HEAT RESISTANCE PROPERTIES OF FRTP COMPOSED OF IN-SITU POLYMERIZATION PA6 AND CF AND GF FABRICS

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1 Introduction
Recently, fiber reinforced thermoplastics (FRTP) are being developed, especially in the field of automobile structures. The advantages of FRTP are not only lightweight as well as FRP but also can be easily recycled and reused because thermoplastics can be remelted and remolded by heat. However, the molding of FRTP with continuous fibers is difficult because of the high viscosity of the matrix.
In-situ polymerizable polyamide 6 (PA6) using anionic ring opening polymerization of ε-Caprolactam could be used as a matrix in order to quickly mold FRTP with the fiber fabrics [1]-[3]. The viscosity of ε-Caprolactam is very low because it is monomer and its polymerization starts after impregnation with fibers. Therefore, the in-situ polymerizable PA6 is supposed to be the one of the most suitable matrix of the FRTP. However, the glass transition temperature (Tg) of PA6 is known as approximately 60 °C and the evaluation of mechanical properties of FRTP using in-situ polymerizable PA6 under a high temperature is important for the practical use.
In the past papers, the improvements of mechanical and thermal properties of thermoplastics with the addition of organic modified nanoclay to resin were reported. There were two kinds of fabrication method of reinforced polymer with the nanoclay. One was a blend and kneading method of molten polymer and nanoclay [4]-[7]. The other was a mixing method of nanoclay to a monomer before polymerization [8]-[11]. The molding techniques and mechanical properties of nanoclay, glass fiber and epoxy hybrid nanocomposites were also reported [12], [13].
In this study, heat resistance properties of the FRTP composed of the in-situ polymerizable PA6 and CF and GF fabrics were examined. The addition of the particle of organic modified nanoclay into the in-situ polymerizable PA6 was examined in order to improve its heat resistance properties.

2 Molding Method
2.1 Materials
The in-situ polymerizable PA6 was obtained from ε-Caprolactam. Sodium salt as an anionic catalyst and hexamethylene diisocyanate as an active agent were used. The melting point of ε-Caprolactam is approximately 70 °C and the viscosity of melted ε-Caprolactam is under 10 mPa·s. The polymerization finishes within one minute. In consideration of the wider application and smaller material cost of FRTP, reinforcing fibers were used in combination of CF fabrics (CF3302H: Toray Industries, Inc.) and GF fabrics (WEA22F-BX: Nitto Boseki Co., Ltd.)

2.2 Molding Condition
The molding method of the FRTP which was composed the in-situ polymerizable PA6 and the CF and the GF fabrics was a VaRTM. The temperature of the molding die was 140°C. This temperature was appropriate one in the past fabrication of CFRTP and GFRTP. The schematic view of the VaRTM is shown in Figure 1. In order to obtain higher bending stiffness and strength, the CF fabrics were stacked upper 2 layers and lower 2 layers and the GF fabric were stacked middle 10 layers. The average of the fiber volume fraction was approximately 42%. The fabricated hybrid FRTP was described as HFRTP. As the result of the sectional observation as shown in Figure 3, in-situ polymerizable PA6 was sufficiently impregnated in the fibers.
specimen was cut to a 10mm width and a 50mm length from the 3mm thickness of the HFRTG plate fabricated with the VaRTM.

3.2 Three Point Bending Test under High Temperatures

In order to evaluate the heat resistance properties of the HFRTG, the three point bending tests under high temperatures were carried out. The test specimens were cut to a 15mm width and a 100mm length from the 3mm thickness of the HFRTG plate. The test speed was 1mm/min and the test temperatures were room temperature, 60, 80 and 120°C, respectively. The five specimens were prepared for each test temperature. In the case of the bending test under the high temperatures, each specimen was set to the heat chamber more than 15 minutes before testing.

3.3 Unreactive Monomer and Absorption Water Content

In order to check the polymerization of ε-Caprolactam might be inhibited by nanoclay, the unreactive monomer content was measured. The content of absorption water was measured at the same time. The measurement methods of unreactive monomer and absorption water content were as follows.

