Mechanical Properties and Dimensional Stabilities of Wood-Polypropylene Composites Prepared using Mechanochemically Acetylated Japanese Cedar (*Cryptomeria japonica*) Wood Meal

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The scale-up of a mechanochemical acetylation operation using 100-L ball mills was performed to produce acetylated Japanese cedar (*Cryptomeria japonica*) wood meal for wood-polypropylene composite (WPC) production. Finely and coarsely acetylated wood meals (AWMs) were successfully produced with approximately 21% and 19% weight percent gains (WPG), respectively, which was close to the theoretical value. The mechanical properties of WPCs showed similar, rather weak strength compared with the AWM-filled WPCs without maleic anhydride-grafted polypropylene (MAPP) as a compatibilizing agent; however, coarse AWM-filled WPCs showed similar or higher mechanical properties than untreated wood meal (UWM)-filled WPCs when MAPP was added. Clear enhancements in the dimensional stability of AWM-filled WPCs were observed, but no significant differences in dimensional stability were observed between WPCs filled with fine and coarse AWMs, even when MAPP was added. Morphological analyses of the fracture surface showed the retention of some wood cell wall structures in coarse AWM, and fine loadings of the thermoplastic into the lumen were clearly observed. These properties were not found on the fracture surface of fine AWM-filled WPCs; therefore, high polymer loadings into the retained wood structure with high interfacial adhesion by MAPP could be suggested for improving the mechanical properties of coarse AWM-filled WPCs.

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INTRODUCTION

Recently, the use of wood-plastic composites (WPCs) has expanded beyond decking and railing to other exterior building products, including roofing, fencing, siding, and window/door profiles (Clemons *et al*. 2013). When WPCs are exposed to outdoor conditions, wood properties such as low thermal stability and high hygroscopicity have generally been considered to be negative factors impacting WPC performance. Chemical modifications of wood materials have been reported not only to prevent or retard these negative effects, but also to improve their properties (Mahlberg *et al*. 2001; Rowell 2013).

It is well known that acetylation is one of the major effective chemical modification methods performed on lignocellulosic materials for the improvement of dimensional stability and biological durability of WPCs (Ibach and Clemons 2007; Ibach *et al*. 2007;

Segerholm *et al*. 2012a,b). These improvements are often explained by the reduction in moisture sorption caused by the acetylation of hydroxyl groups. However, the effects of acetylation on the mechanical properties of WPCs are not always positive. Segerholm *et al*. (2007) reported that when 50 wt.% acetylated wood particles were combined with cellulose acetate propionate or polypropylene (PP), the tensile strength was approximately 40% higher than that of unmodified WPC, whereas their notched impact strength was 20% lower than those of the corresponding unmodified composites. Bledzki *et al*. (2008) found the following effects of acetylation on the mechanical properties of flax fibre-PP composites: tensile and flexural strength were increased because of the increasing degree of acetylation up to 18% and then decreased, whereas the Charpy impact strength was decreased with increasing degree of acetylation. However, increments in tensile and flexural strength were found, depending on the degree of acetylation, when a coupling agent was added. These notable studies suggest that the effects of filler acetylation on its mechanical properties are strongly related to the experimental design, as well as filler properties.

The acetylation of wood materials has often been performed using acetic anhydride (AA) as a liquid phase reaction, with or without catalysts (Rowell 2013). A novel acetylation process using a system involving supercritical carbon dioxide has also been reported (Matsunaga *et al*. 2010). In general, chemical modifications of lignocellulosic materials for WPC production need to undergo a two-step process, *i.e.*, reaction and pulverization, in the course of application. Mechanochemical acetylations that produce acetylated materials in one step have been performed using a vibration mill (Efanov and Galochkin 2006; Kurimoto and Sasaki 2013a) and a pan mill (Zhang *et al*. 2008). However, these applications have rarely been reported for WPC production.

In our series of studies, mechanochemical acetylations (Kurimoto and Sasaki 2013a) of Japanese cedar (*Cryptomeria japonica*) wood meal were successfully performed with a high-speed vibration rod mill at a laboratory scale, and the mechanical properties and dimensional stability of the acetylated wood meal (AWM) and PP composites were reported (Kurimoto and Sasaki 2013b). Whereas these studies revealed the fundamental data of mechanochemical acetylation, a batch of AWM was limited to a few grams by the small scale of treatment. As Zhang *et al.* (2008) mentioned, further scale-up of the mechanochemical production scale has become a challenging exploitation for commercial application. Additionally, no studies have reported on the effect of the scale-up of mechanochemical treatment on the degrees of reaction and pulverization.

Thus, the aim of this study was to investigate the feasibility of AWM production because of the expansion of mechanochemical treatment for WPC production. In this paper, finely and coarsely AWMs were produced using mechanochemical acetylation in the presence of AA and pyridine as a catalyst using a 100-L ball mill, and the mechanical properties and dimensional stabilities of these AWM-filled WPCs were evaluated with or without a compatibilizing agent. The scale-up of mechanochemical acetylation for WPC production was carried out for the first time in this study.

EXPERIMENTAL

Wood Materials

Sawdust of Japanese cedar (*Cryptomeria japonica* D. Don) mixed with both heart- and sapwood was supplied by Akita Pellet Co., Ltd. (Akita, Japan), and wood meal that

passed through a 2.0-mm mesh sieve was used for the mechanochemical acetylation process without delipidation. Spruce wood meal was supplied by Akita Wood Co., Ltd. (Odate, Japan) and used as untreated wood meal (UWM). This UWM was used for actual WPC production; it was ground (passed through a 300-μm mesh sieve) using an industrial-scale hammer mill.

