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The Effects of Wet-Milled Wood Flour on the Mechanical Properties of Wood Flour/Polypropylene Composites

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Abstract: The sizes and shapes of wet ball-milled wood flour were investigated based on their average particle size, size distribution, their solution viscosity, and scanning electron microscopy images. The ball-milling conditions were combinations of rotational speed (150, 200, and 250 rpm) and milling time (1 to 16 h). The average diameter of the wood flours decreased and the degree of fibrillation of the wood fibres increased with the ball-milling time at each rotational speed. Ball-milled wood flours having the same average particle size had similar surface fibrils that were tens to hundreds of nanometres wide. Ball-milling at 200 or 250 rpm could pulverise just as effectively as that at 150 rpm because the size reduction and fibrillation progressed more quickly.
Tensile and bending properties of the composites prepared from the ball-milled wood flour (4 wt% in polypropylene) were evaluated. Morphological changes in the wood fillers had little effect on the properties of the composites. The tensile and bending properties of the composites containing the wood filler were 10% higher than those for the unfilled resin.

INTRODUCTION

Wood–plastic composite (WPC), which uses wood flour as a filler in a polyolefin resin, has seen increased demand, mainly in applications such as decks, door components, and automotive components.[1] WPC has also attracted attention as a way to utilise an unused biomass resource such as forest thinnings. The thinnings can be pulverised into a fine powder and then used as a filler. The functionality of WPC needs to be improved in order to meet the increasing demand for WPC products.

Nanocomposites using a cellulosic material, such as wood fibre that was fibrillated at the nano-scale, have recently received widespread attention because of their high performance. Previous studies reported improved physical and mechanical properties, including strength, thermal stability, and optical transparency for nanocomposites.[2–5] Data for moulded nanocomposites showed that the formation of a micro-fibrous structure on the surface of wood flour by disk-milling improved the mechanical properties.[6] However, to the best of our knowledge, there have been few reports that have evaluated the importance of the size and shape of mechanically-pulverised/fibrillated wood flour.

The authors have been evaluating the performance of WPC using mechanically-pulverised/fibrillated cellulose materials as fillers; the pulverised materials were prepared by disk-milling or ball-milling. Cellulosic materials are usually fibrillated when wet. The authors reported that the mechanical properties and water resistance of bamboo flour/high-density polyethylene (HDPE) composites are enhanced by the addition of micro-fibrillated cellulose prepared by wet ball-milling commercial cellulose powder.[7] Mechanical dry grinding pulverises cellulosic materials into fine particles, and prolonged pulverisation leads to increased flocculation.[8] Excessive pulverisation of the wood flour by dry ball-milling had a negative effect on the mechanical properties of the WPC made with it.[9]

The purpose of this study was to evaluate the effect of the morphology of wet-milled wood flours on the mechanical properties of the composites made with them. The wood flour was fibrillated by wet ball-milling, washed with *t*-butyl alcohol to prevent flocculation, and freeze-dried. The particle sizes and shapes of the wood flour fibrillated under prescribed conditions of rotational speed and milling time were investigated, and the mechanical properties of the composites made with the wood flour were evaluated.

EXPERIMENTAL

Materials

The following raw materials were used: wood flour obtained from Japanese cedar (*Cryptomeria japonica* D. Don) forest thinnings, polypropylene (PP, Kayaku Akzo Co., Tokyo, Japan), and PP resin modified with maleic anhydride (MAPP, Kayaku Akzo Co., Tokyo, Japan) as a compatibilising agent. The PP was a homopolymer powder with a melt flow rate of 2 g/10 min (230°C/2.16 kg) and an average molecular weight of 30,000. The MAPP powder had 4% MA content and a melt flow rate of at least 1000 g/10 min (230°C/2.16kg). Forest thinnings were supplied by the Ibi Forest Resources Utilization Center Cooperative (Gifu, Japan). The average particle diameter of the wood flour was about 170 μm.

