ENHANCEMENT OF FRACTURE TOUGHNES OF COMPOSITE/ADHESIVE INTERFACE BY IN-MOLD PREPARATION USING NANOIMPRINT LITHOGRAPHY

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1 Introduction

Composite materials such as carbon fiber reinforced plastic (CFRP) are widely used as structural materials because of their high specific strength and stiffness. In such structures, adhesive bonding is also widely applied for the joining of composite materials to reduce structural weight and defuse stress concentration.

In order to obtain high adhesion strength, the adherend surface must be prepared adequately; for example, sand blasting and chemical etching etc. are applied. However, these conventional methods increase manufacturing process since they are conducted after molding of composite materials. Furthermore, they cause environmental degradation because of the dust and the use of chemical agents and it is difficult to apply those methods to large-scale structural materials.

In order to solve these problems, in–mold surface preparation using nanoimprint lithography (NIL) has been proposed [1]. In NIL process, microstructures on a mold are pressed onto melted polymeric material at high temperature and the shape of microstructures is transferred by releasing the mold at low temperature [2]. Since nanometer-scale microstructures can be fabricated easily with high accuracy by NIL, it has been applied in semiconductor devices industries and so on; for example, microcapillaries [3], nanometer-scale MOSFETs [4], and a nanofluidic chip for DNA stretching application [5] etc. are produced by NIL technique. In in-mold surface preparation using NIL, silicon wafers with micrometer-scale microstructures fabricated by photolithography technique are embedded on a mold of composites. By forming composites on this mold, the shape of microstructures is transferred onto the surface of composites during curing process. If adherent surface can be obtained by fabricating surface microstructures, since molding composites and surface preparation are able to be conducted at once, it reduces the time and costs required in conventional techniques. Therefore, it is considered that this method is better suited for mass-production process such as automotive industries where future expansion of application of composite materials is expected.

In previous work, some results have been reported that interfacial properties such as adhesive strength or fracture toughness highly depend on surface topography of adherend [6-10]. Therefore, these interfacial properties can be improved by appropriately designing and fabricating microstructures on the surface.

The objective of the present work is to improve interfacial properties by in-mold surface preparation using NIL, especially mode I fracture toughness of composite/adhesive interface is focused. We propose microstructures to improve apparent mode I fracture toughness of adhesive joint. Proposed microstructures are fabricated on CFRP surface and the effect is investigated by DCB test. The test is conducted with changing the size and shape of microstructures and the affection is discussed from cross section observations.

2 Proportion of the shape of microstructures

2.1 Micro concavo-convex structures

We select micro concavo-convex structures shown in Fig. 1 as a shape of microstructures to improve apparent mode I fracture toughness of adhesive joint. When the mode I load is applied to the interface with these microstructures, microscopically the

mode II fracture is occurred at lateral faces of microstructures as shown in Fig. 2. Since mode II fracture toughness is higher than that of mode I [11] in practical adhesion, higher energy is required for crack propagation and improvement of apparent mode I fracture toughness is expected.

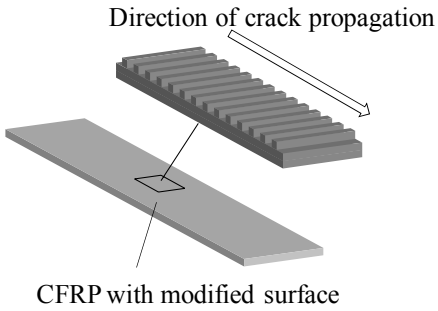


Fig. 1. Micro concavo-convex structures.

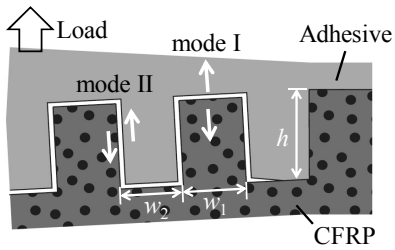


Fig. 2. Fracture mechanism of interface with micro concavo-convex structures.

