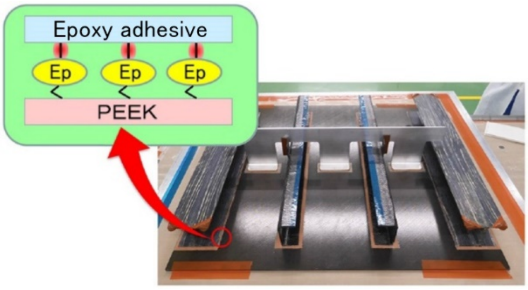
Development of Destructive Surface Modification of PEEK (Poly Ether Ether Ketone) for High Adhesion Strength



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Since the early 1980s, Mitsubishi Heavy Industries, Ltd. (MHI) has continued with research for the application of Carbon-Fiber-Reinforced Plastics (CFRP) in aircraft structures. Poly(ether ether ketone) (PEEK) is a thermoplastic resin that has recently attracted attention as a matrix for CFRP. PEEK is superior mainly in terms of strength, heat resistance and chemical resistance, but has a drawback of having poor adhesive properties. This report presents the destructive surface modifications of PEEK enabling stable adhesion that we developed jointly with each of Kobe University and Kyushu University. The application of these destructive surface modifications can reduce the cost and weight of CFRP structures.

1. Introduction

CFRP, which is a composite material made up of carbon fiber with thermosetting epoxy resin, is widely used in aircraft structures, apart from duralumin, a hard alloy of aluminum. Recently, discussion is going on to shorten the time for forming the parts of aircraft structures by applying thermoplastic CFRP (CFRTP : Carbon-Fiber-Reinforced Thermoplastics) produced by combining with carbon fibers instead of thermosetting epoxy resins. Among the thermoplastic resins, PEEK, which is a super engineering plastic, has often been adopted mainly because of its strength, heat resistance and chemical resistance. This report focuses on adhesion of CFRTP with a PEEK matrix.

With CFRTP, the use of a hot press machine enables parts to be formed at low cost in a short period of time, but it is difficult to form parts that are larger than the molds (such as aircraft skins) unless an autoclave is used. This necessitates the use of a technology to assemble CFRP and CFRTP connected together. If bolted, however, the carbon fiber acting as the primary load transmitter will be disrupted by bolt holes. The strength will be drastically reduced, leading to the increased thickness and weight of structures. Therefore, a joint method requiring no bolts, namely adhesive structure, is preferable.

PEEK exhibits poor adhesive properties, making it impossible to adhere without performing any surface treatment. For this purpose, there is a method called plasma treatment by which functional groups are introduced on the PEEK surface[(1)]. This method, however, has problems such as the diminishing of the chemical modification effect with time and the difficulty in defining the intensity of plasma.

This report describes two types of new, unique methods for PEEK surface modification, one developed jointly with Kobe University and the other with Kyushu University. In these methods, the formation of covalent bonds – strong chemical bonding – is induced at the interface between PEEK and the adhesive. The adhesives we used are epoxy based. This type of adhesive is often

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adopted for aircraft structures because of its superior strength and rigidity.

2. Friedel-Crafts reaction treatment (Kobe University modification)

This chapter summarizes a method to modify the surface of PEEK, which was jointly developed with Kobe University[2]. In the Kobe University modification, epoxy groups are introduced to the surface of PEEK by the Friedel-Crafts reaction in which epoxy groups are allowed to react with the aryl groups in PEEK through the use of Lewis acids. This enables the PEEK surface to be covalently bonded to amines, which are curing agents for epoxy adhesives, through epoxy ring-opening polymerization, resulting in strong adhesion.

2.1 Kobe University modification – procedure

In the presence of epoxy groups, Lewis acids used in the Friedel-Crafts reaction promptly facilitate the opening of the epoxy ring. It is therefore difficult to introduce epoxy groups into PEEK through a single chemical reaction. Two steps were therefore utilized for this purpose (**Figure 1**).