Filler pre-treatment

Ball-milling was performed in a planetary ball mill (Pulverisette 6, Fritsch Japan Co., Ltd., Kanagawa, Japan). For each load, wood flour (13.5 g) and 200 ml of distilled water were milled with 25 balls (20-mm diameter) at the desired rotational speed using a cycle of 10 min of milling followed by a 1 min pause for the prescribed time. The ball-milling conditions are shown in Table 1.

The samples of dried wood flour were prepared as follows. The solid phase of the slurry after ball-milling was separated using a centrifuge (Micro Refrigerated Centrifuge 3700, Kubota Manufacturing Co., Tokyo, Japan) and dehydrated using *t*-butyl alcohol (2-methyl-2-propanol, Wako Pure Chemical Industries Ltd., Osaka, Japan). The samples were fully dehydrated by repeating the centrifugation and dehydration steps, and finally freeze-dried.

Filler characterisation

The viscosity of the ball-milled slurry was measured using an automatic viscometer (DV-III, Eko Instruments, Co., Ltd., Tokyo, Japan) at 25°C. The viscous drag of the slurry against a spindle (which was immersed in the test slurry) was measured by the spring deflection. The shear rate was varied from 0 to 16 s^{-1}. Preliminary tests established that the slurries after ball-milling were thixotropic because their viscosities decreased over time.[10] To evaluate the degree of thixotropy, the thixotropic index (TI ratio) was calculated using the following equation:

$$TI = \eta_a/\eta_b$$

where η_a and η_b are the viscosity values at shear rates a (= 2.4 s^{-1}) and b (= 14.9 s^{-1}).

The average particle size and size distributions of the dried samples were determined using a laser diffraction particle size distribution analyser (Partica LA-950V2, Horiba, Ltd., Kyoto, Japan). The instrument was equipped with two different light sources, a 650-nm red laser diode and a 405-nm blue emitting diode, and used Mie scattering theory to accurately measure particle sizes from 3 mm to 10 nm. Particle sizes were reported as the equivalent spherical diameters of the irregularly shaped particles. The average particle size for a sample was the average calculated from the particle size distribution.

A scanning electron microscope (Miniscope TM1000; Hitachi, Tokyo, Japan)

operating at 15 kV was used to study the sample morphologies.

Sample preparation

The materials were blended at a wood flour/PP/MaPP ratio of 4/91/5 by weight. The blends were mixed in a micro-compounder (Compounder 5; DSM Xplore, Geleen, The Netherlands) at 190°C and 30 rpm for 5 min, and an injection-moulding machine (DSM Xplore) operating at 190°C with an injection pressure of 1.6 MPa was used to prepare specimens for mechanical property testing.

Mechanical properties

The performance of the composites was evaluated by bending and tensile tests. Both tests were carried out according to the Japanese Industrial Standard JIS A 5741 using a universal testing machine (Tensilon RTG-1250; A&D Co., Ltd., Tokyo, Japan). The bending strength (32-mm span, 2-mm/min loading speed) was measured by a three-point bending strength test. The loading rate was 20 mm/min in the tensile test. At least 5 specimens were tested for each composite.

RESULTS AND DISCUSSION

Filler characterisation

Figure 1 shows the relationship between the ball-milling time and the average particle diameter at the different rotational speeds. The average diameter of the particles after ball-milling decreased with increasing milling time at each rotational speed. Figure 2 shows SEM photographs of wood flours that were prepared by ball-milling at 150 rpm for 2, 4, and 16 h. The largest fibre of the wood flour was tens of micrometres wide after milling for 2 h (Figure 2a), and only a few micrometres wide after milling for more than 4 h (Figure 2b and Figure 2c). The surface fibres of the wood flour were fibrillated and were tens to hundreds of nanometres wide. It is believed that the large wood fibres were separated initially, and then the surface fibres were fibrillated. The degree of fibrillation increased with the milling time.

