1 Introduction

Hybrid composite have been researched by many researchers because hybrid fiber or resin gives composite great mechanical performance which composite made from sole fiber or resin does not achieve. Hybrid composites are expected to be highly-functional properties because of eliminating weakness and developing merit each other. Most popular hybrid composite is hybrid fiber composite and two or more different reinforcing fibers such as glass fiber, carbon fiber and aramid fiber are used in one composite[1].

In this study, braiding structure was employed as reinforcements to achieve hybrid fiber structure. In braided fabrics, the fiber bundle called middle end yarn (MEY) can be inserted between braiding fibers in longitudinal direction, so that the excellent mechanical properties were expected. In addition, the braided fabrics by using various kinds of braiding fiber and MEY with different properties can be fabricated. Therefore, concept of hybrid composite can be easily applied by using braiding technology and the mechanical properties of the braided composite can be designed according to the requirements. The concept of fiber hybrid composite was expansively applied to FRTP[2].

The purpose of this study is to clarify the impregnation process of hybrid fiber braided FRTP and relationship between impregnation property and mechanical property. In order to examine the impregnation process, cross-sectional observation of moldings with different molding time and braiding structure was performed. After that, impregnation process of fiber hybrid FRTP for pultrusion was investigated by stopping pultrusion molding in midstream and effect caused by pultrusion speed to impregnation state.

2 Materials and molding method

2.1 Intermediate materials

To clarify the process of impregnation for fiber hybrid FRTP, carbon fiber (T700-50C-12000 (sizing content : 1.1wt%), T700-60E-12000 (sizing content: 0.2wt%), 800tex, TORAY) and aramid fiber (Kevlar29-12000 660tex, TORAY Dupont) were used as the reinforcement while the PA66 resin fiber (L-235T35B PA66235dtex, melting temperature: 265 °C) was used as the matrix resin. Commingled yarns made from these materials are listhed in Table1. “Com-” indicates “Commingled yarn of”, CH and CL indicates carbon fiber with high or low sizing content. Vfi was defined as the Vf of reinforcing fiber at intermediate material. Dispersion ratio was defined as the ratio of dispersion between reinforcing fiber and resin fiber. If dispersion ratio was increased, impregnation distance was decreased.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Reinforcing fiber</th>
<th>Vfi(%)</th>
<th>Dispersion ratio(%)</th>
<th>Contact angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Com-CH</td>
<td>Carbon fiber (1.1wt%)</td>
<td>48</td>
<td>58.6</td>
<td>33</td>
</tr>
<tr>
<td>Com-CL</td>
<td>Carbon fiber (0.2wt%)</td>
<td>48</td>
<td>79.6</td>
<td>8</td>
</tr>
<tr>
<td>Com-A</td>
<td>Aramid fiber</td>
<td>49</td>
<td>68.7</td>
<td>10</td>
</tr>
</tbody>
</table>

2.2 Fabric

The structure of braided fabric for heat compressing was shown in Figure 1. Carbon fiber or aramid fiber and PA66 were commingled and it was used as the braided yarns (BYs) and MEYS. Tubular braided fabric was fabricated with 16BYs and 8 MEYS.

In this study, 5 types of braided fabric were used as specimen for molding. These braided fabrics are listed in Table 2. The left side of sample name means the reinforcement fiber used as braiding yarn and the right side of sample name means the reinforcement fiber used as MEY.
3 Molding method and condition

3.1 Heat compressing

In order to investigate the impregnation state of fiber hybrid FRTP and sole FRTP, braided composite was fabricated by compression machine as shown in Figure 2. Braided fabric was inserted into molding die and was molded. Molding pressure and temperature were kept as 0.1MPa and 290 degree, the molding time was changed as 1, 3, 5, 10, 15min. Finally, braided composite plate (20mm in width, 200mm in length) was molded and the cross-sectional observation was carried out.

