concentrated to approximately 40 nm were used in this experiment. In STXM, shaped and gathered synchrotron radiation X-rays are radiated onto a thin film sample and the absorption intensity of the X rays before and after the transmission (ln (I_0/I): where, I_0 is the intensity of the X rays before the transmission and I is that after the transmission) is measured while the sample location is scanned.

In addition, two-dimensional X-ray absorption images of a target atom near the absorption edge are measured (image stacking measurement) and combined to obtain XANES images of the target element. Furthermore, using linearly polarized synchrotron radiation X-rays makes it possible to obtain two-dimensional images of molecular orbital orientation¹⁾ in the spatial resolution of about 40 nm. In addition, using circularly polarized synchrotron radiation X-rays makes it possible to obtain two-dimensional images of magnetic states such as spin magnetic moment and orbital magnetic moment⁴⁾ in sub-micron resolution. All the experiments in this paper were performed using the compact STXM (cSTXM) installed at BL-13A in the Photon Factory, Institute of Materials Structure Science of the High Energy Accelerator Research Organization. The details of the equipment are specified in the literature cited.^{3, 5)} **2.2 Sample processing**

The thickness of a sample for STXM needs to be adjusted such that the product $(\Delta \mu t)$ of the difference between the linear absorption coefficient before and after the absorption edge $(\Delta \mu)$ and the sam-



ple's thickness (t) becomes approximately one. The CFRP analyzed in this study was a commercially available one (PAN [polyacrylonitrile] based). The estimated tensile strength is 1760 MPa. The estimated elastic modulus is 125 GPa. **Figure 2**(a) is a schematic illustration of the cross section of a carbon fiber. The cross section perpendicular to the fiber axis is defined as the cross section (CS) and that parallel to the fiber axis is defined as the longitudinal section (LS).

An approximately 10- μ m square sample with a thickness of approximately 100 nm was created by FIB (focused ion beam) processing and Ar milling. The sample includes both of the CS of a fiber and the LS of another fiber as shown in Fig. 2(b). In Fig. 2(b), the angle between the direction of the incident electron beams and the normal direction of the thin sample is 35 degrees. In this experiment, XANES imaging was performed for the C *K*-edge of the two regions ((I) interface between the resin and CF, (II) inside of the CS of the CF) shown with the red regions in Fig. 2(b). Figure 2(c) is a transmission electron microscopy (TEM) image of the CS of the thin sample. A ring-like pattern (contrast) was measured inside the CS. The chemical states of this ring will be discussed in 3.2 below.

3. Results and Discussion

3.1 Observation of the interface between the resin and CF

Figure 3(a) is an X-ray absorption image of the region (I) in Fig. 2(b) at energy E=286.5 eV. The image is 70×70 pixels. One pixel is 40×40 nm². E=286.5 eV is equivalent to the excitation energy of a C atom in the C-OH bond to orbit π^* from 1s. In addition, X-ray absorption images discussed in this report are those of synchrotron radiation X-ray linearly polarized to linear horizontal $\rho/2$ (LHR) mode in Fig. 3(a), unless otherwise specified. As shown in Fig. 3(a), a region at the interface between the resin and CF shows absorption contrast different from that of the regions enclosed in the black-dashed lines in Fig. 3(a) was calculated in 8 bits (256 gray levels), it was 86 at the resin section, 162 at the CF section, 224 at the interface, and 20 at the space without sample.

X-ray absorption intensity is decided by the product of the linear absorption coefficient ($\mu = \rho \mu_m$ [ρ : density, μ_m : mass absorption coefficient]) that is decided for each substance and the thickness of a sample, in general. In addition, the absorption originated in a specific chemical bond is proportional to the amount of such bond. Therefore, the contrast difference is decided by the linear absorption coefficient, the thickness of the sample, and the amounts of chemical bonds. The thickness of the sample was adjusted by Ar milling and the thickness of the thin sample is almost homogeneous, so it is difficult to explain that there are significant differences in the thickness



Fig. 2 (a) Schematic illustration of a cross section (CS) and a longitudinal section (LS) of CF, (b) Backscattered electron (BSE) image of the CFRP thin film, (c) Transmission electron microscope (TEM) image of CS of CF and resin



Fig. 3 (a) X-ray absorption contrast image of Area (1) shown in Fig. 2(b) at E=286.5 eV. Black-dashed squares show regions of averaged XANES spectra of (i) resin, (ii) CF(LS), and (iii) the interface used for RGB deconvolution of Fig. 4(c).
(b) Averaged XANES spectra of resin, CF(LS), and the interface in each region shown in Fig. 3(a).