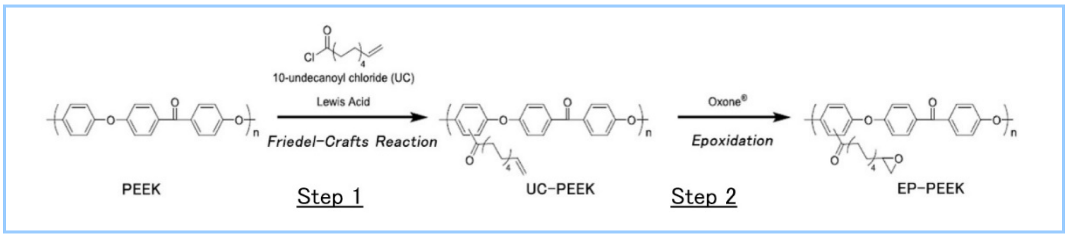

Figure 1 Kobe University modification – procedure

(1) Step 1

The Lewis acid used was a chloroform solution in which aluminum bromide ($AlBr_3$) was dissolved. The surface of PEEK was reacted with 10-undecenoic chloride (UC) and the resulting product is referred to as UC-PEEK. A carbon double bond was thus introduced to the terminal of aryl group in PEEK.

(2) Step 2

To replace the terminal carbon double bond with an epoxy ring, Oxone® (potassium peroxymonosulfate) dissolved in a mixture solvent of acetone and water was dropped on UC-PEEK before stirring. The resulting PEEK has epoxy groups on the surface and is referred to as EP-PEEK.

2.2 Kobe University modification – confirmation of the chemical reaction

To examine whether the chemical reaction had progressed as expected, EP-PEEK was reacted with a fluorinated amine (1H,1H-pentadecafluorooctylamine) to introduce fluorine atoms to the epoxy groups (the resulting product is referred to as Am-PEEK). The X-ray photoelectron spectroscopy (XPS) profiles of Am-PEEK are given in **Figure 2**, which indicates the detection of fluorine. It can be therefore inferred that the reaction took place as expected.

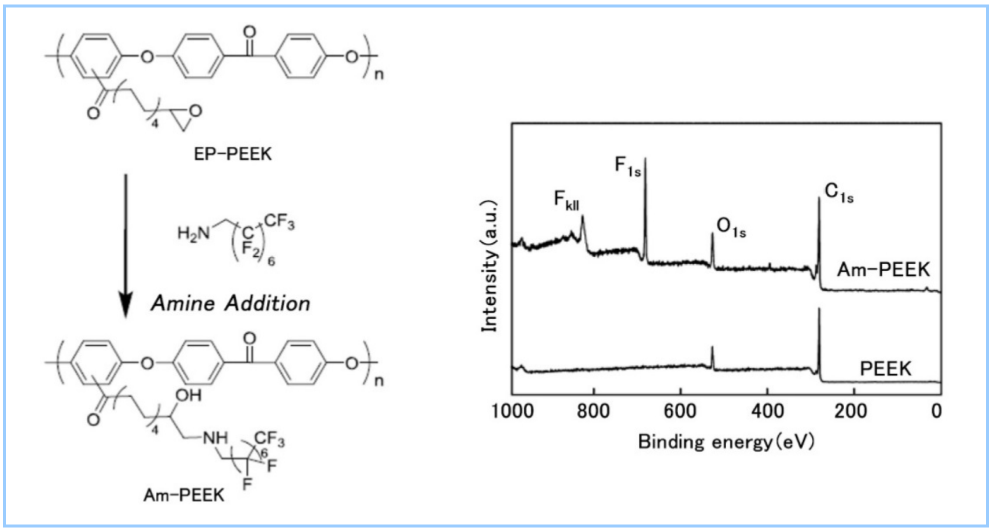

Figure 2 Am-PEEK production process and XPS profiles

Next comes the comparison of the penetration depth of surface modification between the plasma treatment and the Kobe University modification, which was performed by etching the surface using an argon ion cluster beam. For the plasma treatment, plasma was irradiated for 10 seconds at 100 W under an oxygen atmosphere of approximately 1.2 Pa in a vacuum plasma apparatus. The results show that the penetration is deeper with the Kobe University modification than the plasma treatment. The modified layer of Am-PEEK, which is thicker than the plasma treatment, is considered to more effectively prevent or delay the reorientation/migration of functional groups at the surface, resulting in the advantage of a long-lasting modification effect.

As PEEK has some crystallinity, the degree of crystallinity was measured by X-ray diffraction (XRD) before and after the Kobe University modification. The results indicate that PEEK is 28% crystalline before the treatment and 26% after the treatment, showing almost no difference (**Figure 3**). Because of this unaffected degree of crystallinity before and after the treatment, the impact of the treatment on the matrix strength is expected to be small, which is advantageous for the surface modification method.

