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 diffusion 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.

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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 manufacturing of CFRP.^{4)–6)} In CFRP, it is known that the carbon fiber in the composite adsorbs the MW selectively because carbon fiber is heated by Joule heating on the basis of conductive property.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 ununiform heating of CFRTP and thermal decomposition of interfaces between carbon fiber and thermoplastic by difference of thermal conductivities of them.^{5),6)}

In our previous studies, we have found that the thermal degradation of the interface between carbon fiber and matrix was suppressed by using hexagonal boron nitride (h-BN) as fillers for improvement of thermal conductivity of matrix.^{5),6)} Generally, it is necessary for fabrication of thermal conductive path to increase the filler contents in composites. However, high filler contents causes various demerits, such as lowering of fluidity and formability of composites, increasing of material costs and weight, and decreasing of mechanical properties of composites. Therefore, development of novel technique is necessary to improve the performance of filler at low filler content.

h-BN particle is one of layered materials and stacked in numerous 2D single layers by weak van der Waals interaction to form a 3D crystal.⁸⁾ Thermal conductivity of h-BN particle is extremely high in plate-like direction as compared in thickness direction. By increasing the aspect ratio of h-BN particle, percolation of h-BN particle forms the thermal conductive path at low filler contents. Thus, in order to exploit the excellent properties of h-BN particle, h-BN particle must be exfoliated to thin layers.^{9),10)} In our previous reported, we have synthesized the exfoliated h-BN particle with high aspect ratio by mechanical processes.^{11),12)}

In this study, we will demonstrate to improve the thermal and mechanical properties of matrix and CFRTP by adding the exfoliated h-BN particle to matrix resin. Thermal diffusion and propagation of a model composite composed of a single carbon fiber and matrix was observed by a thermo-viewer during MW irradiation. Besides, we evaluated the mechanical and fatigue properties by three-point bending test. We will show how exfoliation of h-BN particle is contributed to physical properties of CFRTP.

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

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Fig. 1. Particle (a) and thickness (b) distribution of used h-BN particles.

Table 1. Average of particle size, thickness and aspect ratio of used h-BN particles

	Particle size, D_{50} (μm)	Thickness, T_{50} (μm)	Aspect ratio, D_{50}/T_{50}
Raw h-BN	13.7	0.162	85
Exfoliated h-BN	13.3	0.059	225

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 collided 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. The amount of carbon fiber was adjusted to be 20 vol.%. 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,

Fig. 2. Diagram of microwave-irradiated composite composed of a single carbon fiber and matrix.

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 (α65, 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_x/T_0) was used as the temperature parameter. Here, T_x 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).

$$\rho_{\text{CFRP}} = \rho_f V_f + \rho_m (1 - V_f) \quad (1)$$

$$S_\sigma = \sigma_{\text{CFRP}} / \rho_{\text{CFRP}} \quad (2)$$

$$S_E = E_{\text{CFRP}} / \rho_{\text{CFRP}} \quad (3)$$

where ρ_{CFRP} , ρ_f and ρ_m are density of CFRP, fiber and matrix, V_f is volume fraction of carbon fiber in CFRP, S_σ is specific strength, σ_{CFRP} is flexural strength of CFRP, S_E is specific rigidity, E_{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 matrixes 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.

Fig. 3. FE-SEM micrographs of the h-BN/PP prepared as matrix. (a) 2.5 vol.% raw h-BN/PP, (b) 5.0 vol.% raw h-BN/PP, (c) 2.5 vol.% exfoliated h-BN/PP.

Table 2. Thermal conductivity of matrix

	Thermal conductivity (W/m·K)		
	Filler contents		
	0 vol.%	2.5 vol.%	5.0 vol.%
PP	0.117	—	—
Raw h-BN/PP	—	0.258	0.534
Exfoliated h-BN/PP	—	0.440	—

Fig. 4. 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 4 shows the thermographic images of single carbon fiber/matrix composites heated for 10 s by MW irradiation, which was obtained using a thermos-viewer. As shown in these images, the heat of single carbon fiber occurred by MW irradiation was diffused hardly in PP composite (a) and 2.5 vol.% raw h-BN/PP composite. On the other hand, in the case of 5.0 vol.%

Fig. 5. Temperature of composites MW-irradiated for 10 s as a function of distance from a single carbon fiber.

raw h-BN/PP composite (d), the heat was diffused widely. These results indicated that the heat of a single carbon fiber produced by MW irradiation was released effectively to matrix by increasing the thermal conductivity of matrix. In the case of 2.5 vol.% exfoliated h-BN/PP composite (c), the thermal propagation behavior was almost similar at half filler contents compared to 5.0 vol.% raw h-BN/PP composite, meaning that the thermal conductive path was formed effectively by increasing the aspect ratio based on the exfoliation of h-BN. Thus, the heat of carbon fiber occurred by MW irradiation was diffused and propagated effectively to matrix by high thermal conductivity of matrix. Furthermore, the exfoliation of h-BN particles lead to improve the thermal properties at low filler contents.

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 temperatures ratio 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

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.

near the carbon fiber, meaning that the PP resin was degraded thermally because the heat of carbon fiber might be not diffused to matrix by low thermal conductivity of matrix. On the other hand, the composite with 2.5 vol.% exfoliated h-BN was not changed after MW irradiation, indicating that the thermal conductive path was formed effectively by increasing the aspect ratio based on exfoliation of h-BN particles as shown in Table 2. Thermal degradation of the composite with exfoliated h-BN was suppressed at low filler content.

Figure 8 shows the specific strength and specific rigidity of CFRTP composites prepared by 20 vol.% carbon fiber and PP. The specific strength of CFRTP composites composed of PP, 5.0 vol.% raw h-BN/PP, and 2.5 vol.% exfoliated h-BN/PP were 4.32×10^3 , 4.81×10^3 , and 5.27×10^3 m, respectively. The specific strength of CFRTP with exfoliated h-BN was increased by 22% compared to PP. Then, the specific rigidity of them were 4.53×10^5 , 5.38×10^5 , and 6.20×10^5 m, respectively. The specific rigidity of CFRTP with exfoliated h-BN was also increased by 37% compared to PP. The specific strengths and specific

Fig. 8. Specific strengths and specific rigidity of CFRTP composites prepared by 20 vol.% carbon fiber and PP. (a) PP, (b) 5.0 vol.% raw h-BN/PP, (c) 2.5 vol.% exfoliated h-BN/PP.

Fig. 9. Fatigue properties of CFRTP composites.

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 1.64×10^3 , 4.58×10^4 , and 9.19×10^5 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.^{13),14)} 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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