Effect of Moisture Absorption at Fabrication Stage on Static and Fatigue Properties for Plain-Woven CF/Epoxy Composites

Yasuhiro NISHIKAWA**, Kazuya OKUBO*** and Toru FUJII***

The effect of moisture absorption on the static and fatigue properties for plain-woven CF/epoxy composites (plain-woven CFRP) was examined when the humidity condition changed at the following stages; mixing of epoxy resin with hardener, laminating of carbon fabrics with epoxy resin, storage before testing and static and fatigue testing. At each stage, the materials were exposed to either completely dry nitrogen gas to isolate the materials from moisture or the laboratory atmosphere. The experimental results showed that the tensile strength and fatigue life of plain-woven CFRP were significantly improved when the materials were protected from moisture absorption at the mixing and laminating stages. This protection improved the resistance of crack growth and interfacial shearing strength at the fiber/matrix interface. Such improvement contributes to the enhancement of the tensile strength and fatigue life of plain-woven CFRP.

Key Words: Tensile Properties, Fatigue, Composite Material, Plain-Woven CF/Epoxy, Moisture Absorption, Interfacial Property

1. Introduction

Mechanical properties of epoxy resin are significantly influenced by moisture absorption in the atmosphere. Therefore, a lot of researches have reported on the effect of moisture absorption during tests on the mechanical properties of composite materials using epoxy resin as matrix(1)–(9). Selzer and Friedrich(3) investigated the influence of moisture on the mechanical properties and failure behavior of CF/epoxy composites. Zhao and Gaedke(6) studied the moisture effect on the interlaminer properties (mode II delamination behavior) of CF/epoxy composites. Fjeldly et al.(9) also examined the CF/epoxy interfacial properties by conducting single fiber fragmentation tests.

In the previous investigations, however, moisture absorption at the fabrication stage (in this study, mixing stage of epoxy resin with hardener and laminating stage of carbon fabrics and epoxy resin) is ignored. The fabrication environment is not dry. According to the reports of Japan Meteorological Agency in 2003, the relative humidity in Kyoto was about 66%. At the fabrication stage, liquid epoxy resin is exposed in the atmosphere. Therefore, moisture absorption would degrade the mechanical properties of composites even if the materials absorbed moisture for a short time.

The material life is divided into the following stages; (1) mixing of epoxy resin with hardener, (2) laminating of carbon fabrics and epoxy resin, (3) storage before testing and (4) testing. The objective of this study is to investigate the effect of moisture absorption at the fabrication ((1) and (2)) stage on the static and fatigue properties of plain-woven CF/epoxy composites (plain-woven CFRP). The fiber/matrix interfacial properties are also evaluated when moisture exists or not.

2. Specimen and Experiment

2.1 Experimental condition

Two conditions were considered at each stage; one was absolutely dry condition (0%RH, 23 ±2°C), and the other was the laboratory condition (60±5%RH, 23±2°C). Magnesia acetate tetrahydrate ((CH₃COO)₂Mg·4H₂O) was put in the fabricating chamber (volume = 0.5 m³) and the testing chamber (volume = 0.05 m³) to obtain the absolutely dry condition. Pure nitrogen gas (N₂ gas, 99.99%) was put into the fabricating and testing chambers with silica gel and magnesium chloride (MgCl₂) to obtain the absolutely dry condition. N₂ gas was continuously put into the
chambers to remove air (oxygen) and moisture. The volumetric flow rate of N₂ gas was 2 m³/h. The pressure in the chambers was almost the same with atmospheric pressure.

2.2 PW-CFRP specimens and testing procedures

PAN based carbon fabric (MITSUBISHI RAYON Co.) was used as reinforcement. The matrix was bisphenol-A type epoxy resin (YUKA SHELL Co.). Acid anhydride (TOTOKASEI Co.) was used as hardener. The density of wefts and warps in carbon fabrics was about 12.5/25 mm (width of fiber bundle = 2 mm). A fiber bundle was consisted of 3 × 10³ single fibers. The thickness of carbon fabrics was about 0.2 mm. Carbon fabrics were dried in a heating oven at 100°C for 2 hours and cooled in the fabricating chamber. Epoxy resin and the hardener were also dried in a vacuum chamber at 60°C for more than 12 hours to remove water before mixing them.

