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ORIGINAL ARTICLE

Preparation of acetylated wood meal and polypropylene composites II: mechanical properties and dimensional stability of the composites

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Abstract Acetylated wood meals of Sugi (*Cryptomeria japonica* D.Don) wood were prepared by mechanochemical processing using a high-speed vibration rod mill. Weight percent gain (WPG) of the acetylated wood meals ranged from 7.0 to 35.5 %. Wood–plastic composites (WPCs) containing 50 % acetylated woods were produced by an injection molding technique. The polymer matrix used was polypropylene homopolymer. Maleic anhydride-grafted polypropylene (MAPP) was also used as a compatibilizing agent. The mechanical properties of WPCs in bending and tensile tests were independent of WPG of acetylated wood meals, and the test values for WPCs containing acetylated wood meals were lower than that of unmodified wood meal. The use of MAPP increased bending and tensile strength, but no effect on bending modulus was found. An increase in WPG significantly decreased water absorbability and thickness swelling of WPCs as measured by dimensional stability tests. These results demonstrated that mechanochemical processing is a promising technique for preparing WPC material with improved dimensional stability. The future challenge is to inhibit the decreases in mechanical properties of WPCs containing acetylated wood meals.

Keywords Wood–plastic composite · Acetylation · Mechanochemical processing · Dimensional stability

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Introduction

Wood–plastic composites (WPCs) are used in many outdoor products. Due to encapsulation of the wood meals by the plastics, WPCs have high dimensional stability on short-term resistance tests. However, moisture uptake occurs slowly in outer WPCs as they are exposed to long-term humidity or contact with water [1–3].

This study describes the preparation of acetylated wood meals through mechanochemical processing, and the resulting acetylated wood meals are used as materials for WPC production, because the use of chemically modified wood such as acetylation is known as a method to improve dimensional stability and biological durability of WPCs [2–5].

In the first part of this two-part paper [6], we prepared acetylated wood meals with the desired weight percent gain (WPG) through mechanochemical processing with acetic anhydride (AA) and pyridine in a high-speed vibration rod mill. Acetyl content of the acetylated wood meals after saponification changes in the FT-IR spectra before and after pulverization, and the water vapor sorption isotherms strongly suggested modification of the hydroxyl groups of the wood into acetyl groups.

In this report, injection molded WPCs with different WPG and compatibilizing agent levels were prepared, and mechanical properties in bending and tensile tests and water absorbability and swelling in 40 °C water were examined.

Experimental

Materials

Sapwood of Sugi (*Cryptomeria japonica* D.Don) was ground through a Wiley mill (Cutting mill ISO-9001,

Mitamura Riken Kogyo, Tokyo, Japan) and the wood meals passing 2.0 mm and retained on 1.0 mm mesh sieves were used without prior processing such as soxhlet extraction. The amount of ethanol–benzene solubles (1:2 [v/v]) was 0.99 %. Special grade AA and pyridine were used as the reaction reagent and catalyst, respectively, for acetylation.

The plastic material used was an industrial grade of polypropylene (Novatec-PP, MA3, Japan Polypropylene Corporation), with a melt flow rate of 11 g/10 min and a density of 0.90 g/cm^3 (JIS K 7210). The bending strength and modulus according to JIS K 7171 were 43 MPa and 1.5 GPa, respectively. The tensile strength and modulus were 35 MPa and 1.6 GPa (JIS K 7161), respectively. Maleic anhydride-grafted polypropylene (MAPP, Umex 1010, Sanyo Chemical Industries, Ltd.) was used as a compatibilizing agent.

Acetylation using vibration rod mill

Acetylation of the wood particles was performed using a high-speed vibration rod mill (CMT, TI-100 type, Tokyo, Japan). Oven-dried wood particle (5.0 g), AA (1.25–5.0 g), pyridine (0.188–0.75 g), and an A-type of rod (CMT, Tokyo, Japan) were placed into vessels, and then the vessels were set on the mill and run for 30–120 min under mechanical pulverization. After reaction, the treated wood meal was washed with deionized water, and filtered using a glass-fiber filter (Toyo, GA-100, pore size 1.0 μm). The detail procedures are described in the previous paper [6]. The average WPG values for acetylated wood meals were 7.0, 18.0, 28.0 and 35.5 % with AA amounts of 25, 50, 75 and 100 phr, respectively (Table 1).

