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Physical and chemical imaging of adhesive interfaces with soft X-rays

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Adhesion is an interfacial phenomenon that is critical for assembling carbon structural composites for next-generation aircraft and automobiles. However, there is limited understanding of adhesion on the molecular level because of the difficulty in revealing the individual bonding factors. Here, using soft X-ray spectromicroscopy we show the physical and chemical states of an adhesive interface composed of a thermosetting polymer of 4,4'diaminodiphenylsulfone-cured bisphenol A diglycidyl ether adhered to a thermoplastic polymer of plasma-treated polyetheretherketone. We observe multiscale phenomena in the adhesion mechanisms, including sub-mm complex interface structure, sub-µm distribution of the functional groups, and molecular-level covalent-bond formation. These results provide a benchmark for further research to examine how physical and chemical states correlate with adhesion, and demonstrate that soft X-ray imaging is a promising approach for visualizing the physical and chemical states at adhesive interfaces from the sub-mm level to the molecular level. Check for updates

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he development of carbon-based structural composites including carbon-fiber-reinforced plastics (CFRPs) has contributed substantially to the development of technologies reducing CO₂ emission and moving society towards a low carbon future by reducing the weight of aircraft and automobiles¹⁻³. However, development of these next-generation mobilities faces a great challenge: how to assemble CFRPs efficiently. Steel/alloy-based vehicles have long been assembled using bolted joint and arc welding techniques. These conventional joining methods are not well-suited for CFRPs because bolts increase weight, bolt holes reduce the stiffness of CFRPs, and arc welding does not work for joining polymer-based structures^{2,3}. Adhesive bonding is a promising alternative to traditional joining methods because it maintains the lightweight and high-durability advantages of CFRPs with higher productivity¹⁻³. Reliable adhesive bonding of CFRPs for next-generation transportation will require a comprehensive understanding of adhesion, from the macroscopic to the molecular levels.

It is common knowledge that the interplay of the mechanical, physical, and chemical interactions between adhesives and adherends determines adhesive bonding characteristics¹. A macroscopic understanding of adhesive bonding has been achieved by means of the tensile-shear strength test¹. On the other hand, developing a molecular-level understanding of adhesive bonding presents challenges due to the complexity of multiple bonding mechanisms at adhesive/adherend interfaces. The molecular-level adhesion mechanism has been in general evaluated based on the chemical states of individual materials or rather simplified systems (e.g., ultrathin films on substrates)^{4,5}. For instance, bisphenol A diglycidyl ether (DGEBA, Fig. 1a), a thermosetting epoxy polymer, has been investigated as one of the model adhesive materials. The epoxy groups in DGEBA can be covalently bonded with the amino groups in a curing agent 4,4'diaminodiphenylsulfone (DDS, Fig. 1a) to form a cross-linked DGEBA-DDS structure, wherein the hydroxy (OH) group is a possible chemical reaction site for adhesion with adherends^{6,7}. Also, polyetheretherketone (PEEK, Fig. 1a) is a promising thermoplastic polymer matrix for CFRPs^{8–11}. For adhesion on an inert PEEK surface, the wettability and chemical reactivity of PEEK must be improved using surface modifications^{12–16}. Plasma treatment is a widely-used technique to introduce hydrophilic reactive functional groups on the target surface¹⁷. In addition, plasma treatment introduces a sub-µm-level surface roughness (Fig. 1b and Supplementary Fig. 1), which can contribute to mechanical interlocking^{17,18}. Even for such typical adhesive materials, direct experimental observation of the interfacial chemical bond in the bonded structure has been missing to our knowledge. One potential experimental approach to developing a molecular-level understanding of adhesion is to visualize the geometric structures of the adhesive interface and their local chemical-state analysis.

Synchrotron X-ray microprobes have enabled us to extend the elucidation of geometric, electronic, and chemical states from ideal model systems to practical applications¹⁹. In this article, using soft X-ray spectromicroscopy²⁰, we shed light on the possible physical and chemical origins of adhesion at the plasmapretreated DGEBA-DDS/PEEK interface. X-ray fluorescence (XRF) imaging enabled us to characterize the physical structure of the adhesive interface, where two different bond failure modes existed. Furthermore, by performing microprobe soft X-ray absorption spectroscopy (XAS), we were able to directly observe the interfacial covalent bonds due to the esterification of the OH group in DGEBA-DDS with the carboxy (COOH) group at the plasma-treated PEEK surface.

