Reusing Recycled Fibers in High-Value Fiber-Reinforced Polymer Composites: Improving Bending Strength by Surface Cleaning

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Abstract

Glass fiber-reinforced polymer (GFRP) composites and carbon fiber-reinforced polymer (CFRP) composites were recycled using superheated steam. Recycled glass fibers (R-GFs) and recycled carbon fibers (R-CFs) were surface treated for reuse as fiber-reinforced polymer (FRP) composites. Treated R-GFs (TR-GFs) and treated R-CFs (TR-CFs) were characterized by scanning electron microscopy (SEM) and remanufactured by vacuum-assisted resin transfer molding (VARTM). Most residual resin impurities were removed by surface treatment. Analysis indicated no adverse effect of surface treatment on bending strength. The mechanical properties of the TR-GF reinforced polymer (TR-GFRP) and TR-CF reinforced polymer (TR-CFRP) composites were determined and compared with those of R-GF reinforced polymer (R-GFRP) and R-CF reinforced polymer (R-CFRP). The bending strengths of R-GFRP (26%) and R-CFRP (49%) were very low, compared to that of virgin glass fiber-reinforced polymer (V-GFRP) and that of virgin carbon fiber-reinforced polymer (V-CFRP). The bending strength of TR-GFRP composites was improved to about 90% of that of V-GFRP, and the bending strength of TR-CFRP composites was improved to about 80% of that of V-CFRP.

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1. Introduction

The use of fiber-reinforced polymer (FRP) composites as high-performance materials is increasing in the aerospace, military, automobile, and sports industries. However, FRP is one of the most difficult materials to separate into elemental components (e.g., fiber, filler, and polymers). As a result, for many years FRP materials have been incinerated or used for landfill without any recyclings [1, 2]. Although researchers have developed new technologies [3-8] to recycle FRP, fibers obtained through these technologies are either short or fluffy, and they are not treated after recycling by those technologies. Orderly longer recycled fibers are more valuable. Thus, we developed a new recycling technology using a steam system. Our previous studies [9, 10] indicated that recycling FRP by superheated steam is optimal, making it possible to obtain long fibers with little decline in tensile strength.

The performance of FRP depends on fiber and resin characteristics. In particular, the interfacial adhesion between fibers and resin plays an important role in improving the mechanical behavior of FRP. Good interfacial adhesion between fiber and resin is necessary to ensure effective load transfer from one fiber to another through the resin. Generally, the methods of enhancing interfacial bonding strength can be classified into two fundamental categories: modifying the fibers and applying a toughened resin [11-13]. The interfacial characteristics between fiber and resin depend mainly on the fiber surface.

High-value recycled reinforced fiber with high performance can be remanufactured into FRP for reuse. In this study, the resin impurities that remained on the fibers would affect the performance of recycled fiber-reinforced polymer (R-FRP). Therefore, it was necessary to treat the surface of recycled fibers to enhance the interfacial bond between fibers and resin in a composite. We removed the residual resin impurities by soaking the recycled fiber in solution. Treated recycled glass fibers (TR-GFs) and recycled carbon fibers (TR-CFs) were remanufactured by vacuum-assisted resin transfer molding (VARTM), and the bending properties of the

R-FRP composites were determined and compared.

2. Materials and methods

2.1 Manufacturing of virgin fiber-reinforced polymer *(V-FRP)*

Commercially available unidirectional glass fibers, purchased from Unitika Ltd., were used as the reinforcement fiber of GFRP. Unsaturated polyester resin, obtained from Showa Highpolymer Co., Ltd., was used as the matrix in the present work. Pamekku N was chosen as the hardener and was purchased from Nof Corporation. Unsaturated polyester resin and hardener were 100 and 0.8 parts by weight. PAN-based T300 carbon-fiber fabrics used in the present study were produced by Toray Industries Inc. Epoxy resin obtained from Nagase ChemteX Corporation was used as the matrix of carbon fiber reinforced polymer (CFRP). Hardener was also purchased from Nagase ChemteX Corporation. Epoxy resin and hardener were 100 and 27 parts by weight. These materials are listed in Table I. The prepregs were fabricated by VARTM, cut into scrap ($50 \times 200 mm^2$), and recycled by superheated steam.

2.2 Recycling of V-FRP

Samples were fed into the chamber of a superheated steam recycling instrument and heated in the absence of oxygen. Glass fiber reinforced (GFRP) samples were heated at 370°C for 30min [9]. CFRP samples were heated at 340°C for 30min [10]. After the experiment, samples were cooled to room temperature.

