EVALUATION OF THE FRACTURE TOUGHNESS OF COMPOSITE/ADHESIVE INTERFACE APPLIED BY IN-MOLD SURFACE MODIFICATION UNDER MODE II LOADING

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1 Introduction

Composite materials such as carbon fiber reinforced plastics (CFRPs) are anticipated to be used regularly in automotive industries to reduce the weight of structures in a bid to decrease fuel consumption. In industries, where large-scale production occurs, efficiently manufactured composite structures are essential [1]. The efficiency of manufacturing composite structures depends on the molding process and secondary fabrication processes such as trimming or surface modification. Despite the wide use of adhesively bonded joints in fiber reinforced plastic structures to avoid stress concentration and for weight reduction, additional surface modification is required to achieve high adhesion strengths [2, 3].

Conventional surface modification techniques such as sand blasting or emery papers, plasma treatment, and chemical etching, which are used as secondary fabrication processes, are excessively time consuming to be applied to mass production. Furthermore, workers without appropriate protection gear may be exposed to the air borne carbon particulates produced or to the harmful chemicals used in these processes [4]. To improve the production of FRP structures, it is essential to reduce the number of secondary processing steps.

To address this issue, we have investigated an in-mold surface modification process that uses imprint lithography to produce adhesive joints on composite surfaces [5]. We also confirmed that the apparent steady state fracture toughness \( G_{\text{im}} \) increased with increase in the aspect ratios of the concavo-convex microstructures [6, 7].

With regard to the improvement of adhesive strength or interfacial fracture toughness by utilizing microstructures on the adherend, some studies have been reported [8-12]. Under macroscopic mode II loading on the micropattern, cohesive failure of the adhesive is constantly included in addition to the interfacial failure. Therefore, the crack resistance and crack propagation behaviors may be largely affected by the fracture toughness of the adhesives in addition to the configuration of the microstructure of the adherend surface. Therefore, in the present study, we investigate the effects of the micropattern and adhesive properties on the interfacial fracture toughness and crack propagation under macroscopic mode II loading. The aspect ratio of the microstructures was varied by the in-mold surface modification. To evaluate interfacial fracture toughness, we have conducted end notched flexure (ENF) tests using CFRP/adhesive interfaces containing microstructures. In addition, we microscopically observed crack propagation in the CFRP/adhesive interfaces during ENF tests to clarify the relationship between interfacial fracture toughness and fracture behavior.

2 Material and method

2.1 In-mold surface modification

Concavo-convex microstructures were fabricated on the CFRP surface by in-mold surface modification. This surface modification follows the nanoimprint lithography procedure, which is a pattern-transferring technique in which microstructures of a mold are pressed into low-viscosity plastics at a high temperature and patterns are transferred by demolding at a low temperature [13-15]. The technique was introduced during the curing of
composites. Figure 1 shows the schematic of the in-mold surface modification process and the panel/stiffener structure to demonstrate the use of the technique. The specific processes involved in the in-mold process used in this study are listed below.

1) Microstructures were fabricated on a silicon wafer by photolithography or on an aluminum plate using a milling machine.

2) After coating the mold surface with a releasing agent (ChemTrend, Chemlease #70), the carbon/epoxy prepregs (Mitsubishi rayon, Pyrofil #380) were stacked on the mold. In this study, the stacking sequence was [0/90]_{2S}, with the concave and convex directions set to 90°. Thus, the fiber direction on the top layer was oriented with the convex features.

3) The prepregs were cured in two steps over the glass transition temperature under a pressure of 0.6 MPa (at 85 °C for 1 h and at 135 °C for 3 h), which allowed the molten matrix resin to flow into the microstructures of the mold.

4) The microstructures were transferred to the CFRP by demolding at room temperature.

According to these processes of works, microstructures will be transferred to CFRP surface like Figure 2. These microstructures enhance the resistance of crack propagation of CFRP/adhesive interface, since crack penetrates concavo-convex of the microstructures under mode II loading.
EVALUATION OF THE FRACTURE TOUGHNESS OF COMPOSITE/ADHESIVE INTERFACE APPLIED BY IN-MOLD SURFACE MODIFICATION UNDER MODE II LOADING

Figures 3(a) and (b) show the images of the mold for in-mold surface modification with microstructures on its Si surface fabricated by photolithography and the imprinted surface of CFRPs acquired with a scanning electron microscope. The concavo-convex structures were transferred by the mold during the in-mold process. Using this mold, the concavo-convex features in the scale of 10–100 µm can be fabricated in Figure 3 (b). Figures 4(a) and (b) show the images of the mold for in-mold surface modification with microstructures on its Al surface fabricated by milling and the imprinted surface of CFRPs acquired with a scanning electron microscope. Using this mold, the concavo-convex features in the scale of >100 µm can be fabricated in Figure 4 (b). To observe the crack propagating process with ease, we tested the surfaces with concavo-convex microstructures of >100 µm in size, similar to that shown in Figure 4(b).

