Use of Hollow Colloids for Generating Nanovoids to Mitigate the Brittle Fracture of Carbon Fiber-Reinforced Thermoplastics

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Abstract

To reduce the risk of brittle fracture of carbon fiber-reinforced thermoplastics (CFRTPs) based on poly(methyl methacrylate) (PMMA) that have excellent mechanical properties, hollow PMMA colloids were used to do surface modification of the carbon fibers. Making the hollow PMMA colloids adsorbed on the carbon fibers by electrodeposition enhanced the interfacial properties, such as the interfacial shear strength and impregnation ratio of the CFRTP, resulting in improved mechanical properties. Three-point bending tests confirmed the improved fracture toughness of the fabricated CFRTP. During the fracture of the CFRTP, the nanovoids generated from hollow PMMA colloids attached to the carbon fibers in the CFRTP enabled the delamination of the carbon fibers from the PMMA resin, thus reducing the risk of brittle fracture of the CFRTP, while the high bending strength was maintained.

Keywords: CFRTP, Nanovoid, Interfacial properties, Brittle fracture, Hollow colloid

1. Introduction

Carbon fiber-reinforced thermoplastics (CFRTPs) are recyclable composite materials that can be applied as construction materials in transport equipment owing to their light weight [1, 2]. They have good recyclability and can be manufactured easily using thermoplastics remolded by heating [3-5]. However, for application in automobiles, the CFRTPs should be safe and reliable. In general, as the mechanical properties of composite materials are enhanced with higher interfacial properties, the possibility of brittle fracture increases without interfacial peeling, thus increasing the risk of fracture [6]. Such fracture could harm the human body in a traffic accident. The interfacial properties between the carbon fibers and thermoplastic resin of CFRTPs are not sufficiently optimal to lead to excellent mechanical properties [7]. Therefore, various surface modification techniques have been developed to improve the interfacial properties, such as surface adhesion between the thermoplastic resin and carbon fiber. For example, nanomaterials and plasma are used to enhance the surface adhesion between the thermoplastic resin and fiber [8-12]. Recently, polymer colloids were adsorbed on the carbon fiber surface through electrostatic interactions [13] or by electrodeposition [14, 15] to enhance the mechanical properties. The interfacial shear strength (IFSS) was controlled by varying the amount of adsorbed polymer particles, and the impregnation ratio of the thermoplastic resin defined in the section of 2.2 was increased to enhance the bending strength of CFRTP [14, 15]. However, as the mechanical properties are improved, the CFRTP composites become brittle, thereby increasing the risk of fracture. In a previous study, the morphologies of fractured CFRPs were analyzed after destructive testing [16].

It is speculated that voids present in the CFRTP negatively affect the mechanical properties [17, 18]. In the present study, we focused on nanovoids in the CFRTP and their effect on the mechanical properties because the impregnation ratio was not decreased by the nanovoids.

Hollow poly(methyl methacrylate) (PMMA) colloids, which can be readily synthesized by various methods [19-22], were used to induce nanovoids in CFRTP by employing the polymer colloidal technique that was developed in our previous study [23]. Nanovoids are believed to function as delamination points in the CFRTP during fracture. The effects of nanovoids on the interfacial and mechanical properties were studied through the three-point bending tests, cross-sectional observations, and fragmentation tests. Finally, the failure mode of the CFRTPs was evaluated.

2. Experimental

2.1 Preparation of PMMA colloid and surface modification of carbon fibers

Solid or hollow PMMA particles (Sekisui Kasei) shown in **Fig. 1a and 1b** captured by transmission electron microcopy (TEM, JEM-2100 plus, JEOL) were dispersed in distilled water (WG250, Yamato Scientific) using sodium lauryl sulfate (SDS, Fujifilm Wako Pure Chemical Industries, Ltd.) to prepare a colloidal suspension. PMMA powder (1.2 g), distilled water (450 g), and SDS (2 g) were added to a 600 mL screw-top vial and sonicated for 30 min using an ultrasonic cleaner (US-5KS, SND) to disperse the polymer particles. The zeta potential of the particles was measured to be in the range -67.5 – -82.6 mV using a ZETASIZER Nano-ZS instrument (Malvern Panalytical).