Results and discussion

Soft X-ray imaging. For soft X-ray imaging of the adhesive interface, a cross-section of the DGEBA-DDS/PEEK interface was magnified at the sample surface by oblique polishing (Fig. 1b). The exposed cross-section was introduced into a trifluoroacetic anhydride (TFAA) atmosphere, which can fluorinate the OH



Fig. 1 Chemical and physical structures of the sample. a Chemical structures of DGEBA, DDS, PEEK, and the curing reaction of DGEBA-DDS. **b** Oblique polishing. The geometrical directions of the sample before polishing (*X*, *Y*, and *Z*) and after polishing (*X*_p, *Y*_p, and *Z*_p) are indicated along with the corresponding illustration. Examination using an atomic force microscope (AFM) revealed hill-and-valley structures at the plasma-treated PEEK surface. Uncured DGEBA-DDS was adhered to the plasma-treated PEEK surface via the curing reaction of DGEBA-DDS. The cross-section of the DGEBA-DDS/ PEEK interface was exposed by polishing the *X*-*Y* plane of the adhered sample at the oblique angle of 2°. The depth distribution along the Z direction was reflected in the *Y*_p direction. The TFAA treatment was applied to the exposed cross-section. XRF imaging was performed at the *X*_p-*Y*_p plane. **c** Microprobe XRF spectra (*hv* = 780 eV) in the regions of DGEBA-DDS and PEEK. A soft X-ray beam from SPring-8 synchrotron radiation was focused by the Fresnel zone plate (FZP) and the order sorting aperture (OSA). XRF spectra were measured using a silicon drift detector (SDD). The XRF image was obtained by scanning the sample in the *X*_p and *Y*_p directions.



Fig. 2 Soft X-ray imaging of the DGEBA-DDS/PEEK cross-section. a An optical microscope image of the DGEBA-DDS/PEEK cross-section. XRF images were measured in the dashed-square region. The XAS spectra in Fig. 3 were measured at region X. **b** N K α and F K α images at hv = 780 eV. To identify the contrast difference between the N K α and F K α images, the F K α image was normalized by the N K α image (labeled F/N K α). The interface region is indicated by the dashed line. **c** The upper panel shows O K-edge XAS spectra at regions I, II, and III. XAS spectra (colored thin solid curves) were measured at five different neighboring spots, and the dotted curve indicates their averaged data. The lower panel shows XAS spectra for the PEEK and DGEBA-DDS bulk materials.

group²¹, enabling OH-group imaging via F K α XRF. As shown in Fig. 1c, the microprobe XRF spectra at the incident photon energy (*hv*) of 780 eV exhibited a stronger F K α (i.e., OH) signal at DGEBA-DDS than at PEEK. The element concentration distribution of the adhesive cross-section can be imaged by distinguishing the XRF energy emitted from the sample.

Figure 2a shows the optical microscope image of the adhesive cross-section, where the dark and bright areas correspond to the areas of PEEK and DGEBA-DDS, respectively. The complex structural pattern existed in the DGEBA-DDS area and was found to originate from the delamination of DGEBA-DDS as judged from the height-profile analysis using the scanning white-light interferometry (Supplementary Fig. 2). Three chemical states can exist in the DGEBA-DDS area due to: the presence of DGEBA-DDS [case (i)], the exposure of PEEK without the plasma-treated surface [case (ii)], and the exposure of the plasma-treated surface of PEEK [case (iii)]. Determining the type of adhesive delamination is an important issue in the science and technology of adhesion and can be resolved by using XRF imaging combined with XAS, which is sensitive to the local chemical environment²²⁻²⁵. In case (i), the XRF image should show the N Ka and F Ka signals from the amine and OH groups in DGEBA-DDS, respectively. Both the N Ka and F Ka signals should vanish in case (ii), and only the F Ka signal should be detected from the plasma-treated PEEK surface in case (iii).

