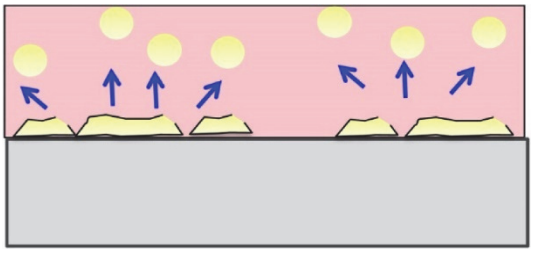
Study to Improve Reliability Control Technology of Adhesive Bonding in Composite Structures: Systematic Evaluation of Bonding Process Factors to Determine Their Degrees of Influence



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Adhesively bonded composite structures can transfer loads efficiently and are expected to contribute to reducing assembly costs. However, the current status of reliability given to this joining method by the certification authorities such as the Civil Aviation Bureau is low. In this report, the process factors that can affect the adhesive strength were extracted, and their degrees of influence were evaluated quantitatively. The results can be used as the foundations for devising an appropriate bonding process, which is considered to help greatly improve the reliability of adhesive bonding.

1. Introduction

When compared to mechanical fastening such as bolting, adhesive bonding of composite materials can transfer loads efficiently through the structures and lead to structural weight reduction. It is therefore desirable to broaden its application to transportation equipment such as aircraft, whose fuel efficiency and environmental impact need to be improved. Co-curing bonding is a process of curing simultaneously uncured composite materials and an adhesive. As covalent bonds are formed at the interface, this is considered to be a robust and highly reliable method. However, difficulties arise when bonding large, complicated parts such as aircraft structures. Although it is preferable for this reason to use the secondary bonding method in which cured composite parts are joined, this method has issues with bonding stability and integrity. The certification guidelines by the Civil Aviation Bureau advise that its application should be limited because of the low reliability.

In this report, the bonding process factors that can affect the adhesive strength were extracted, and their degrees of influence were evaluated. The goal is to improve the reliability of adhesive bonding in the assembly, because it can be an alternative to the conventional bolting in the assembly of aircraft composite structures.

2. Systematic evaluation of the bonding process factors to determine their degrees of influence

To evaluate the impact of variable factors in the bonding process on the adhesive strength, a composite material in use for aircraft structures was used to prepare adhesively bonded test samples under conditions in which the bonding process factors were varied systematically. An adhesive strength test was then conducted using coupon specimens. Specifically, the composite material used was a laminate of Toray's T800S/3900-2B, while Syensqo's FM309-1M was used as a film adhesive. The curing temperature for the sample preparation was 180°C, which is the condition recommended by each manufacturer.

2.1 Extraction of variable factors in bonding process

Of the bonding processes used for the major structures of an aircraft, the widely applied method is as follows: a film adhesive is placed between the pre-cured base materials (substrates) or

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between a pre-cured substrate and an uncured prepreg, before bagging and heating in an autoclave/oven to cure under pressure. Based on this bonding method, the variable factors in the bonding process, which can affect the adhesion performance, were extracted. As regards the bonding pretreatment, the commonly applied peel ply method was selected. In this pretreatment, a layer called peel ply is laid upon the outer surface of a composite laminate for purposes such as surface protection/treatment during composite material fabrication. The peel ply is peeled off before bonding.

The results of extraction are shown in **Table 1**. Quality defects during materials production were excluded, because such materials with poor quality were removed by the pre-shipment inspection.

Table 1 List of variable factors in bonding process

Stage(s) of process	Variable process factor(s)	Possible adverse effect(s)	Affected component		
			Interface	Adhesive	Substrate
Substrate fabrication	Temperature and time for fabrication	Thermal degradation of substrate	✓	—	✓
	Use of wrong peel plies	Unsuitable materials for bonding	✓	—	—
Substrate storage to drying	Temperature/humidity, and time for storage Temperature and time for drying	Moisture absorption of the substrate	✓	✓	✓
Adhesive storage	Temperature/humidity and time for storage	Premature adhesive curing Moisture absorption	✓	✓	—
Peel ply removal to adhesive application to bagging	Cleanliness level of work environment	Bonding surface contamination	✓	✓	—
	Work environment	UV degradation of substrate resin	✓	—	✓
	Time of exposure after removal	Exposure of bonding surface to air	✓	—	—
	Adhesive's exposed temperature and time	Lowered wettability	✓	✓	—
Curing	Temperature and time	Insufficient adhesive curing	✓	✓	—
	Pressure	Insufficient void prevention Lowered wettability	✓	✓	—