Table 2 5 types of braided fabric.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>A/A</th>
<th>CH/CH</th>
<th>CL/CL</th>
<th>A/CH</th>
<th>A/CL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Braided yarn</td>
<td>Com-A</td>
<td>Com-CH</td>
<td>Com-CL</td>
<td>Com-A</td>
<td>Com-A</td>
</tr>
<tr>
<td>Middle end yarn</td>
<td>Com-A</td>
<td>Com-CH</td>
<td>Com-CL</td>
<td>Com-CH</td>
<td>Com-CL</td>
</tr>
</tbody>
</table>


3.2 Pultrusion

The pultrusion line is shown in Figure 3. Braided fabrics were pulled into the pultrusion die having a cylindrical hole. During the passage into the die, the resin fiber of the braided fabric melted and impregnated into reinforcing fiber. A preheating die and a molding die were prepared for the forming of the pipe. The braided fabrics were pre-heated in the preheating die up to near melting temperature (160 °C) of the resin fiber for easier impregnation. The molding die had the cylindrical hole with 18 mm diameter and diameter of the mandrel was 15mm, so the cylindrical tube with 1.5mm thickness was obtained by this pultrusion system. The molding die is shown in Figure 4. The length of the molding die was 1500 mm, which was separated into 8 heating zones. The temperature at each sections of the molding die was set at 290, 290, 290, 290, 285, 280, 275°C from the entrance side, respectively. The mandrel had also a heater and set at 230°C during pultrusion. The pipe was pulled out continuously by pulling system.

3.3 Stopping pultrusion in midstream

In order to investigate the impregnation process during molding, pultrusion molding was interrupted. Then the sample inside of the molding die was taken out and cross-sectional observation of the composite cut in each position corresponding to (a) to (e) in Figure 5 was carried out by using optical microscopy. In this stopping pultrusion in midstream, braided fabrics of A/A, A/CL and CL/CL were used as specimen.

4 Experiments

- **Figure 2** Heat compressing.
- **Figure 3** Pultrusion system.
- **Figure 4** Positions of heaters.
- **Figure 5** The points measuring impregnation ratio.
4.1 Dispersion ratio
In order to quantitatively evaluate the dispersion state of fibers in intermediate material, dispersion ratio was defined. The intermediate material was inserted into heat-shrinkable tube and the tube was deflated by heating. Then, the tube was formed into cylindrical shape and fibers were densely packed. The tube was embedded in a resin, and then cross-sectional observation was performed.

Figure 6 shows the definition of dispersion ratio. First, straight lines were drawn on the parabola with each 30 degree on the cross-sectional photograph. There was a continuous reinforcing fiber and resin fiber along the diameter line on the cross-sectional photograph of fiber bundle. The length of reinforcing fiber and resin fiber along the diameter line were measured. Dispersion ratio was expressed by Eq.(1). The value that average distance of first fiber-assembly to second fiber-assembly divided by total distance of both fibers was calculated. Each dispersion ratio was defined by subtracting the value from 1. As average distance of fiber area are becoming small, dispersion ratio comes close to 100%, and the minimum value is 50%.

\[
\text{Dispersion ratio} \left(\%\right) = 1 - \left(\frac{\sum a_i \text{ or } b_i}{n} \cdot \frac{1}{\sum a_i \cdot b_i}\right) \cdot 100 \quad (1)
\]

Draw a line on the parabola
The length of reinforced fiber and resin fiber respectively on the line were measured.

4.2 Cross-sectional observation
The cross section of each molding was observed with the optical microscope. For the observation on cross section, the samples were emery grinded (#100~#2,000) and buffed (alumina particle, average particle size: 100 nm) after they were embedded in epoxy resin. After cross-sectional observation, un-impregnation ratio of each specimen was calculated. The definition of un-impregnation ratio is shown in Figure 7. Un-impregnation ratio was defined as the area of un-impregnation area divided by the area of a fiber bundle.