Figure 3 shows the particle size distributions after milling at (a) 150 rpm for 16 h, (b) 200 rpm for 8 h, and (c) 250 rpm for 8 h. Two peaks were observed in Figure 3b and 3c, while only one peak was observed in Figure 3a. The peak centred at about 0.4 μm was less than 1 μm wide (Figure 3b and 3c). This suggested two possibilities: the wood flour was ground to sizes finer than 1 μm, or that the wood flour was ground into fibres having extremely high aspect ratios, which the instrument measured exclusively in the width direction. To explore these two possibilities, the TI ratio was examined.

The relationship between the ball-milling time and the TI ratio is shown in Figure 4. The TI ratio decreased with the ball-milling time at each rotational speed; the TI ratios for ball-milling at 200 and 250 rpm for 8 h were not higher compared with those for the other conditions (Figure 4). It is known that fibre orientation leads to an increase in fluidity. Therefore, orientation of the wood fibres would increase the TI ratio because the decrease in apparent viscosity increased with the shear stress. This result indicated that material smaller than 1 μm in size that was obtained by ball-milling at 200 rpm for 8 h and 250 rpm for 8 h was not high-aspect-ratio wood fibres, but rather small wood-flour particles.

Figure 5 shows the relationship between the average particle diameter and the TI ratio. The TI ratio decreased drastically for particle sizes below about 20 μm, while the TI ratio remained stable for those above 20 μm. This finding suggested that the water retention ability of the wood flours with particle sizes below 20 μm increased with increasing degree of fibrillation, which consequently improved the stability of the wood flour slurries. Figure 5 also shows that the TI ratio was the same for the same particle size obtained under the different milling conditions. This result suggested that there was little difference in the shapes of same-sized wood flours. SEM was used to study their shapes. Figure 6 shows SEM photographs of the milled wood flours, each of which had an average particle diameter of about 10 μm after ball-milling at (a) 150 rpm for 16 h, (b) 200 rpm for 8 h, and (c) 250 rpm for 8 h. It was observed that the surface fibres of the wood flours were fibrillated with the fibrils from tens to hundreds of nanometres wide; the largest fibres were several micrometres wide. The results of the TI ratios and the SEM photographs revealed that there was little difference in the shapes of same-sized wood flours prepared under the different milling conditions. Ball-milling at 200 or 250 rpm could be just as effective for pulverising as that at 150 rpm because the

size reduction and fibrillation of the surface fibres progressed over a short period of time. The particles smaller than 1 μm that were observed in the particle size distribution for slurries prepared at 200 rpm for 8 h and 250 rpm for 8 h could have been nano-sized fibrils on the surfaces of the wood flours that had broken off during the milling process. Summarising, 1) the large fibres of the wood flour were fiberised and fibrillation of the surface fibres increased with ball-milling time, 2) little difference in the shapes and the degree of fibrillation of the fibres as observed for same-sized wood flours, and 3) size reduction and fibrillation of the surface fibres could be carried out efficiently by ball-milling at high rotational speeds.

Bending testing

The measured mechanical properties are shown in Table 2. Figure 7a and Figure 7b show the relationship between the ball-milling time and the modulus of rupture (MOR) of the composite, and between the ball milling time and the modulus of elasticity (MOE), respectively. As shown in Figure 7, the MOR and MOE were not affected by the ball-milling time at the different rotational speeds. Morphological changes such as size reduction and increase in degree of fibrillation were observed for milled wood flours as a function of the ball-milling time, as described above. The formation of a micro-fibrous structure improved the mechanical properties of composites containing 70 wt% of wood flour because of interactions such as hydrogen bonding and entanglements among the micro-fibres. [6] In this study, interaction among the fibrous wood fillers was not believed to have developed in the composites because the filler content was low (4 wt%). Thus, the bending properties of the composites might not have been affected by the degree of fibrillation of the wood flour. As shown in Figure 7, the low loading of the wood flour nevertheless affected the bending properties of the composites because the MOR and MOE of the composites were about 10% higher than those for the control (containing only PP).