✓: Yes, —: No

2.2 Bonding process factors: systematic collection of data about their degrees of influence

Of the factors extracted in Section 2.1, the six factors listed below were selected as variables for the evaluation of influence, because these factors are likely to exhibit large fluctuations and control difficulty. The prepared specimen measures 160 mm in length and 20 mm in width. The double cantilever beam (DCB) test was conducted based on ASTM D5528, to obtain the mode-I energy release rate (G_{IC}).

(1) Bonding surface contamination
(2) Thermal degradation of substrate
(3) Moisture absorption of substrate
(4) Ultraviolet (UV) degradation of substrate resin
(5) Exposure of bonding surface to air
(6) Lowered wettability

(1) Bonding surface contamination

Bonding surface contamination is generally considered to be one of the most adversely influential factors in the bonding process. Strict precautionary control of the work area is normally required. However, as excessive control may lead to an increase in the production cost, the relationship between the amount of contaminant and the adhesive strength needs to be understood to set an appropriate control level. However, data that have been collected in this regard are still insufficient.

A silicone release agent, which is regarded as the highest risk among the chemicals used

on the manufacturing site, was selected as a contaminant and Henkel's Frekote 700-NC was used in this test. A small amount of the release agent, which had been diluted with hexane, was uniformly applied onto the surface of a pretreated substrate, using Sono-Tek's ultrasonic spray coating system. The application was carried out with varying amounts of the release agent. **Figure 1** shows the ultrasonic spray coating system in operation.

Polyester peel ply A, which had been placed on the surface of a substrate, was peeled off. The release agent was then applied to the bonding surface of the substrate. The film adhesive FM309-1M was used for bonding in an autoclave. For comparison, the co-cured bonding was also examined. In co-curing, uncured prepregs were stacked to have the same layered structure as the substrates, before bonding. **Figure 2** shows the G_{IC} values plotted against the amount of contaminant on the x axis, for two types of specimens (i.e., "peel ply" and "co-cure"). The error bar in the figure represents the maximum and minimum values of four test specimens (n = 4). In the "peel ply" specimens, the level of toughness at zero contamination was more or less maintained until the amount of contaminant reached 16 mg/m^2, but it dropped sharply through to 31 mg/m^2. Partial interfacial failure was observed even at 16 mg/m^2. On the other hand, the "co-cure" specimens retained a high level of toughness at 31 mg/m^2, even after which the declining trend was gradual. Although visual inspection of the specimen at 31 mg/m^2 suggested a mixed mode of failure (≈40% interfacial), it was difficult to draw a clear distinction from cohesive failure. Thus, it is highly likely that the failure occurred at the near-interface adhesive layer containing the release agent.