The test specimens were cut into 10mm×50mm and dried in the vacuum furnace of 60°C. After 24hour the each weight of each specimen \( M_0 \) was measured. Next, these specimens were soaked in the 80°C water during 72 hours and their weights were measured as \( M_2 \). At last these specimens were dried over 72 hours under 60°C and the each weight \( M_1 \) was measured. The unreactive monomer content \( M_u \) and absorption water content \( M_a \) were calculated by equation (1) and (2), respectively.

\[
M_u[\%] = \frac{M_0 - M_1}{M_0} \times 100 \quad (1)
\]
\[
M_a[\%] = \frac{M_2 - M_0}{M_0} \times 100 \quad (2)
\]
3.4 Degree of Crystallinity

The degree of crystallinity of in-situ polymerizable PA6 was calculated by equation (3). Where, the heat of fusion $\Delta H_m$ was measured by differential scanning calorimeter from the room temperature to $250 \degree C$ with the heating rate of $10 \degree C / min$. The heat of fusion of perfect crystal of PA6 $\Delta H_m^{100\%}$ is estimated $188 \ J/g$ based on the report of Dole and others[14].

$$DC[\%] = \frac{\Delta H_m}{\Delta H_m^{100\%}} \times 100 \quad (3)$$

4 Results of DMA and Bending Test

The results of the DMA test of the HFRTP are shown in Figure 4. The local maximum of tan$\delta$ indicated the glass transition temperature (Tg) and it was near $50\degree C$. However, the storage modulus of the HFRTP over the Tg was not drop down because the PA6 became already to crystalize.

The bending strength and modulus of the HFRTP are shown in Figure 5 and Figure 6 respectively. The bending strength decreased according to the increase of the testing temperatures. Although the bending modulus slightly decreased with the higher temperature, its value kept about $80\%$ of that of the room temperature. Figure 7 shows the representative stress strain curves under the each test temperature. After the peak stress, the stress kept almost the same value until the maximum strain and the maximum strain at the each test temperature showed the almost same value of $1.6\%$. In order to reveal the fracture mode, the microscopic observations were carried out. Some local separations of carbon fibers were observed at the outermost layer just before the maximum stress (Figure 8). Then a failure of CF layer at the compressive side occurred (Figure 9) and the stress slightly dropped (Figure 7). However the GF layer and the CF layer of tensile side were not damaged and kept the high stress for a short time. The final failure of HFRTP occurred at the tensile side (Figure 10). Under the higher temperature than the room one, the failure behavior was almost same as the room temperature. But a wrinkle buckling of CF layer appeared (Figure 11) near the maximum stress instead of the local separation spots. The wrinkle buckling was caused by the softening of the matrix under the high temperature over the Tg.
Fig. 7 Stress strain curve of HFRTP under high temperatures

Fig. 8 Initial damage at compression side of HFRTP (RT)

Fig. 9 Fracture mode at compression side of HFRTP (RT)

Fig. 10 Fracture mode at tension side of HFRTP (RT)

Fig. 11 Initial damage at compression side of HFRTP (80°C)

5 Experiment of Addition of Nanoclay

5.1 organic modified nanoclay

For the purpose of improving heat resistance properties, the addition of organic modified nanoclay to the matrix was examined. The organic modified nanoclay was modified an ammonium ion with inorganic mineral montmorillonite (Cloisite15A: Southern Clay Products, Inc.) The chemical constitution and particle size were shown in Figure 12 and Table 1, respectively.
HEAT RESISTANCE PROPERTIES OF FRTP COMPOSED OF IN-SITU POLYMERIZATION PA6 AND CF AND GF FABRICS

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_3 - \text{N}^\ominus - \text{HT} & \\
\text{HT} & \text{Where, HT is Hydrogenated Tallow (~65\% C18; ~30\% C16; ~5\% C14)}
\end{align*}
\]

Fig. 12 Chemical constitution of Colisite 15A

Table 1 Particle size and contents of Colisite 15A

<table>
<thead>
<tr>
<th>Content (by volume)</th>
<th>10% less than</th>
<th>50% less than</th>
<th>90% less than</th>
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<tr>
<td>Typical dry particle size</td>
<td>2µm</td>
<td>6µm</td>
<td>13µm</td>
</tr>
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</table>

5.2 Comparison of In-situ PA6 to In-situ PA6 with nanoclay

As first trial test, 1, 2 and 3 weight \% of organic modified nanoclay particles were added to the in-situ polymerizable PA6. The net PA6 plate and the PA6 with the nanoclay plates were fabricated by using VaRTM facilities as the same temperature condition of the HFRTP molding. The nanoclay particles were dried in the vacuum furniture of 40\°C more than 24 hour before the addition and were mixed them to the molten monomer before polymerization. The photograph of all specimens is shown in Figure 13. The color of PA6 changed gradually to brown from white with the increase of the contents of the nanoclay. The microscopic image of section for the 2 weight \% specimen was shown in Figure 14. For all of the specimens, the PA6 and the nanoclay particles were mixed uniformly.