Carbon fibers (HTS40, Toho Tenax Co., Ltd.) with an average fiber diameter of 7.3 μm and a tensile strength of 4.22 GPa were treated for 60 min with acetones in several vats to remove the sizing agents as shown in **Fig. S1** and then immersed in the PMMA colloid to allow the adsorption of the negatively charged PMMA particles on their surfaces via electrodeposition [24]. In this manner, 3,000 carbon fibers were attached to the positive electrode (AD-8724D, A&D) because of the negative charge of the PMMA colloid. The morphologies of the PMMA colloid-modified carbon fibers were investigated by field-emission scanning electron microcopy (FE-SEM, JSM-7500FA, JEOL), and **Fig. 1c** shows the FE-SEM image. Before the FE-SEM observations, the specimen was covered with a thin osmium film by vapor deposition (OPC60A, Filgen, Inc.). To determine the amount of PMMA particles adsorbed on the carbon fibers, thermogravimetric analysis (STA7200, Hitachi, Ltd.) was performed to heat the sample up to 500 °C at a nitrogen flow rate of 50 mL/min. As a result, the adsorbed amount of PMMA particles on the carbon fibers was measured to be 0.02 g/m^2. The corresponding coverage of carbon fibers was calculated to be 0.009 assuming the coverage of complete monolayer adsorption of PMMA particles was 1.0.

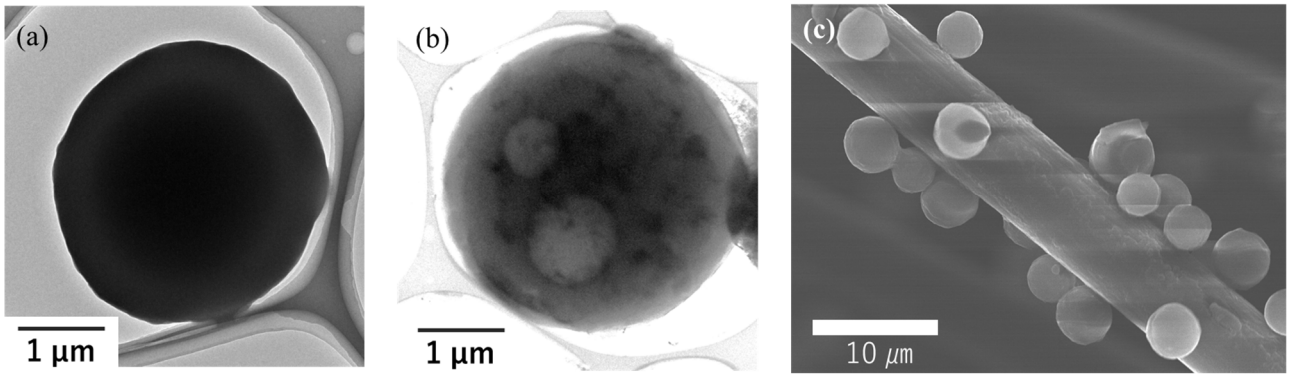

Fig. 1 Morphologies of PMMA particles and carbon fibers: (a and b) TEM images of the solid and

hollow PMMA particles and (c) FE-SEM image of the hollow PMMA colloid-modified carbon fiber prepared at an electrodeposition voltage of 30 V for 30 s.