Fig. 4 Residual curves of each region in Fig. 3(a) after SVD analyses of (A) resin/CF(LS) and (B) resin/CF(LS)/interface are shown in (a) and (b), respectively. (c) RGB (red: resin, green: CF(LS), blue: third phase) color-deconvoluted image of the interface between resin and CF(LS). The twoway arrow is the polarization of LHR mode of X-ray beams.

of the resin and CF sections. Actually, it was confirmed that the maximum height roughness (Rz) was approximately 20 nm by atomic force microscopy (AFM). Therefore, we assume that there was a third phase with the linear absorption coefficient and chemical state different from those of the resin and fiber at the interface between the resin and fiber.

To examine whether a third phase exists, image stacking measurement was carried out at the energy region of C K-edge in the regions in Fig. 3(a). Figure 3(b) shows the average spectra of the regions enclosed with the black-dashed broken lines in Fig. 3(a). The spectra were normalized at E=292 eV (excitation from 1s to σ^* in the C-C bond). Regarding the average spectra at the resin section (i) and interface (iii) in Fig. 3(a), an absorption peak due to the excitation from 1s to π^* in the C=C bond was seen at 284.8 eV; an absorption peak due to the excitation from 1s to π^* in the C-OH bond at 286.5 eV; an absorption peak due to the excitation from 1s to σ^* in the O(C-H)R bond at 288.3 eV; and an absorption peak due to the excitation from 1s to σ^* in the C-C bond at 292 eV.⁶ However, their intensity ratios differ between (i) and (iii). Typical epoxy resin has these chemical bonds and functional groups.⁷⁾ On the other hand, regarding the average spectra at the CF section (ii) in Fig. 3(a), an absorption peak due to the excitation from 1s to π^* in the C=C bond was observed at 285.2 eV and another peak due to the excitation from 1s to σ^* in the C-C bond at 292 eV.⁶⁾

In a previous research, diffraction peaks originated in graphite were observed by the CF powder method of X-ray diffraction $(XRD)^{8)}$. The C *K*-edge XANES spectrum results at the CF section in our experiment are consistent with the results of this previous re-

search. It has been confirmed that the CF is an aggregate of the laminate structures of graphene sheets. The results above suggest that the third phase at the interface is a substance consisting of functional groups similar to those of the resin, but their abundance ratios vary. A coating is applied to improve the adhesiveness between the CF and resin in processes for manufacturing CFRP before embedding the CF into the resin. The third phase for which the existence was suggested in our study could be this coating layer.

To further examine if this third phase exists, the spectra at each pixel $(I_n(E) \ (n=1 \ to \ 4900))$ in Fig. 3(a) were analyzed by singular-value decomposition (SVD)⁹⁾ with the average spectra in Fig. 3(b) (i) to (iii) $(I_{resin}(E), I_{CF}(E), \text{ and } I_{interface}(E), \text{ respectively})$. The SVD analysis was carried out under conditions (A) and (B) shown below. The fitting spectra $I'_n(E)$ for conditions (A) and (B) are expressed as shown below.

Condition (A): Two spectra of the resin (i) and CF (ii)

$$I'_{n}(E) = a_{n, \text{resin}} I_{\text{resin}}(E) + a_{n, \text{CF}} I_{\text{CF}}(E)$$
(1)

Condition (B): Three spectra of the resin (i), CF (ii), and interface (iii)

 $I'_n(E) = b_{n, resin} I_{resin}(E) + b_{n, CF} I_{CF}(E) + b_{n, interface} I_{interface}(E)$ (2) Where, $a_{n, resin}, a_{n, CF}, b_{n, resin}, b_{n, CF}$ and $b_{n, interface}$ are real constants. Figure 4(a) shows the average residual spectra of the regions enclosed with the black-dashed lines in Fig. 3(a) by fitting under condition (A). Figure 4(b) shows that under condition (B). As shown in Fig. 4(a) and 4(b), the spectra could be fitted with almost no residues at the resin section (i) and CF section (ii). Meanwhile, the spectra at the interface (iii) under condition (B) could be fit similarly to those at sections (i) and (ii), but when they were fitted only by the spectra

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at the resin and CF under condition (A), many residues remained and thereby these mixed spectra could not explain such action. Therefore, this result also shows that there exists a substance with chemical states different from those of the resin and CF in the region (iii) in Fig. 3 (a). The coefficients ($b_{n, resin}$, $b_{n, CF}$ and $b_{n, interface}$) at the spectra in the fitting under condition (B) were used to color Fig. 3 (a) in red, green, and blue (RGB). Figure 4 (c) shows the results. This shows that the thickness of the coating layer at the interface between the resin and CF is approximately 100 nm and it has permeated into the resin in spots in the range of approximately 300 nm. Through such spectrum analysis by two-dimensional XANES imaging, desirable types and thickness of the coating layers and desirable extents of the permeation into resin could be proposed to make CFRP stronger.