4.3 3-point bending test
The three-point bending test was conducted to estimate the mechanical properties. In this test, INSTRON type-4206 was used as the universal testing machine. Conditions of the experiment were as indicated below: span length was 80mm, specimen length was 110mm, and testing speed was 3mm/min.

5 Results
5.1 Investigation of intermediate material
In order to investigate the intermediate material, dispersion ratio and contact angle was measured as shown in Table 3. Dispersion ratio of Com-CL was the highest, that of Com-CH was the lowest. Contact angle of Com-CL was the lowest, that of Com-CH was the highest. According to these results, it was considered that impregnation property of Com-CL was best and Com-CH was poorest because of those impregnation distance and wettability.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Reinforcement fiber</th>
<th>Dispersion ratio (%)</th>
<th>Contact angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Com-CH</td>
<td>CF (1.1wt%)</td>
<td>58.6</td>
<td>33</td>
</tr>
<tr>
<td>Com-CL</td>
<td>CF (0.2wt%)</td>
<td>79.6</td>
<td>8</td>
</tr>
<tr>
<td>Com-A</td>
<td>AF</td>
<td>68.7</td>
<td>10</td>
</tr>
</tbody>
</table>

5.2 Impregnation state for heat compressing
Cross-sections of moldings consisted from sole material molded by each condition (molding time: 1min, 15min) are shown in Figure 8 to Figure 10. Cross-sections of consisted from hybrid material molded by each condition (molding time: 1min, 15min) are shown in Figure 11 and Figure 12. According to Figure 8 to Figure 12, it was clarified that un-impregnation area and the area of resin-rich were decreased with increasing of molding time. Relationship between un-impregnation ratio of sole material (CH/CH, CL/CL, A/A) is shown in...
Figure 13. Relationship between un-impregnation ratio of hybrid material (A/CH, A/CL) is shown in Figure 14 and Figure 15. According to Figure 13, each un-impregnation ratio of CF with 1.1wt% of sizing content at all time was higher than that of CF with 0.2wt% of sizing content. It is because that Com-CH had low dispersion ratio and poor wetting ability because of the high sizing content. According to Figure 14, un-impregnation ratio of CH in fiber hybrid structure was decreased compared to that of CH in sole structure. The quantity of contacted resin of Com-AF around CF was increased in the case of Fiber hybrid structure of AF/CF (1.1wt %) According to Figure 15, in the case of fiber hybrid braided fabric which has MEY with CF of 0.2wt% sizing content, the un-impregnation ratio of MEY was increased at all molding time. The thermal conductivity of CF (80~800(W/mK)) was higher than AF (2~4(W/mK)), so that MEY of CF had longer essential molding time than BY of AF. Here, essential molding time was defined as the molding time over melting temperature. The time to melting temperature of AF was longer than that of CF because of low thermal conductivity of AF.
5.3 3-point-bending test

Specimens for 3-point-bending test were same as press molding and its molding was 15min. The result of three-point bending test was shown in Table 4. According to Table 4, comparing CH/CH and CL/CL, bending modulus and strength of CL/CL were twice higher than that of CH/CH and comparing A/CH and A/CL, bending modulus and strength of A/CL were higher than that of A/CH. The cause of these results was difference of un-impregnation ratio. It was clarified that bending modulus and strength were increased with decreasing un-impregnation ratio.

Relationship between bending modulus or strength and un-impregnation ratio was shown in Figure 16 and Figure 17. These relationships were made by CH/CH and CL/CL. According to Figure 16 and Figure 17, it was clarified that bending modulus and strength were increased with decreasing of un-impregnation ratio. This result suggested that it was important making design to decrease un-impregnation ratio.

5.4 Stopping pultrusion in midstream

Cross-sections of A/A, CL/CL and A/CL made by molding method of stopping pultrusion in midstream were shown in Figure 18 to Figure 20. In these pictures, width, void and un-impregnation area were decreased in taper area of (a) to (d), but cross-section of near tapa end (d) and straight area of (e) were similar. According to this result, it was clarified that impregnation were performed only tapa area and not mostly performed in straight area.