2.2 Fabrication of CFRTPs and evaluation of their interfacial and mechanical properties

The CFRTP was prepared as follows. 12,000 carbon fibers sandwiched between six sheets of PMMA films (HBS006H, Mitsubishi Chemical) of 12 × 205 mm dimensions were hot-pressed at 240 °C , and pressures of 0.3 and 14 MPa for 3 and 2 min, respectively, using a heat press machine (SA-303, TESTER SANGYO Corporation). The hot-pressing temperature of 240 °C exceeds the melting point of PMMA but is suitable for enhancing the bending strength, as shown in the Supplementary **Fig. S2**. As PMMA particles were cross-linked, their melting point was higher. The hot-pressed fibers were then quenched by placing them between two steel plates cooled with water at 25 °C to obtain the prepreg. Then, three prepregs were used to fabricate a unidirectional CFRTP specimen of 2 mm thickness by a prepreg-based hot-press method at a temperature of 240 °C and pressures of 0.3 and 14 MPa for 5 min each [25, 26] as shown in the Supplementary **Fig. S2**. This high pressure procedure at 14 MPa would generate nanovoids in the CFRTP reducing the sizes of the voids in the hollow PMMA particles adsorbed on the carbon fibers.

For the evaluation of the IFSS (τ_m) of a single carbon fiber, fragmentation tests were performed through a tensile testing machine (10073B, Japan High Tech Co, Ltd.) under an optical microscope (MS-804, MORITEX Corporation). The specimen was prepared as follows: a single carbon fiber that was sandwiched between two PMMA films (HBS006H, Mitsubishi Chemical) was hot-pressed at the

temperature of 240 °C and pressures of 3 and 14 MPa for 3 and 2 min, respectively, using a heat press machine (SA-303, TESTER SANGYO Corporation). The film was then quenched by placing it between two steel plates cooled with water at 20 °C, and then cut into strips having a gauge length of 30 mm and width of 2 mm. These strip specimens were tested until the fragmentation process was saturated, which occurred at a tensile strain of ~15%. The average length of the fragmented carbon fibers (<*L*>) was determined by conducting the fragmentation tests on five samples. The IFSS between the resin and carbon fiber was calculated using Eq. 1 [27].

$$\tau_m = \frac{D\sigma_f}{2l_c}, \qquad (1)$$

where the effective length (l_c) is given by,

$$< L > = \frac{3}{4} l_c. \qquad (2)$$

The average diameter of the carbon fiber was measured by the diffraction of a He-Ne laser beam from the fiber. The tensile strength of the carbon fibers (σ_f) of length l_c was estimated by the Weibull analysis of the results of the single-fiber tensile tests carried out using a tensile testing machine (SDW-1000SS-E-SL, IMADA SEISAKUSHO CO., LTD.) operated at a crosshead speed of 1 mm/min and a gauge length of 25 mm [28].

To evaluate the impregnation ratio of PMMA, the difference between the total volume calculated from the dimensions of the CFRTP specimens and the volume of the carbon fibers, V_{cal}, was calculated. The volume of the PMMA resin in the CFRTP samples, V_{weight}, was determined as a difference between the weights of the carbon fibers and CFRTP divided by the density of the PMMA

film. The impregnation ratio of the PMMA resin was defined as V_{weight} divided by V_{cal}.

The cross-sections of the CFRTP were examined by FE-SEM to observe the nanovoids. The specimen for FE-SEM was prepared by the embedding method using a photocurable resin (ARONIX, TOAGOSEI Co., Ltd.), and then was cut and polished by a grinding machine (ML-150P, MARUTO INSTRUMENT CO., LTD.). Before the FE-SEM observations, the samples were covered with a thin Os film by vapor deposition (OPC60A, Filgen, Inc.).

To measure the bending strength (σ) of the CFRTP, the three-point bending test was performed using a tension and compression testing machine (SDW-1000SS-E-SL, IMADA SEISAKUSHO CO., LTD.). The specimens with a fiber ratio of 30 vol%, as calculated from the masses of PMMA films used in the fabrication of the CFRTP and the carbon fibers and the length, width and thickness of the CFRTP, were loaded at a crosshead speed of 5 mm/min. The bending strength of the CFRTP was calculated follows [15]:

$$\sigma = \frac{3FL}{2wh^2}, \qquad (3)$$

where L is the distance between the supporting points, and h (2 mm) and w (100 mm) are the thickness and width of the CFRTP specimen, respectively, and F is the load. The bending strength at maximum F is defined as σ_{max}. After the bending tests, the risk of brittle fracture of the CFRTPs was evaluated by FE-SEM studies.

