Improvement of thermal and mechanical properties of carbon fiber reinforced plastic composite with exfoliated hexagonal boron nitride particles

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Improvement of thermal and mechanical properties of carbon fiber reinforced thermoplastic (CFRTP) was studied by incorporating exfoliated hexagonal boron nitride (h-BN) with high aspect ratio into matrix resin composed of polypropylene (PP). The thermal diffusivity and propagation of model CFRTP composite composed of a single carbon fiber and matrix was investigated by microwave (MW) irradiation. As result, the thermal propagation of composite with 2.5 vol.% exfoliated h-BN was even similar to that of composite with 5.0 vol.% raw h-BN. Furthermore, the thermal degradation of the composite was suppressed by the exfoliated h-BN at low filler content. Moreover, three-point bending test showed that the specific strength and the specific rigidity of CFRTP composite composed of 2.5 vol.% exfoliated h-BN/PP were increased by 22 and 37%, respectively, as compared to matrix with only PP. The mechanical property of CFRTP with 2.5 vol.% exfoliated h-BN/PP was higher than that of CFRP with 5.0 vol.% raw h-BN/PP. Furthermore, the number of failure cycles of CFRTP composite composed of exfoliated h-BN was increased by one orders as compared to raw h-BN one. Thus, the addition of exfoliated h-BN into matrix resin had a significant influence on the thermal and mechanical properties of CFRTP.

Key-words: Carbon fiber reinforced thermoplastic, Hexagonal boron nitride, Exfoliation, Microwave, Thermal propagation, Mechanical properties

1. Introduction
Carbon fiber reinforced plastic (CFRP) is attracting attention due to its strong mechanical and lightweight properties at automobile, airplane, and aviation industries fields. Especially, carbon fiber reinforced thermoplastic (CFRTP) using matrix resin, such as polypropylene and polyamide, has been focused from viewpoint of formability, recyclability and repair capability.1-3

Generally, CFRTP is pressed to fabricate various shapes after heating by an infrared heater, resulting that CFRTP is manufactured with a long time. Therefore, the novel forming process of CFRTP with a short time has been expected. Recently, we have reported a microwave (MW) irradiation process for the manufacture of CFRP.4-6 In CFRP, it is known that the carbon fiber in the composite absorbs the MW selectively because carbon fiber is heated by Joule heating on the basis of conductive properties.7 And then, MW energy is directly converted into heat, resulting that CFRTP is heated rapidly from inside of the composite. However, MW processing causes the nonuniform heating by an infrared heater, resulting that CFRTP is heated uniformly from inside of the composite. Consequently, a three-point bending test showed that the specific strength and specific rigidity of CFRTP composite composed of exfoliated h-BN were increased by orders as compared to raw h-BN one. Thus, the addition of exfoliated h-BN into matrix resin had a significant influence on the thermal and mechanical properties of CFRTP.

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2. Experimental procedure
2.1 Materials
All materials were used as received without further purification. Commercially available carbon fiber (HTA-12K, 7.0 μm average diameter, Toho Tenax, Japan) was used as a single carbon fiber for thermal characterization. Discontinuous carbon fiber (Torayca MLD-1000, 150 μm average fiber length, Toray, Japan) was used for mechanical characterization. Polypropylene (PP, Noblen 808 DOI http://dx.doi.org/10.2109/jcersj2.16032
Z144, Sumitomo Chemical, Japan) was used as thermoplastic of a CFRTP model composite. Hexagonal boron nitride (h–BN, UHP–1, Showa Denko, Japan) was used as filler in this work.