2.3 Treatment of recycled fibers

Recycled fibers were fixed by wire netting and soaked in solution to keep them in order. R-GFs were soaked in acetone for 4h and in detergent for 24h at room temperature respectively. They were then cleaned by an ultrasonic washing machine for 1h. R-CFs were soaked in acetone for five days at room temperature and in N-Methyl-2-pyrrolidinone (NMP) for three days at 200°C respectively. They were then cleaned by an ultrasonic washing machine for 1h. These conditions are listed in Table II. Treatment time mentioned in Table II was selected according to our preliminary testing experiments. TR-GFs and TR-CFs were remanufactured by VARTM after drying. Figure 1 presents a schematic view of the experiment.

2.4 SEM

Samples of R-GFs, R-CFs, virgin glass fibers (V-GFs), and virgin carbon fibers (V-CFs) were analyzed using scanning electron microscopy (SEM) (Hitachi S-3000N) to determine the morphology and diameter of the fibers, as well as visual signs of residual resin impurities. The microscope was operated in high-vacuum mode, and images were obtained through a secondary electron detector.

2.5 Mechanical Testing

The mechanical properties of V-FRP, R-FRP, and TR-FRP composites were evaluated on an AUTO GRAPH (Shimadzu AG-20KND). The bending strength of the composites was measured by applying a three-point bending test according to the JIS K7017 standard procedure. The bending strength was taken as the average value of five tests.

3. Results and discussion

3.1 Recycling of V-GFRP and treatment of R-GFs

3.1.1 Surface morphology

The surface morphologies of R-GFs (Fig. 2 (a)) and V-GFs (Fig. 2 (b)) were examined by SEM at a magnification of 1000×. Considerable quantities of nubbles were clearly clinging to the surfaces of R-GFs (Fig. 2 (a)), whereas V-GFs exhibited a cleaner, smoother surface (Fig. 2 (b)). Unsaturated polyester resin impurities remaining on the fiber's surface would spoil the interfacial adhesion between fibers and new resin when they were remanufactured into recycled GFRP (R-GFRP). High-performance R-GFRP requires good interfacial adhesion. Therefore, surface treatment of R-GFs should be performed to improve interfacial adhesion between fibers and new resin.

Figure 3 (a) depicts the surface morphology of TR-GFs soaked in detergent for 24h and cleaned by an ultrasonic washing machine for 1h after soaking. Figure 3 (b) depicts that of TR-GFs soaked in acetone for 4h and cleaned by an ultrasonic washing machine for 1h after soaking. All were analyzed at a magnification of 1000×. The nubbles that could be observed clinging to the surfaces of TR-GFs were fewer and smaller than those depicted in Fig. 2 (a). Figure 3 (b) reveals a cleaner, smoother surface than Fig. 3 (a). It was nearly the same as that of V-GFs. The results indicated that both detergent and acetone effectively removed unsaturated polyester resin impurities from the fiber's surface, although acetone was more effective than detergent. It was possible to improve interfacial adhesion between fibers and new resin when they were remanufactured into TR-GF reinforced polymer (TR-GFRP).

3.1.2 Mechanical properties

Detergent and especially acetone effectively removed the remaining unsaturated polyester resin impurities. However, whether the solutions would affect the fiber soaked in them was not determined. Therefore, V-GFs were soaked in two different solutions and then fabricated to treated virgin glass fiber-reinforced polymer (TV-GFRP). The bending strength of TV-GFRP was measured and compared with that of V-GFRP.

Figure 4 compares the bending strengths of V-GFRP (circle), TV-GFRP reinforced by virgin glass fiber treated with detergent (triangle), and TV-GFRP reinforced by virgin glass fiber treated with acetone (square). The bending strengths of the three types were nearly the same. Thus, neither detergent nor acetone affected the bending strength of TV-GFRP. These solutions may be considered for unsaturated polyester resin impurity removal in the future.

The results presented in section 3.1.1 indicate that both detergent and acetone effectively removed unsaturated polyester resin impurities. Although the surface was cleaner than that of R-GFs, whether the bending strength would be improved by detergent and acetone, and how much it would be improved had not been determined. Thus, the bending strengths of V-GFRP, R-GFRP, and TR-GFRP were measured and plotted in Fig. 5.