3. Results and discussion

3.1 Influence of the PMMA colloid on the interfacial properties of the CFRTP

To investigate the influence of the PMMA colloid on the interfacial properties of the CFRTP, fragmentation tests and cross-sectional studies were carried out. **Fig. 2** shows the influence of the surface modification on the IFSS between PMMA resin and the carbon fibers, and the impregnation ratio. Evidently, the IFSS increased when the carbon fibers were coated with PMMA particles (**Fig. 2a**). In particular, solid PMMA particles are more effective than hollow PMMA particles in improving the IFSS because of the presence of voids between the carbon fiber and PMMA resin in the latter [29]. In the case of carbon fibers with hollow PMMMA particles, however, the surface adhesion between carbon fiber and PMMA was strengthened partially by PMMA originated from the particles, which suggested the slippage between carbon fiber and the resin would be hard to be occurred during the three-point bending test. A recent study demonstrated that the adsorption of polymer particles on the carbon fiber effectively enhances the IFSS [15, 27]. The impregnation ratio, which was calculated from the volumes by measuring the mass and length of the fabricated CFRTP, increased after the surface modification with the PMMA colloids (**Fig. 2b**).

The cross-sectional images of the CFRTP obtained from surface-modified carbon fibers are shown in **Fig. 3**. The results are similar to those obtained in our previous study [15]. However, the impregnation ratios of the CFRTP prepared using carbon fibers modified with solid and hollow PMMA particles were almost the same (**Fig. 2b**).

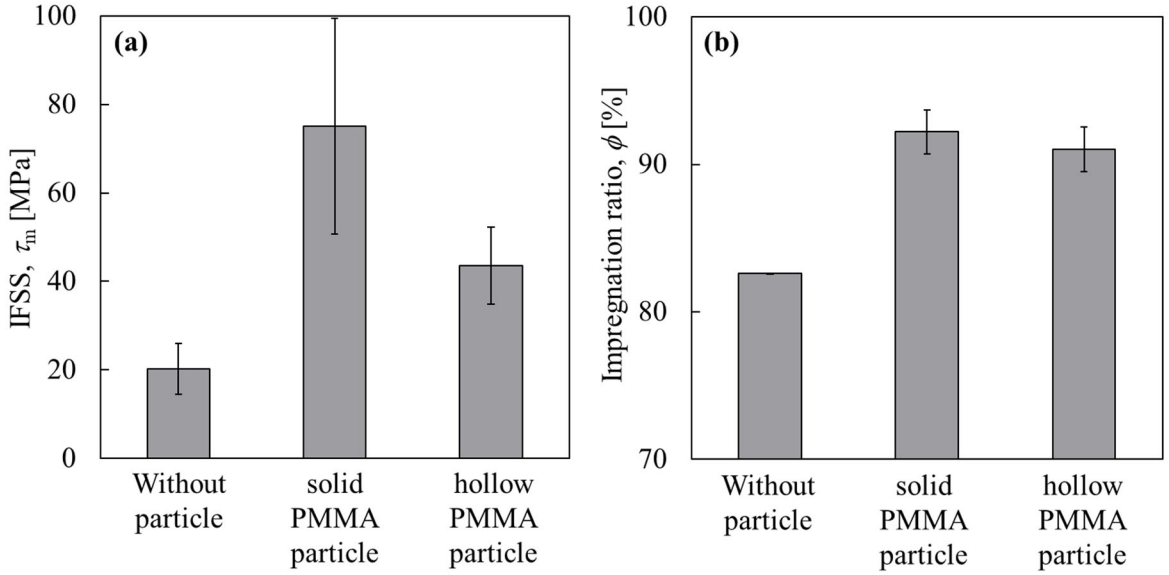

Fig. 2 Effect of surface modification on the (a) IFSS between the carbon fiber and PMMA and (b) impregnation ratio.