Figure 2b shows the XRF images of the adhesive cross-section measured at the dashed-square region in Fig. 2a. The N Ka image exhibited a complex distribution, which follows the structural pattern in the optical microscope image, and the distribution of F Ka was partially different from that of N Ka. The signaled region in the contrast difference between F Ka and N Ka (labeled F/N Ka) indicated the presence of the OH group and the absence of the amine group. We found three types of chemical states in the area of DGEBA-DDS, labeled I, II, and III. Region I showed the N Ka and F Ka signals, indicating the presence of DGEBA-DDS [case (i)]. Indeed, the microprobe O K-edge XAS spectrum in region I exhibited the characteristics of DGEBA-DDS (Fig. 2c). In region II, both the N Ka and F Ka signals were negligibly weak, and the corresponding XAS spectrum exhibited the characteristics of PEEK. Therefore, region II reflected the absence of



Fig. 3 Schematics of the adhesion failure determined by XRF imaging. **a** Presence of DGEBA-DDS. Both the N K α and F K α signals were observable in region I. **b** In region II, neither N K α nor F K α signals were observable due to the substrate failure. In region III, only the F K α signal was observable due to the interfacial failure.

DGEBA-DDS and the exposure of PEEK without the plasmatreated surface [case (ii)]. In region III, the N K α signal was missing, while the F K α signal was detected. We can conclude that DGEBA-DDS was removed in region III, and the surface of PEEK with the OH group was exposed [case (iii)]. The adhesion failure modes determined from the XRF imaging are shown in Fig. 3. Because region II showed the surface of PEEK without the OH group, the delamination of DGEBA-DDS in region II can be attributed to the substrate failure. On the contrary, region III, which showed the topmost surface of PEEK with the plasmainduced OH group, can be explained by the interfacial failure. The substrate failure might have originated from overtreatment by the oxygen plasma, resulting in the unexpectedly poor adhesion^{10,12}.

As demonstrated here, multichannel XRF imaging enabled us to characterize both the physical and the chemical structures of the adhesive interface at a μ m scale. Furthermore, molecular-level insights about the adhesive interface can be assessed by microprobe XAS. In fact, the XAS spectrum in region I exhibited a shoulder-like feature at hv = 531.5 eV, which reflected the interfacial chemical reaction as discussed in the next section.

Local chemical-state analysis. Two different adhesion failures revealed by the XRF imaging could be governed by the chemical interaction between the adhesive and the adherend. To discuss the local chemical interaction at the adhesive interface, we



Fig. 4 Microprobe XAS measurements of the DGEBA-DDS/PEEK cross-section. a O K-edge XAS spectra by the partial-fluorescence-yield method. The XAS measurement positions 1-15 are indicated together with the corresponding O K α and F K α images measured at hv = 780 eV. The interface region is indicated by the white dot curve in the XRF images. **b** Line shape analysis using three Gaussian components for the pre-edge peak in XAS of 1, 10, and 15 after background subtraction. Energy distribution of features A and B in XAS is also shown. **c** Line shape analysis using four Gaussian components for the pre-edge peak in XAS of 1, 9, 10, and 15. The intensity distribution of features B₁ and B₂ in XAS is also shown. Fitting data for all XAS spectra are given in Supplementary Fig. 3. Error bars in panels b and c are defined as the standard deviation in the least-squares fitting using the Gaussian function.

measured the microprobe XAS spectra at the uniformly polished interface region (labeled X in Fig. 2a). The COOH group and the OH group induced by the plasma treatment on the PEEK surface can react with DGEBA-DDS through esterification and etherification, respectively. In the O K-edge XAS spectra, the esterification can be reflected in the π^* -derived pre-edge peak, while the etherification can be reflected in the σ^* -derived broad feature. In the following paragraphs, we describe the evidence for the esterification.

Figure 4a shows the microprobe O K-edge XAS spectra of the DGEBA-DDS/PEEK cross-section measured at regions 1–15,

which are indicated by filled circles along with the corresponding O and F K α images. The XAS spectra of the adhesive cross-section exhibited a pre-edge peak at hv = 530-533 eV consisting of features A, B, and C, and the pre-edge fine structure was dependent on the measurement position, suggesting the possibility of interfacial esterification in the bonded structure.