3.2 Inside the CF

Next, the region (II) (inside of the CS of the CF) in Fig. 2 (b) was subject to image stacking measurement to analyze chemical states in the CS. **Figure 5**(a) shows the average spectra of the resin, matrix, and inner ring sections of the CS. The spectra were normalized at E=292 eV as is the case with the spectra in Fig. 3 (b). The figure shows that there are no differences in the spectra at the matrix and inner ring sections of the cross section of the CF. A ring structure was observed in TEM and X-ray absorption images. However, there were no changes in the C *K*-edge spectra. The X-ray absorption intensity was higher at the ring section. These results show that the density is possibly higher at the ring section.

Lastly, for the average spectra of the LS (the green line in Fig. 3(b)) and CS (the green line in Fig. 5(a)), the intensity ratios (π/σ ratio: (absorption intensity for 1s to π^*) / (absorption intensity for 1s to σ^*)) of the absorption peaks originated in the excitation from 1s to π^* and 1s to σ^* were compared. Due to the relative relationship between the direction of a linearly polarized light beam and the direction of a molecular orbital, the absorption intensity with the excitation to the molecular orbital changes.¹) When the polarized X-ray beam is in parallel to the molecular orbital, the absorption is the strongest. When they cross at right angles, it is weakest (not absorb). Figure 5(c) shows the average spectra of the CS and LS obtained from two linearly polarized light beams (LHR mode and LVS [linear vertical $\sigma/2$] mode) that cross at right angles. The spectra were nor-

malized at E=292 eV. The π/σ ratio of the CS spectra did not change by the polarization. On the other hand, at the LS, the π/σ ratio of LHR polarization is smaller than that of LVS. This shows that the π molecular orbitals oriented to the direction of the LVS polarization. Therefore, it is assumed that the laminated structures of graphene sheets stretch to the fiber axis direction in the CF as shown in the schematic illustration of Fig. 5 (d) and it is an assembled structure of domains where the π orbitals in the scale equal to or smaller than the measured STXM spatial resolution (approximately 40 nm) oriented to various directions at the CS.

4. Conclusion

In this study, the chemical state distribution of CFRP was analyzed by STXM. The conclusion is shown below.

- (1) The analysis of the X-ray absorption spectra obtained by image stacking of the C K-edge region revealed the existence of a third phase (assumed to be a coating layer) at the interface between the resin and CF of the CFRP. We have succeeded in finding that its thickness is approximately 100 nm and to what extent it has permeated into the resin. From such information, desirable types and thickness of coating layers and desirable extents of permeation into resin are proposed to make CFRP stronger.
- (2) The C K-edge X-ray absorption spectra at the ring pattern observed in the CS of the CF were measured. The chemical state around the carbon of the CF matrix section is equivalent to that at the ring section, so the reason why the contrast was observed in the TEM and X-ray absorption images is possibly because of the difference of the density.
- (3) The differences in the absorption spectra of the two linearly polarized synchrotron radiation X-rays that cross at right angles have revealed that the π molecular orbitals oriented perpendicular to the fiber axis in the carbon fiber. There are also at least no domains more than 40 nm (the spatial resolution of the STXM used in this study) in which π orbitals oriented in the CS.

This study used CFRP as an application example of STXM. STXM is a method that can obtain two-dimensional images of (1) atomic species, (2) valences, (3) functional groups, (4) molecular orbital orientation, (5) magnetic information, and other items in the



Fig. 5 (a) Averaged XANES spectra of resin (red), CF(CS) (green), and inner ring in CF(CS) (blue) in (II) of Fig. 2(b). (b) RGB (red: resin, green: CF(CS), blue: inner ring in CF(CS)) color-deconvoluted image in (II) of Fig. 2(b). Two-way arrow shows the polarization of LHR of X-ray beams. (c) Averaged XANES spectra of CS and LS of CF using two types of polarized X-ray. These spectra are normalized by the intensity at 292 eV. (d) Schematic illustration of the distribution of graphene sheets in CF. Blue and red two-way arrows are the thickness and plane directions of graphene sheets, respectively.

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spatial resolution of approximately 40 nm, being applicable to various composite materials. Regarding microscopes using synchrotron radiation X-rays in the future, the spatial resolution could be enhanced due to the advance of optical devices; the brightness was stronger by using next-generation synchrotron radiation light sources; the sensitivity could be improved by higher coherence; and the spatial resolution was higher. Many of the raw materials, products, and by-products that Nippon Steel & Sumitomo Metal Corporation handles are composite materials in a broad sense. We will further advance the technique for analyzing chemical states using microscopes as an analysis technique that accelerates all material and process development by Nippon Steel & Sumitomo Metal.

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