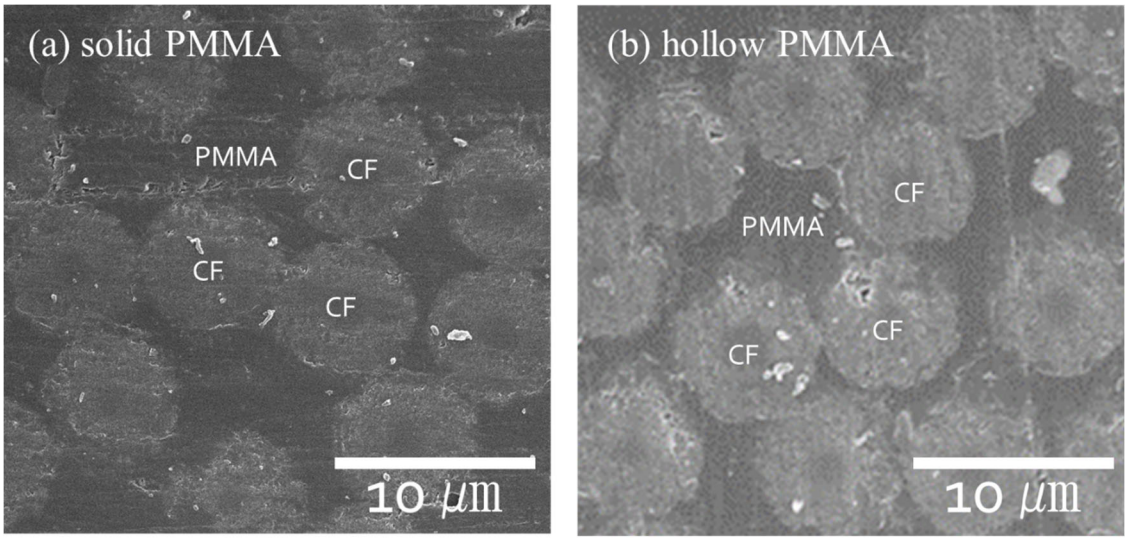

Fig. 3 Cross-sectional FE-SEM images of the CFRTP prepared using carbon fibers modified with (a) solid PMMA particles and (b) hollow PMMA particles.

For a detailed analysis of the cross-section of CFRTPs, high-magnification FE-SEM images were captured (**Fig. 4)**. Evidently, hollow PMMA colloids induced nanovoids and cracks in the CFRTP, as indicated by the white arrows in **Fig. 4b**. The hollow parts of the hollow PMMA particles were

compressed and broken to form nanovoids under the high pressure during the fabrication of CFRTP. As a result, the IFSS obtained for the specimen using hollow PMMA particles was smaller than that of the specimen using solid PMMA particles.