Feature A due to the O $1s \rightarrow \pi^*$ transition at the carbonyl (C=O) group²⁶ appeared at the constant hv of 530.84 eV in regions 1–8, and exhibited an exponential-like energy shift in regions 9–15, indicating the depth distribution of the chemical species. According to the gas-phase core excitation spectra²⁷, the

pre-edge energy of the C=O group with aromatic hydrocarbons was 0.1 eV lower than that with aliphatic hydrocarbons. Feature A at regions 1–8 and 9–15 can be explained by the C=O group with aromatic rings and that with aliphatic species, respectively. The formation of the C=O group with aliphatic species originated from the C–C bond scission around the C=O site in PEEK by plasma-induced oxygen radicals. In this region, we found evidence for covalent-bond formation by analyzing feature B, which was missing in the bulk areas of PEEK and DGEBA-DDS (Fig. 2c).

From the line shape analysis (Fig. 4b), feature B appeared at hv = 531.52 eV in regions 1–9, and became visible at the higherhv side of 531.67 eV from region 10. The total energy shift in feature B was 0.15 eV. In the gas-phase core excitation spectra²⁷, the pre-edge peak derived from the COOH group appeared at a higher-hv side than that derived from the C=O group. Furthermore, the pre-edge energy of carboxylic acids (R-COOH) was about 0.2 eV lower than that of the carboxylate esters (R-COO-R')^{27–29}. Based on these results, feature B at hv= 531.52 eV can be ascribed to the COOH group induced by the plasma treatment. Feature B at hv = 531.67 eV can be ascribed to the formation of an ester bond between the COOH group on the PEEK surface and the reactive OH and/or remanent epoxy groups in DGEBA-DDS, which indicates covalent-bond formation at the adhesive interface.

Because different chemical species contributed to feature B in XAS, we performed an additional line shape analysis by considering the coexistence of the COOH group (B_1) and the ester bond (B_2) as shown in Fig. 4c. The contribution of the ester bond (B₂) rapidly attained a maximum between spectra 9 and 10, which corresponds to the interface region as determined from the O Ka and F Ka images. The maximum intensity of B₂ was observable in regions 10-13 due to the large probing depth along the Z_p direction of the fluorescence-yield O K-edge XAS of about 380 nm (see, "Methods"), which was able to detect the buried interface beneath DGEBA-DDS. The detection of B₂ in the thicker DGEBA-DDS region (regions 14 and 15) might have originated from the plasma-induced surface roughness of PEEK, which introduces an ununiform thickness of DGEBA-DDS affecting the detection probability for the buried interface.

We briefly discuss the other spectral features in the pre-edge peak. Our previous experimental and theoretical work demonstrated that feature C originated from the OH… π interaction in DGEBA-DDS as well as the background of lower-hv pre-edge peaks²⁶. In addition, the O 1s $\rightarrow \pi^*$ transition at the sulphonyl (S=O) group in the DDS unit existed around hv = 532 eV, and its contribution to the XAS spectral feature was rather weak due to the small spatial distribution of the π^* orbital at the S=O site²⁶. We can, therefore, conclude that these chemical states contributed to a non-covalent bond rather than a covalent one.

Based on these observations, in Fig. 5, we show the proposed adhesion mechanism at the DGEBA-DDS/PEEK interface pretreated by atmospheric pressure plasma. Before the plasma treatment (Fig. 5a), the C=O group existed in PEEK (A). After the plasma treatment (Fig. 5b), plasma-induced oxygen radicals introduced the bond scission of PEEK and the formation of hydrophilic groups such as COOH (B₁), as confirmed by X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 4). After adhesion (Fig. 5c), the OH group and/or the remanent epoxy group in DGEBA-DDS were able to form an ester bond with the plasma-induced COOH group on PEEK (B₂). The formation of the ester bond and the complex interface structure contributed to the adhesive strength from the viewpoints of the covalent bond and the macroscale mechanical interlock, respectively.