Figure 5 compares the bending strengths of V-GFRP (circle), R-GFRP reinforced by R-GFs (diamond), TR-GFRP reinforced by R-GFs treated with detergent (triangle), and TR-GFRP reinforced by R-GFs treated with acetone (square). The bending strength of R-GFRP was 26% that of V-GFRP (Fig. 5). The bending strength of

TR-GFRP treated with detergent was slightly higher than that of R-GFRP, at 29% that of V-GFRP. The bending strength of TR-GFRP treated with acetone was nearly the same (94%) as that of V-GFRP. Although the quantity and volume of nubble clinging to the surfaces of TR-GFs decreased, the bending strength of TR-GFRP treated with detergent improved only slightly. In contrast, that of TR-GFRP treated with acetone greatly improved. Acetone very effectively removed the unsaturated polyester resin impurities, although it cost more than detergent. To sum up, it was possible to obtain high-performance TR-GFRP by treating R-GFs with acetone.

3.2 Recycling CFRP and treating R-CFs

3.2.1 Surface morphology

The surface morphologies of R-CFs (Fig. 6 (a)) and V-CFs (Fig. 6 (b)) were examined by SEM (Fig. 6) at a magnification of 1000×. Many epoxy resin impurities could be observed on the surfaces of R-CFs, whereas V-CFs had cleaner, purer, and smoother surfaces. Epoxy resin impurities would spoil the interfacial adhesion between fibers and new resin when remanufactured into recycled CFRP (R-CFRP). As with R-GF, in order to obtain high-performance R-CFRP, surface treatment of R-CFs should be performed to improve interfacial adhesion.

Figure 7 (a) depicts the surface morphology of TR-CFs that were soaked in acetone for five days and cleaned by an ultrasonic washing machine for 1h after soaking. Figure 7 (b) illustrates the surface morphology of TR-CFs that were soaked in NMP at 200°C for three days and cleaned by an ultrasonic washing machine for 1h after soaking. All were analyzed at a magnification of 1000×. Many impurities were observed on the surfaces of the TR-CFs depicted in Fig. 7 (a). In contrast, fibers depicted in Fig. 7 (b) had clean, smooth surfaces. Although some nubbles were clinging to the surfaces of TR-CFs, their surfaces were nearly the same as those of V-CFs. The results of surface treatment indicated that acetone very effectively removed unsaturated polyester resin impurities but not epoxy resin impurities. However, NMP was very effective and possibly improved interfacial adhesion between fibers and new resin.

3.2.2 Mechanical properties

Although the solutions effectively removed remaining epoxy resin impurities, whether the solutions would affect the fiber soaked in them was undetermined. Therefore, V-CFs were soaked in two different solutions and then fabricated to form treated virgin carbon fiber-reinforced polymer (TV-CFRP). The bending strength of TV-CFRP was measured and compared with that of V-CFRP.

Figure 8 compares the bending strengths of V-CFRP (circle), TV-CFRP reinforced by virgin carbon fiber treated with acetone (triangle), and TV-CFRP reinforced by virgin carbon fiber treated with NMP at 200°C (square). The bending strengths of these three types of CFRP were nearly the same. Therefore, neither acetone nor NMP affected the bending strength of TV-CFRP. Based on the results presented in section 3.2.1, NMP could be considered as a solution for removing epoxy resin impurities in the future.

The results presented in section 3.2.1 indicated that NMP effectively removed epoxy resin impurities. Although it was determined that acetone did not effectively remove epoxy resin impurities, it was not determined whether bending strength would be improved by acetone or NMP, and how much it would be improved. Therefore, the bending strengths of V-CFRP, R-CFRP, and TR-CF reinforced polymer (TR-CFRP) were measured (Fig. 9).

Figure 9 compares the bending strengths of V-CFRP (circle), R-CFRP reinforced by R-CFs (diamond), TR-CFRP reinforced by R-CFs treated with acetone (triangle), and TR-CFRP reinforced by R-CFs treated with NMP at 200°C (square). The bending strength of R-CFRP was 49% that of V-CFRP (Fig. 9). The bending strength of TR-CFRP treated with acetone was 51% that of V-CFRP. The bending strength of TR-CFRP treated with NMP at 200°C was 78% that of V-CFRP. Bending strength was thus significantly improved by treatment with NMP. NMP very effectively removed epoxy resin impurities, and it was possible to obtain high-performance TR-CFRP by treating R-CFs with NMP. Although NMP costs more than acetone, if the R-CFs can be reused in high-value TR-CFRP, it is still a significant solution for treating R-CFs. Compared to TR-GFRP, amount of improved bending strength distinctly fall in the case of TR-CFRP could be ascribed to not only poor adhesion between epoxy resin impurities on CF and resin but also poor adhesion between CF and resin. This explanation was supported by observations made under the SEM and shown in Fig. 10, where the features on the fracture surface of failed samples shown was demonstrated. The V-CFRP showed good river patterns in the resin-rich regions and considerable resin adherence to the CF (Fig. 10(a)). TR-CFRP, on the other hand, didn't show a bundle of fibers with considerable resin adherence (Fig. 10(b)). Some regions showed rough CF stained with epoxy resin impurities, meanwhile, some regions showed hardly any smearing of resinous material and smooth CF. Furthermore, if the bending strength needed to be improved, other methods could be considered, such as plasma treatment, coupling agents and so on.