Tensile testing

Figure 8 shows the relationships between the ball-milling time and the tensile strength. The tensile strength depended on the rotational speed, contrary to the bending test results. The tensile strength increased with the ball-milling time, especially at the

rotational speeds of 200 and 250 rpm; this finding might be ascribed to the presence of sub-micron wood-flour particles, as previously stated. Dry wood flour was used to make the composites, and the fine particles could have adhered to the fibre surfaces. The tensile strengths of the composites were about 10% higher than those for the control (containing only PP). This improvement was attributed to an increase in the bonded area between the PP and the wood flour. Although the state of dispersion of the wood flour in the composites was not directly observed, the increased tensile strength can be ascribed to a greater surface area because of the fine particles.

CONCLUSIONS

The sizes and shapes of wet ball-milled wood flours were studied as functions of changing milling conditions, i.e., the rotational speed (150, 200, and 250 rpm) and the milling time (1 to 16 h). The effects of morphological differences of the milled wood flours on the mechanical properties of the composites made with them were evaluated.

The particle size of the wood flour decreased and the degree of fibrillation of the surface wood fibre increased with the ball-milling time at each rotational speed. SEM analyses showed that the surface wood fibres had fibrils that were tens to hundreds of nanometres wide. Although morphological changes such as size reduction and increased surface fibrillation were observed for longer ball-milling times, differences in the mechanical properties of the composites made with them were small. The absence of strong interactions between the wood filler fibres in the composites because of the filler loading (4 wt%) may be one explanation. The MOR, MOE, and tensile strength of the composites were about 10% higher than those of the control (containing only PP). Closer examination of the state of dispersion of the wood filler in the composites is needed to better understand the effect of the filler content on the mechanical properties.

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Table and Figure captions

Table 1. Ball-milling conditions.

Table 2. Mechanical properties: the standard deviation is shown in parentheses

Figure 1. Relationship between ball-milling time and average particle diameter at different rotational speeds.

● : 150 rpm, ■ : 200 rpm, ▲ : 250 rpm.

Figure 2. SEM photographs of ball-milled wood flours prepared at 150 rpm for (a) 2 h, (b) 4 h, and (c) 16 h.

Figure 3. Particle size distributions after ball-milling at (a) 150 rpm for 16 h, (b) 200 rpm for 8 h, and (c) 250 rpm for 8 h.

Figure 4. Relationship between ball-milling time and TI ratio.

● : 150 rpm, ■ : 200 rpm, ▲ : 250 rpm.

Figure 5. Relationship between average particle diameter and TI ratio.

● : 150 rpm, ■ : 200 rpm, ▲ : 250 rpm.

Figure 6. SEM photographs of ball-milled wood flours after milling at (a) 150 rpm for 16h, (b) 200 rpm for 8 h, and (c) 250 rpm for 8 h.

Figure 7. Relationship (a) between MOR and ball-milling time and (b) between MOE and ball-milling time.

▲: Control, ○ : 150 rpm, □: 200 rpm, ◊ : 250 rpm.

Figure 8. Relationship between tensile strength and ball-milling time.

▲: Control, ○ : 150 rpm, □: 200 rpm, ◊ : 250 rpm.

Table 1

Rotational speed (rpm)	Milling time (h)				
	1	2	4	8	16
150	−	○	○	○	○
200	−	○	○	○	−
250	○	○	○	○	−