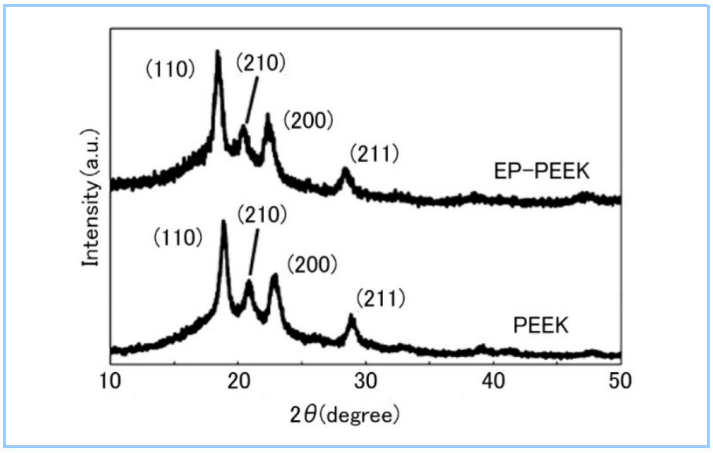

Figure 3 XRD profiles after Kobe University modification

2.3 Kobe University modification – strength properties

As shown in **Figure 4**, the single lap shear test was conducted using the specimens treated by the Kobe University modification, to assess the adhesion shear strength.

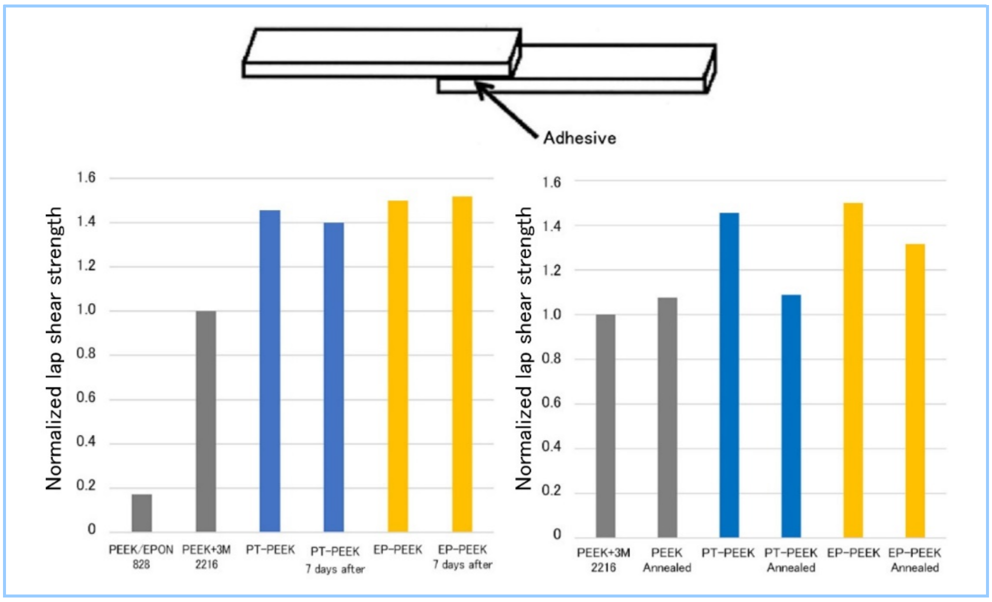

Figure 4 Kobe University modification – lap shear strength test results
(Left: lasting effect, right: lap shear strength after thermal annealing)

The specimen material used was a carbon fiber composite with a PEEK matrix. For comparison, two types of adhesives were used: 3M Scotch-Weld 2216 B/A Gray (referred to as 3M 2216) and an EPON™ Resin 828 curing agent, 1-methylimidazole. With regard to the treatment before adhesion, the specimens treated with plasma (referred to as PT-PEEK) were also tested in order to compare with the Kobe University modification. The adhesive joint area is 13 mm × 13 mm.

In this test, shear strength data were collected for (1) different types of adhesives, (2) specimens adhered after being left for 7 days from the treatment to confirm the lasting effect of modification and (3) those adhered after the post-treatment annealing at 150°C to evaluate the robustness of surface modification. The results are given in Figure 4. The data shown therein were normalized by considering the shear strength of PEEK joints adhered using 3M 2216 without surface treatment as 1.0.