The laminate was fabricated by the hand-lay up method. The laminate had 6 layers. The thickness of the laminate was about 1.3 mm and the area was 300 × 200 mm². The volume fraction of carbon fibers was about 51.5%. The specimens measuring 25 × 200 mm² were cut out of the laminate as cooled with compressed air. The geometry and dimensions of the specimen are shown in Fig. 1. The specimens are classified as listed in Table 1. AD (All Dry) specimen is dried at all stages. MD (Mixing, storage and testing Dry) specimen is dried in except for the laminating stage. SD (Storage and testing Dry) specimen is dried in except for the mixing stage, the laminating stage. BA (BAsic) specimen absorbs moisture at all stages. Mixing, laminating and storage periods were 15 minutes, 15 minutes and 1 month, respectively. Fatigue testing period was more than 2 hours.

Tensile tests were conducted at a cross-head speed of 0.5 mm/min by using a universal testing machine. A servo-controlled hydraulic testing machine was used for the fatigue tests. In fatigue tests, the specimen was subjected to cyclic loads having a sinusoidal wave at a frequency of 6 Hz and a stress ratio of 0.1. The internal damage state was observed from the side of the specimen by using an optical microscope.

2.3 Evaluation of fiber/matrix interfacial properties

Double cleavage drilled compression (DCDC) tests(10)(11) and microbond tests(12)(13) were conducted to examine the fiber/matrix interfacial properties. DCDC test is a useful method for evaluating the crack propagation behavior and interfacial fracture energy at the fiber/matrix interface. Microbond test is one of the methods to measure the fiber/matrix interfacial shear strength.

Figure 2 shows the geometry and dimensions of the DCDC specimen. A fiber bundle was embedded in the center of the specimen. The DCDC specimen was subjected to cyclic compressive loads having a sinusoidal wave at a frequency of 6 Hz and a stress ratio of 0.1. The fiber volume fraction of this specimen is very small (about 0.1%). This specimen, from a macroscopic viewpoint, is considered as isotropic and homogeneous materials. Therefore, the energy release rate range ∆G is given by the following equation(10).

\[
\Delta G = \frac{(1 - \nu^2)}{E} \frac{f(a/d)\Delta \sigma(\pi d)^{1/2}}{2}
\]

Where \( \nu \) is Poisson’s ratio of epoxy resin, \( E \) is Young’s modulus, \( a \) is the crack length, \( d \) is the diameter of a circular hole, \( \Delta \sigma \) is the range of the compressive stress, \( \delta \) is the crack opening displacement and \( \sigma \) is the compressive stress.

Figure 3 shows the geometry and dimensions of the microbond specimen and the schematic view of testing method. Micro-vises were set near a resin droplet and a fiber bundle was pulled out from a resin droplet (cross-head speed = 0.5 mm/min). The interfacial shearing strength \( \tau \) is given by the following equation.

\[
\tau = \frac{P}{\pi d l}
\]
Where $P$ is the maximum shearing load, $d$ (12 – 18 $\mu$m) is the diameter of a fiber bundle and $l$ (80 – 100 $\mu$m) is the length of the embedded fiber bundle.

3. Results and Discussion

3.1 Moisture absorption properties of epoxy resin

The moisture absorption properties of liquid and consolidated epoxy resin were examined. Liquid epoxy resin on a glass plate (diameter = 60 mm) was exposed in the laboratory condition. The epoxy resin specimen (volume = $25 \times 50 \times 3$ mm$^3$), which was consolidated in absolutely dry condition, was put in the laboratory condition. The mass of each epoxy resin was measured by using an electronic balance. The moisture absorption rate $R$ is given by the following equation.

$$R = \frac{(m - m_0)}{A}$$

Where $m_0$ is the mass of epoxy resin, $m$ is the mass after moisture absorption and $A$ is the exposed area in the laboratory atmosphere.

Figures 4 and 5 show the variation in the moisture absorption rate with respect to the exposed time for liquid epoxy resin and consolidated epoxy resin. The moisture absorption rate of liquid epoxy resin was $1.5 \times 10^{-6}$ g/mm$^2$ and the moisture absorption rate of consolidated epoxy resin was $0.18 \times 10^{-6}$ g/mm$^2$ after 60 minutes as shown in Fig. 4. Therefore, it is important to control the humidity condition at the fabrication stage, especially the laminating stage because liquid epoxy resin comes in contact with the atmospheric air and the amount of moisture absorption increases.

The mass fraction of absorbed moisture, the tensile strength and Young’s modulus of epoxy resin are listed in Table 2. The tensile strength and Young’s modulus of each epoxy resin were not affected by the fabricating condition.