Table 2

Rotational speed (rpm)	Milling time (h)	Modulus of elasticity (GPa)	Modulus of rupture (MPa)	Tensile strength (MPa)
150	2	1.9 (0.1)	65.4 (2.9)	39.1 (1.1)
150	4	1.7 (0.3)	63.4 (2.7)	39.8 (0.7)
150	8	2.0 (0.1)	65.7 (2.0)	39.5 (0.7)
150	16	2.0 (0.1)	66.8 (3.0)	39.4 (0.6)
200	2	1.9 (0.1)	67.3 (1.7)	39.6 (0.5)
200	4	1.9 (0.2)	66.2 (2.4)	40.1 (0.7)
200	8	1.9 (0.1)	66.8 (2.1)	40.5 (0.4)
250	1	1.8 (0.2)	64.4 (1.8)	38.9 (0.5)
250	2	2.0 (0.1)	66.0 (0.6)	39.9 (0.8)
250	4	1.9 (0.1)	63.1 (0.5)	41.1 (0.9)
250	8	2.0 (0.1)	67.2 (4.1)	41.7 (0.5)
Control	(Pure PP)	1.7 (0.1)	59.1 (2.8)	37.5 (1.5)

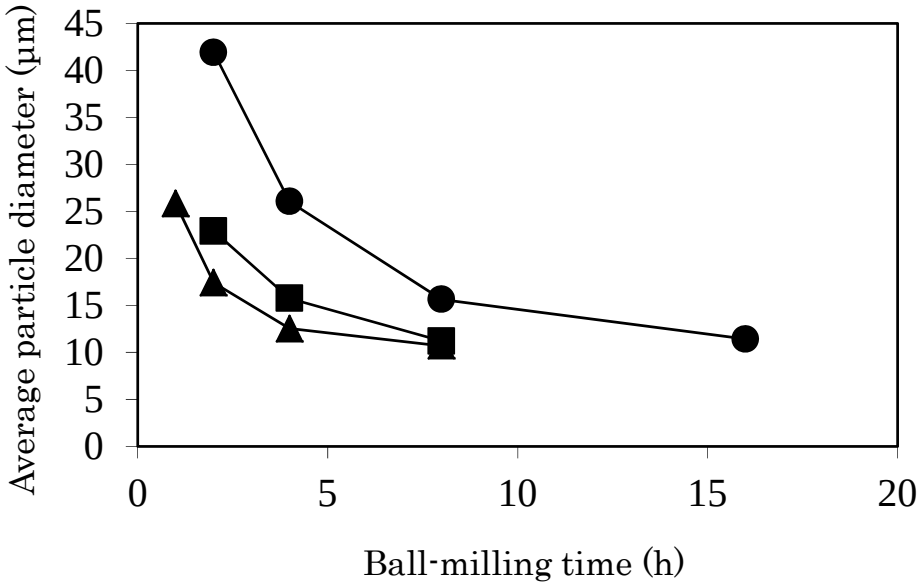
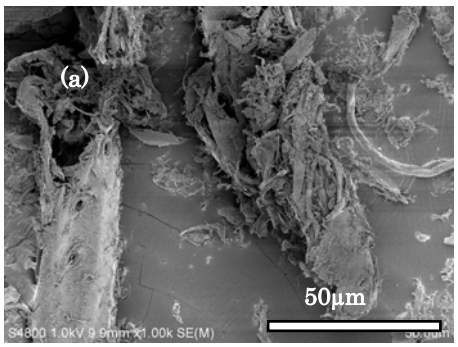
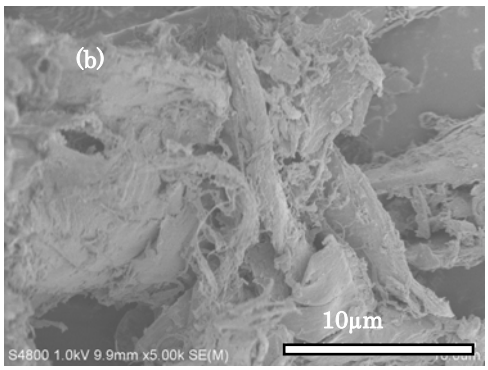

Average particle diameter (μm)
45
40
35
30
25
20
15
10
5
0
0
5
10
15
20
Ball-milling time (h)

Fig.1


(a)
50μm
S4800 1.0kV 9.9mm x1.00k SE(M)