To calculate essential molding time, temperature history was measured and shown in Figure 21. Essential molding time was defined as product set both of the time in which material was in taper zone of the molding die and the time in which material temperature was over melting temperature. Essential molding time can be calculated by temperature history and pultrusion speed. According to Figure 21, it was clarified that essential molding time was 9 min in this pultrusion design.

Relationships between un-impregnation ratio and essential molding time were shown in Figure 22 to Figure 24. In these figure, dot line show end of...
molding die. In figure 22 to figure 24, first, impregnation did not start before 0 min of essential molding time because resin did not melt in this time. Second, it was clarified that un-impregnation ratio was decreased until tapa end same as cross-sections of A/A, CL/CL and A/CL. In Figure 24, in the case of fiber hybrid braided fabric which has MEY CL, the un-impregnation ratio of MEY was increased at all molding time. This phenomenon was caused by same reason as A/CL made by heat compression in 5.2.

Figure 18 Impregnation process of A/A.

Figure 19 Impregnation process of CL/CL.

Figure 20 Impregnation process of A/CL.

Figure 21 Temperature history of pultrusion.

Figure 22 Relationship between un-impregnation ratio and essential molding time of A/A.
IMPRESSIONATION PROCESS FOR FIBER HYBRID BRAIDED THERMOPLASTIC COMPOSITES

5.5 Difference of impregnation process by heat compressing and pultrusion.
Differences of impregnation process by heat compressing and pultrusion were shown in Figure 25 and Figure 26. Difference of aramid fiber was shown in Figure 25 and difference of carbon fiber was shown in Figure 26.

In Figure 25, the curve pultrusion was in upper side comparing to the curve of heat compressing. It is considered that the reason of this gap between two curves was caused by difference of molding pressure.

In Figure 26, it is considered that the curve of pultrusion can be shifted to left by more pre-heating and the difference of convergent point was caused by molding pressure from difference molding method.

According to these result, this pultrusion system must be improved by adding longer pre-heater for longer pre-heating time and making some system for adding more pressure to braided fabric. If these system developed these system, molding which has same quality as made by heat compressing will be able to molded continuously.

5.6 Effect of pultrusion speed to impregnation state of molding
In this section, to investigate effect of pultrusion speed to molding condition, pultrusion for A/CL was performed with several pultrusion speed (30, 50, 100, 150 mm/min). Molding condition was same as 3.2. Cross-sections of each speed was shown in Figure 27 to Figure 30 in order of pultrusion speed of slowness. In Figure 29 and Figure 30, pipe outer diameter s were not constant because cooling at exit of molding die was not enough. In addition, it was clarified that one layer was broken because of increasing of pultrusion friction in these Figures.

Relationship between un-impregnation ratio and pultrusion speed was shown in Figure 31. According to Figure 31, it was clarified that un-impregnation
ratio was increased with increasing of pultrusion speed. It was because that essential molding time was decreased because of decreasing of staying time in molding die if pultrusion speed was increased. Responding to these result, it was considered that extending molding die and decreasing of pultrusion friction would be beneficial for improving of pultrusion speed.

6 Conclusions

By investigation of intermediate material, the wettability of CF with lower sizing content of 0.2wt % was better than that of CF with higher sizing content of 1.1wt %.

By comparing cross-sectional observation of sole or hybrid FRTP with various molding times, it was clarified that impregnation process in same fiber bundle was changed according to the combination of AF and CF. It is considered that these results can be applied to various design of molding FRTP like pultrusion.

By investigating impregnation process of pultrusion by stopping pultrusion molding in midstream, it was clarified that impregnation was performed in only tapa area in molding die and aramid fiber filled the role of insulator to carbon fiber same as heat-compress molding.

By investigate relationship between molding state and pultrusion speed, it was clarified that molding state was made worth with increasing pultrusion speed because of decreasing essential molding time and increasing pultrusion friction.

7 Reference