### Table 2 Mechanical properties of epoxy resin

<table>
<thead>
<tr>
<th></th>
<th>Mass Fraction of Moisture</th>
<th>Tensile strength</th>
<th>Young’s modulus</th>
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</thead>
<tbody>
<tr>
<td>AD</td>
<td>0.068 [mass%]</td>
<td>36.2 [MPa]</td>
<td>3.7 [GPa]</td>
</tr>
<tr>
<td>MD</td>
<td>0.075 [mass%]</td>
<td>36.5 [MPa]</td>
<td>3.7 [GPa]</td>
</tr>
<tr>
<td>SD</td>
<td>0.079 [mass%]</td>
<td>38.6 [MPa]</td>
<td>3.6 [GPa]</td>
</tr>
<tr>
<td>BA</td>
<td>0.56 [mass%]</td>
<td>38.2 [MPa]</td>
<td>3.8 [GPa]</td>
</tr>
</tbody>
</table>

3.2 Static and fatigue properties of plain-woven CFRP

The variation in the tensile strength for the stage environment is shown in Fig. 6. Figure 7 shows the variation in Young’s modulus of plain-woven CFRP. Figure 6 shows that average tensile strengths of AD, MD, SD and BD specimens were 961 MPa, 891 MPa, 849 MPa and 841 MPa, respectively. Average strength of AD specimen was 70 MPa higher than that of MD specimen. This result shows that the tensile strength of plain-woven CFRP is significantly improved if the materials are protected.
from moisture absorption at the laminating stage. Average strength of MD specimen was 42 MPa higher than that of SD specimen owing to protection from moisture absorption at the mixing stage. Average strength of SD specimen, however, was almost the same with that of BA specimen.

Figure 7 shows that Young’s modulus of each specimen was 63 GPa in average. Young’s modulus was not affected by the fabricating condition.

Figure 8 shows S–N diagrams obtained in fatigue tests. In this figure, the fatigue life of AD specimen was longer than that of MD specimen and the fatigue life of MD specimen was longer than that of SD specimen. These results show that the fatigue life of plain-woven CFRP is improved if the materials are protected from moisture absorption at the fabrication stage.

The fatigue life of SD specimen was almost the same with that of BA specimen. BA specimen is exposed in the atmosphere for about 1 month (storage and testing periods). However, it takes more than 2 months up to saturated moisture absorption for consolidated epoxy resin as shown in Fig. 5. Therefore, the effect of moisture absorption at storage and testing stages on the fatigue life of plain-woven CFRP is not a little under the condition of this study.

The photographs of internal damage state for plain-woven CFRP are shown in Fig. 9. According to the observation, a lot of transverse cracks initiated for AD and MD specimens. However, local delamination at the cross over point between warp and weft for AD specimen was a little, compared with MD specimen.

3.3 Fiber/matrix interfacial properties

It is well known that the hydroxyl in epoxy resin easily bonds to H₂O molecular. This chemical link weakens the strength of the bond between carbon fibers and epoxy resin. Therefore, the improvement of the fiber/matrix interfacial properties is expected if plain-woven CFRP is fabricated without moisture absorption.

Figure 10 shows the relationship between the fatigue crack growth rate and crack growth resistance (energy re-
Fig. 10 Relationship between energy release rate range and fatigue crack growth rate

Fig. 11 Photograph of fracture surface of DCDC specimen

The interfacial shearing strengths of AD and MD-microbond specimens are shown in Fig. 12. At all range of cumulative fracture probability, the shearing strength of AD-microbond specimen was higher than that of MD-microbond specimen.

These results show that the improvement of the fiber/matrix interfacial properties contributed to the enhancement of the tensile strength and fatigue life of plain-woven CFRP.

4. Conclusions

The effect of moisture absorption at the fabrication (mixing and laminating) stage on the static and fatigue properties was examined for plain-woven CF/epoxy composites. The fiber/matrix interfacial properties were also evaluated when moisture exists or not. The present study is summarized as follows.

1 ) It is important to control the humidity condition at the fabrication stage, especially the laminating stage, because liquid epoxy resin comes in contact with the atmospheric air and the amount of moisture absorption increases.

2 ) If the materials are protected from moisture absorption at the fabrication stage, the tensile strength and fatigue life of plain-woven CFRP are significantly improved.

3 ) The protection from moisture absorption at the fabrication stage improved the fiber/matrix interfacial properties. Such improvement contributed to the enhancement of the tensile strength and fatigue life of plain-woven CFRP.

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