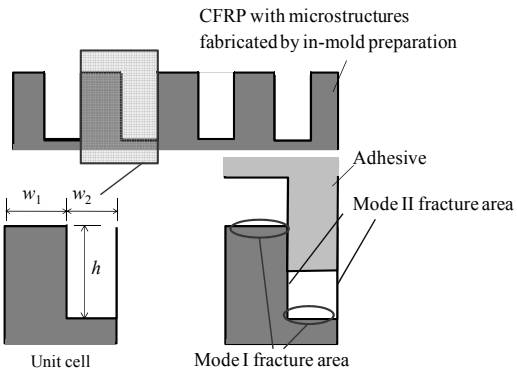


Fig. 3. Model for constructing the equation describing apparent mode I fracture toughness.

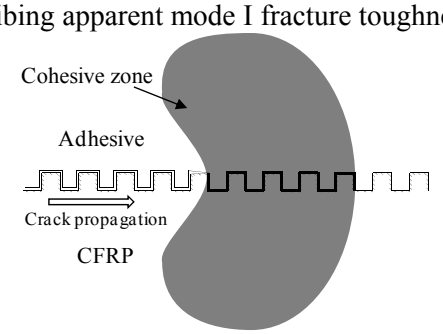


Fig. 4. Cohesive zone around the crack tip.

2.2 Effect of microstructures

In order to build a simple estimating equation of the effect of the microstructures, we regard micro concavo-convex structures as the repeat of a unit cell as shown in Fig. 3.

Total energy E required to fracture at the CFRP/adhesive interface in the unit cell is described as follow.

$$E = (w_1 + w_2)G_{IC} + 2hG_{IIC} \qquad (1)$$

Here, G_{IC} and G_{IIC} are pure mode I and mode II fracture toughness, w_1 is the width of the convexity, w_2 is the width of concavity and h is the height.

The size of microstructures fabricated in this study is micrometer-scale. Considering Cohesive Zone Model (CZM), which is one of the most commonly used tool to investigate interfacial fracture [12], since the length of cohesive zone is generally millimeter-scale [12, 13], several microstructures are contained in the cohesive zone (Fig. 4). Under crack prppagation, energy is dissipated by peeling of microstructures on composites and adhesive in the cohesive zone. In CZM, since fracture toughness is calculated from the energy dissipation in the cohesive zone, surface with proposed microstructures can be macroscopically regarded as "frat surface". Therefore, apparent mode I fracture toughness G_A is obtained by dividing E (eq. (1)) by macroscopic adhesion area w_1+w_2 as follow as the fracture energy per apparent unit area.

$$G_A = \frac{(w_1 + w_2)G_{IC} + 2hG_{IIC}}{w_1 + w_2} = G_{IC} + 2AG_{IIC} \qquad (2)$$

Where A is the aspect ratio described like

$$A = \frac{h}{w_1 + w_2} \qquad (3)$$

In this study, the shape of micro concavo-convex is evaluated by this aspect ratio A. From eq. (2), it is expected that apparent fracture toughness improves by fabricating micro structures compared with flat surface and A affect the effect of in-mold surface preparation.

3. In-mold surface preparation using NIL

Micro concavo-convex structures are fabricated on the surface of CFRP by in-mold surface preparation using NIL. In this method, microstructures are manufactured on the surface of silicon wafer by

photolithography technique. Since each crystal plane of silicon has a different etch rate, silicon is etched anisotropically and diverse shapes are able to be fabricated on the surface [14]. Fig. 5 shows the process of in-mold surface preparation and an example of the application of in-mold surface preparation.

The process consists of two parts: fabricating microstructures on the mold by photolithography technique (Fig. 5(a)) and transferring the shape of microstructures to the surface of CFRP (Fig. 5(b)). The steps in the first part shown in Fig. 5(a) are follows.

(1-1) o-Aminophenol (OAP) and then positive photoresist are spin-coated on a silicon wafer with a silicon dioxide (SiO_2) layer and exposed to intense ultraviolet light through a photo mask.

(1-2) The exposed photoresist is removed with tetramethyl ammonium hydroxide.

(1-3) The oxidized layer is removed with ammonium hydrogen fluoride.

(1-4) Silicon is etched with potassium hydroxide.

(1-5) A Mold for CFRP is fabricated by embedding the Si wafer into an Al plate.

