1 Introduction

Over the past few decades, fiber reinforced plastics (FRP) have been developed as the foremost material for products in fields such as mechanical, electrical, architectural, and structural engineering. Carbon fiber reinforced plastic (CFRP) has especially attained a prominent position in use as structural materials for aeronautical and space engineering. Application in this industry requires further reduction in weight to satisfy the demand for higher fuel efficiency.

Recently, a number of experimental and analytical techniques have been proposed to evaluate the fracture toughness for mode I[1], mode II[2], mixed mode[3] with several combinations of carbon fiber and matrix resin. Previous attempts to improve the interlaminar fracture toughness of CFRP laminates has shown various useful results. Namely, a certain level of toughening technique has already been achieved by inserting an interleaf (interlayer) between the CFRP Prepregs[4]. T800H/3900-2, with a heterogeneous interlayer consisting of fine thermo plastic particles, has shown high compressive strength after impact (CAI). Ionomer interleaved CFRP laminates have shown higher toughness under mode I[5] and II deformations[6].

Furthermore, it was confirmed that Zanchor technique[7] has been achieved high fracture toughness and high fatigue property for CFRP laminates made by vacuum-assisted resin transfer molding (VaRTM).

In recent years, carbon nanotubes and carbon nanofibers have received a great deal of attention in the aeronautical, biological, electrical and mechanical sciences, and engineering fields. Since discovery of the carbon nanotube in the 1970s[8,9] and the publication in Nature[10] clarifying the structure of the carbon nanofibers, carbon nano tubes and carbon nanofibers have received a great deal of attention in the aeronautical, biological, electrical and mechanical sciences, and engineering fields.

Due to CNF's superiority in electrical conductivity, MWCNT or vapor grown carbon fiber `VGCF' has established a strong presence in the storage battery field as the conductive filler. Carbon nanotubes and nanofibers have been applied as the toughening filler of the structural material for resin or metal based composites[11,12]. They are suitable for this application as they also have excellent mechanical properties such as elastic moduli, strength, fracture toughness, and flexibility compared with the traditional carbon fiber which are based on polyacrylonitrile (PAN).

In the present study, we implemented an alternative way to increase the interlaminar fracture toughness and fatigue property of CFRP laminates by inserting carbon nanofibers between the CFRP laminates composed of woven fabric[13,14]. Carbon nanofiber was employed as reinforcement for the interlayers for mode I fracture toughness tests. CNF, VGCF(SHOWA Denko K.K.) and MWNT-7(Hodogaya Chemical Co.,LTD.), were used for the reinforcement of the CFRP laminate. The carbon fiber of twill woven fabric was used as main composition materials in the present study.
Table 1 Specification of carbon nanofiber.

<table>
<thead>
<tr>
<th>CNF</th>
<th>Diameter [nm]</th>
<th>Length [μm]</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGCF</td>
<td>150</td>
<td>7</td>
<td>Multiwall</td>
</tr>
<tr>
<td>MWNT-7</td>
<td>40 - 90</td>
<td>4</td>
<td>Multiwall</td>
</tr>
</tbody>
</table>

Table 2 CFRP Specimens for DCB tests.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>CNF Type</th>
<th>Amount of CNF [g/m²]</th>
<th>Thickness [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Laminate</td>
<td>–</td>
<td>–</td>
<td>4.19</td>
</tr>
<tr>
<td>MWNT7-10</td>
<td>MWNT-7</td>
<td>10</td>
<td>4.25</td>
</tr>
<tr>
<td>MWNT7-20</td>
<td>MWNT-7</td>
<td>20</td>
<td>4.26</td>
</tr>
<tr>
<td>MWNT7-30</td>
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<td>MWNT7-40</td>
<td>MWNT-7</td>
<td>40</td>
<td>4.39</td>
</tr>
<tr>
<td>VGCF-5</td>
<td>VGCF</td>
<td>5</td>
<td>4.15</td>
</tr>
<tr>
<td>VGCF-10</td>
<td>VGCF</td>
<td>10</td>
<td>4.23</td>
</tr>
<tr>
<td>VGCF-20</td>
<td>VGCF</td>
<td>20</td>
<td>4.25</td>
</tr>
</tbody>
</table>

The static and fatigue property of mode I crack was investigated by double cantilever beam (DCB) tests. The experimental results showed that the interlaminar fracture toughness and fatigue crack growth resistance can be improved by inserting the CNF interlayer on the CFRP laminates fabricated by VaRTM process with woven fabric.