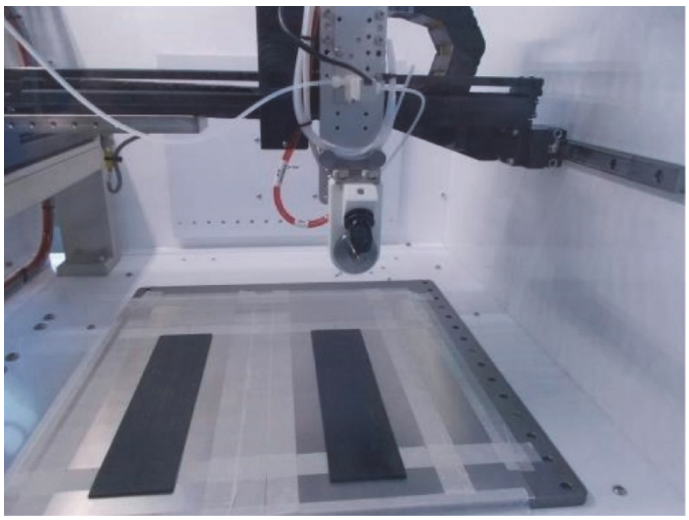

Figure 1 Ultrasonic spray coating system in operation

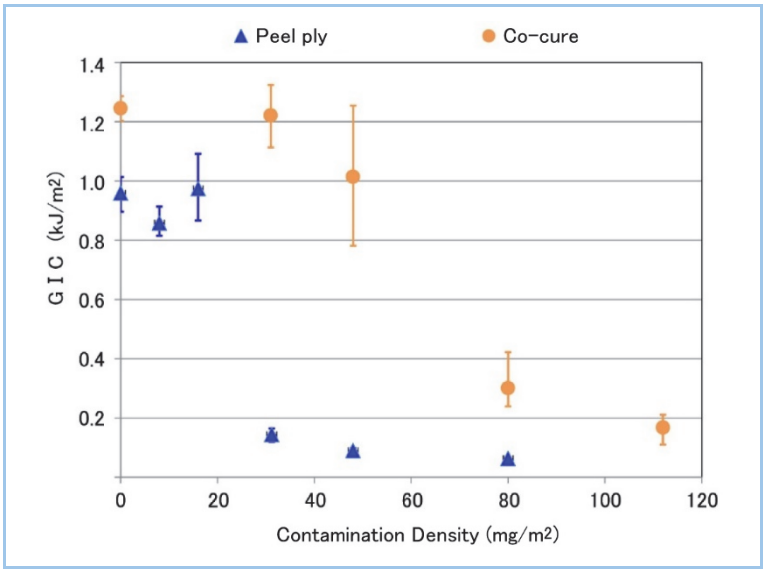

Figure 2 Relationship between amount of contaminant (release agent) and adhesive strength

(2) Thermal degradation of substrate

Assuming that the substrate may be kept over a long time at the upper limit of temperature tolerance during curing, the impact of such substrate heating on the adhesion was investigated. After being cured under the conditions recommended by the manufacturer, the substrate underwent heating at 190°C in an oven. The bonded samples were prepared, before specimens were cut out from these samples and G_{IC} values were obtained. **Figure 3** shows the variation in G_{IC}, plotted with the substrate heating time on the x axis. The error bar in the figure represents the standard deviation of n = 4, which also goes for the graphs in the following sections. When compared to the baseline conditions (i.e., with no heating), the heated specimens had a tendency to show lower G_{IC} values, but the impact of heating on the adhesive strength remained small regardless of the varying heating time. All the fractures that occurred under any of the given conditions exhibited a mixed mode of failure: cohesive (adhesive) and substrate. Substrate failure became significantly predominant with heating. Even then, no interfacial failure was observed. It is therefore considered that the impact of this process factor on the adhesive strength is small.

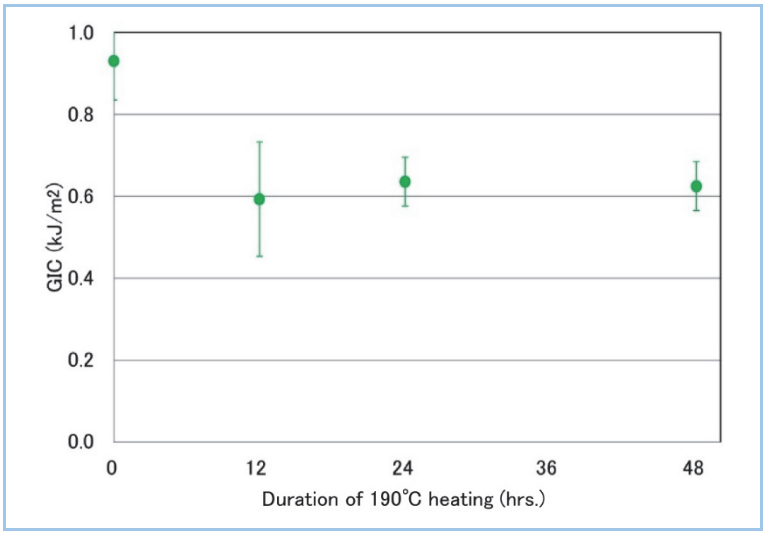

Figure 3 Relationship between heating time of substrate and G_{IC}

(3) Moisture absorption of substrate

The moisture absorbed by the substrate before bonding evaporates at the time of bonding, which is known to have an adverse effect on the adhesion. In the actual manufacturing process, drying by heating is often conducted before bonding. However, from the production schedule and cost points of view, there is a need to minimize this step or skip it entirely if possible. Having been immersed in warm water, the substrates with varying amounts of moisture absorption were used for bonding without being dried. G_{IC} was then obtained as in the previous section.