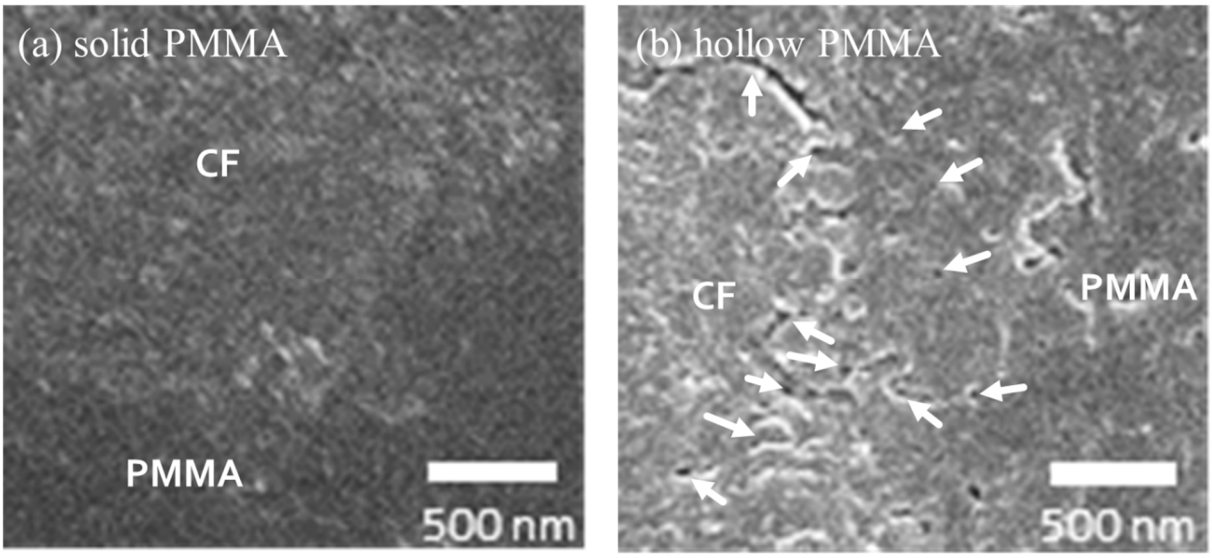

Fig. 4 Cross-sectional FE-SEM images of the CFRTPs prepared using carbon fibers modified with (a) solid PMMA particles and (b) hollow PMMA particles. The white arrows in (b) indicate the nanovoids and cracks in the CFRTP.

3.2 Bending properties of the CFRTP based on PMMA colloid-modified carbon fibers

The CFRTPs were fabricated using three types of carbon fibers viz., carbon fibers without any particles, carbon fibers with solid PMMA particles, and carbon fibers with hollow PMMA particles. Three-point bending tests were carried out to evaluate the bending properties of the CFRTPs in terms of σ_{max}, and the result is shown in **Fig. 5**. σ_{max} increased because of the improvement in the interfacial properties, such as surface adhesion and impregnation ration of the resin, after the surface modification of the carbon fibers. These results agree well with the results of our previous study [14, 15]. However,

the side views and the cross-sectional views of the CFRTPs prepared using solid and hollow PMMA particles after the three-point bending test showed significantly different features.

To investigate the effect of nanovoids on the fracture toughness of the CFRTPs, the fractured CFRTPs after the three-point bending tests were examined by FE-SEM (**Fig. 6)**. Although the CFRTPs with surface-modified carbon fibers exhibited similar bending strengths, they showed different modes of failure. The CFRTP prepared using solid PMMA particles showed brittle fracture without cracks (**Fig. 6a and 6a′**), whereas that prepared using hollow PMMA particles showed clear cracks and delamination between the PMMA resin and carbon fibers (**Fig. 6b and 6b′**). The nanovoids formed in the CFRTP from the hollow PMMA particles adsorbed on the carbon fibers are speculated to be the origin of cracks and delamination points of fracture of the CFRTP as a result of the three-point bending test [30, 31]. Additionally, at τ_m = 42.7 MPa, interfacial peeling of the CFRTP was observed in our previous work, and the results of this study agree well with those [15]. Generally, brittle fracture decreases the safety and reliability of materials. Therefore, electrodeposition of hollow PMMA particles was carried out to improve the fracture toughness of the CFRTP and reduce the risk of brittle fracture of the material during its rupture.

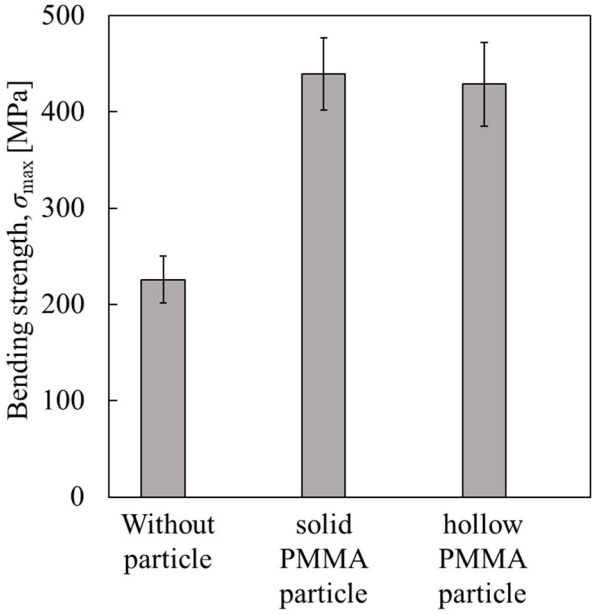

Fig. 5 Effect of surface modification using solid or hollow PMMA particle on the bending strength of the CFRTPs.