The concavo-convex microstructures fabricated on the CFRP surfaces are defined in terms of the aspect ratio (A). A is the ratio of the concavo-convex depth \( h \) to the sum of widths \( w_1 \) and \( w_2 \) (shown in Figure 4 (b)) and is expressed by Eq. (1).

\[
A = \frac{h}{(w_1 + w_2)} \tag{1}
\]

In the present study, the Al mold surface was divided into four areas, as shown in Figure 4 (a). Thus, four types of microstructures were simultaneously fabricated on the CFRP with \( A \) values of 0.13, 0.15, 0.19, and 0.25. For the \( A \) values ranging from 0.13 to 0.25, the height was set at a constant value of 150 µm and the width was changed to 600, 500, 400, and 300 µm, as shown Table 1, for the four different \( A \) values. For comparison, a flat surface without any surface treatment was also fabricated. To note, the \( A \) value of the flat surface is zero.

<table>
<thead>
<tr>
<th>Aspect ratio ( A )</th>
<th>0.13</th>
<th>0.15</th>
<th>0.19</th>
<th>0.25</th>
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</thead>
<tbody>
<tr>
<td>Width ( w_1 = w_2 ) [µm]</td>
<td>600</td>
<td>500</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>Depth ( h ) [µm]</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
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</table>

Table 1 Values of width and depth of the concavo-convex for each aspect ratio.
2.2 ENF testing

Under macroscopic mode II loading, the crack resistance of CFRP/adhesive interfaces containing microstructures varies microscopically depending on the location of the crack position within the concavo-convex shape. However, the objective of this study was not to obtain the precise crack-propagation resistance on a microscopic scale but to evaluate the macroscopic crack-propagation resistance as a practical indicator of the effect of using the proposed surface modification instead of conventional treatments. For evaluating the surface modification effects, we assumed that the concavo-convex microstructures macroscopically possess a flat surface and the apparent mode II fracture toughness values were calculated from the ENF tests based on JIS K7086 [16]. The apparent fracture toughness corresponds to the total energy dissipation (including that in the fracture process zone) divided by the macroscopic crack length.

The ENF test specimens were fabricated by the following protocol. Two CFRP adherends were used. The surface of one of the CFRP adherends was polished by #100 abrasive paper, and the surface of the other was treated by the in-mold process. Then, the two CFRP adherends were bonded together using the epoxy adhesives (3M DP-100 clear) for 48 h at room temperature by curing. Teflon sheets (0.1 mm in thickness) were inserted between the two adherends at both edges to introduce an initial crack and to control the thickness of the adhesive layer. Then, the adhesive DP-100 clear will henceforth be termed as Epoxy A. In Figure 5, CFRP/adhesive interface with microstructures are indicated. Any initial delamination of CFRP/adhesive interface can not be seen. Where, to clarify the mechanical properties of the adhesives, tensile tests and single edge notched bend (SENB) tests were performed based on the Japan industrial standards (JIS) K7161 and ASTM D5045-99 standards [17,18], respectively. The tensile specimens and SENB tests specimens of Epoxy A was cured for 48 h at room temperature. Where, the values of the Young’s modulus (E) and Mode I fracture toughness (GIC) of the adhesive are shown in Table 2. Then, Epoxy A indicates brittle fracture property. After the bonding process, the bonded CFRP plates were sliced to designated sizes, as shown in Figure 6. Three ENF specimens were prepared for each A value. In Figure 6, the schematic of ENF testing set up are also shown.

Figure 7 indicates ENF testing set up. The ENF tests were performed using a universal testing instrument (Shimadzu, AGS-I) with the rate of compression at the loading point set to 1.5 mm/min. The crack length was measured with a measuring microscope (Pika Seiko, PRM-2) and the crack propagation behavior at the CFRP/adhesive interface was observed using a digital microscope.
After the crack had propagated, the specimen was fully unloaded. Then, the lengths between the supported points and loading point were changed and the ENF tests were repeated four or five times by changing the location of the loading point. The average values obtained from several points at the initial critical load were calculated and expressed as the apparent mode II interfacial fracture toughness at a particular $A$ value. The representative load-displacement curves were showed during the ENF testing, in Figure 8.