(b)
10μm
S4800 1.0kV 9.9mm x5.00k SE(M)

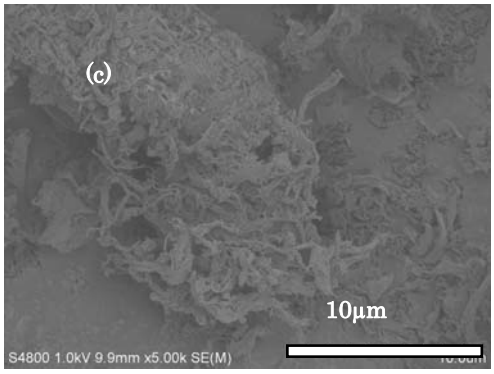
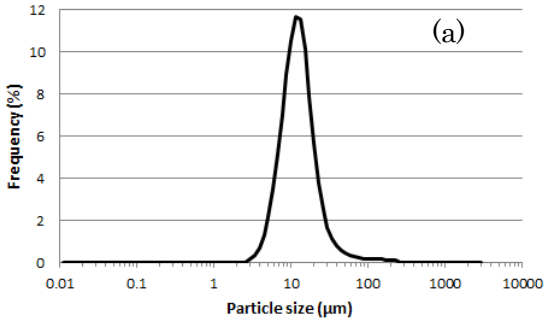
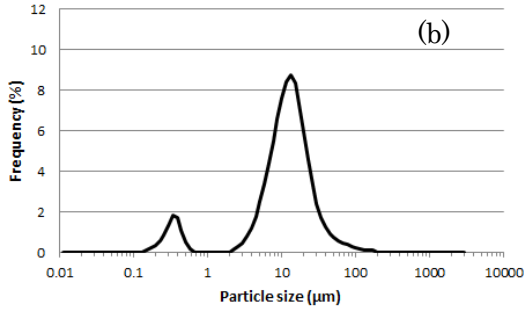

(c)
10μm
S4800 1.0kV 9.9mm x5.00k SE(M)

Fig.2


(a)
Frequency (%)
12
10
8
6
4
2
0
0.01
0.1
1
10
100
1000
10000
Particle size (μm)


(b)
Frequency (%)
12
10
8
6
4
2
0
0.01
0.1
1
10
100
1000
10000
Particle size (μm)

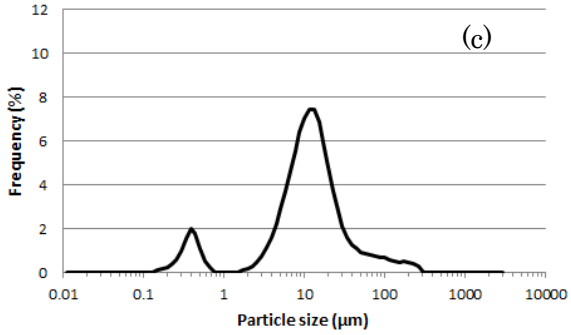

(c)
Frequency (%)
12
10
8
6
4
2
0
0.01
0.1
1
10
100
1000
10000
Particle size (μm)