Table 1. Compositions of Acetylation Mixture

Abbreviation	Wood Meal (g) (phr)	Acetic Anhydride (g) (phr)	Pyridine (g) (phr)
FAWM	5000 (100)	2500 (50)	375 (7.5)
CAWM	6000 (100)	3000 (50)	450 (7.5)

Production of Acetylated Wood Meal

Mechanochemical acetylation

Two types of mechanochemical acetylation were performed using a 100-L ball mill (AXB-100, Seiwa Giken Co., Ltd., Hiroshima, Japan) in this study. One used a low wood content (5 kg/vessel) with a long pulverization time (72 h) to produce finely acetylated wood meal (FAWM), and the other used a high wood content (6 kg/vessel) with a short pulverization time (28 h) to produce coarsely acetylated wood meal (CAWM). Five or six kilograms of oven-dried *C. japonica* wood meal was mechanochemically pulverized for 72 or 28 h, respectively, together with 50 parts per hundred wood meal (phr) of AA (min. 97.0%, Wako Pure Chemical Industries Ltd., Osaka, Japan) as a reaction reagent and 7.5 phr of pyridine (min. 99.5%, Wako Pure Chemical Industries Ltd., Osaka, Japan) as a catalyst. Half of the amount of the mixture of AA and pyridine solution was added to the vessel at the beginning of the process, then the other half was separately added 15 min after the process was started. The compositions of the acetylation mixture (Table 1) were determined based on the authors' previous work (Kurimoto and Sasaki 2013a). The ceramic ball to wood meal mass ratios for the production of FAWM and CAWM were 12:1 and 10:1, respectively, with 30 kg each of two ball sizes ($\varphi = 30$ mm, mass = *ca.* 48 g and $\varphi = 25$ mm, mass = *ca*. 30 g). The rotational speed of the ball mill was fixed at 30 rpm. For the measurement of weight percent gain (WPG) and particle size distribution of the treated wood meal, a few grams of the samples were collected periodically for the analysis of particle size distribution. Each collected sample was diluted with deionized water immediately and filtered using a glass-fiber filter (Advantec (USA), GA-100, 0.44 mm thickness, $\varphi = 70$ mm, pore size 1.0 μm); then they were washed with deionized water until the pH of the filtrates became neutral. The samples were then oven-dried to a constant weight at 105 °C. After undergoing the mechanochemical process, the treated wood meals with the reaction residue of acetate and pyridine mixtures were immediately soaked in approximately 40 L of tap water in the receiving vessel and then filtered using filter paper (Advantec (USA), No. 1, 0.20 mm thickness, $\varphi = 300$ mm, pore size 6.0 μm). Finally, they were washed until the pH of the filtrates became neutral and oven-dried at 80 °C for 48 h to produce approximately 6 or 7 kg of FAWM or CAWM samples, respectively.

Analysis of particle size distribution

Particle size distributions of AWMs and UWM were classified using four types of mesh sieve: 53, 106, 500, and 1000 μm. After careful measurement of each dry weight, the relative distribution rates were measured from the sum of each five fraction, *i.e.*, < 53, 53 to 106, 106 to 500, 500 to 1000, and > 1000 μm.

Measurement of weight percent gain

The WPG of the treated wood meal was calculated from the quantification of free acetate liberated by sample saponification. It was assumed that the number of accessible hydroxyl groups might increase because of the enlarged surface area of the wood particle during the mechanochemical process. Therefore, to ensure the uniformity of each WPG, the free acetate content was analyzed for every classified particle.

After the classification of wood meal into different particle sizes, approximately 0.3 g (d.w.) of each sample with 25 mL of 0.5 N KOH ethanol solution was left for 48 h at 50 °C for saponification. After centrifugation (10,000 rpm, 2 min), 255 μL of 0.5 N H_2SO_4 aq. and 505 μL of deionized water were added to 250 μL of KOH ethanol solution and well-stirred. Quantification analysis was performed on a Shimadzu (Japan) LC-10AD high-performance liquid chromatograph (HPLC) equipped with a Shimadzu SPD-10AV UV-VIS detector. Five microliters of the above solution was injected into the column (Hitachi (Japan) LaChrom C18-AQ, 250 mm x 4.6 mm i.d.), and the amount of free acetate was quantified using a three-point calibration curve (10, 20, and 30 w/v% in 0.5 N KOH ethanol solution). The column was used with eluents of 5 mM KH_2PO_4, 0.34 mL of 85% (w/w) H_3PO_4, and 10 mL of ethanol at 0.8 mL/min. Detection was performed at 210 nm.

Quantified free acetate was regarded as the amount gained from the original wood meal, and WPG_{part} for every particle size was calculated using the following equation,

$$WPG_{part} \ (\%) = 100 \times \frac{W_a}{W_0} - G_0 \tag{1}$$

where W_a is the weight (g) of free acetate quantified by HPLC, W_0 is the weight (g) of the oven-dried sample, and G_0 is the free acetate rate (1.4%) of untreated original wood meal quantified by HPLC. Each of the calculated WPG_{part}, *i.e.*, < 53, 53 to 106, 106 to 500, 500 to 1000, and > 1000 μm, was multiplied by content percentage and then summed to determine the WPG of the AWMs.
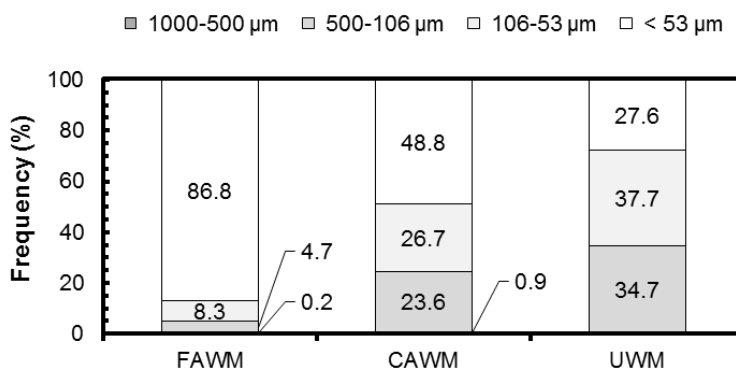

Fig. 1. Particle size distributions of AWMs and UWM used for WPC production

Manufacturing of Wood-Polypropylene Composites

Prepared AWM and PP (Novatec-PP, MA3, Japan Polypropylene Co., Ltd., Tokyo, Japan) were dried under vacuum at 60 °C for 24 h before use. Particle size distributions of the AWM fillers are shown in Fig. 1. Maleic anhydride-grafted polypropylene (MAPP, Umex 1010, Sanyo Chemical Industries Co., Ltd., Tokyo, Japan) was added as a compatibilizing agent. These three materials were combined according to the formations listed in Table 2. Well-dried materials were mixed uniformly for 15 min at 190 °C using a

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twin-screw kneading machine (S1 KRC kneader, Kurimoto Co., Ltd., Osaka, Japan) and pelletized. Then, pellets were crushed for 10 s using a crush mill (WDL-1, Osaka Chemical Co., Ltd., Osaka, Japan).