2.2 Exfoliation of h–BN particles
Exfoliated h–BN particle was prepared based on our previous report.11) Aqueous h–BN slurry was prepared using distilled water. The prepared h–BN slurry was collidated at 150 MPa by the wet–jet milling (PRE03–20–SP, Genus, Japan). After then, the wet–jet milled h–BN slurry was dried. The particle size distribution, thickness distribution and aspect ratio of h–BN particle are shown in Fig. 1 and Table 1. Here, the median values were used as the particle size and the thickness, and the aspect ratio of h–BN particle was calculated from the median particle size ($D_{50}$) and the median thickness ($T_{50}$). These parameters were measured based on our previous reports.11)12)

2.3 Preparation of test specimens
Single carbon fiber/matrix composites were prepared for thermal characterization. PP pellets were mixed with h–BN particles at 180°C by an uniaxial kneading equipment (IMC–TAD3, Imoto Machinery, Japan). The rotational speed of screw was adjusted to be 25 rpm. The amount of h–BN particle was adjusted to be 2.5 or 5.0 vol.%. The matrix film was prepared at 180°C by hot press machine (AH–10TD, As One, Japan). After a single carbon fiber was sandwiched between two prepared matrix films, the composite film was hot–pressed at 180°C. The thickness and diameter of composite film was adjusted to be 0.50 and 16 mm, respectively. Furthermore, CFRTP specimen was prepared for mechanical characterization. Prepared PP/h–BN pellets were mixed with discontinuous carbon fiber at 180°C by an uniaxial kneading equipment. The rotational speed of screw was adjusted to be 20 rpm. After kneading, the prepared pellets were hot–pressed at 180°C to be 10 mm × 60 mm × 4.0 mm for three–point bending test.

2.4 Characterization
The morphology of prepared matrix was observed by a field emission scanning electron microscopy (FE–SEM, S–4300, Hitachi, Japan). In order to observe h–BN particle in composite, resin of cross section was removed by UV–ozone (PL16–110D, Sen Lights, Japan) irradiation for 1 h. Thermal conductivity of matrix was measured by a laser flash equipment (TC–7000, ULVAC, Inc.). The thermal diffusion and propagation of the composite composed of a single carbon fiber and matrix were evaluated as follows. The test specimen was heated by MW apparatus (FDU–201VP–07, Fuji Electronic Industrial, Japan) as shown in Fig. 2. The MW irradiation was performed by a single–mode applicator with semiconducting generation source at 2.45 GHz frequency. The MW power was adjusted at 0.10 W. The thermal diffusion and propagation of the composite were observed by a thermos–viewer with a digital camera (g65, Sony, Japan), which was placed on top of the composite. In order to correct the variation of temperature between various samples, the temperature ratio ($T_s/T_0$) was used as the temperature parameter. Here, $T_s$ and $T_0$ show temperatures at $x$ and 0.0 mm position, respectively. The thermal diffusion and propagation test was performed by measuring three samples. The mechanical properties of prepared CFRTP composites were measured by three–point bending test using an autograph apparatus (AG–IS, Shimadzu, Japan). The indenter speed was fixed at 5.0 mm/min. The specific strength and the specific rigidity of CFRTP composite were calculated as following Eqs. (1)–(3).

\[
\rho_{\text{CFRP}} = \rho_{\text{f}} V_{\text{f}} + \rho_{\text{m}} (1 - V_{\text{f}}) \\
S_p = \frac{\sigma_{\text{CFRP}}}{\rho_{\text{CFRP}}} \\
S_t = \frac{E_{\text{CFRP}}}{\rho_{\text{CFRP}}}
\]

where $\rho_{\text{CFRP}}$, $\rho_{\text{f}}$, and $\rho_{\text{m}}$ are density of CFRP, fiber and matrix, $V_{\text{f}}$ is volume fraction of carbon fiber in CFRP, $S_p$ is specific strength, $\sigma_{\text{CFRP}}$ is flexural strength of CFRP, $S_t$ is specific rigidity, $E_{\text{CFRP}}$ is flexural modulus.

Furthermore, the fatigue property of CFRTP composite was also evaluated by three–point bending fatigue test using a fatigue testing machine (L5kN, Shimadzu, Japan). The frequency, the maximum stress, and the stress ratio were fixed at 1.0 Hz, 30 MPa, and 0.10, respectively.