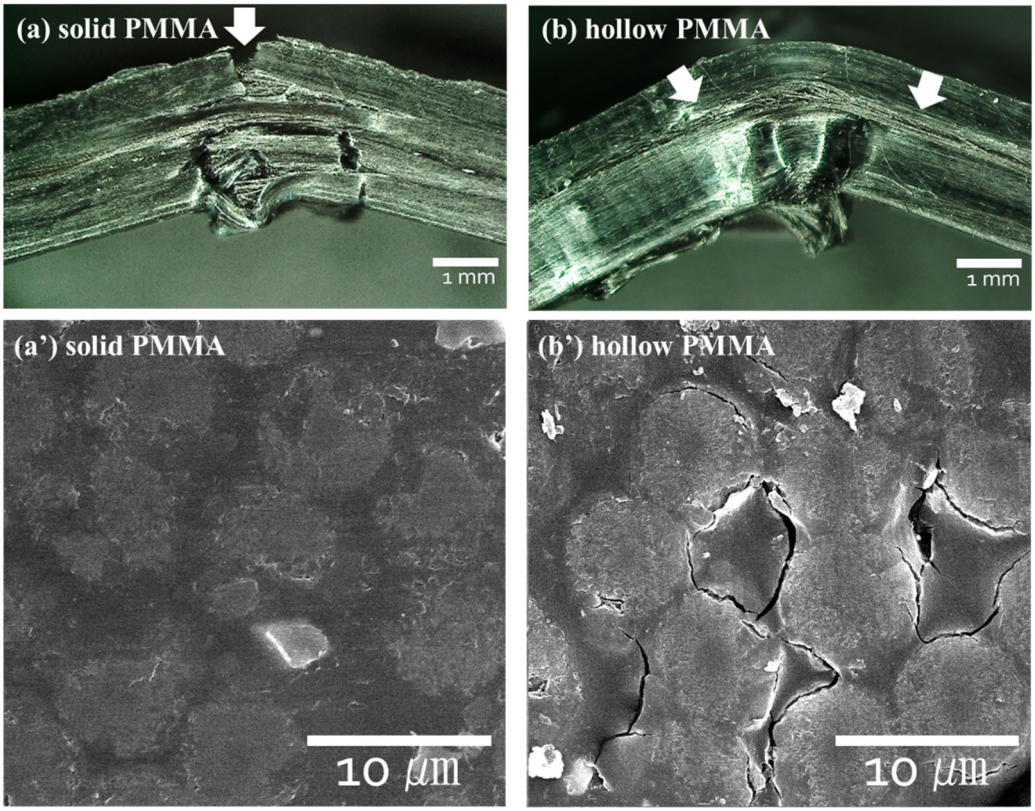

Fig. 6 Side-view and cross-sectional FE-SEM images of the CFRTPs prepared using carbon fibers modified with (a) solid PMMA particles and (b) hollow PMMA particles after the bending tests. The white arrow in (a) indicates the brittle fracture point, and the white arrows in (b) indicate the

delamination points.

Conclusions

The risk of brittle fracture of CFRTPs with high bending strength was decreased by modifying the carbon fibers with hollow PMMA colloids via electrodeposition. The influence of such surface modification on the bending property of the CFRTP was clarified by tension and compression tests. Thus, we demonstrated that the surface modification of the carbon fibers with hollow PMMA colloids enhances the bending strength of the CFRTP by improving the interfacial properties. Furthermore, the presence of nanovoids enabled delamination between PMMA resin and the carbon fibers, thereby reducing the risk of brittle fracture. The hollow PMMA colloids enhanced the safety and reliability of the CFRTP, while the high bending strength was maintained.

Supporting Information

The scheme of treatment of carbon fibers is shown in **Fig. S1**. **Fig. S2** shows the influences of the molding temperature on the bending strength of CFRTP using carbon fibers modified with solid or hollow PMMA particles. The schemes of fabrication of prepreg and CFRTP are illustrated in **Fig. S3**.

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