Atmospheric Pressure Plasma Treatment for Composites Bonding

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Bonded joints, with which the number of fasteners to be used is reduced, are effective for the reduction of the weight of a composite structure. However, the challenge for bonded joints is to increase reliability, and the stabilization of surface treatment is indispensable. Therefore, we focused on atmospheric pressure plasma treatment, which can be easily automated, as a stable surface treatment. The effects of the treatment on the surface of composite materials and its adhesiveness were evaluated and its effectiveness was verified.

1. Introduction

Composite materials are lightweight and have high strength, and their application to the structures of aerospace vehicle has been increasing. At present, as with metal structures, composite structures are joined mainly using fasteners, but the bearing strength is low, and the parts thickness must be increased. Therefore, to reduce the weight of a structure, it is desirable to apply a bonded joint rather than a bolted joint. As can be seen in Figure 1, with a bonded joint, the parts thickness at a joint is reduced, the fastener weight is reduced, and in turn, the sealing compounds applied around the fasteners to mitigate electromagnetic effects in a fuel tank is also reduced, resulting in weight reduction. Furthermore, by reducing labor intensive drilling, fastening or sealing operations, adhesively-bonded composite structures can also allow cost saving.

For the application of bonded joints, however, the reliability must be increased. To that end, the stabilization of surface treatment is indispensable.

The surface treatment for composite materials that are generally used at present are sanding, grinding, etc. These methods are performed manually, resulting in non-uniform surface quality as well as higher labor cost.

The peel ply method by which polyester fabrics are applied on the composite material surface and peeled off before bonding is an effective method. But if curing is conducted under inappropriate conditions or if inappropriate peeling is conducted, the polyester components may remain on the surface or the adherend may be damaged at the time of peeling, resulting in a risk of not expressing sufficient adhesive strength.1

Therefore, a more stable surface treatment for composite materials is required. Mitsubishi Heavy Industries, Ltd. (MHI) has been promoting the development of a surface treatment technology using atmospheric pressure plasma treatment, which allows easy automation of the equipment and an increase in adhesive strength through the activation of the surface.2

This report describes the results of the evaluation for the effect and the adhesiveness of atmospheric pressure plasma treatment on the surface of carbon fiber/epoxy composite materials for aircraft.

Figure 1  Comparison between joint with fasteners and bonded joints

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2. Atmospheric pressure plasma treatment

In atmospheric pressure plasma treatment, the surface of the composite material is radiated with active plasma and thereby is decontaminated and activated. It has the advantages of obviating the use of water and allowing easy automatization.

As can be seen in Figure 2, contaminants exist on the surface before treatment. Through atmospheric pressure plasma treatment, active oxygen radicals react with the contaminants, removing them as CO₂ or H₂O. In addition, the active functional groups containing oxygen, such as the hydroxyl group (OH), carbonyl group (C=O) and carboxyl group (COOH), are produced on the CFRP surface. The active functional groups contribute hydrogen bonding with the adhesive, resulting in the expression of a strong adhesive force compared to Van der Waals force.

3. Effects of plasma treatment on composite materials to which mold releasing elements migrate adherend

Contaminants migrated by the mold release agent (organo silicon compound) and the release film (fluoropolymer), which are used in composite cure process, adhere to the surface of a composite material. Usually, the contaminants are removed by sanding, etc., before bonding. A composite material to which contaminants produced by the release film have adhered was subjected to atmospheric pressure plasma treatment using FPE20 (manufactured by Fuji Machine Mfg. Co., Ltd.), and the following evaluations were conducted:

1. Calculation of the surface free energy by measurement of the contact angle
2. Surface elemental analysis by XPS (X-ray Photoelectron Spectroscopy)
3. Acquisition of the Mode-I fracture toughness (GIC) value by DCB (Double Cantilever Beam) test

3.1 Calculation of surface free energy by measurement of contact angle

Water and diiodomethane were dropped on the surface before and after atmospheric pressure plasma treatment, the contact angles were measured, and the surface free energy was calculated by the Owens-Wendt method. As can be seen in Figure 3, the larger the number of treatments, the larger and the more active the surface free energy became. In particular, the polar component that contributes to hydrogen bonding increased, showing that the state of the surface became suitable for bonding.
3.2 Surface elemental analysis by XPS

XPS analysis was conducted on the surface before and after atmospheric pressure plasma treatment, and the existence ratio of elements other than hydrogen was calculated. As can be seen in Figure 4, the larger the number of treatments, the greater the rate of oxygen became. This shows that a functional group containing oxygen has been formed on the surface. On the other hand, it was found that fluorine couldn't be completely removed through atmospheric pressure plasma treatment, and some remained. It is considered that the reason why the surface free energy increased even if fluorine remained on the surface is that the effect of activation by oxygen is significant.