Image of the surface of the mold observed by scanning electron microscope (Keyence, VE-8800) is presented in Fig. 5(a). It shows that fine micro concavo-convex structures are fabricated perpendicular to the surface of the silicon wafer.

Fig. 5(b) shows the process of the pattern-transferring part and schematic of molding CFRP stiffener with adhesion area as an example of application of this method. Follows are the steps in this part.

(2-1) CFRP prepregs are stacked on the mold.

(2-2) The prepregs are cured at a specific temperature. During curing, a resin contained in CFRP flows into the cavities of the mold.

(2-3) After the CFRP is cured, it is released from the mold.

Fig. 6 shows images of the surface and its cross sectional view of cured CFRP. Cross sectional view is observed using field emission-scanning electron microscope s4500 produced by Hitachi. As compared with the SEM image of the mold in Fig. 5(a), it is confirmed that the shape of microstructures are successfully transferred. The widths of microstructures are from 26 to 32 μm and the

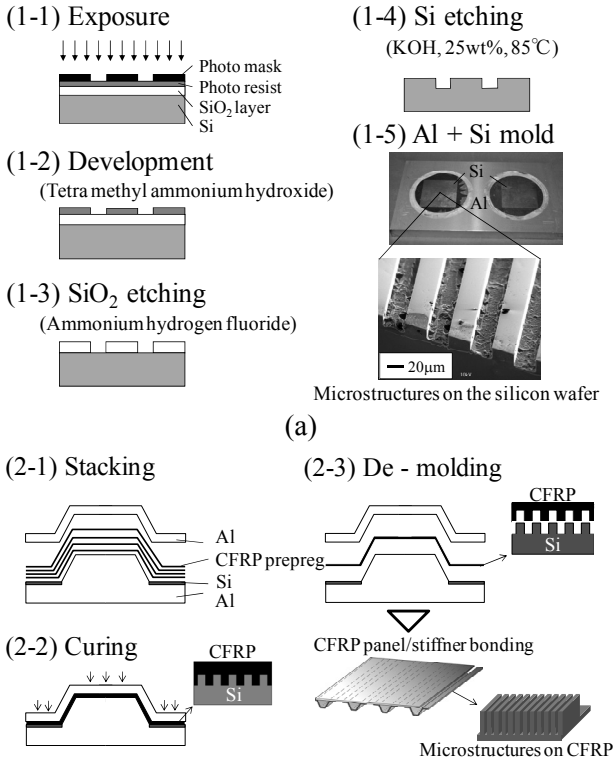
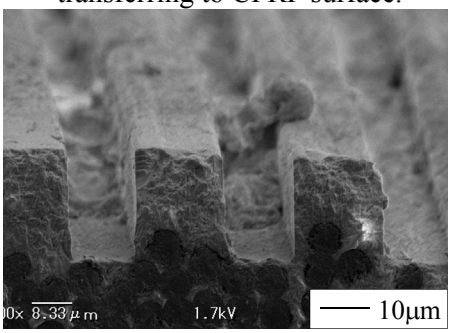
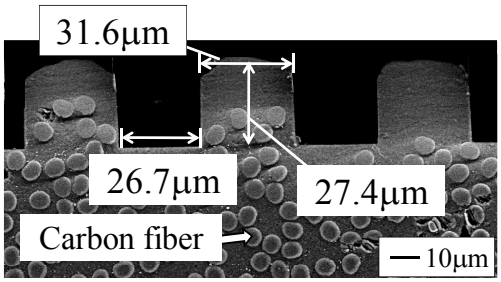


Fig. 5. Process of in-mold surface preparation using NIL and example of application: (a) part of fabricating microstructures and (b) part of pattern-transferring to CFRP surface.



(a)



(b)

Fig. 6. (a) SEM image of microstructures on CFRP and (b) FE-SEM image of their cross sectional view.

heights are about 30 μm. Fig. 6 shows that carbon fibers are included in micro convexities. Therefore, microstructures are also considered as composite materials.