Figure 4 shows the relationship between the amount of moisture absorbed by the substrate and G_{IC}. The baseline amount of moisture absorption approximates 0.3-0.5%, which was measured after the substrate was dried at 105°C in an oven for 3 days. G_{IC} decreased gradually from the baseline conditions, as the amount of moisture absorption increased; the gradient became sharp around the amount exceeding 1%. The fracture observation after the DCB test suggests that, in general, the absorption of moisture mainly causes cohesive failure, but the occurrence of substrate failure may become frequent depending on the amount of moisture absorbed by the substrate. Thus, the impact of this factor cannot be overlooked, even if the immersion in warm water is in a relatively short time. When the parts to be bonded are stored in a place with no control systems for temperature and humidity, the process of drying by heating before bonding is very likely to be required.

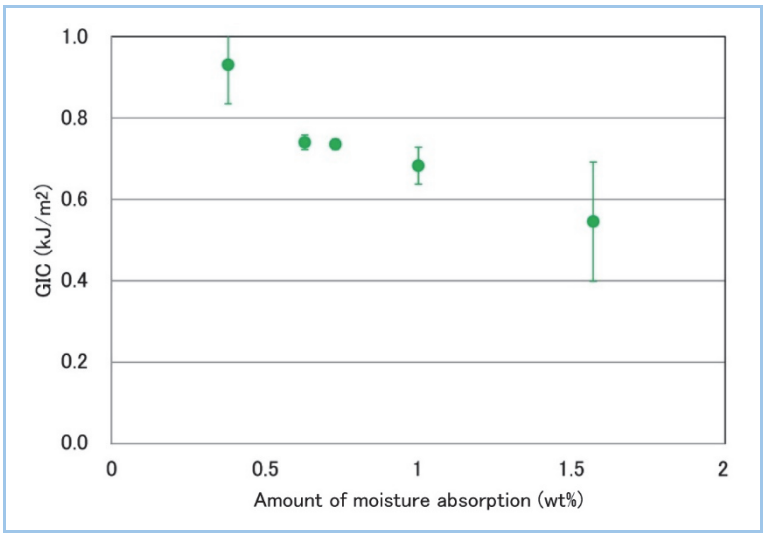

Figure 4 Relationship between amount of moisture absorbed by substrate and G_{IC}

(4) Ultraviolet (UV) degradation of substrate resin

Epoxy resins are generally known to decompose by exposure to UV light, leading to degradation. After being exposed to varying amounts of UV radiation through the peel ply using a UV lamp, the substrates were bonded together to measure G_{IC}.

Figure 5 shows the relationship between the amount of exposure to UV-A through the peel ply and G_{IC} (given as the average of n = 2). All the fractures that occurred under any of the given conditions exhibited a mixed mode of cohesive failure and substrate failure. As the variation in G_{IC} is small within the measured range of the UV exposure amount, the impact of this factor is considered low under the generally expected storage conditions and work periods.

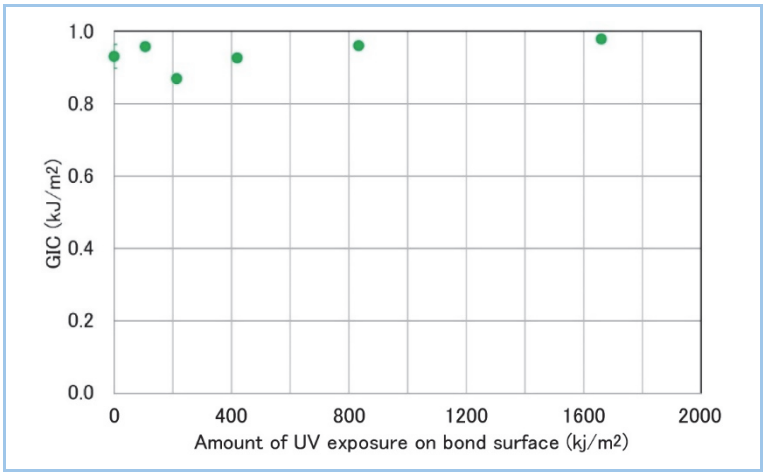

Figure 5 Relationship between amount of UV exposure on bond surface and G_{IC}

(5) Exposure of bonding surface to air

From the viewpoint of contamination prevention, it is generally considered important to bond as quickly as possible after pretreatment. Even with no contamination, long-time exposure to air may cause the resin on the bonding surface to change chemically, which can affect the adhesion.