Fig. 5 Schematics of the adhesion mechanism of DGEBA-DDS on plasmatreated PEEK. a Untreated PEEK sample. The C=O group in PEEK appeared as feature A in XAS. **b** Plasma-treated PEEK sample. Plasma-induced oxygen radicals introduced the bond scission of PEEK and the formation of a COOH group, which appeared as feature B₁ in XAS. **c** The DGEBA-DDS/ PEEK interface. The curing reaction of the DGEBA monomer with the DDS curing agent is also shown. The epoxy group in DGEBA is covalently bonded with the amino group in DDS to form a cross-linking structure of DGEBA-DDS. The unreacted epoxy group in the DGEBA unit forms an ester bond with the plasma-induced COOH group on the PEEK surface, which appeared as feature B₂ in XAS.

Conclusion. We used soft X-ray spectromicroscopy to visualize the geometric and chemical states of the archetypal adhesive interface. We succeeded in revealing the molecular-level origins of the adhesion as well as its unexpected failure at the adhesive interface, which had remained an unexplained phenomenon. Currently, the correlation between the chemical-state distribution and the mechanical properties at the adhesive interface remains unclear – this relationship needs to be clarified to enable further innovation of adhesion technology for next-generation mobilities. As conventional bolted joint and arc welding techniques can be managed using torque and amperage, respectively, adhesive bonding must be controlled by specific critical factors for adhesion such as the presence or absence of chemical bonds that have larger bond enthalpies than the intermolecular forces^{30,31}, and their spatial distribution. Our present study serves as a benchmark for a systematic soft X-ray microprobe examination of adhesive interfaces with different adhesion parameters to pave the way for developing a comprehensive understanding of adhesive interfaces from a range spanning the sub-mm scale to the molecular level.

Methods

Soft X-ray spectromicroscopy. The soft X-ray spectromicroscopy experiments were performed at the soft X-ray undulator beamline BL17SU of SPring- 8^{20} , 3^{2-34} . The energy resolving power ($h\nu/\Delta E$) was about 9000 in the present work. The incident photon energy $h\nu$ was calibrated by measuring (i) the Au 4f core-level photoemission spectra of gold using both the first- and second-order peaks and (ii) the O K-edge XAS spectrum of a gas-phase O₂ molecule. For XRF and XAS measurements, the higher-order incident photon beam was suppressed using a higher-order cutoff mirror system based on a Ni-coated mirror. As shown in Fig. 1, the incident soft X-ray beam was focused by the Fresnel zone plate (FZP), and the first-order diffraction beam was irradiated on the sample through the order sorting aperture (OSA). The energy and intensity of the fluorescent soft X-rays emitted from the sample were analyzed using a silicon drift detector (SDD) for measuring XRF and partial-fluorescence-yield XAS. XRF images were obtained by scanning

the sample in the X and Y directions. The angle between the incident X-ray beam axis and the fluorescent X-ray beam axis was 90°, and the incident angle was 26.5° with respect to the surface normal. Other details, such as the optics system, are described in ref. ²⁰.

Because focused X-ray beams quickly introduce radiation damage to molecular materials, we characterized the radiation damage for DGEBA-DDS and PEEK, as presented in refs. ²⁶ and ³⁵. In the present work, XRF and XAS measurements were performed under helium atmosphere (*ca.* 1×10^5 Pa) and a defocused beam configuration to reduce radiation damage. The diameter of the incident X-ray beam was 0.95 µm in the full-width at half maximum (FWHM) of the Gaussian distribution. To compensate for the lowering of the spatial resolution due to the defocused beam configuration, the depth cross-section of the DGEBA-DDS/PEEK interface was magnified 28.65-times on the sample surface by the 2°-off oblique polishing as described below.