Fig.3

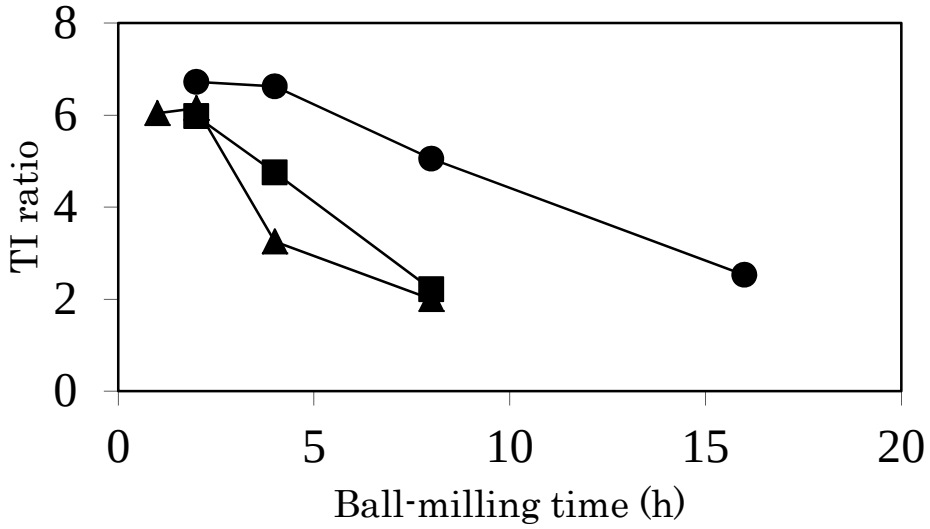


Fig.4

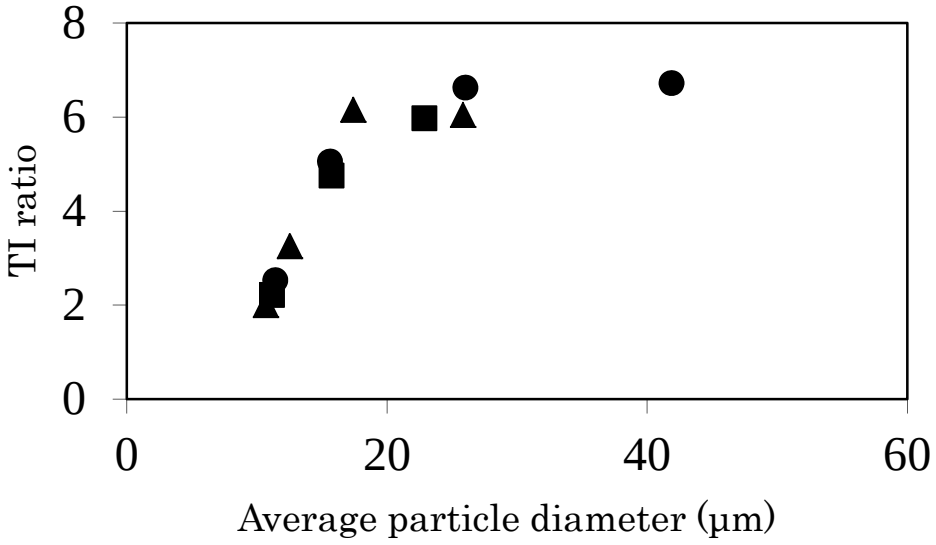
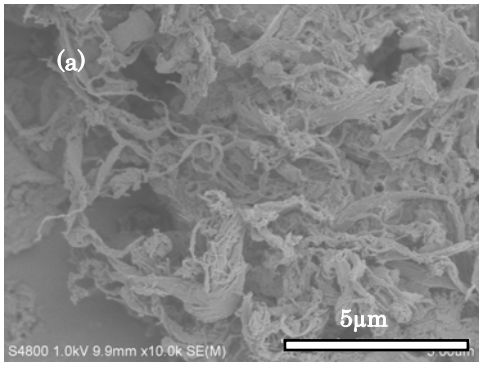
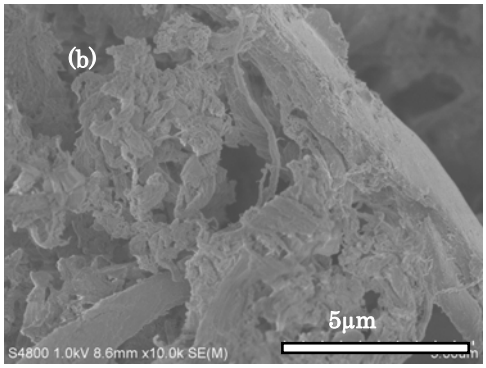