The injection molding procedure was based on a previous study (Kurimoto and Sasaki 2013b). The crushed granules were well dried under vacuum at 60 °C and fed into the head of an injection-molding machine (type IMC-1167, Imoto Machinery Co., Ltd., Kyoto, Japan) and heated at 210 °C for 5 min. The molten material was injected into dumbbell-shaped molds to produce 75-mm (l) x 2-mm (t) x 5-mm (minimum width) composites for the tensile test according to the Japanese Industrial Standard (JIS) K7162 (1994) and bar-shaped molds to produce 80-mm (l) x 4-mm (t) x 10-mm (w) composites for the bending and swelling test according to JIS K7171 (1994) using a hand press.

Table 2. Combination of the Materials for WPC Production

Wood Meal Type	Abbreviation	Wood (%)*	PP (%)*	MAPP (%)*
Fine, acetylated	FAWM	50	50	0
		49	49	2
Coarse, acetylated	CAWM	50	50	0
		49	49	2
Untreated (control)	UWM	50	50	0
		49	49	2

 * Value indicates weight percent

Mechanical Properties

Bending tests were conducted at room temperature using a universal testing machine (RTC-1325, Orientec Co., Ltd., Tokyo, Japan) according to JIS K7171 (1994). Bar-shaped specimens were well dried under vacuum at 60 °C for 24 h before testing and then tested at a crosshead speed of 2 mm/min. The distance between the supports was fixed at 64 mm. Three replicates were performed for each WPC. Bending strength was calculated from the ultimate force on the dimensions of its cross-section and the distance of the supports. Bending modulus was calculated from the linear region of the load-deflection curve.

Tensile tests were conducted at 20 °C and 65% relative humidity (RH) using a tensile and compression testing machine (type AL5KN, Minebea Co., Ltd., Tokyo, Japan). Dumbbell-shaped specimens were well dried under vacuum at 60 °C for 24 h before testing and then were tested at a crosshead speed of 2 mm/min. For each WPC condition, five replicates were tested. Tensile strength was calculated from the ultimate force on the dimensions of its cross-section (minimum width and thickness).

Dimensional Stability

The water absorbability and swelling property of WPCs under each condition were determined according to JIS K7209 (2000) and JIS A5905 (2003). For both tests, the boiled water absorption method was chosen with some modification to shorten the test period and to evaluate the advanced water absorbability of AWM-filled WPCs. Bar-shaped specimens for each bending test were well dried under vacuum at 60 °C for 24 h before testing. Three specimens of WPCs for each condition were soaked in boiled, deionized water. After 24 h, any water adhering to the WPC surface was immediately removed using a paper towel. Water absorbability and dimensional swellings were calculated from the changes in weight, width, and thickness of each specimen.

Morphological Characterization of Fracture Surface

After the tensile test, WPC specimens were well dried under vacuum at 60 °C for 24 h and one side of each fracture surface was coated with gold using a sputter coater (JFC-1200 fine coater, JEOL, Tokyo, Japan). Each fracture surface was observed with a scanning electron microscope (SEM, S-3400N, Hitachi, Tokyo, Japan) to distinguish any morphological characteristics.

Statistical Analysis

One-way analysis of variance (ANOVA) followed by Tukey-Kramer honest significant difference (HSD) comparisons were performed using JMP version 9.0.3 (SAS Institute Inc., Cary, NC, USA), with a significance level of $P < 0.05$. Statistically different groups are shown in Figs. 4, 5, 6, and 7 with different letters, and the error bars indicate standard deviation (SD).

RESULTS AND DISCUSSION

Mechanochemical Acetylation

For the production of the two types of wood meal with different particle sizes distributed in AWM, enlarged mechanochemical acetylation was demonstrated using a 100-L ball mill. The results of time-courses of particle size distribution and WPGs during the treatments are shown in Fig. 2. From our previous study (Kurimoto and Sasaki 2013a), the number of moles in dried *C. japonica* meal of accessible hydroxyl groups was calculated to be 0.00963 mol/g, which confirms the results of Hill and Jones (1996). If all of the accessible hydroxyl groups could be replaced by acetyl groups, 40.5% WPG would be obtained. In this study, 50 phr of AA was used; therefore, the theoretical WPG value was calculated to be 20.6%.

When producing FAWM (Fig. 2(a)), the WPG value reached a ceiling after approximately 10 h of pulverization, and after 72 h, 21.4% of WPG was obtained. After 72 h of pulverization, FAWM consisted of 86.8% particles with sizes lower than 53 µm.
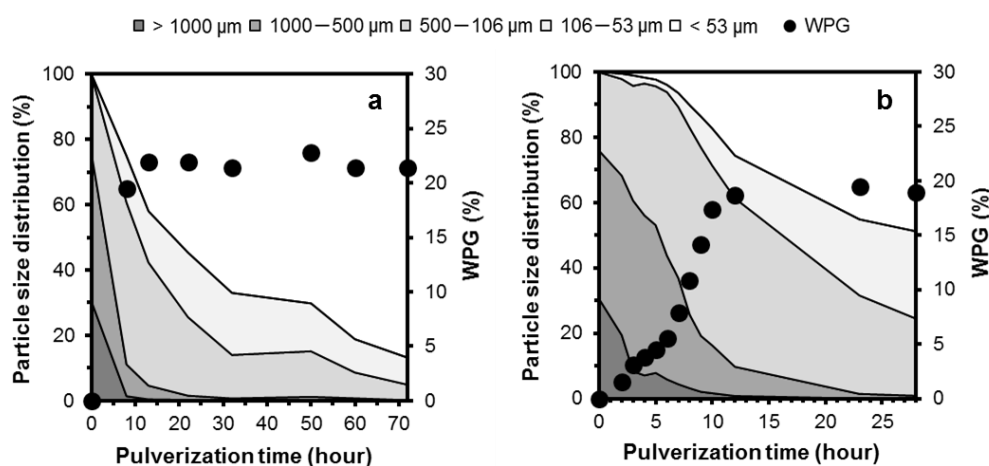
**Fig. 2.** Time-course of particle size distribution and WPGs during the production of (a) FAWM and (b) CAWM samples

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Frequent samplings were taken during CAWM production (Fig. 2(b)) to observe the increment of WPG in the early period of the mechanochemical process. It was found that the WPG value started to increase rapidly, not linearly, after 8 h of pulverization and reached a ceiling after 12 h. After 28 h of pulverization, 18.9% WPG was obtained.