The results of the DMA test of the all specimens are shown in Figure 15 and 16. The storage modulus of the plates with the nanoclay was improved. The decrease of the storage modulus after Tg was lower by the addition of the nanoclay more than 1 weight \%.

Next, the results of bending test of the net PA6 specimen and the PA6 specimens with the nanoclay under the room temperature and 60\°C are shown in Figure 17-20. When the PA6 was added nanoclay more than 2 weight \%, the bending modulus and strength were 15\% and 30\% larger than those of the net PA6 under room temperature. The bending modulus and strength of PA6 added 3 weight \% of the nanoclay were also about 50\% and 30\% larger than those of the net PA6 under 60\°C.

In addition, the measurement results of the content of the unreacted monomer and absorption water are listed in Table 2 and Table 3, respectively. The unreacted monomer content and the content of absorption water of the PA6 with the nanoclay were little increased according to the amount of the nanoclay. Since these values were less than 1 weight \%, the organic modified nanoclay is considered not to inhibit polymerization of ε-Caprolactam. On the other hand, the degree of crystallinity of the PA6 with nanoclay was lower than the net PA6 (Table 4). However, the degree of crystallinity was reported approximately 23 \% for the standard PA6 and was approximately 40\% for the in-site PA6 polymerized under 140\°C [2]. Therefore the addition of nanoclay did not affect the degree of crystallinity.

Fig.13 In-situ PA6 with nanoclay and net PA6

Fig.14 Observation of PA6 with nanoclay 2wt %
Fig. 15 Results of DMA of PA6 with nanoclay compared with net PA6 (Storage modulus)

Fig. 16 Results of DMA of PA6 with nanoclay compared with net PA6 (Tangent delta)

Fig. 17 Bending modulus of PA6 with clay and net PA6

Fig. 18 Bending strength of PA6 with clay and net PA6

Fig. 19 Stress strain curve under RT

Fig. 20 Stress strain curve under 60°C
HEAT RESISTANCE PROPERTIES OF FRTP COMPOSED OF IN-SITU POLYMERIZATION PA6 AND CF AND GF FABRICS

6 Conclusions

The heat resistance properties of the HFRTFP composed the in-situ polymerizable PA6 and the CF and the GF fabrics were reported. Although the bending modulus at the higher temperature was kept the almost same value under the room temperature, the bending strength decreased according to the increase of the testing temperatures. The fracture modes of the HFRTFP under room temperature were a break of carbon fibers at the tension side following after a failure of carbon fiber at the compression side.

In order to improve the heat resistance properties, organic modified nanoclay particles expected the improvement of the mechanical properties of polymers were added into the matrix. When the nanoclay particles of 1 to 3 weight % were added to the in-situ polymerizable PA6, the mechanical properties were improved with the nanoclay particles more than 2 weight %.

References


Table 2 Content of unreactive monomer

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<thead>
<tr>
<th></th>
<th>net PA6</th>
<th>PA6 + 1wt%</th>
<th>PA6 + 2wt%</th>
<th>PA6 + 3wt%</th>
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<tr>
<td>Content of unreactive monomer [%]</td>
<td>0.34</td>
<td>0.27</td>
<td>0.64</td>
<td>0.80</td>
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Table 3 Content of absorption water

<table>
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<th>PA6 + 1wt%</th>
<th>PA6 + 2wt%</th>
<th>PA6 + 3wt%</th>
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<tbody>
<tr>
<td>Content of absorption water [%]</td>
<td>5.3</td>
<td>5.3</td>
<td>7.4</td>
<td>7.7</td>
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Table 4 Degree of crystallinity

<table>
<thead>
<tr>
<th></th>
<th>Hm [J/g]</th>
<th>DC [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>net PA6</td>
<td>86.5</td>
<td>46.0</td>
</tr>
<tr>
<td>PA6 + clay 1wt%</td>
<td>73.3</td>
<td>39.0</td>
</tr>
<tr>
<td>PA6 + clay 2wt%</td>
<td>78.6</td>
<td>41.8</td>
</tr>
<tr>
<td>PA6 + clay 3wt%</td>
<td>74.1</td>
<td>39.4</td>
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