4 Experiments

4.1 Specimen and the experimental method

In order to evaluate the effect of surface preparation using NIL on the apparent mode I fracture toughness, DCB tests is conducted. Fig. 7 shows the configuration of the specimen. Specimens are fabricated by adhering CFRP laminates. The CFRP laminates is formed using CFRP prepreg PYROFIL#380 produced by Mitsubishi Rayon. The stacking sequence is $[90_6]_T$.

Epoxy resin (Kokusai Chemical, Z-2/H-07) is utilized as an adhesive. Teflon sheet is inserted during adhering to manufacture an initial crack.

From eq. (2), since it is expected that aspect ratio A of microstructures affects apparent mode I fracture toughness, 3 kinds of adherend is prepared: A=0 (flat surface), 0.19 and 0.40.

Fig. 8 shows testing set up. The test is carried out using a tensile testing machine (Shimadzu, AG-I) under displacement control at 0.2 mm/min. The length of crack is measured by microscope. Since it is usually assumed that the contribution of the adhesive layer to the overall compliance is negligible [15], mode I fracture toughness G is calculated as well as mode I interlaminar fracture toughness (JIS K 7086) as follows.

$$G = \frac{3}{2(2H)}\left(\frac{P}{B}\right)^2 \frac{(B\lambda)^{\frac{2}{3}}}{\alpha_1} \qquad (4)$$

Here, λ is compliance of specimen calculated with

$$\lambda = \frac{\delta}{P} \qquad (5)$$

where $2H$ is the thickness of the DCB specimen, B is the width of the specimen, P is the applied load during the test, δ is the crack opening displacement (COD), and α_1 is the coefficient concerning flexural rigidity of adherend.

4.2 Results and discussion

Typical load-COD curves obtained from DCB tests are shown in Fig. 8. Crosshead displacement is utilized as a COD. In all specimens, the load is seen to decrease as the crack length increases. In the tests, stick-slip growth of crack is confirmed. In other words, the crack propagation is not continuous but the repeat of rapid growth and arrest phase. Crack is grown at the point denoted by symbols (■, ○, and □) in Fig. 8.

The loads of those points are used to calculate fracture toughness by eq. (4). This is because it is considered that fracture toughness at the crack initiation is more critical in actual structures. Fig. 9

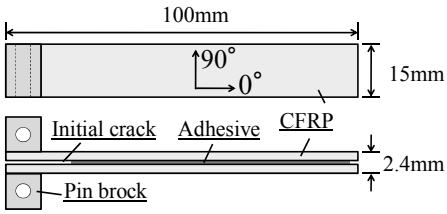


Fig. 7. Configuration of the DCB specimen.

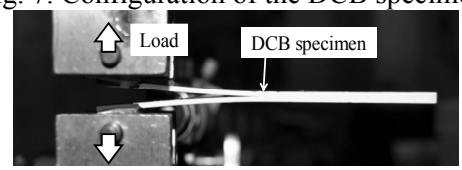


Fig. 8. Picture of the experimental setup.

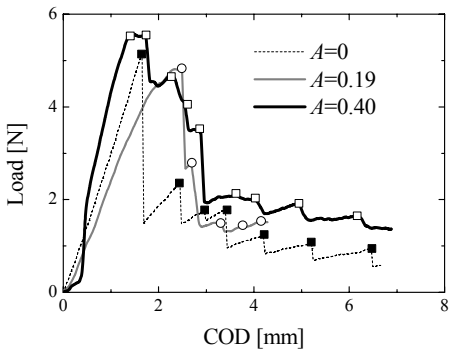


Fig. 8. Load-COD curves during DCB tests.

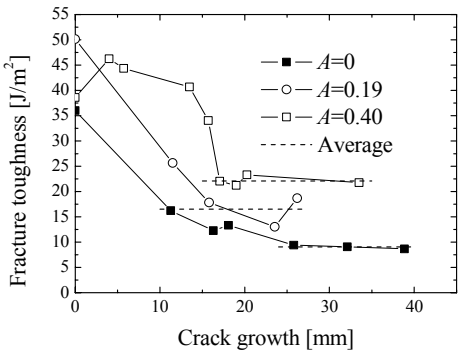


Fig. 9. Fracture toughness as a function of the crack growth.

presents fracture toughness of each specimen shown in Fig. 8 as a function of the length of the crack growth. Dashed line shows average values when fracture toughness become constant as the crack grows and these are regarded as the apparent mode I fracture toughness of each specimen. Table 1 shows average of apparent mode I fracture toughness and standard deviation about each aspect ratio *A*. It is

Table 1 Values of apparent mode I fracture toughness obtained DCB tests.