Comparing the results of these two processes, mixing higher amounts of wood meal and AA (Fig. 2(b)) delayed the increment of WPG and particle pulverization for approximately 2 to 3 h; however, results within approximately ±2% of the theoretical values of WPG were successfully achieved for both processes. In addition, the time-course of WPG values of these two mechanochemical processes using a 100-L ball mill followed almost the same tendencies compared with our previous study using a high-speed vibration rod mill (Kurimoto and Sasaki 2013a), except the serpentine curve was observed at the WPG increment phase.

Figure 3 shows SEM micrographs of AWMs and UWM made with particles that passed through a 53-μm mesh sieve. It is clear that longer pulverization time led to the aggregation of AWMs. Plenty of aggregated AWM particles were observed in FAWM after 72 h of mechanochemical processing (Fig. 3(a) and (b)), while aggregated particles were scarce in CAWM after 28 h of mechanochemical processing (Fig. 3(c) and (d)).
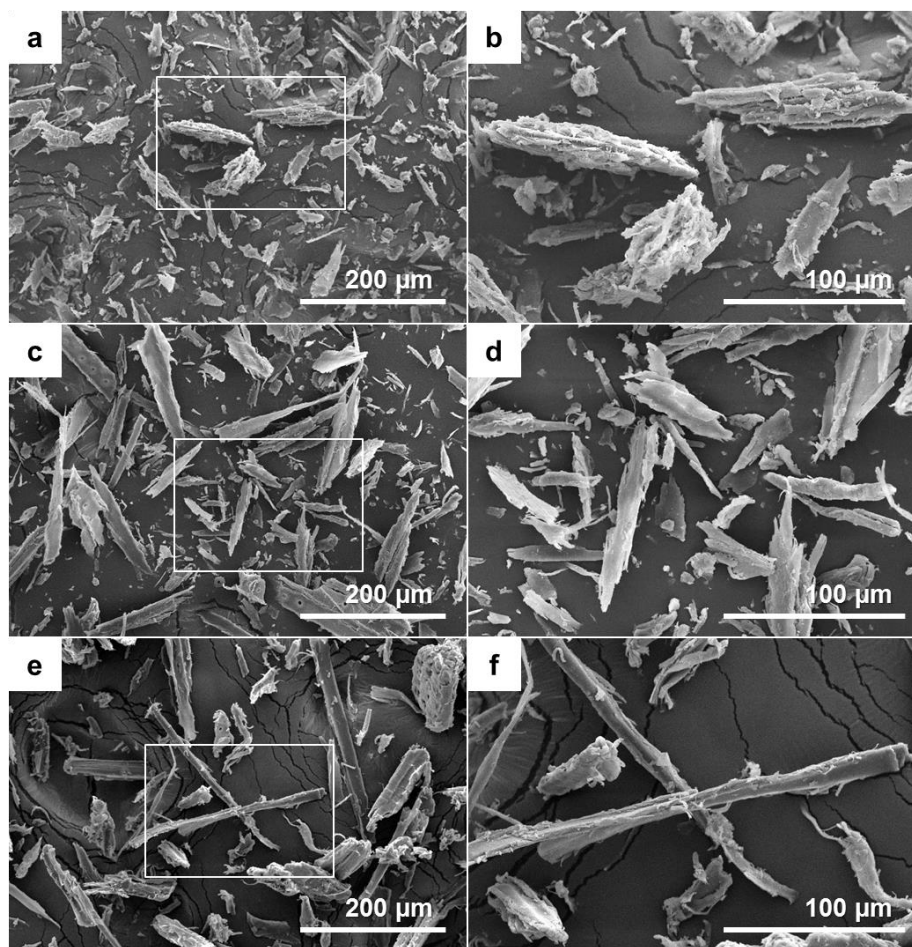

Fig. 3. SEM micrographs of 53-μm-mesh-sieve-passed (a) and (b) FAWM and (c) and (d) CAWM with (e) and (f) UWM samples; (b), (d), and (f) are enlargements of the white squares in (a), (c), and (e), respectively, from 200x to 500x.

The CAWM particles were found to be flat-sharp configurations, and these edges were subject to fluffy-like fibrils. The pulverization time of the ball milling process could be the major factor determining the characteristics of these two AWMs. In addition, none of the aggregations were observed and particles with high length-to-diameter (L/D) ratio were found in UWM (Fig. 3(e) and (f)). At the beginning of the mechanochemical process, the inside of the vessel may become damp under the pulverizing conditions of AA and the catalyst, then gradually become dry by decreasing AA with the evaporation of reaction residue into the dead volume part. It is difficult to compare the properties of wood particles with others produced by wet (Isa *et al*. 2014) and dry (Makise *et al*. 2012) ball milling processes; however, aggregated configurations of FAWM seemed rather similar to the particles produced by the dry ball milling process.