The test results show that (1) there was almost no adhesion strength when specimens were bonded without surface treatment using an EPON^{TM} Resin 828 curing agent (1-methylimidazole) as an adhesive, while a certain level of adhesion strength was observed in the case of 3M 2216. Higher adhesion strength was obtained when 3M 2216 was used in combination with the Kobe University modification.

(2) Regarding the lasting effect of modification, the shear strength was reduced in 7 days from the plasma treatment, but remained unchanged for the specimens treated by the Kobe University method (i.e., EP-PEEK).

(3) When it comes to the robustness of surface modification, the decline in the shear strength after annealing was also smaller with the Kobe University modification than the plasma treatment. This is presumably because the penetration of surface modification by the Kobe University modification is deeper than the plasma treatment, preventing the reorientation of functional groups more effectively and therefore resulting in less decline in the shear strength.

3. Polymer brush formation modification (Kyushu University modification)

Given in this chapter is a summary of the treatment method developed with Kyushu University[3][4]. The Kyushu University modification focuses on the chemical structure of PEEK consisting of units of benzophenone, which is a photoinitiator. PEEK is irradiated with ultraviolet (UV) ray to generate free radicals within it, leading to the formation of a dense polymer brush with epoxy groups (**Figure 5**).

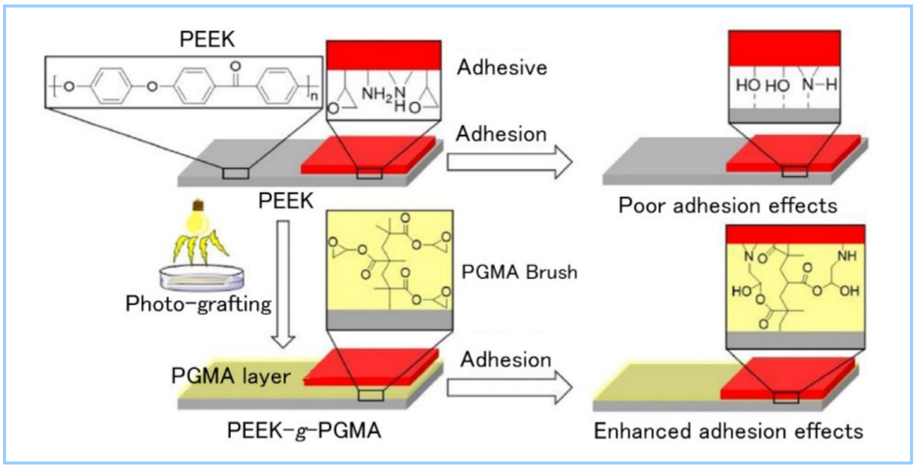

Figure 5 Schematic illustration of Kyushu University modification

3.1 Kyushu University modification –procedure

After cleaning, PEEK was immersed in glycidyl methacrylate (GMA) and was irradiated with UV ray (wavelength: 240-400 nm) at room temperature. In this way, poly(glycidyl methacrylate) (PGMA), which has many epoxy functional groups, was introduced to the surf ace of PEEK. The resulting product is referred to as PEEK-g-PGMA. The standard duration of UV irradiation is 120 minutes. The irradiation intensity in the following confirmation test is of two levels: low (2 mW/cm^2) and high (8 mW/cm^2), which are respectively referred to as PEEK-g-PGMA$_{2\text{-}120}$ and PEEK-g-PGMA$_{8\text{-}120}$. The effect of modification was thus evaluated.

3.2 Kyushu University modification – confirmation of the chemical reaction

Figure 6 shows the XPS profiles of C1s binding energy for PEEK-g-PGMA. For comparison, the profiles of the PEEK specimens that were UV-irradiated at 2 and 8 mW/cm^2 for 120 minutes are also given in Figures 6-b' and 6-c', respectively. PEEK (Figure 6-a) has three peaks, each at 284.5 eV for the C-C bond, 286.5 eV for the C-O bond and 291.1 eV, the somewhat broad peak of which is attributed to aromatic rings (π-π^* bond satellite peak). The figures indicate that UV irradiation or the introduction of PGMA induces the COO bond at 288.7 eV. The molar ratio of the C-O bond to C-C bond remained almost unchanged in the case of performing only UV irradiation. When PGMA was introduced, however, the proportion of the C-O bond was increased. This suggests that PGMA has been successfully grafted on the surface of PEEK. In a comparison between PEEK-g-PGMA$_{2\text{-}120}$ and PEEK-g-PGMA$_{8\text{-}120}$, the latter shows higher intensities of COO bond and C-O bond, indicating deeper surface modification.