Radiation damage. To assess radiation damage in the sample materials, we determined the absorbed dose (D_a) . From the 1/e of the exponential-like intensity decay of the XAS feature as a function of the X-ray dose, we previously evaluated the critical absorbed dose (D_a^{-c}) ; 3.45 MGy for the OH group in DGEBA-DDS and 14.52 MGy for the C=O group in PEEK^{26,35}. Here, D_a is equal to the kinetic energy released in the material (Kerma) under the charged-particle equilibrium. Kerma is expressed as the product of the irradiated photons and the absorbed energy per unit mass by one photon,

$$D_{\rm a} = \text{Kerma} = N_{\rm ph} t_{\rm dose} \times \frac{E_{\rm p}[1 - T(E)]}{\lambda S \rho} (\text{Gy})$$

where $N_{\rm ph}$, $t_{\rm dose}$, $E_{\rm p}$, T(E), λ , S, and ρ represent the photon flux, the photon dose time, the photon energy, the transmission probability of the materials, the photon attenuation length, the photon beam size, and the density of the materials, respectively. $N_{\rm ph}$ was about 0.25×10^9 ph s⁻¹ in the present experimental setup. *S* on the sample surface was about $5.13 \,\mu\text{m}^2$ in the ±3 σ confidence interval, where σ is the attended denicities of the Gaussian distribution.

is the standard deviation of the Gaussian distribution. We calculated λ and T(E) using ref. ³⁶ by considering the monomer chemical structure of TFAA-treated DGEBA-DDS ($C_{35}H_{35}N_2O_5F_5$, $\rho = 1.22$ g cm⁻³) and PEEK ($C_{19}H_{12}O_3$, $\rho = 1.44$ g cm⁻³). We determined λ to be 850 nm at O Ka ($h\nu = 530$ eV) and 1650 nm at F Ka ($h\nu = 780$ eV) for DGEBA-DDS and 730 nm at O Ka and 1400 nm at F Ka for PEEK. Under the assumption that the mobile surface layer of the adherend to form the adhesion interface was 10 nm³⁷, T(E) of the interface layer was calculated to be 0.98924 at O Ka and 0.99333 at F Ka for DGEBA-DDS and 0.98634 at O Ka and 0.99292 at F Ka for PEEK. Using these values, D_a/t_{dose} was calculated as 0.04 MGy s⁻¹ for O Ka of DGEBA-DDS, 0.02 MGy s⁻¹ for F Ka of DGEBA-DDS, 0.05 MGy s⁻¹ for O Ka of PEEK, and 0.02 MGy s⁻¹ for F Ka

Both XRF and XAS measurements in this work were obtained by considering the threshold of the radiation damage based on D_a/t_{dose} : the XRF images were measured at 1 s per pixel (0.02–0.05 MGy per pixel). The pre-edge fine structures at the interface regions were observable at 3.20 MGy per spectrum, which is lower than the critical absorbed dose for the weak OH… π interaction in DGEBA-DDS.

Probing depth. The XRF and XAS data were obtained by measuring fluorescent X-rays using SDD, which was located at a direction of 63.5° from the surface normal of the sample as shown in Fig. 1b. Fluorescent X-ray measurement is an inherent bulk-sensitive method. Using ref. ³⁶ considering the monomer chemical structure of TFAA-treated DGEBA-DDS with $\rho = 1.22 \text{ g cm}^{-3}$, λ of the O K-edge X-rays was 850 nm for DGEBA-DDS. At the present measurement geometry without considering the self-absorption effect^{38,39}, the probing depth for O K-edge XAS could be calculated as 380 nm along the Z_p direction, which enabled the detection of the buried interface. The detection probability for the buried interface was dependent on the thickness of DGEBA-DDS on PEEK. From the atomic force microscope, the surface roughness of PEEK induced by the plasma treatment was about 350 nm in the peak-to-peak value. The plasma-induced surface roughness of PEEK introduces the unuiform thickness of DGEBA-DDS in the order of hundreds of nanometers, which affects the detection probability for the buried interface.

Line profile analysis of XAS. Before conducting line profile analysis, the background of all XAS spectra was subtracted considering the arctangent-type background. After the background subtraction, line shape analysis was performed under the assumption that three Gaussian-type components contributed to the pre-edge peak (Supplementary Fig. 3). To reproduce the tail structures of the pre-edge peaks, the Gaussian width of the lowest- and highest-energy components A and C were used as 0.70 eV and 0.90 eV, respectively. The Gaussian width of the other component B was set to be the same as the lowest-energy component A (0.70 eV). These Gaussian widths were broader than that estimated from the O 1s core-hole lifetime of about 3-6 fs^{40,41}. The peak area and centroid energy of Gaussian components A–C were used as the free parameters for the least-squares fitting.