Mechanical Properties of WPCs

The bending strength and modulus of FAWM and CAWM-filled WPCs are shown in Fig. 4. The densities of WPC specimens were between 1.06 and 1.09 g/cm^3. The results of the bending tests using WPCs without a compatibilizing agent indicate that statistically, no differences were found between the strength and modulus of WPCs filled with FAWM or CAWM. Furthermore, UWM-filled WPCs showed the highest bending strength (44.2 ± 1.57 MPa) and modulus (4.64 ± 0.14 GPa). The increment of the L/D ratio has been reported to beneficially affect WPC mechanical properties (Segerholm *et al*. 2007; Migneault *et al*. 2009); therefore, particle configuration might be affected by these results.
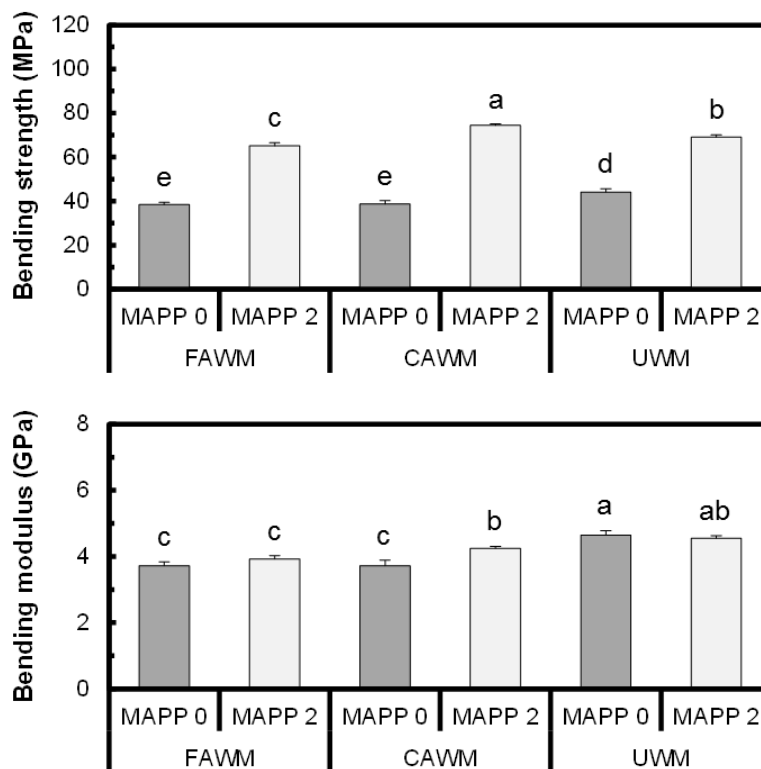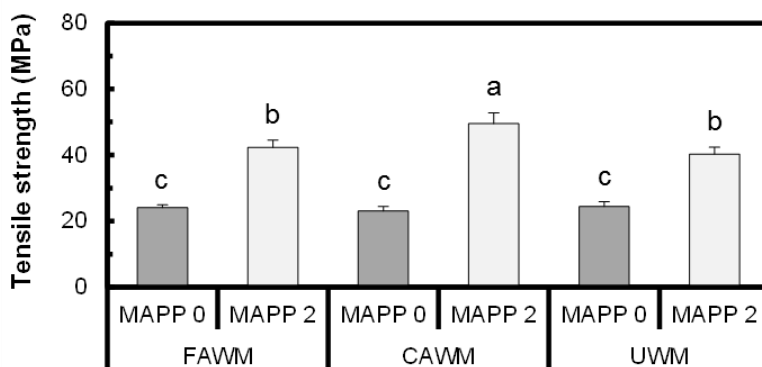

Fig. 4. Bending strength (above) and modulus (below) of FAWM- and CAWM-filled WPCs. The error bars indicate the ranges of standard deviations and the same letters indicate no significant difference at *P* <0.05 (Tukey-Kramer HSD test).

When 2 phr of MAPP was added, the bending properties remarkably increased, with some reflection of the AWM characteristics. Samples filled with CAWM showed the highest bending strength (74.4 ± 0.65 MPa) and had almost twice the value of the sample without MAPP. Samples filled with FAWM also showed good value; however, it was significantly weaker than the samples filled with not only CAWM but also UWM. The bending modulus of CAWM-filled WPCs showed significantly higher value than the FAWM-filled WPCs, and it was raised to a similar value as the sample filled with UWM.

The tensile strengths of FAWM and CAWM-filled WPCs are shown in Fig. 5. For WPCs without a compatibilizing agent, no differences were found between the tensile strengths of WPCs filled with FAWM, CAWM, and UWM. When 2 phr of MAPP was added, the samples filled with CAWM showed significantly higher tensile strength (49.6 ± 3.18 MPa), almost 2.2 times higher than the sample without MAPP. The tensile strength of samples with FAWM also increased to the same degree compared with that of UWM. Because of the differences in mechanochemical processing and the proportions of the material combinations for WPCs, the observed values were rather different from those in our previous study (Kurimoto and Sasaki 2013b).

In this study, similar or rather weak strength values were observed for AWM-filled WPCs without MAPP; however, CAWM-filled WPCs showed similar or higher mechanical properties than UWM-filled WPCs when 2 phr of MAPP was added. Segerholm *et al*. (2007) mentioned that the higher mechanical properties in the AWM-filled WPCs could be a result of better adhesion or molecular interaction between AWMs and PP, although the higher *L/D* ratio could contribute to improvements in the mechanical properties. According to the results in this study, however, FAWM-filled WPCs showed good mechanical properties, close to UWM-filled WPCs, even when particles featured low *L/D* ratios with aggregations. Therefore, more factor-definitive experiments are needed for evaluating the mechanical properties of WPCs filled with mechanochemically produced AWMs.
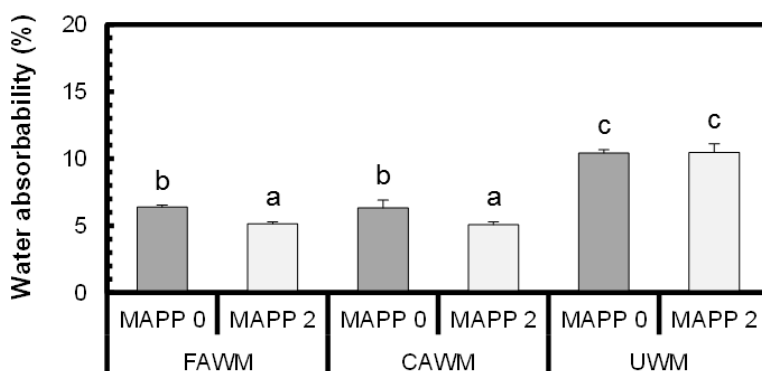

Fig. 5. Tensile strength of FAWM- and CAWM-filled WPCs. The error bars indicate the ranges of standard deviations and the same letters indicate no significant difference at *P* < 0.05 (Tukey-Kramer HSD test).

Dimensional Stability of WPCs

Figure 6 shows the water absorbability values of all samples after soaking in boiling water for 24 h. Improvements in hydrophobicity were clearly observed by filling with AWMs. The absorbability of AWM-filled WPCs were approximately half that of UWM-filled WPCs. In addition, the properties of AWMs did not affect water absorbability.