Aspect ratio *A*	0	0.19	0.4
Apparent fracture toughness [J/m^2]	9.0	16.5	22.1
Standard deviation	0.29	2.5	0.8

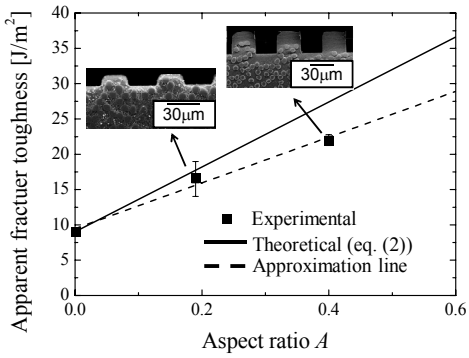
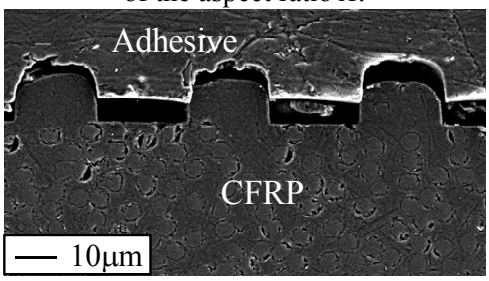
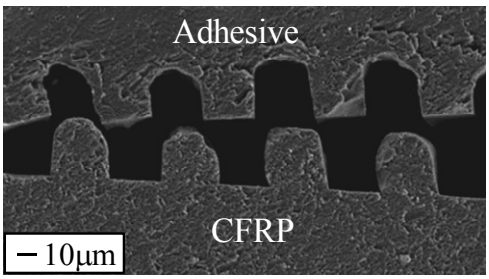


Fig. 10. Apparent fracture toughness as a function of the aspect ratio *A*.



(a)



(b)

Fig. 11. FE-SEM images of CFRP/adhesive interface: (a) *A*=0.19 and (b) *A*=0.40.

confirmed that apparent fracture toughness is improved by in-mold surface preparation compared to specimen with flat interface (*A*=0). Fig. 10 shows apparent mode I fracture toughness as a function of the aspect ratio *A*. The theoretical line calculated from eq. (2) and the approximation line obtained from experimental results are also shown. G_{IC} and G_{IIC} used in calculation by eq. (2) are obtained from preparatory experiments: G_{IC} = 9.0 J/m^2, G_{IIC} = 23.0 J/m^2. As shown in Fig. 10, it is found that experimental results show linear enhancement as *A* increases and it is the same tendency as theoretical values calculated by eq. (2). It is considered that difference between theoretical value and experimental results is caused by simplicity of eq. (2). In other words, it is caused by that in eq. (2) an effect of the corner of microstructures, residual stress in adhesive and so on is not considered, and this is a future work.

FE-SEM images of CFRP/adhesive interfaces after crack propagation shows that fracture is occurred at interfaces (Fig. 11). From these observations, it is indicated that the mode II fracture is occurred microscopically at lateral faces of microstructures. Since the proportion of mode II fracture area enlarges as the aspect ratio *A* increases, the fracture toughness enhances as the increase of *A* like Fig. 10.

5. Conclusions

In-mold surface preparation using NIL was applied to the surface of CFRP. Since this method can be included in the process of molding composites, it reduces the time and costs required in conventional techniques.

As the microstructures which improve apparent mode I fracture toughness of composite/adhesive interface, micro concavo-convex structures were proposed. Since these microstructures introduce mode II fracture area microscopically into the path of crack, apparent mode I fracture toughness is enhanced. According to DCB tests, it was confirmed that the apparent mode I fracture toughness become stronger as the aspect ratio *A* increased. Observations of interfaces of CFRP/adhesive show that the enhancement of the fracture toughness is caused by the increase of mode II fracture area as *A* increased.

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