3. Results and discussion
Figure 3 shows FE–SEM micrographs of the h–BN/PP prepared as matrix. As shown in these FE–SEM images, it was observed that h–BN particles in all matrices were oriented in the planar direction. Because the aspect ratio of h–BN particles was high, h–BN particles would be oriented by hot–pressing. Furthermore, the number of h–BN particles in 2.5 vol.% exfoliated h–BN/PP matrix (c) was increased obviously by exfoliation of h–BN compared to 2.5 vol.% raw h–BN/PP matrix (a). The morphology of h–BN particles in matrix (c) was almost same as compared to 5.0 vol.% raw h–BN/PP matrix (b). Moreover, the exfoliated h–BN particles were uniformly dispersed in the matrix resin. Thus, it was suggested that the number of h–BN filler was increased apparently by exfoliation of h–BN particles as compared to raw h–BN.
Thermal conductivity was diffused hardly in PP composite (a) and 2.5 vol.% raw h-BN/PP, (b) 5.0 vol.% raw h-BN/PP, (c) 2.5 vol.% exfoliated h-BN/PP.

Furthermore, the thermal conductivities were increased by adding h-BN particles in matrix was formed effectively by exfoliation of h-BN particles. The position of a single carbon fiber was heated selectively by MW irradiation. In the position of 1.0 mm, the temperature ratios of matrix composed of PP, 2.5 vol.% raw h-BN/PP, 2.5 vol.% exfoliated h-BN/PP, and 5.0 vol.% raw h-BN/PP were 0.31, 0.44, 0.49, and 0.52, respectively. The temperature ratio of the composite with 2.5 vol.% exfoliated h-BN was highest as compared to other three composites. Moreover, in the distantly position of carbon fiber, the temperature ratio of the composite using exfoliated h-BN particles was also higher than that of PP and 2.5 vol.% raw h-BN composites, suggesting that the heat was propagated efficiently to matrix by exfoliating h-BN particles as compared raw h-BN/PP particles.

**Figure 4** shows the thermographic images of single carbon fiber/matrix composites heated for 10 s by MW irradiation. (a) PP, (b) 2.5 vol.% raw h-BN/PP, (c) 2.5 vol.% exfoliated h-BN/PP, (d) 5.0 vol.% raw h-BN/PP.

**Table 2** shows the thermal conductivities of matrix. Thermal conductivities were increased by adding h-BN particles as filler. Furthermore, the thermal conductivity of 2.5 vol.% exfoliated h-BN/PP matrix was much increased as compared to 2.5 vol.% raw h-BN/PP matrix, suggesting that thermal conductive path of h-BN particles in matrix was formed effectively by exfoliation of h-BN particles.

**Figure 5** shows the temperature ratio of composites MW-irradiated for 10 s as a function of distance from a single carbon fiber. The position of a single carbon fiber is represented as 0.0 mm. The temperature ratios at 0.0 mm position in MW-irradiated single carbon fiber/matrix composites were highest in all samples, indicating that the carbon fiber was heated selectively by MW-irradiation. In the position of 1.0 mm, the temperature ratios of matrix composed of PP, 2.5 vol.% raw h-BN/PP, 2.5 vol.% exfoliated h-BN/PP, and 5.0 vol.% raw h-BN/PP were 0.31, 0.44, 0.49, and 0.52, respectively. The temperature ratio of the composite with 2.5 vol.% exfoliated h-BN was highest as compared to other three composites. Moreover, in the distantly position of carbon fiber, the temperature ratio of the composite using exfoliated h-BN particles was also higher than that of PP and 2.5 vol.% raw h-BN composites, suggesting that the heat was propagated efficiently to matrix by exfoliating h-BN particles as compared raw h-BN particles.

**Figure 6** shows the photographs of single carbon fiber/matrix composites during MW irradiation for 10 s. As shown in photographs, the center of the composite of PP matrix (a), which was the position of carbon fiber, was melted rapidly by MW irradiation. Furthermore, it was also observed that the melting of the composite of 2.5 vol.% raw h-BN/PP (b) was caused along with the length direction of heated carbon fiber by MW irradiation. On the other hand, the matrix with 2.5 vol.% exfoliated h-BN/PP and 5.0 vol.% raw h-BN/PP were not melted by MW irradiation, indicating that the heat of carbon fiber was not accumulated near the interface between carbon fiber and matrix and diffused to the matrix due to high thermal conductivity of matrix.