Interestingly, 1.2% to 1.3% higher values were observed for AWM-filled WPCs without the addition of MAPP. These increments were not clearly found in our previous study, in which WPCs were soaked in 40 °C water for eight weeks (Kurimoto and Sasaki 2013b). Advanced testing may be able to show the improvements in hydrophobicity caused by the addition of MAPP. Clemons *et al.* (2013) mentioned that the anhydride portion of MAPP reacts with a cell wall polymer hydroxyl group to form an ester bond, and then the PP polymer attached to the anhydride intertangles into the PP network, thereby bonding the two together. Therefore, our results suggest that the high hydrophobic stability of AWM-filled WPCs with MAPP was caused by the chemical bonding of MAPP among PP and AWM.

Fig. 6. Water absorbability of FAWM- and CAWM-filled WPCs soaked in boiling water for 24 h. The error bars indicate the ranges of standard deviations and the same letters indicate no significant difference at $P < 0.05$ (Tukey-Kramer HSD test).

Figure 7 shows the width and thickness swelling of AWM-filled WPCs. When MAPP was added, the swelling rates observed were lower than half those of UWM-filled WPCs. In addition, no differences were observed between FAWM and CAWM-filled WPCs, similar to the results of the water absorbability tests. These results, together with the improvements in hydrophobicity, suggest that the combination of mechanochemically produced AWMs with MAPP might promote high dimensional stability of WPCs.
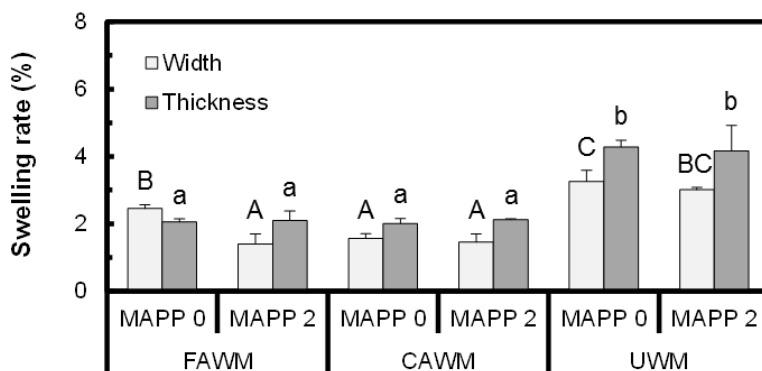
Fig. 7. Width and thickness swelling of FAWM- and CAWM-filled WPCs soaked in boiling water for 24 h. The error bars indicate the ranges of standard deviations and the same letters indicate no significant difference at $P < 0.05$ (Tukey-Kramer HSD test).

## Fracture Surface Characterization in Scanning Electron Microscope

Fracture surfaces after the tensile tests of WPC samples were characterized by SEM micrographs at fixed magnifications (Fig. 8). Plenty of wood particle traces such as cavities and molds were observed together with gaps between PP and particles on the samples without MAPP (Fig. 8(a), (c), and (e)). When MAPP was added, dissociated wood particles were often found on the fracture surfaces of CAWM- or UWM-filled WPCs (Fig. 8(d) or 8(f)), but seldom on that of FAWM-filled WPCs (Fig. 8(b)). These differences can be explained by the proportions of large particles with high *L/D* ratios. Clemons *et al.* (2013) mentioned that without MAPP, the wood fibers were pulled from the PP, whereas with the addition of MAPP, the adhesion between the PP and fibers was improved sufficiently such that the fibers were broken during the composite failure. These characteristics were clearly shown in the present observations, and good interfacial adhesion between the PP and mechanochemically produced AWMs was observed when MAPP was added.
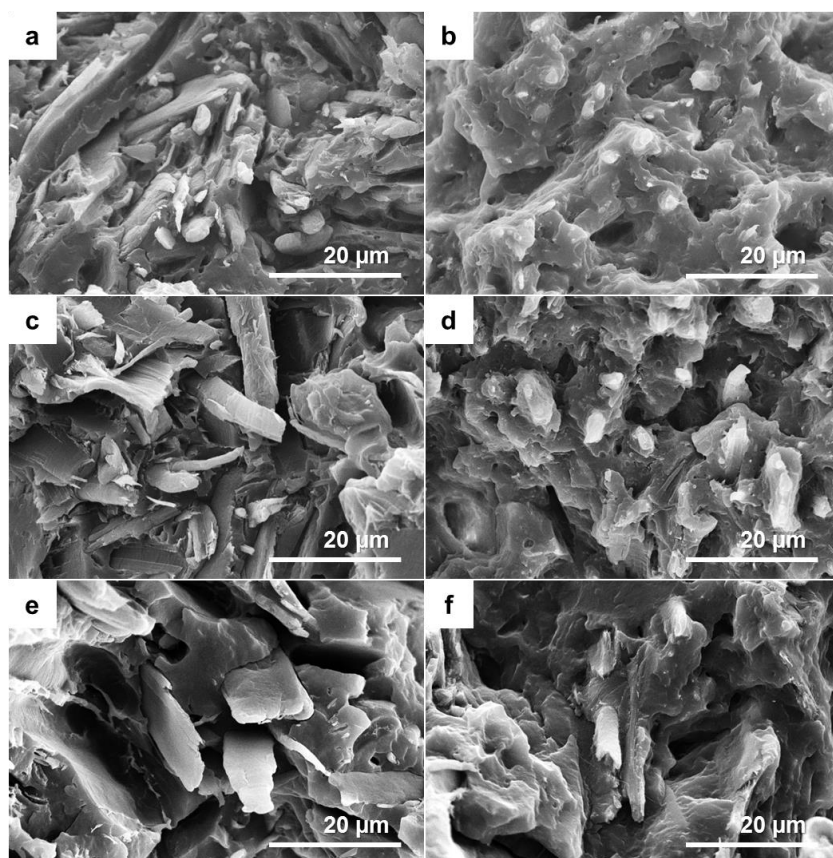
Fig. 8. SEM micrographs of the fracture surface of WPC specimens after the tensile test. FAWM-filled WPC (a) without MAPP and (b) with MAPP; CAWM-filled WPC (c) without MAPP and (d) with MAPP; and UWM-filled WPC (e) without MAPP and (f) with MAPP. The magnification of all micrographs was fixed at 2000x.