After the peel ply was removed, the bonding surface was covered with another peel ply to prevent contamination as much as possible. The substrates were exposed to air in an oven at 110°C, before bonding together. G_{IC} was then obtained as in the previous sections.

Figure 6 shows the relationship between exposure time, contact angle of water, and G_{IC}. The contact angle tended to increase up to the exposure time of 24 hours, which indicates that the surface was contaminated or changed chemically with atmospheric components. However, no marked changes in the G_{IC} value were observed up to the exposure time of 48 hours; the

fractures also exhibited a mixed mode of cohesive failure and substrate failure. Normally, as the assembly in the manufacturing process can be completed in 24 hours after the peel ply removal, it was confirmed that the impact on the adhesion is low even if there is surface contamination or chemical change due to the exposure.

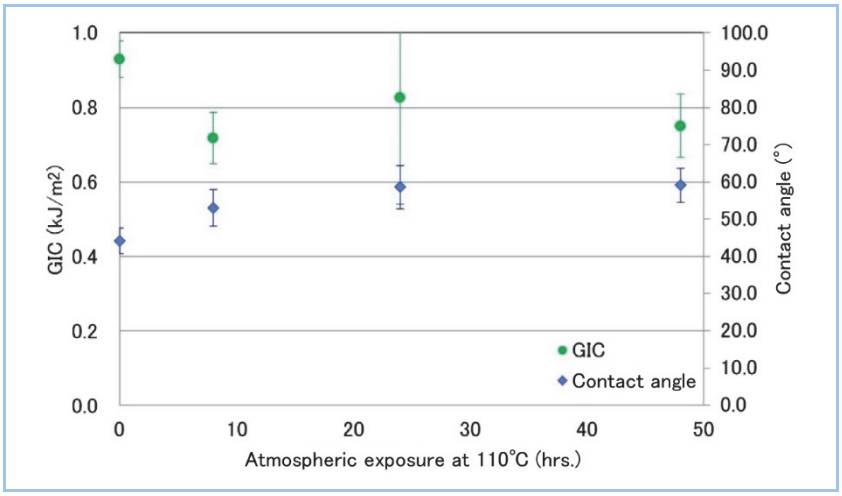

Figure 6 Relationship between time of bonding surface exposure to air, contact angle, and G_{IC}

(6) Lowered wettability

To produce good adhesion, the bonding surface needs to be wetted by an adhesive. The degree of wetting is indicated by a property called wettability. The quality of static wettability is determined by the surface energy difference between the adhesive and the substrate. The adhesion becomes better when the adhesive has a smaller surface energy and the substrate a larger surface energy. As the surface energy of an adhesive normally depends on the molecular structure of the adhesive, it is unlikely to be affected by the bonding process. However, from the viewpoint of whether the adhesive is spread throughout during the curing reaction, it is considered possible that curing of the adhesive occurs before the above-mentioned static energy equilibrium is reached (i.e., before the adhesive is spread throughout). The viscosity of the adhesive and the pressure during the bonding process may thus affect the adhesion. Therefore, wettability was selected to obtain data on its influence.

As regards the bonding surface of the substrate after pretreatment, it is expected that the surface energy decreases with time, from the data on contact angle in Figure 6. To conduct a severe test of wettability, the influence of viscosity and pressure was combined with the surface energy reduction by the exposure of the pretreated bonding surface to an environment at a temperature of 110°C for 48 hours. **Table 2** shows the results. In the lowered wettability test process, the adhesive was heated at 120°C for 105 minutes to increase the viscosity.

The results show no noticeable changes in the mode of failure or fracture toughness energy, thus indicating that the impact of the lowered wettability on the adhesive strength remains small if the change in the surface energy is relatively small, such as may occur during manufacturing.

Table 2 Impact of lowered wettability

	Test conditions			Test results		
	Adhesive viscosity [Poise]	Curing pressure [kPa]	Change with time	Void	GIC (kJ/m^2) (average of n = 4)	Failure mode
Normal process	1,000	400	Nil	Nil	0.93	Cohesive / substrate
Lowered wettability process	22,000	175	110°C 48 hours	Nil	1.06	Cohesive / substrate

3. Discussion

The evaluation results in Section 2.2 indicate that the key contributors in reducing the adhesive strength are the following two: factor (1) bonding surface contamination and factor (3) moisture absorption of the substrate before bonding. Factor (1), in particular, poses the highest risk from the viewpoints of the degree of impact and detectability.

