Mechanical Characteristics of C/C Composites Modified with Micro-Sized Glass Fibers

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Abstract: The purpose of this study is to investigate the mechanical characteristics of C/C (Carbon-Carbon) composites, where the carbon precursor contains micro-sized glass fibers. The carbon fiber bundle was dipped in the phenolic resin in which micro-sized glass fibers were dispersed uniformly and winding in order to fabricate unidirectional CFRP (Carbon-Fiber-Reinforced-Plastic) preform. The CFRP preform was carbonized at high temperature with inert atmosphere to fabricate the C/C composites as follows. The preform was heated up to 1273 K and then kept for 1 hr. In second phase, the preform was heated again up to 1773 K and then kept for 1 hr. The test results showed that the bending strength of C/C composites carbonized at 1273 K decreased compared with that of CFRP preform. However, the bending strength of modified C/C composites was increased when the carbonized temperature exceeded 1773 K. Unmodified C/C composites showed almost constant bending strength and modulus with respect to the carbonized temperature. These results suggested that the SiC synthesization between glass fibers and carbon matrix was effectively obtained during the carbonizing procedure.

Keywords: C/C Composites, Glass Fiber, Carbonized Temperature, Mechanical Characteristics, SiC

1. Introduction

A carbon-carbon (C/C) composite is known as one of the excellent high performance composite materials because of its high mechanical properties, despite its low density, and also because of its high durability in high temperature environments [1, 2]. Because of their excellent properties, it is expected that C/C composites are applied not only to structural materials for aerospace vehicles [3, 4] but also to those of commercials vehicles. Generally, inter-laminar shear strength of C/C composites was relatively poor compared with that of other composite materials [5, 6]. In order to improve the inter-laminar shear strength of C/C composites, modifications of carbon matrix to SiC by metal infiltration [7] or chemical vapor deposition (CVD) [8] have been investigated. However, the conventional SiC modification methods not only require long process time [9], but also may have defects such as thermal cracks during modification process [10]. An effective SiC modification technique of C/C composites that improves shear strength without long process time is required. One of the authors proposed a novel method that synthesizes the SiC and charring of C/C composites was conducted simultaneously by adding the glass fiber to carbon precursor and demonstrated its effect on the frictional characteristics [11].

Therefore, the purpose of this study is to investigate the mechanical characteristics of C/C composites, where the carbon precursor contains micro-sized glass fiber. The effects of carbonized temperature on the mechanical characteristics of C/C composites were evaluated. In this study, the preform plate of CFRP was prepared by a filament winding technique. The pitch-based carbon fiber bundle was dipped in the phenolic resin, in which the micro-sized glass fiber was dispersed uniformly, and then winding to the bobbin with controlled tensions and winding pitch in order to fabricate unidirectional CFRP preform. The CFRP preform was carbonized at high temperature with inert atmosphere to fabricate the C/C composites. The mechanical properties of C/C composites were characterized under four-point bending load.

2. Materials and Method

2.1 Raw materials

A 3K pitch-based carbon fiber (XN-20-30S: Nippon Graphite Fiber Co., Ltd.) and phenolic resin (PHENOLITE 5010: DIC Co., Ltd.) were used for reinforced fiber and carbon precursor resin of C/C composites matrix, respectively. Micro-sized glass fibers (CENTRAL GLASS Co., Ltd.) were used as an additive material, in which the diameter and length were approximately 11 µm and 100 µm, respectively. The micro-sized glass fiber was added to the phenolic resin, where the weight fraction was controlled to be 1.0 mass% with respect to the phenolic resin. Table 1 shows the mechanical characteristics of raw materials. Table 2 also shows the chemical composition of micro-sized glass fiber.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density [g/cm³]</th>
<th>Fineness [g/km]</th>
<th>Tensile strength [MPa]</th>
<th>Elastic modulus [GPa]</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Carbon fiber</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.10</td>
<td>70</td>
<td>3000</td>
<td>196</td>
<td>462</td>
</tr>
<tr>
<td>(b) Glass fiber</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.54</td>
<td>1113</td>
<td>72.6</td>
<td>3430</td>
<td></td>
</tr>
<tr>
<td>(c) Phenolic resin</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>1.05</td>
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</tbody>
</table>