4. Conclusions

R-GFs were treated with detergent and acetone, and R-CFs were treated with acetone and NMP. The bending strengths of FRP reinforced with treated recycled fibers were evaluated, and the effect of solutions on surface treatment and bending strength was determined. The following conclusions can be drawn from the present investigations.

(1) It is possible to recycle reinforced fibers from FRP, and to remanufacture them into high-value R-FRP for reuse.

(2) Acetone effectively removes unsaturated polyester resin impurities, with no adverse effect on the bending strength of TV-GFRP. The bending strength of R-GFRP could be dramatically improved (from 26% to 94%) through treatment with acetone. NMP effectively removes epoxy resin impurities, with no adverse effect on the bending strength of TV-CFRP. The bending strength of R-CFRP could be significantly improved (from 49% to 78%) through treatment with NMP.

The price of reinforced fiber, especially CFs, is very high. If reinforced fiber can be recycled and remanufactured into TR-FRP with as high a performance as possible, the value of TR-FRP will be greater than the recycling cost, and the recycling of FRP can be carried out continuously without assistance from government. These results increase the probability that this method will be widely used in the future.

Acknowledgments

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Figure captions

Fig. 1. Schematic view of the experiment.

Fig. 2. SEM micrographs of fibers at 1000× magnification (a) R-GFs, (b) V-GFs.

Fig. 3. SEM micrographs of TR-GFs at 1000× magnification (a) detergent, (b) acetone.

Fig. 4. Bending strength of V-GFRP and TV-GFRP (1) reinforced by V-GFs, (2) reinforced by V-GFs treated with detergent, and (3) reinforced by V-GFs treated with acetone

Fig. 5. Bending strengths of V-GFRP, R-GFRP and TR-GFRP (1) reinforced by V-GFs, (2) reinforced by R-GFs, (3) reinforced by R-GFs treated with detergent, and (4) reinforced by R-GFs treated with acetone

Fig. 6. SEM micrographs of fibers at 1000× magnification, (a) R-CFs, (b) V-CFs.

Fig. 7. SEM micrographs of TR-CFs at 1000× magnifications (a) acetone, (b) NMP.

Fig. 8. Bending strength of V-CFRP and TV-CFRP (1) reinforced by V-CFs, (2) reinforced by V-CFs treated with acetone, and (3) reinforced by V-CFs treated with NMP

Fig. 9. Bending strength of V-CFRP, R-CFRP and TR-CFRP (1) reinforced by V-CFs, (2) reinforced by R-CFs, (3) reinforced by R-CFs treated with acetone, and (4) reinforced by R-CFs treated with NMP

Fig. 10. SEM micrographs of fracture surface of samples at 1000× magnification (a) V-CFRP, (b) TR-CFRP

Table 1

Materials for specimens

Type	**Resin**	**Hardener**	**Fiber**
GFRP	Unsaturated polyester resin	Pamekku N	Unidirectional glass fiber
	(Showa High polymer, Japan)	(Nof, Japan)	(Unitika, Japan)
CFRP	Epoxy resin XNR6815	XNH6815	Cloth carbon fiber fabrics
	(Nagase Chemtex, Japan)	(Nagase Chemtex, Japan)	(Toray, Japan)

Table 2

Solutions for surface treatment

Recycled fibers	Surface treatment conditions		
	Solution	Temperature	Time
R-GFs	Acetone (Junsei Chemical, Japan)	Room temperature	4h
	Detergent (Kao, Japan)	Room temperature	24h
R-CFs	Acetone (Junsei Chemical, Japan)	Room temperature	5 days
	NMP (Kanto Chemical, Japan)	200°C	3 days