Manufacturing of composites

Acetylated wood meal and polypropylene (PP) were mixed uniformly for 15 min at 190 °C using a twin-screw kneading machine (S1 KRC kneader, Kurimoto Ltd., Osaka). The acetylated wood meal was dried under vacuum at 60 °C for at least for 24 h before use. MAPP was also mixed according to the formulations shown in Table 2.

Table 1 Composition of acetylation mixtures and average WPG yielded

No.	Wood meal/AA/Pyridine (phr by weight)	Pulverization time (min)	Average WPG (%)
1	100/25/3.75	30	7.0
2	100/50/7.5	40	18.0
3	100/75/11.25	90	28.0
4	100/100/15.0	120	35.5

Table 2 Material combinations for WPCs

Wood material (%)	PP (%)	MAPP (%)
Acetylated, 50	50	0
Acetylated, 45	45	10
Unmodified, 50	50	0
Unmodified, 45	45	10

All percentages are weight percent

After kneading, the mixture was left at room temperature, and then was crushed for 10 s using a crush mill (WDL-1, Osaka Chemical Co. Ltd., Osaka).

Two types of molded specimens were produced by injection molding. One was for the tensile test, using a mold of type 1BA with dimensions of 75 mm (l) × 2 mm (t) × 5 mm (minimum breadth) according to JIS K 7162. The other was used for the bending test and had dimensions of 80 mm (l) × 4 mm (t) × 10 mm (b), according to JIS K 7171. Before injection, the crushed material was dried under vacuum at 60 °C for at least for 24 h. The dried sample was then fed into a head of an injection-molding machine (type IMC-1167, Imoto Machinery Co., Ltd., Kyoto) and heated at 210 °C for 5 min. Next, the heated material was injected into a die using a hand press, and the molded specimen was left until its temperature decreased to room temperature because of the relaxation of elasticity in the specimen.

For the composites with unmodified wood meal, the wood meals with 1.0–2.0 mm size were ground until the wood meal passing through a 106-μm sieve using a Wiley mill, and it was used as the same manner as the composites with acetylated wood meals.

Bending test

Three-point bending tests were conducted at room temperature using a universal testing machine (RTC-1325, Orientec Co., Ltd., Tokyo) according to JIS K 7171. Test specimens were dried under vacuum at 60 °C for at least for 24 h before the test, and then were loaded at a movable crosshead speed of 2 mm/min. The distance between supports was 64 mm. Three replicates were tested for each condition. Bending strength was obtained from the ultimate force on the dimensions of its cross-section and the distance of supports. Bending modulus was calculated from the linear region of the load–deflection curve.

Tensile test

Tensile tests were conducted at 20 °C and 65 % RH using a universal testing machine (RTC-1150, Orientec Co., Ltd., Tokyo) according to JIS K 7113. Test specimens were

dried under vacuum at 60 °C for at least for 24 h and then were loaded at a movable crosshead speed of 5 mm/min. Initial distance between clamps was 30 mm. Three replicates were tested for each condition. Tensile strength was calculated from the ultimate force on the dimensions of its cross-section (minimum breadth and thickness).

Dimensional stability test

Water absorbability (WA) and swelling on thickness (TS) of the WPCs were determined using JIS A 5905. Three specimens of type 1BA form were used for each formulation. Before the test, samples were dried under vacuum at 60 °C for at least for 24 h. The samples were soaked in deionized water (100 mL) in a glass tube under constant of 40 °C. After the predetermined time, water on the surface of the samples was removed immediately using a soft paper. Weight and thickness from swelling then were measured. WA and TS were calculated from Eqs. 1 and 2:

$$WA(\%) = (W_w - W_{vd})/W_{vd} \times 100 \quad (1)$$

where W_w is the weight (g) of WPC after soaking in water and W_{vd} is the weight (g) of WPC before soaking.

$$TS(\%) = (T_w - T_{vd})/T_{vd} \times 100 \quad (2)$$

where T_w is the thickness (mm) of WPC after soaking in water and T_{vd} is the thickness (mm) of WPC before soaking.