Fig.5


(a)
5μm
S4800 1.0kV 9.9mm x10.0k SE(M)


(b)
5μm
S4800 1.0kV 8.6mm x10.0k SE(M)

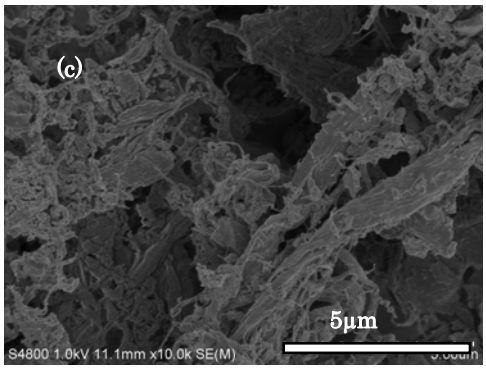

(c)
5μm
S4800 1.0kV 11.1mm x10.0k SE(M)

Fig.6

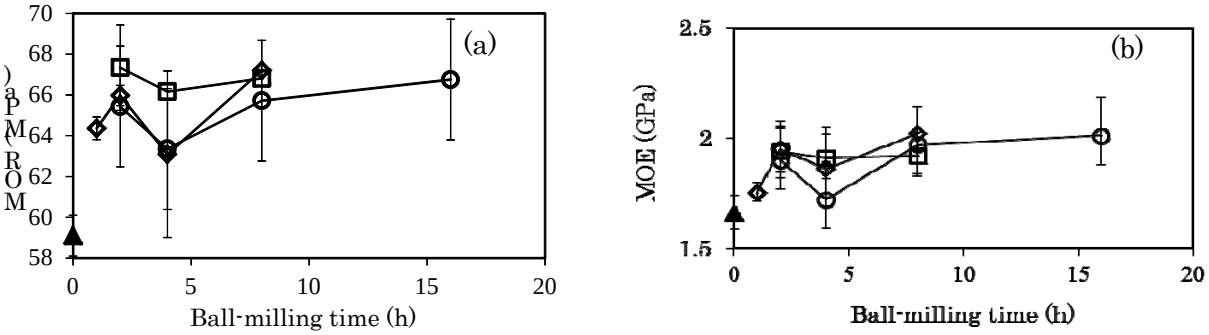

(a)
70
68
66
64
62
60
58
0
5
10
15
20
Ball-milling time (h)
(b)
2.5
2
1.5
MOE (GPa)
0
5
10
15
20
Ball-milling time (h)

Fig.7

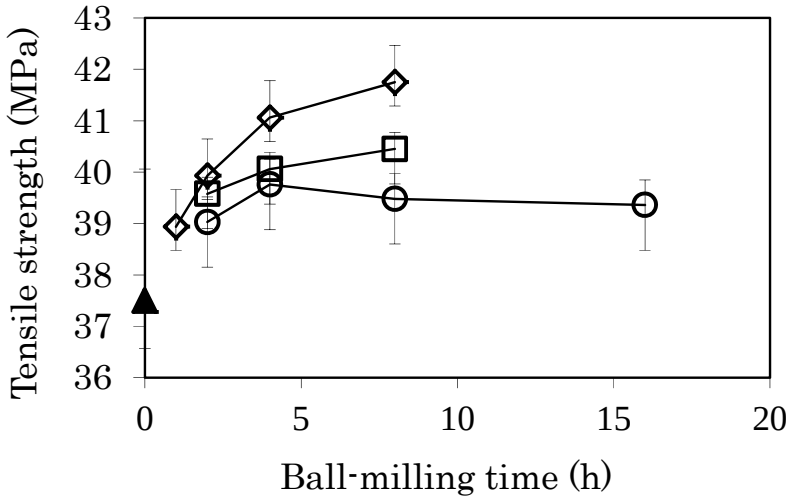

Tensile strength (MPa)
43
42
41
40
39
38
37
36
0
5
10
15
20
Ball-milling time (h)

Fig. 8