Table 1 Mechanical and physical characteristics of raw materials

2.2 Fabrication of C/C composites

The unidirectional preform plate of CFRP was fabricated by a filament winding technique. The pitch-based carbon fiber bundle was dipped in the phenolic resin in which the micro-sized glass fiber was dispersed uniformly, and then winding to the bobbin with controlled tensions and winding pitch in order to fabricate unidirectional CFRP preform. The CFRP preform was carbonized at high temperature with inert atmosphere to fabricate the C/C composites. The mechanical properties of C/C composites were characterized under four-point bending load.

Figure 2 shows the normalized weight change of the matrix shows the filament winding machine used in this study.
2.2 Fabrication of C/C composites

The unidirectional preform plate of CFRP was fabricated by employing a filament winding technique. Figure 1 shows the filament winding machine used in this study. The carbon fiber bundle was dipped into a phenolic resin in which micro-sized glass fiber was dispersed uniformly. The dipped bundle was wound onto a cubic bobbin with hoop winding configuration under controlled tensions and winding pitch. In this study, the applied tension and winding pitch were controlled to be 3.5 N and 3.0 mm, respectively. The wound CFRP preform was precured in the oven at 353 K for 24 hr. After this process, the CFRP preform was heat pressed at 423 K under 15 MPa for 1 hr to cure the phenolic resin matrix. The fiber volume fraction of the fabricated CFRP preform was approximately 67%.

The fabricated CFRP preform plate was cut in parallel with the fiber direction to fabricate 80×15×3 mm³ coupon type specimens using a diamond cutter. The C/C composites were obtained by being well charred through the following two processes. In first phase, the preform was heated up to 1273 K at 1.0 K/min of elevation rate and then kept for 1 hr in a ring furnace filled with argon gas. At 1273 K, it was believed that the SiC synthesis does not occur. In second phase, the preform was heat treated again up to 1773 K at 1.5 K/min of the elevation rate and then kept for 1 hr. At 1773 K, SiC synthesis may occur. After heating, the preform was cooled gradually.

2.3 Four point bending test

The mechanical properties of the C/C composites were characterized under the four-point bending load by using a universal testing machine (EZ-L: SHIMADZU Co., Ltd.). Lower span, upper span, and cross head speed of the four-point bending test were set to 51 mm, 17 mm, and 1.0 mm/min, respectively. The bending stress and strain were simply calculated using the following Eq.(1) and Eq.(2):

\[ \sigma_B = \frac{PL}{wL^2} \]  
\[ \varepsilon_B = \frac{4.75tL}{L^2} \]  

Here, \( P \), \( \delta \), \( L \), \( w \), and \( t \) denote the applied bending load, deflection, lower span length, width of specimen, and thickness of specimen, respectively. At least five specimens were tested to investigate the bending properties.

3. Results and Discussions

3.1 Weight change and pore of C/C composites

Figure 2 shows the normalized weight change of the matrix due to charred treatment. The test results showed that the weight of the matrix was drastically decreased when the specimen was charred over 1273 K even if the glass fiber was present (Modified) or absent (Unmodified) at its matrix. This weight diminution can be explained using the carbon yield of phenolic matrix.

The test results also revealed that the weight diminution of specimen was increased when the matrix was modified.

Table 2 Chemical composition of micro-sized glass fiber

<table>
<thead>
<tr>
<th>Types of glass</th>
<th>Percentage [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>53</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15</td>
</tr>
<tr>
<td>CaO</td>
<td>21</td>
</tr>
<tr>
<td>MgO</td>
<td>2</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>8</td>
</tr>
<tr>
<td>Na₂O+K₂O</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Fig. 3 Cross section of the specimens.

Fig. 2 Normalized weight change of the matrix.
This result would be explained as follows; because of presence of the glass fiber, the volume of the phenolic resin in the specimen would be decreased. Therefore, the weight diminution of the modified matrix was decreased compared with that of the un-modified matrix. Fig.3 also shows the cross section of the specimens. When the specimen was charred over 1273 K, the amount of pore was increased even if the glass fiber was present or absent at its matrix. These pores would have been generated using the liberation of decomposed phenol matrix according to temperature elevation.