2 CFRP Specimens

Twill woven fabric of carbon fiber C06347B (TORAY) has been used for the base material of CFRP. Epoxy resin “DENATOOL” (Nagase Chemtex Corp.) has been used for the matrix, where XNR6809 is base resin and XNH6809 is curing agent.

In order to reinforce between the woven fabric layer by making nanofiber/resin interlayer, MWNT-7 (Hodogaya Chemical Co., LTD.) and VGCF (Showa Denko K. K.) have been introduced. In the CFRP specimens, carbon nanofiber interlayer was inserted between 10th and 11th woven fabric in the vacuum-assisted resin transfer molding (VaRTM) process as shown in Fig.1(B). The specifications, diameters and length, of the MWNT-7 and VGCF are shown in Table 1.

At first, mixed slurry of CNF and epoxy resin was made using a planetary centrifugal mixer (SR500, THINKY USA Inc.). The quantity of the CNF was controlled by area density of CNF [g/m²]. When the area density of CNF is \( X [g/m^2] \), the weight fraction of the CNF should be controlled to \( 0.25 \times X \text{ wt}[%] \) in the mixed slurry. After making a pair of the preform composed of 10 layer woven fabric, the
mixed slurry was applied on the preform and the preforms were stacked inserting polyimide film (Thickness 30µm) to make an artificial crack in the CFRP laminate as shown in Fig.1.

Wrapping up the preform by sealant tape and bagging film, then epoxy resin is put in the preform with vacuum assist as shown in Fig.2. After filling up with resin in the woven fabric preform, resin was cured by heating with an electric furnace. Primary curing is 2 hours by 80°C in 4 hours, and it carried out secondary curing is 2 hours by 130°C.

From the CFRP laminate obtained by VaRTM process, a CFRP laminated beams (20mm width, 150mm length) were cut out for the double cantilever beam (DCB) specimens for the fracture toughness tests and fatigue crack propagation tests.
DCB specimens in the present study are shown in the Table 2.

Since the base materials of CFRP are textiles, it is difficult to define clearly the thickness of the CNF interlayer. However, it seems that the thickness of CNF interlayer is about 60 – 120 µm as long as it judges from Table 1.

3 Experimental Procedure

In the present study, fracture toughness tests for crack opening mode (Mode I) have been carried out (Fig.3). For static mode I test, a universal material testing machine AGS-J-5kN, SHIMADZU Co.(Fig.4) was used. The aluminum tabs were attached to the opening end of a DCB specimen, and the mode I tests were carried out by giving compulsive displacement to the DCB specimen through a pair of hinge, where the cross head rate was specified to 0.5mm/min.

On the other hand, an electric fatigue testing machine Electro Pulse E3000, Instron Co.(Fig.5) was used for the fatigue crack propagation tests of mode I. The fatigue tests were carried out with load control of the frequency 5Hz where the maximum and minimum loads were specified to 42N and 8.4N (load ratio = 0.2), respectively. The fracture toughness of the DCB testing were evaluated by modified compliance calibration method[15,16]. The side section of the specimen was ground by the Emery paper and it was painted white to observe the crack extension. Observing the crack front by the digital camera (SONY α700 with close-up lens), the crack length was measured continuously in the DCB tests.

4 Experimental Results

4.1 Static mode I fracture toughness test

Figure 7 and 8 show the relations between crack growth ∆a and fracture toughness $G_{ic}$ in static DCB tests estimated by modified compliance calibration method. In the case of MWNT-7 (Fig.8), the fracture toughness of CFRP/MWNT-7 laminates reaches almost twice as much as that of base CFRP laminate in the initial stage of crack propagation.

As the cracks extend, the ratio $G_{ic}$ (Interlayer)/$G_{ic}$(Base laminate) increases and reaches about 3 in the region of the crack length $\Delta a > 40$mm. The area density of CNF 20g/m² and 30g/m² give relatively high fracture toughness as shown in Fig.8.
On the other hand, as shown in Fig. 8, the influence of the VGCF interlayer is not so large in fracture toughness $G_I$ like the case of COD v.s. load in Fig. 4. It seems that the effect of VGCF interlayer is at most about 20% in the case of 5-10 g/m² area density of CNF.

SEM images of the fracture surfaces after static DCB tests are shown in Fig. 8, 9 and 10 for the MWNT-7 interlayer case; area density 10g/m², 30g/m² and 40g/m², respectively. Comparing Fig. 8 and Fig. 9, there is no difference between the fracture surfaces of MWNT-7 10g/m² and that of 30g/m². On the fracture surface of MWNT-7 40g/m², condensation of some carbon nano fiber exists on the fracture surface. It is thought that the fracture in the CNF interlayer becomes in brittleness by condensation of a fiber. Therefore, it seems that the fracture toughness value fell in the case of CNF area density 40g/m².
4.2 Mode I fatigue Tests

Mode I fatigue crack growth tests were carried out for CFRP laminate toughened with MWNT-7 interlayer which gives high fracture toughness in the static mode I test. Figure 11 shows the relation between the extension of the crack length $\Delta a$ and cycles for the mode I crack fatigue tests. As shown in Fig.11, the number of cycles which results in final unstable fracture increased sharply using MWNT-7 interlayer.