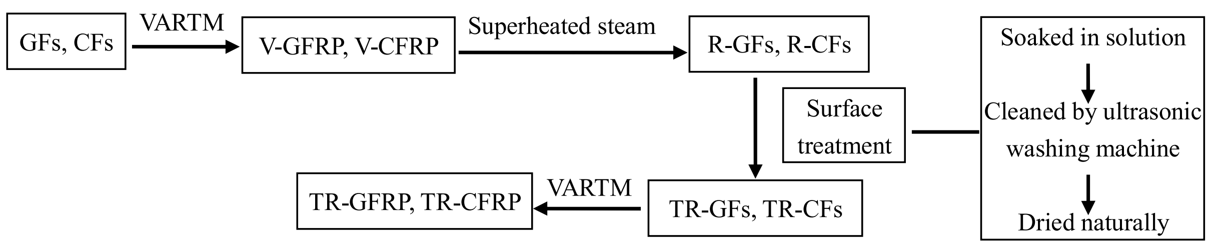
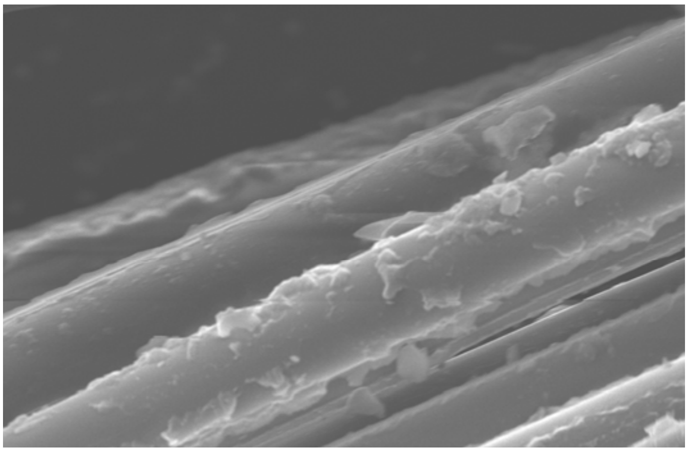
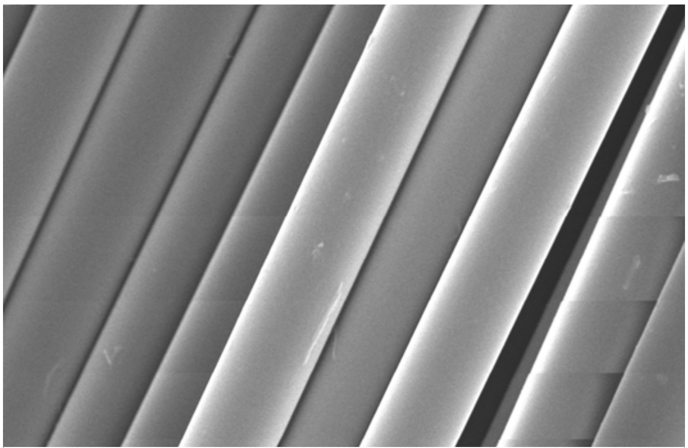


Fig.1



10μm

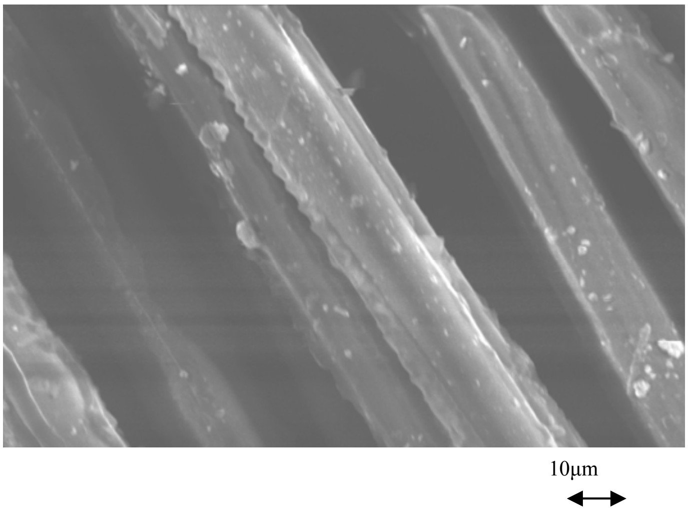
(a)



10μm

(b)