The contact angle of water on the surface was also measured. PEEK (without surface modification) has a water contact angle of 79.3° ± 1.8°, while PEEK-g-PGMA$_{2\text{-}120}$ shows a lower angle of 62.2° ± 2.3°. In the case of PEEK with a surface that was spin coated with PGMA, the value is 63.0° ± 2.9°, which is close to that of PEEK-g-PGMA$_{2\text{-}120}$.

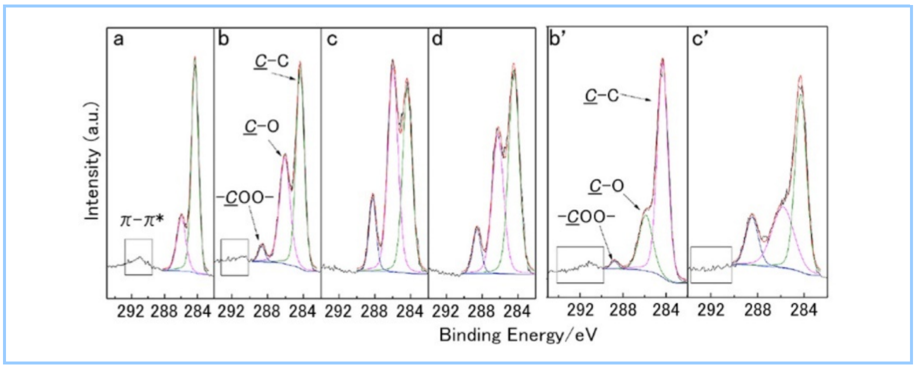

Figure 6 XPS profiles of C1s for CFR-PEEK (a), PEEK-g-PGMA$_{2\text{-}120}$ (b), PEEK-g-PGMA$_{8\text{-}120}$ (c), spin coated PGMA (d), PEEK UV-irradiated at 2 m/W/cm^2 for 120 min (b') and PEEK UV-irradiated at 8 mW/cm^2 for 120 min (c')

3.3 Kyushu University modification – strength properties

The single lap shear test was conducted using the specimens treated by the Kyushu University modification .

The specimen used was PEEK (thin and thick films: 0.2 mm and 4 mm in thickness) and the adhesive used was EPON™ Resin 828 with ethylenediamine as a curing agent. The size of the specimen is 5 mm × 20 mm, while the adhesive joint area is 5 mm × 5 mm. The test results are given in **Figure 7**. The data shown therein were normalized by the lap shear strength of PEEK-g-PGMA$_{2\text{-}60}$ joints. When compared with the untreated specimen, the adhesion strength of PEEK-g-PGMA$_{2\text{-}120}$ was improved by a factor of approximately 6. While keeping the UV irradiation intensity constant at 2 mW/cm^2, a lap shear strength test was conducted with the varying duration of irradiation from 20 to 120 minutes. It has been shown that longer exposure results in higher adhesion strength. Prolonged exposure to UV light is considered to increase the amount of grafted PGMA. This therefore indicates that the adhesion strength is directly correlated with the amount of covalent bonds created by the chemical reaction between epoxy groups in PGMA and amines in the adhesive.