The highest bending and tensile strengths were found for CAWM-filled WPCs with MAPP; therefore, more detailed observations were performed for the identification of their typical morphological characteristics (Fig. 9). Some of the wood cell wall structures were retained in CAWM, and fine loadings of the thermoplastic into the lumen were clearly observed (Fig. 9(a) and (b)). These properties were not found on the fracture surface of

FAWM-filled WPCs. Generally, a higher polymer loading yields a higher WPC hardness (Ibach and Rowell 2013). Large particles with such structures were not found from the observations of the particles passed through a 53-µm mesh sieve shown in Fig. 3. However, plenty of different sizes of cell wall structures were present in the original CAWM (data not shown). On the other hand, these structures were rare in the original FAWM. Ayrilmis and Kaymakci (2013) demonstrated that when wood cells collapse, the penetration of thermoplastics into the wood structure almost always ceased. In this study, wood structures were frequently retained without collapse after 28 h of mechanochemical processing, but were not retained after 72 h of processing. Additionally, Gacitua *et al*. (2010) mentioned that significant damage occurs to the wood particles during size reduction and thermo-mechanical processes such as hammer milling and extrusion-injection molding. The thermoplastic loadings into the lumen were also found on the fracture surface of UWM-filled WPCs (Fig. 9(c) and (d)); however, most of the wood structures showed a thinner configuration than that of CAWM. During UWM production, therefore, disintegration of the wood structure might have occurred because of the hammer milling process. Thus, high polymer loadings into the retained wood structure with high interfacial adhesion by MAPP can be suggested to affect the mechanical properties of CAWM-filled WPCs. Thus, mechanochemical acetylation using a ball mill is a potentially useful method for producing higher-quality AWMs (*i.e.*, less affected during mechanical processes) for WPCs; also, the increase in the scale suggests the feasibility of increased production of AWMs.
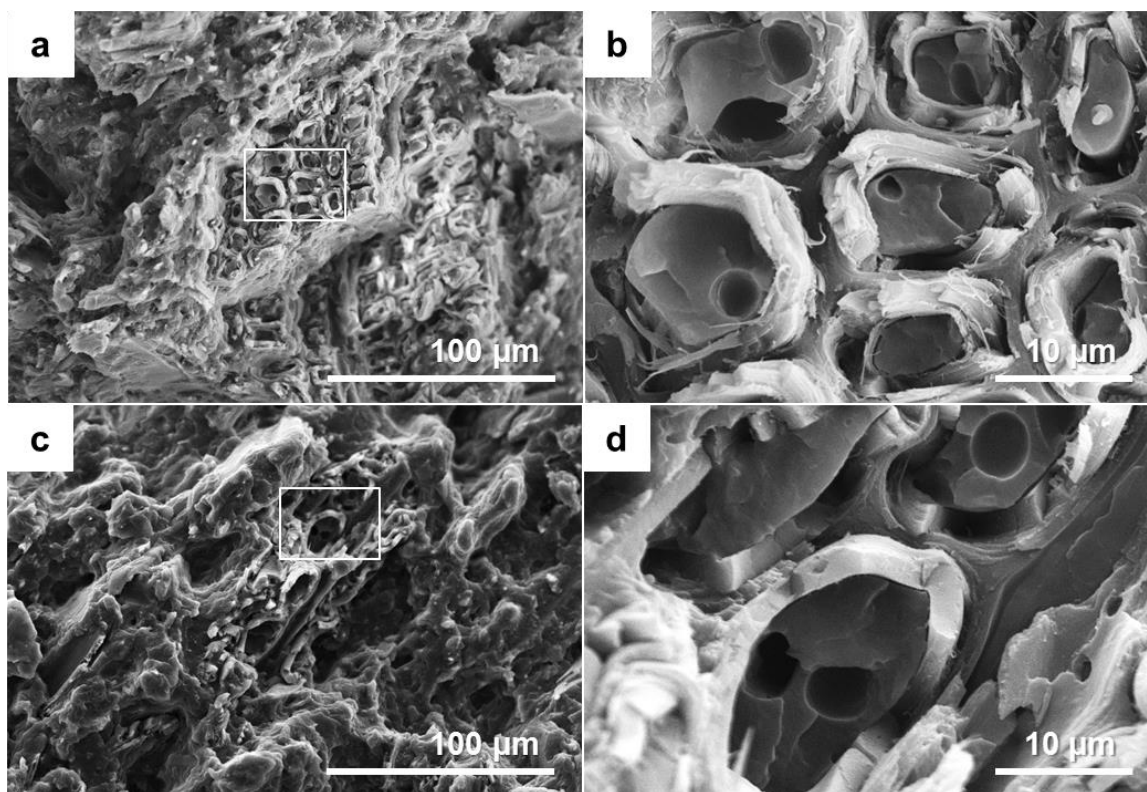
Fig. 9. Specific SEM micrographs of the fracture surface of WPC specimens after the tensile test. (a) and (b) CAWM-filled WPCs with the addition of MAPP and (c) and (d) UWM-filled WPCs with the addition of MAPP; (b) and (d) are enlargements of the white squares in (a) and (c), respectively, from 500x to 3000x.

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CONCLUSIONS

1. In this study, large-scale mechanochemical acetylation was performed using a 100-L ball mill for the first time. Two types of AWMs consisting of fine and coarse particle size distributions were successfully produced with the expected WPG values; furthermore, aggregations of wood particles were frequently observed in FAWM.

2. According to the improvement in compatibility with the addition of MAPP, CAWM-filled WPCs showed the highest mechanical properties, and FAWM-filled WPCs also showed good qualities not inferior to UWM-filled WPCs. Higher improvements in dimensional stabilities were definitively observed for both WPCs as well.

3. Morphological analyses of the fracture surface of CAWM-filled WPCs only showed the fine thermoplastic loading into the lumens of less mechanically affected wood structures; therefore, it was suggested that mechanochemical conditions considered for the production of less mechanically affected AWMs are needed for producing AWM-filled WPCs of higher quality.