### 3.2 Bending characteristics of C/C composites

Fig.4 and Fig.5 show the typical bending stress-bending strain ($\sigma_B$-$\varepsilon_B$) diagrams of the un-modified and modified specimens. Fig.6 and Fig.7 also show the average bending strength and modulus of the specimens. Here, the bending modulus was simply calculated using the slope of $\sigma_B$-$\varepsilon_B$ diagram range from 50 to 150 MPa. In Fig.6, the bending strength of the charred specimen was drastically decreased comparing with that of the un-charred specimen. When the matrix of the specimen was modified using the glass fiber, the bending strength was improved compared with that of the un-modified specimen. Moreover, the bending strength of the modified specimen was improved with increase in the charred temperature. In Fig.7, the bending modulus estimated using the slope of $\sigma_B$-$\varepsilon_B$ diagrams was slightly decreased when unmodified specimen was charred. However, at modified specimen, the bending modulus was almost same even if the specimen was charred or un-charred. Fig.8 shows the side view observation during the bending test. The observation results revealed that mode II inter-laminar shear failure was initially occurred even if the glass fiber was present or absent at its matrix. Hence, mode II inter-laminar shear strength might had been improved when the matrix was modified using the glass fiber and charred at 1773 K.

### 3.3 Fractured surface of C/C composites

Fig.9 shows the fractured shear surface of specimens. When the specimen was charred with over 1273 K, the fiber breakage due to thermal deformation of matrix was observed. Moreover, the smoothed surface of the fiber was observed even if the glass fiber was present or absent at its matrix. This result suggested that the delamination between the fiber and matrix also occurred because of thermal deformation of the matrix. Therefore, the bending strength of the charred specimen was drastically decreased compared with that of the un-charred specimen. However, when the matrix was modified using the glass fiber and charred at 1773 K, the nanosized fiber like structure was observed at the position where the glass fiber might has existed, as shown in Fig.10. The element analysis of this fiber like structure was conducted using SEM-EDX. Fig.11 shows the result of the element analysis. The significant peaks of C and Si were confirmed. These result suggested that the nanosized SiC fiber were synthesized using the proposed method. According to previous study of Shimoo et al. [12], the β-SiC nanofiber has been synthesized when graphite was exposed to SiO gas over a temperature of 1700 K. These results suggested that the added glass fiber enhanced when the matrix was modified using the glass fiber, the crack bridging between layers would be occurred. Therefore, the mode II inter-laminar shear strength was improved even if the glass fiber was present or absent at its matrix. Hence, mode II inter-laminar shear strength might had been improved when the matrix was modified using the glass fiber and charred at 1773 K.
1700 K. These results suggested that the added glass fiber would be gasified over 1700 K and generate SiO gas as follows,

$$S_iO_2(s) + 3C(s) = S_iO(g) + CO(g)$$

(3)

Then, the SiO gas and CO gas would be reacted and synthesized β-SiC nanofiber as follows,

$$S_iO(g) + 3CO(g) = S_iC(s) + 2CO_2(g)$$

(4)

Because of the presence of synthesized β-SiC nanofiber, the crack bridging between layers would be occurred. Therefore, the mode II inter-laminar shear strength was enhanced when the matrix was modified with glass fiber and charred with 1773 K.

4. Conclusions

In this study, the glass fibers were added to the carbon precursor of C/C composites, and its effect of the bending characteristics was investigated. The following conclusions were given as:

[1] The weight change because of the charred of C/C composite was almost constant even if the glass fibers were present or absent at its matrix.

[2] When the matrix of the C/C composite was modified using the glass fibers, the bending strength was improved compared with that of the un-modified C/C composite.

[3] Due to the presence of the synthesized β-SiC nanofibers, mode II inter-laminar shear strength was enhanced when the matrix was modified using the glass fibers and charred at 1773 K.

Acknowledgement

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References