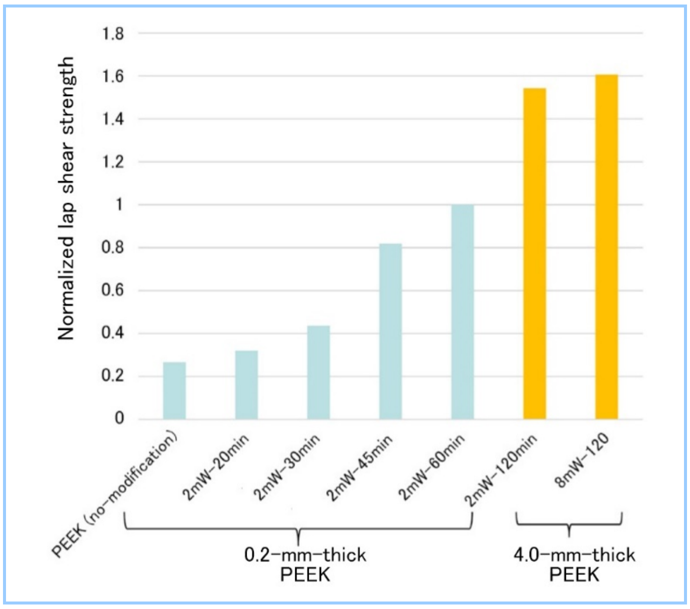

Figure 7　Kyushu University modification – lap shear strength test results

4. Test panel production evaluation

As described above in joint research with two universities, the surface modification technologies for PEEK, the adhesive properties of which are poor, have been established by testing with coupons. As a preliminary evaluation to apply these technologies for assembling actual aircraft structures, the skin-stringer panel, which is one of the main components of an aircraft structure, was test-produced in our company. **Figure 8** provides a schematic of the structure. Two I-shaped stringers on the outer edge and clips are made of CFRTP using PEEK, the skin is made of a thermosetting composite material (CFRP) and the rib is made of an aluminum alloy. As the Kobe University modification is a method of immersion in a solution, it is suitable to treat large parts with complicated shapes. On the other hand, the Kyushu University modification involves only UV irradiation, not requiring a long time or much labor. Therefore, the stringers were treated using the Kobe University modification and the clips were treated with the Kyushu University modification. The obtained parts were assembled by adhesion. A photograph of the completed test panel is presented in **Figure 9**.

Based on this test panel production, we estimated the cost and weight. The results show that the cost for assembly is expected to be reduced by about 30%, compared with the conventional bolting assembly of composite materials. With regard to the weight, the estimated reduction by the assembly with adhesives is approximately 15%.

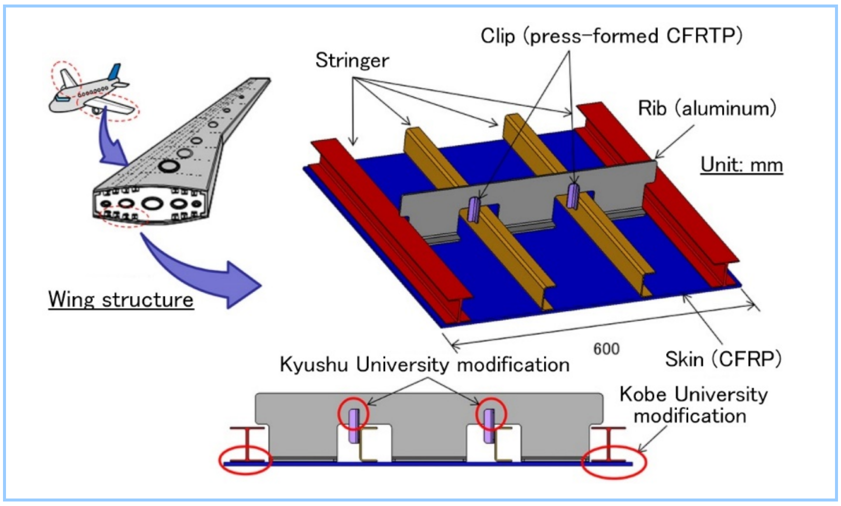

Figure 8　Schematic of skin-stringer panel

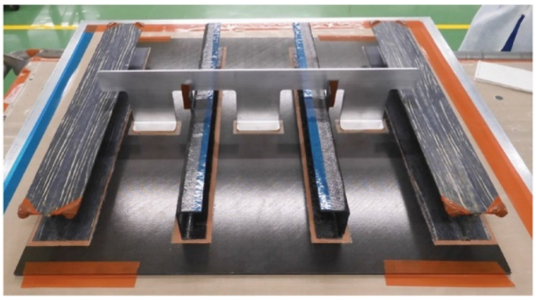

Figure 9 Photograph of completed skin-stringer panel

5. Conclusion

PEEK is known to have poor adhesive properties. In this development effort, we developed and established surface modification treatments that make it possible to adhere, through joint research with Kobe University and Kyushu University. In either treatment, epoxy groups are introduced to the surface of PEEK, thereby inducing a chemical reaction with the curing agent in the adhesive (an amine) to explicitly realize the formation of the strongest chemical bonding called a covalent bond. By applying these destructive surface modifications for the test-production of a small skin-stringer panel in our company, we estimated the weight and cost. The results indicate that assembly with adhesives has a weight and cost reducing effect. Moving forward, we will expand their application to actual-scale aircraft structures. PEEK is also known to be highly biocompatible because of its stability as well as its superior strength, sliding with low friction, etc. As such, we expect that these technologies will also be useful in fields other than aircraft.

The results presented in this report were obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

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