ACKNOWLEDGMENTS

REFERENCES CITED

Ayrilmis, N., and Kaymakci, A. (2013). "Fast growing biomass as reinforcing filler in the thermoplastic composites: *Paulownia elongata* wood," *Industrial Crops and Products* 43, 457-464. DOI: 10.1016/j.indcrop.2012.07.050

Bledzki, A. K., Mamun, A. A., Lucka-Gabor, M., and Gutowski, V. S. (2008). "The effects of acetylation on properties of flax fibre and its polypropylene composites," *eXPRESS Polymer Letter* 2(6), 413-422. DOI: 10.3144/expresspolymlett.2008.50

Clemons, C. M., Rowell, R. M., Plackett, D., and Segerholm, B. K. (2013). "Wood/nonwood thermoplastic composites," in: *Handbook of Wood Chemistry and Wood Composites*, 2nd Edition, Rowell, R. M. (ed.), CRC Press, Boca Raton, FL, pp. 473-508. DOI: 10.1201/b12487-17

Efanov, M. V., and Galochkin, A. I. (2006). "Mechanochemical acetylation of aspen wood," *Chemistry of Natural Compounds* 42(5), 627-628. DOI: 10.1007/s10600-006-0238-8

Gacitua, W., Bahr, D., and Wolcott, M. (2010). "Damage of the cell wall during extrusion and injection molding of wood plastic composites," *Composites: Part A* 41(10), 1454-1460. DOI: 10.1016/j.compositesa.2010.06.007

Hill, C. A. S., and Jones, D. (1996). "The dimensional stabilisation of Corsican pine sapwood by reaction with carboxylic acid anhydrides. The effect of chain length," *Holzforschung* 50(5), 457-462. DOI: 10.1515/hfsg.1996.50.5.457

Ibach, R. E., and Clemons, C. M. (2007). "Effect of acetylated wood flour or coupling agent on moisture, UV, and biological resistance of extruded woodfiber-plastic composites," in: *Wood Protection 2006*, Barnes, H. M. (ed.), Forest Products Society, Madison, WI, pp. 139-147.

Ibach, R. E., and Rowell, R. M. (2013). "Lumen modifications," in: *Handbook of Wood Chemistry and Wood Composites*, 2nd Edition, Rowell, R. M. (ed.), CRC Press, Boca Raton, FL, pp. 599-625. DOI: 10.1201/b12487-21

Ibach, R. E., Clemons, C. M., and Schumann, R. L. (2007). "Wood-plastic composites with reduced moisture: Effects of chemical modification on durability in the laboratory and field," in: *Proceedings of the 9th International Conference on Wood & Biofiber Plastic Composites*, Stark, N. M. (ed.), Forest Products Society, Madison, WI, pp. 259-266.

Isa, A., Toyoda, T., Suzuki, S., Kojima, Y., Ito, H., Makise, R., and Okamoto, M. (2014). "The effects of wet-milled wood flour on the mechanical properties of wood flour/polypropylene composites," *Journal of Wood Chemistry and Technology* 34(1), 20-30. DOI: 10.1080/02773813.2013.817431

JIS A5905 (2003). "Fiberboards," Japanese Standards Association, Tokyo, Japan.

JIS K7162 (1994). "Plastics-Determination of tensile properties – Part 2: Test conditions for moulding and extrusion plastics," Japanese Standards Association, Tokyo, Japan.

JIS K7171 (1994). "Plastics – Determination of flexural properties," Japanese Standards Association, Tokyo, Japan.

JIS K7209 (2000). "Plastics – Determination of water absorption," Japanese Standards Association, Tokyo, Japan.

Kurimoto, Y., and Sasaki, S. (2013a). "Preparation of acetylated wood meal and polypropylene composites I: Acetylation of wood meal by mechanochemical processing and its characteristics," *Journal of Wood Science* 59(3), 209-215. DOI: 10.1007/s10086-012-1319-x

Kurimoto, Y., and Sasaki, S. (2013b). "Preparation of acetylated wood meal and polypropylene composites II: Mechanical properties and dimensional stability of the composites," *Journal of Wood Science* 59(3), 216-220. DOI: 10.1007/s10086-012-1316-0

Mahlberg, R., Paajanen, L., Nurmi, A., Kivistö, A., Koskela, K., and Rowell, R. M. (2001). "Effect of chemical modification of wood on the mechanical and adhesion properties of wood fiber/polypropylene fiber and polypropylene/veneer composites," *Holz als Roh- und Werkstoff* 59(5), 319-326. DOI: 10.1007/s001070100232

Makise, R., Okamoto, M., Hasegawa, T., Ito, H., Minamino, J., Isa, A., Suzuki, S., and Kojima, Y. (2012). "Effect of the shape of pulverized wood flour on the mechanical properties of wood-plastic composites," *Proceedings of the 11th Pacific Rim Bio-Based Composites Symposium* (BIOCOMP 2012), pp. 461-466.

Matsunaga, M., Kataoka, Y., Matsunaga, H., and Matsui, H. (2010). "A novel method of acetylation of wood using supercritical carbon dioxide," *Journal of Wood Science* 56(4), 293-298. DOI: 10.1007/s10086-009-1098-1

Migneault, S., Koubaa, A., Erchiqui, F., Chaala, A., Englund, K., and Wolcott, M. P. (2009). "Effects of processing method and fiber size on the structure and properties of wood-plastic composites," *Composites: Part A* 40(1), 80-85. DOI: 10.1016/j.compositesa.2008.10.004

Rowell, R. M. (2013). "Chemical modification of wood," in: *Handbook of Wood Chemistry and Wood Composites*, 2nd Edition, Rowell, R. M. (ed.), CRC Press, Boca Raton, FL, pp. 537-597. DOI: 10.1201/b12487-20

Segerholm, B. K., Walkenström, P., Nyström, B., Wålinder, M. E. P., and Brelid, P. L. (2007). "Micromorphology, moisture sorption and mechanical properties of a biocomposite based on acetylated wood particles and cellulose ester," *Wood Material Science and Engineering* 2(3-4), 106-117. DOI: 10.1080/17480270801906175

Segerholm, B. K., Ibach, R. E., and Wålinder, M. E. P. (2012a). "Moisture sorption in artificially aged wood-plastic composites," *BioResources* 7(1), 1283-1293. DOI: 10.15376/biores.7.1.1283-1293

Segerholm, B. K., Ibach, R. E., and Westin, M. (2012b). "Moisture sorption, biological durability, and mechanical performance of WPC containing modified wood and polylactates," *BioResources* 7(4), 4575-4585. DOI: 10.15376/biores.7.4.4575-4585

Zhang, W., Zhang, X., Liang, M., and Lu, C. (2008). "Mechanochemical preparation of surface-acetylated cellulose powder to enhance mechanical properties of cellulose-filler-reinforced NR vulcanizates," *Composites Science and Technology* 68(12), 2479-2484. DOI: 10.1016/j.compscitech.2008.05.005