![Figure 4](image)

**Figure 4** Change in the ratio of surface elements by the number of atmospheric pressure plasma treatments

3.3 Acquisition of Mode-I fracture toughness value by DCB test

For the specimen bonded using the epoxy film adhesive, a DCB test, which is sensitive to the effects of surface treatment, was conducted (Figure 5). The specimen was opened starting at the release film in which a part of the specimen was inserted when it was bonded, and crack propagated. From the load displacement curve, the Mode-I fracture toughness value was obtained. In addition, the failure mode for the fracture surface where crack propagated was evaluated. If the surface treatment is good, a cohesive failure in which crack propagate inside the adhesive occurs, and if the surface treatment is not good, an adhesive failure in which crack propagate between the adherend and the adhesive occurs.

![Figure 5](image)

**Figure 5** DCB test and failure mode

The results of the DCB test are presented in Figure 6. With the material used in this test, even if fluorine remained on the surface, the surface was activated by plasma treatment, thereby increasing the fracture toughness value and changing the failure mode from mainly adhesive failure to mainly cohesive failure and adherend failure, resulting in stabilization. The fracture toughness value when the number of treatments is 2 and the fracture toughness value when the number of treatments is 10 are almost the same. It is considered that when the surface free energy is increased to approximately 45 mN/m, sufficient fracture toughness is attained.

These results show that sanding can be replaced with atmospheric pressure plasma treatment. For aircraft structures, in the surface treatment process, sanding is conducted with water being manually applied. When atmospheric pressure plasma treatment is adopted and automated in place of sanding, not only can the process time be reduced through automation, but the drying process...
can be eliminated because water is not used. As a result, it is expected that the pretreatment time can be reduced to 1/9. Furthermore, manual operation may cause unevenness in terms of quality and damage to carbon fibers on the surface depending on the operator's skill level, but automated plasma treatment can reduce these risks and contribute to increased quality.

Figure 6  Change in Mode-I fracture toughness value by the number of atmospheric pressure plasma treatments for a composite material contaminated with fluorine

4. Effects of plasma treatment on composite material to which peel ply elements remain adherent

In surface treatment using polyester peel ply, the temperature and time for curing composite materials are limited. If excessive heating occurs due to any problems, etc., during the manufacturing of parts, the amount of polyester remaining on the surface increases and the adhesive force is lowered. As a result, the disposal of the parts or sanding treatment is required. If it is found that the adhesive strength cannot be ensured after an airframe is manufactured, significant modifications must be conducted, causing a large loss. Therefore, it is important to reduce the adhesive strength reduction risk.

For a composite material to which polyester components remain adhered, atmospheric pressure plasma treatment using FPE20 Type 2 was conducted and XPS and DCB tests were implemented in the same manner as described in Section 3. As can be seen in Figure 7, by the treatment, the functional group arising from oxygen was introduced to the surface, the fracture toughness value increased and the failure mode changed from mainly adhesive failure to mainly cohesive failure and adherend failure, resulting in the stabilization of the surface. It is considered that this is because the polyester component that is made up of C, H and O was decomposed by active oxygen radicals.

Figure 7  Effect of atmospheric pressure plasma treatment on the composite material on which peel ply components remain
In addition, the change in the surface over time after atmospheric pressure plasma treatment was evaluated. The composite material was kept for 7 days in a high-temperature and high-humidity environment and a low-temperature and low-humidity environment, which were assumed in the manufacturing process. As a result, there was no change in the amount of oxygen or the fracture toughness value and the failure mode on the surface, and it was verified that the effect of the treatment was maintained.

These results show that in atmospheric pressure plasma treatment, the adhesive strength reduction risk when the peel ply method is used can be reduced. This leads to increased flexibility of manufacturing through the expansion of the allowable range of temperatures and time during the curing of composite materials and contributes to stable production.

5. Conclusion

This report demonstrated that the adhesive strength of a composite material with adhesive strength reduction factors can be increased through the application of atmospheric plasma treatment to the material and that atmospheric pressure plasma treatment is effective as a replacement for the sanding method and for reducing the risks of the peel ply method.

To apply it to aircraft structures, etc., it is necessary to establish a quality assurance method in the future. We will conduct the setting of a proper range of treatment conditions, the development of a method of guaranteeing the effect of the treatment and the evaluation of structural element tests, etc. We will contribute to the substantial reduction of the number of man-hours and the treatment time required, as well as to increased quality through the commercialization of this method.

References