Fig.2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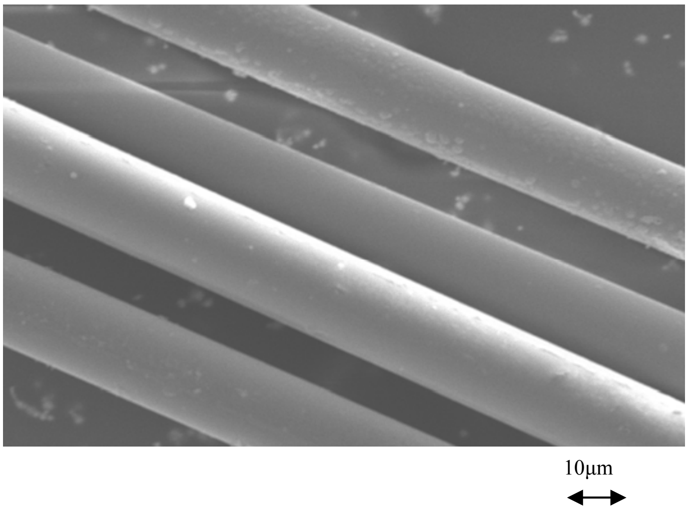
(a)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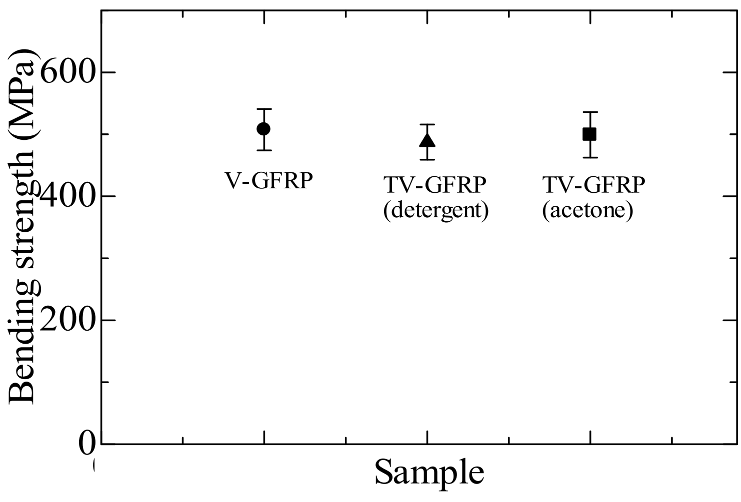
(b)

Fig.3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600
400
200
0
V-GFRP
TV-GFRP
(detergent)
TV-GFRP
(acetone)
Sample

Fig.4

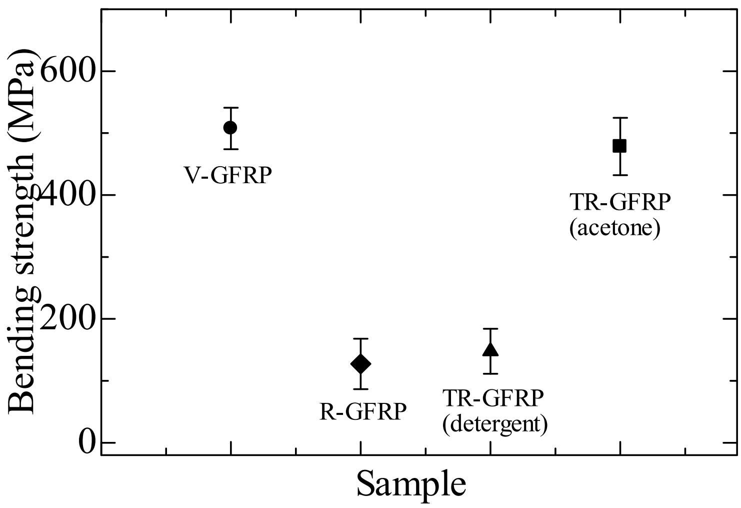
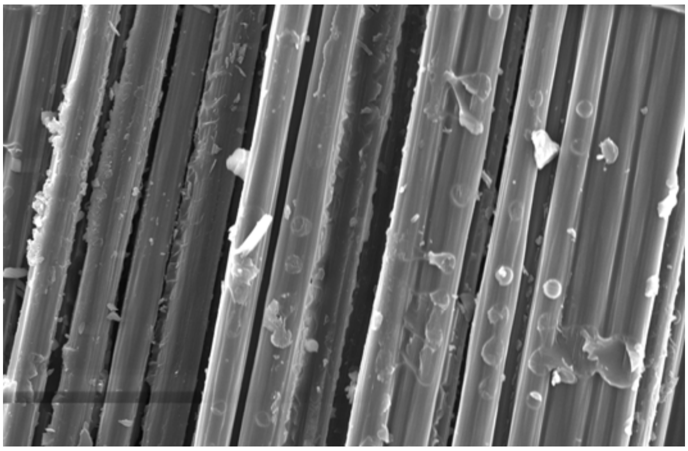
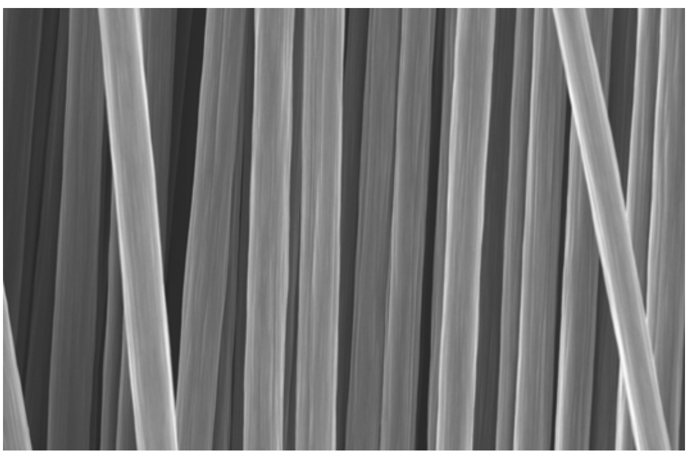