**Table 2 Young’s modulus and mode I fracture toughness**

<table>
<thead>
<tr>
<th></th>
<th>Epoxy A</th>
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<tbody>
<tr>
<td>Young’s modulus $E$</td>
<td>2.29</td>
</tr>
<tr>
<td>[GPa]</td>
<td></td>
</tr>
<tr>
<td>Mode I fracture toughness $G_I$ [J/m$^2$]</td>
<td>3886</td>
</tr>
</tbody>
</table>

### 3 Result and discussion

#### 3.1 Results and discussion of the ENF tests

The apparent mode II interfacial fracture toughness ($G_{II}$) was calculated by Eq. (2).

$$G_{II} = \frac{9a_1^3 P_C^2 C_1}{2B(2L^2 + 3a_1)}$$  \hspace{1cm} (2)

where $P_C$ is the initial critical load, which was determined from the intersection of the initial elastic line and the offset line with a slope of 5% lower than that of initial elastic line in the typical load-displacement curves. $C_1$, $B$, and $L$ are the loading point compliance of the initial critical load, width of the specimen, and length between the loading point and support point, respectively. The estimated value of the crack length $a_1$ at the initial critical loading was calculated by Eq. (3).

$$a_1 = \left[ \frac{C_0}{C_0} + \frac{2}{3} \left( \frac{C_0}{C_0} - 1 \right) L \right]^{\frac{3}{2}}$$ \hspace{1cm} (3)

where $C_0$ is the loading point compliance of the initial elastic line.
Figure 9 showed the relationship between $G_{II}$ and $A$ of each specimen containing the microstructure using Epoxy A and B used as the adhesives, respectively. The values of $G_{II}$ of the in-molded specimens (with $A > 0$) were higher than that of the specimens with a flat surface (with $A = 0$) for each adhesive, as shown in Figure 9. In Figure 9, $G_{II}$ was almost constant for the in-molded specimens (with $A > 0$). Further, $G_{II}$ of the in-molded specimen for $A = 0.25$ was nearly 4.5 times higher than that of the specimen with a flat surface without any surface modification (with $A = 0$).

Since the interfacial fracture toughness of CFRP/adhesive was comparatively low at $A = 0$ (Figure 9), the fracture toughness of the modified interface of CFRP/adhesive may be mainly affected by the cohesive fracture toughness of the CFRP rather than the interfacial fracture toughness of CFRP/adhesive. Thus, the lack of dependence of fracture toughness of the modified interface of CFRP/adhesive on the aspect ratio can be indicated, because the length of cohesive failure of the CFRP was constant regardless of the aspect ratio.

3.2 Process of crack propagation

In the case of in-molded surface (at $A = 0.13$–0.25), Interfacial failure and cohesive failure of CFRP portion were indicated along to entire CFRP/Epoxy A interface. SEM image of CFRP concavo-convex are shown in Figure 11 (a) and (b). These images show the state of cohesive failure of CFRP surface respectively. Because of the penetration of crack to the micro concavo-convex structures, three-dimensional cohesive failure can be confirmed in Figure 11 (a) and (b).

Since the interfacial fracture toughness of CFRP/Epoxy A was comparatively low at $A = 0$ (Figure 9), the fracture toughness of the modified interface using Epoxy A may be mainly affected by the cohesive fracture toughness of the CFRP rather than the interfacial fracture toughness of CFRP/Epoxy A. This agrees well with the observation of interfacial failure occurring first at the CFRP/Epoxy A interface, followed by the cohesive failure of the CFRP. Furthermore, the lack of dependence of fracture toughness of the modified interface using Epoxy A on the aspect ratio can also be explained, bearing in mind that the length of cohesive failure of the CFRP was constant regardless of the aspect ratio.

4 Conclusion

The present study investigated the effects of the presence of a microstructural pattern on the adherend and the properties of the adhesive on the interfacial fracture toughness and crack propagation under macroscopic mode II loading. The microstructural pattern was fabricated using the in-
mold surface modification by imprint lithography. Because the method proposed here allows for surface treatments to be carried out simultaneously during the formation of the composite materials, time and cost involved in the overall production are lower than that required in conventional techniques.

To experimentally evaluate the behavior of the CFRP/adhesive interface containing concavo-convex microstructures subjected to macroscopic mode II loading, we performed ENF tests using the epoxy adhesive (Epoxy A: 3M DP-100 clear). When compared to the crack resistance of flat surfaced specimens (with A = 0), the crack resistance of the in-molded specimens (with A > 0) improved. The interfacial fracture toughness of CFRP/adhesive was rather low and the improvement in the resistance to crack propagation was independent of A. This was because the fracture toughness of the modified interface using the adhesive was mainly affected by the cohesive fracture toughness of CFRP whose length was constant regardless of A.

References