In respect of the mechanism of factor (1) reducing the adhesive strength, some of the contaminants on the bonding surface are detached because of the effects of viscosity/temperature and diffuse into the adhesive, while the remaining contaminants stay at the interface to inhibit the bonding. **Figure 7** shows the observation results of the distribution of silicon atoms in the adhesive using the field emission electron probe micro analyzer (FE-EPMA) under the conditions of two different amounts of contaminant applied: In the 16 mg/m^2 adhesive (with no reduction in the adhesive strength), silicon atoms are dispersed across the adhesive, while for the 31 mg/m^2 adhesive (with reduction in the adhesive strength), their localized concentration at the interface is seen in addition to dispersion across the adhesive. Such concentrated silicon atoms are considered to function as the bonding inhibitor. **Figure 8** is a schematic diagram of the mechanism of contamination reducing the adhesive strength.

On the other hand, as regards how factor (3) affects the adhesive strength, it is considered that strength reduction can be caused by the change in the mechanism of resin curing reaction because of water molecules diffusing into the adhesive from the substrate during curing. The exact mechanism of the reaction has yet to be revealed by further research.

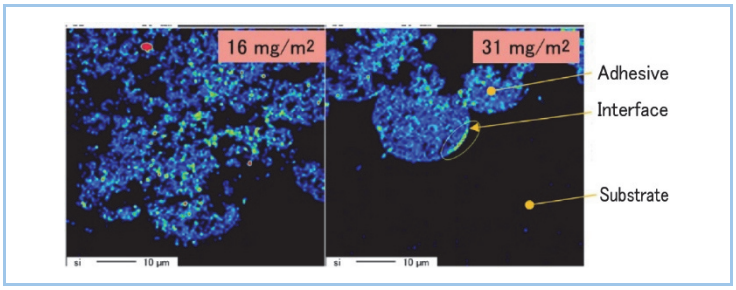

Figure 7 Distribution of silicon atoms (with use of FE-EPMA)

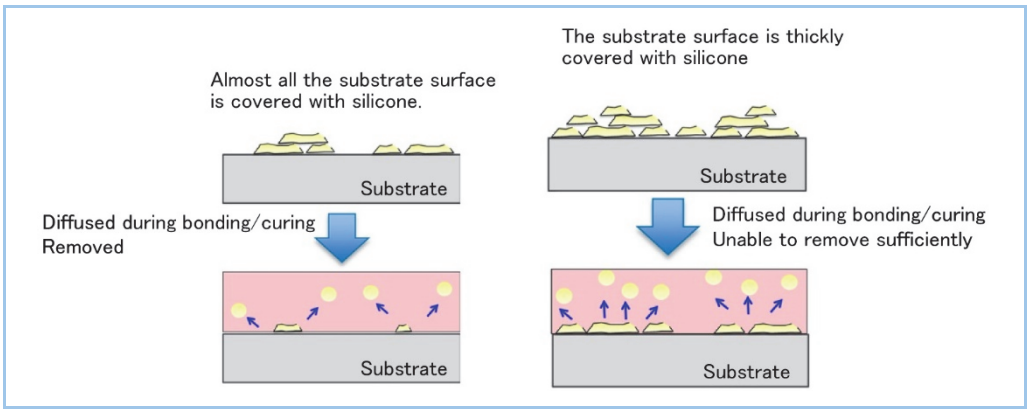

Figure 8 Schematic diagram of contaminants diffusing into adhesive

4. Conclusion

Based on the materials and processes in use for actual aircraft assembly, the process factors that can affect the adhesive strength were extracted to quantitatively evaluate their degrees of influence. The results indicate that bonding surface contamination and moisture absorption of the substrate before bonding have large adverse effects on the adhesive strength, and help to set specific control targets for contamination and moisture absorption. By separately devising the methods for measuring these influencing factors, an appropriate bonding process can be established. This is considered to greatly contribute to improving the reliability of adhesive bonding.

In this study, adhesive toughness was measured based on the DCB test. The impact on

fatigue strength is yet to be evaluated.

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Reference

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