Fig.5



10μm

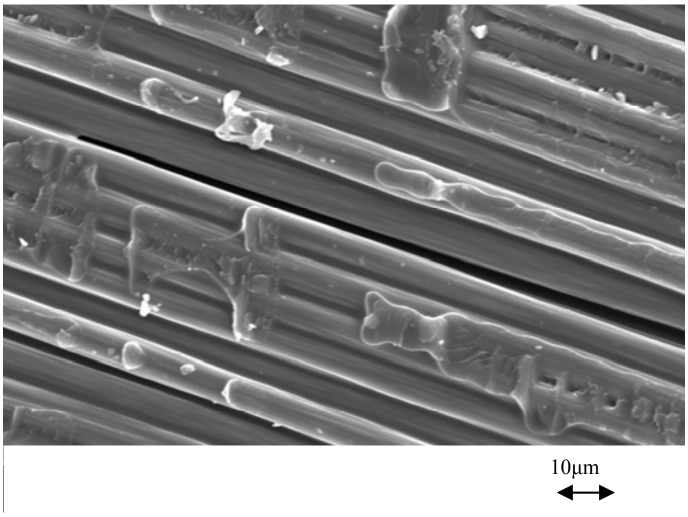
(a)



10μm

(b)

Fig.6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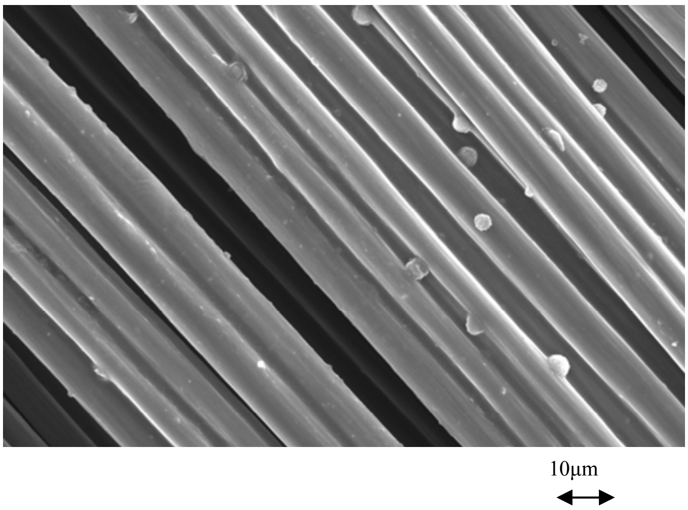
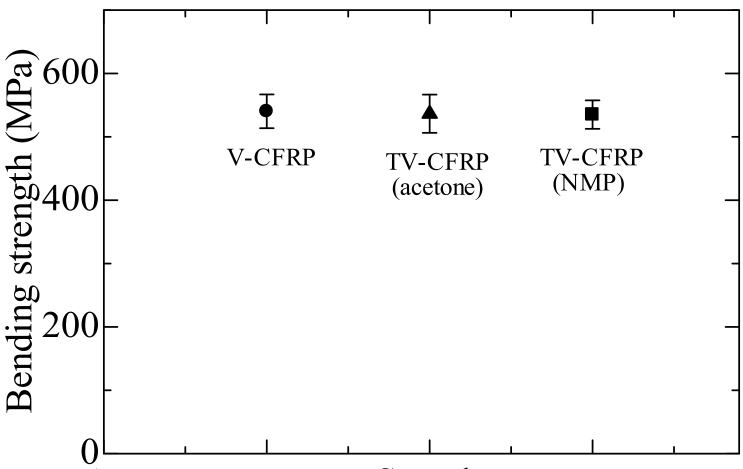
(a)