**Figure 7** also shows the single carbon fiber/matrix composites of 2.5 vol.% raw h-BN/PP (a) and 2.5 vol.% exfoliated h-BN/PP (b) after MW irradiation for 3 min. As shown in the photographs, the composite with 2.5 vol.% raw h-BN was decomposed.

**Table 2.** Thermal conductivity of matrix

| Thermal conductivity (W/m·K) | Filler contents |
|------------------------------|----------------|
| PP                           | 0.117          |
| Raw h-BN/PP                  | 0.258          |
| Exfoliated h-BN/PP           | 0.440          |

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4. Conclusion

In this study, we investigated the thermal and mechanical properties of matrix and CFRTP composite by adding the exfoliated h-BN particles in matrix. The thermal propagation of CFRTP model composite composed of a single carbon fiber and matrix

[Image 56x324 to 283x399]

Fig. 6. Photographs of single carbon fiber/matrix composites during MW irradiation for 10 s. (a) PP, (b) 2.5 vol.% raw h-BN/PP, (c) 2.5 vol.% exfoliated h-BN/PP, (d) 5.0 vol.% raw h-BN/PP.

Fig. 7. Photographs of single carbon fiber/matrix composites after MW irradiation for 3 min. (a) 2.5 vol.% raw h-BN/PP, (b) 2.5 vol.% exfoliated h-BN/PP.

rigidities of CFRTP composites were increased by adding h-BN particles compared to matrix resin of PP. Furthermore, the mechanical properties of CFRTP with 2.5 vol.% exfoliated h-BN/PP was higher than that of CFRTP with 5.0 vol.% raw h-BN/PP. Thus, the exfoliation of h-BN particles led to improvement of the mechanical property of CFRTP at a small amount of fillers. Figure 9 also shows the fatigue properties of CFRTP composites. The maximum stress was fixed at 30 MPa. The number of cycles to failure of CFRTP composite composed of PP, 5.0 vol.% raw h-BN/PP, and 2.5 vol.% exfoliated h-BN/PP were $1.64 \times 10^7$, $4.58 \times 10^4$, and $9.19 \times 10^5$ cycles, respectively. Compared to non-BN samples, the number of cycles to failure of 5.0 vol.% raw h-BN/PP composite was increased by about two orders. Furthermore, the number of failure cycles of the composite composed of exfoliated h-BN was increased by one order as compared to raw h-BN one. It is known that mechanical properties of the composite filled with fillers rely on the efficiency of stress transfer across the interface, meaning that high aspect ratio of plate-like particles, such as h-BN, leads to improvement of mechanical properties of composite. These results indicated that the cracks would propagate through the matrix extensively by the increase of the number of h-BN particles caused by the exfoliation. The exfoliation of h-BN particles also improved the mechanical reliability of the composite.

4. Conclusion

In this study, we investigated the thermal and mechanical properties of matrix and CFRTP composite by adding the exfoliated h-BN particles in matrix. The thermal propagation of CFRTP model composite composed of a single carbon fiber and matrix
was enhanced by adding h–BN particles as high thermal conductive filler. Furthermore, the thermal propagation of the composite with exfoliated h–BN particles was improved at low filler content as compared to raw h–BN particles. By the exfoliation of h–BN particles, the heat was propagated to matrix efficiently. Moreover, in the case of the composite with exfoliated h–BN particles, the thermal degradation was not occurred when irradiating microwave. Thus, the exfoliation of h–BN particles led to enhancement of thermal property of the CFRTP composite because the exfoliated h–BN with high aspect ratio formed thermal conductive path efficiently in the composite. Furthermore, the specific strength and specific rigidity of CFRTP with exfoliated h–BN particles were increased by 22 and 37%, respectively, as compared to matrix without h–BN particles. Then, the fatigue property of the CFRTP with exfoliated h–BN particles was increased by about three orders as compared to non–BN samples. One important consequence of the present work is that the exfoliation of h–BN particles will contribute to improve the thermal and mechanical properties of CFRTP.

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