In the base CFRP laminate, brittle fracture occurred in the experimental final stage. By about $2 \times 10^5$ cycles, the base laminate was broken completely. On the other hand, in MWNT-7/CFRP, the brittle fracture was controlled by means of inserting the CNF interlayer and relatively slow crack propagation was observed until the crack reach 80 mm in length.

Relationship between crack propagation rate $da/dN$ and the energy release rate range $\Delta G_I$ is shown in Fig.12. Here, $da/dN$ for all MWNT laminates for the region(A) with a small energy release rate $100 < \Delta G_I < 300 \ [J/m^2]$ and that for the region(B) with a large energy release rate $300 < \Delta G_I < 1000 \ [J/m^2]$ are considered, respectively.

In the region (A) as shown in Fig.12, the crack propagation rate of MWNT-7/CFRP decreased as compared with the case of base laminate. That is, when these results are compared by same energy release rate range, the crack propagation rate of base laminate is the highest. On the other hand, as shown in the resion (B), the range in which the stable crack growth observed was expanded until the $\Delta G_I$ reaches 1000[J/m$^2$] in MWNT-7/CFRP. As a result, it was confirmed that the characteristic of fatigue crack extenstion was improved introducin CNF interlayer.

Although the specimens which are toughened with the CNF interlayer generally shows the good characteristic of fatigue crack propagation, it is confirmed that the best result can be obtained by CNF interlayer of 20 g/m$^2$ for the mode I fatigue crack. Figures 13 and 14 show the fracture surfaces of the base CFRP laminate and that of MWNT-7/CFRP laminate after mode I crack fatigue tests in the region (A). In the initial stage of crack propagation, the crack propagates in the CNF interlayer as shown in Fig.14.

Figures 15 and 16 show the fracture surfaces in the region (B). In this region, the aspect of fracture surface of base laminate in Fig.15 seems to be almost same to that of the initial stage of the crack propagation as shown in Fig.13. On the other hand, for the MWNT-7/CFRP laminate in Fig.14, the morphology of fracture surface changed since the crack path moved on the interface between woven fabric layer and CNF interlayer.

Since the fracture toughness inside of the CNF interlayer is larger than that between CNF interlayer and CF woven fabric layer, the crack tends to extend.
so that a layer with high fracture toughness may be avoided.

The fatigue crack characteristic of the specimen toughened with CNF interlayer is still better than base laminate. This is because, it has influenced that the interlaminar fracture toughness between the CNF interlayer/woven fabric is higher than the fracture toughness between the woven fabric in the base laminate, and that crack progress is controlled by generating of micro bridging of CNF.

5 Conclusions

In the present study, mode I fracture toughness and mode I fatigue crack property of CFRP woven fabric laminate toughened with carbon nanofiber interlayer (VGCF and MWNT-7) have been investigated.

The static mode I fracture toughness of CNF/CFRP laminates reaches 2 times that of the base laminates at the initial stage of the crack propagation in the MWNT-7 case. In the domain in which the crack fully progressed, the fracture toughness reaches 3 times that of the base laminate although there are variations in data. From static mode I DCB tests, the effect of VGCF interlayer was restrictive although sufficient effect for MWNT-7 interlayer was accepted.

For the mode I fatigue crack tests, only MWNT-7 interlayer was applied. By introducing MWNT-7 interlayer, the number of cycles which a final fracture produces increased to 1.5 or more times compared with the case of base laminate. The fracture toughness (upper limit of the energy release rate range $\Delta G_{\text{max}}$) in fatigue crack extension amounts to 1000[J/m$^2$] in the MWNT-7/CFRP and 300[J/m$^2$] in the base laminate. Therefore, it was confirmed that fracture toughness on the fatigue test increases to about 3 times that of base laminate by introducing CNF interlayer.

According to the kind of CNF, the difference arose in the result greatly as shown in the experimental results. Although the fracture surfaces were observed by SEM, the main reason about the difference of a result is not clarified.

It is necessary to further examine what kind of fiber is effective on to the interlaminar fracture toughness and the fatigue crack property of CFRP laminates toughened with CNF interlayer.

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References