10μm

(b)

Fig.7


Bending strength (MPa)
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400
200
0
V-CFRP
TV-CFRP
(acetone)
TV-CFRP
(NMP)
Sample

Fig.8

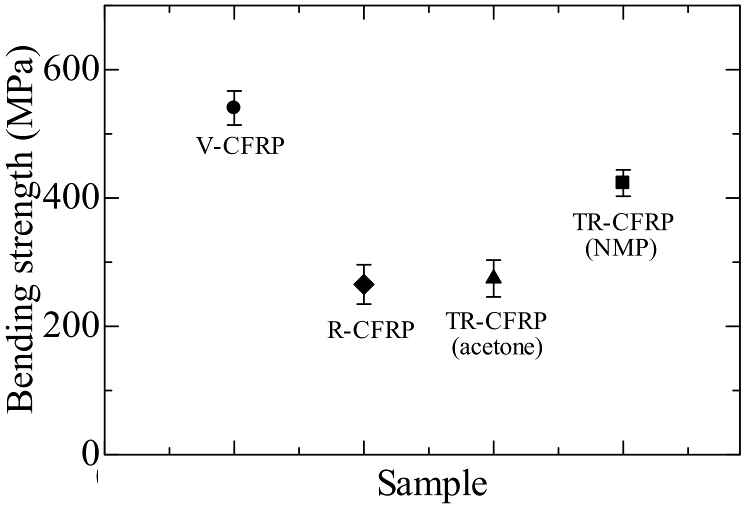
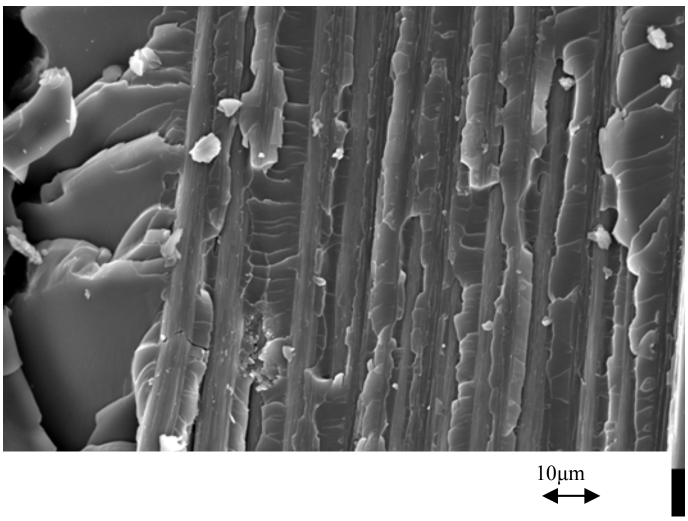
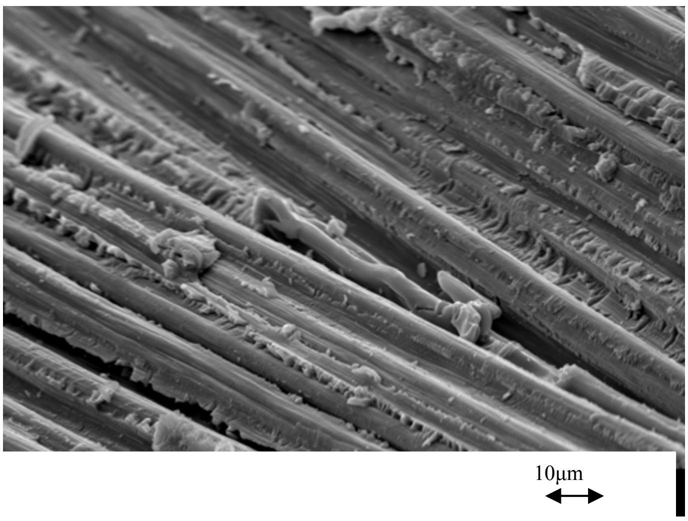


Fig.9



(a)



(b)

Fig. 10