As shown in Supplementary Fig. 1, hill-and-valley microstructures existed on the plasma-treated PEEK surface within the 10 μm square range. The maximum height difference was about 360 nm, resulting in an inhomogeneous thickness distribution in the DGEBA-DDS layer. If the oblique polishing angle was very

shallow (i.e., 2° with respect to surface in the present work), such a large thickness distribution was not negligible in the XAS measurements with the sample scan step of 5 μ m.

Sample preparation 1: adhesive bonding. The PEEK substrate used was a commercialized product (VICTREXTM PEEK $450G^{TM}$) that was cleaned with 2-butanone before the plasma treatment. The PEEK surface was further cleaned and functionalized using an atmospheric pressure plasma unit from FUJI corporation (Tough Plasma FB20). The plasma was generated by a gas mixture of nitrogen (60 L min⁻¹) and dry air (20.6 L min⁻¹). The distance between the plasma exit nozzle and the PEEK surface was 5 mm. The effects of the plasma treatment on the PEEK surface were confirmed by the contact angle and XPS (Supplementary Fig. 4). The degree of the plasma treatment was controlled by the plasma irradiation time and the treatment cycle, as determined from the double cantilever beam test. The plasma treatment condition that resulted in the strongest adhesive strength (*ca.* 1500 J m⁻²) was used for the present sample (Supplementary Fig. 5).

The DGEBA-DDS/PEEK sample was prepared using the following steps. (i) DDS powder (D0089, Tokyo Chemical Industry Co., Ltd.) was introduced into a liquid DGEBA resin (jER1001, Mitsubishi Chemical Corp.) kept at around 70 °C with a molar ratio of DGEBA: DDS = 2:1. (ii) The mixture of DGEBA and DDS was stirred at 110 °C for 10 min. and subsequently at 120 °C for 20 min., and then dropped onto the plasma-treated PEEK surface. (iii) Next, the DGEBA-DDS/PEEK sample was heated at 180 °C for 2 h under a vacuum condition for the curing reaction.

Sample preparation 2: oblique polishing. The DGEBA-DDS/PEEK sample was mechanically polished using a mechanical polisher unit from Ikegami Seiki Co. (IS-polisher ISPP-1000). The interface cross-section structure was exposed on the sample surface by an oblique polishing angle of 2° resulting in a magnification factor of 28.65. To reduce the mechanical damage to the interface structure, we used the weight canceller application of ISPP-1000 for low load polishing without embedding the sample. XRF imaging and XAS measurements were obtained by analyzing soft X-rays emitted from the polished cross-section. Even after such careful polishing, we observed substantial roughness on the sample surface due to the partial delamination of DGEBA-DDS from the PEEK substrate, originating from the inhomogeneous adhesion properties.

Sample preparation 3: TFAA treatment. To efficiently visualize the OH distribution in the sample, the DGEBA-DDS/PEEK cross-section was modified by TFAA [(CF₃CO)₂O], which can fluorinate the OH group as follows²¹:

$$R - OH + (CF_3CO)_2O \rightarrow R - O - CO - CF_3 + CF_3COOH$$

The DGEBA-DDS cross-section sample was introduced into the TFAA atmosphere at room temperature and atmospheric pressure for 1 h. After the treatment, the sample was introduced to a vacuum environment to remove the unreacted TFAA from the sample. The degree of the TFAA treatment was confirmed by AlK α XPS (Supplementary Fig. 6).

Data availability

The experimental data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions

H.Y., M.O., N.Y., and T.H. designed the experiments. H.Y., T. Ishihara, and M.O. performed the experiments and the instrumental setup. K.H., N.Y., and K.T. prepared the samples for the experiments. O.T., H.Y., and T.H. discussed the theoretical considerations of XAS spectra in the present system. T. Ishikawa supervised the project on behalf of RIKEN. All authors contributed to interpreting the results and writing the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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