Results and discussion

Bending properties

The bending strength and modulus of WPCs are shown in Fig. 1. In addition, Table 3 shows the density of samples used in the tests because the density significantly affected the properties. No large differences were found in the density of samples with different WGP and MAPP levels.

In the samples without MAPP, no large differences were found in the bending strength and modulus of WPCs at all WPG levels, where average values are 35.5 MPa and 2.6 GPa, respectively. These are decreased by 19 and 31 %, respectively, comparing to those of unmodified wood meals. A use of compatibilizing agent increases mechanical strength because it also improved interfacial interactions and/or formation of ester bonds [7, 8]. Therefore, greater bending strength was found for samples with MAPP at each WPG, indicating the increases in deformation at plastic region of WPCs. In contrast, since the MAPP gives no effects on the stiffness of untreated and acetylated wood meals and PP, no effect on bending modulus was found between the samples with and without MAPP.

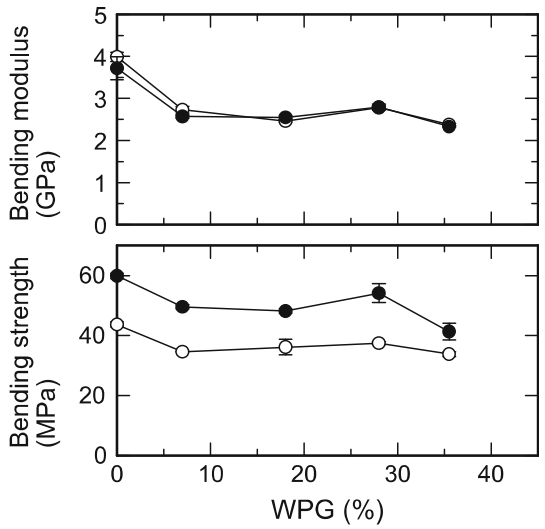

Fig. 1 Influence of WPG on bending properties of WPCs. *closed circle* with MAPP, *open circle* without MAPP. Note: The *plotted values* are means of three replicates and the *error bars* indicate ranges of standard deviations

Table 3 Average density of WPCs in bending tests (g/cm^3)

WPG (%)	With MAPP	Without MAPP
Control	1.101 (0.003)	1.053 (0.009)
7.0	1.053 (0.020)	1.027 (0.004)
18.0	1.032 (0.044)	1.025 (0.018)
28.0	1.007 (0.018)	1.039 (0.008)
35.5	1.033 (0.011)	1.012 (0.018)

Values in the parenthesis are standard deviation

Minato et al. [9] have reported that the specific dynamic Young's modulus (E'/r) of acetylated wood decreased with increasing the WPG. This can be explained by the swelling of matrix substances in the wood cell wall. The E'/r of wood was proportional to that of the cell wall, whereas the E′ depended on the anatomical features including density. Therefore, the significant reduction in E'/r due to acetylation indicated the reduction in the stiffness of cell wall. In the case of the WPCs with acetylated wood meals, it seemed that the same swelling of matrix substances would decrease the mechanical properties in bending tests, comparing to those with untreated wood meal. In addition, the matrix substances in WPCs decreased with increasing the WPG, when the ratio of wood meal to PP was kept constant. This also affects the mechanical properties of WPCs.

On the subject of bending properties of WPCs containing acetylated wood, negative results have been reported. Segerholm et al. [5] and Seki et al. [10] showed the decreases in bending strength and modulus of WPCs prepared from PP and acetylated wood flour. The values of the composites without MAPP were decreased by 5–15 % and

10–15 %, respectively, comparing to those of unmodified wood. Seki et al. [10] explained the reason by a decrease in Young's modulus of the acetylated wood.

The decreased rates in bending strength and modulus obtained here are greater than those of the literatures. It was possible that mechanochemical processing using the vibration rod mill could give damage to wood meals, when they were subjected to elevated temperatures and pressures due to frictional heat and impact strength for long time. In addition, surface properties and morphology of the wood meals and crystallinity of cellulose would be changed. Therefore, the greater decrease rates may be explained by the degradation and decrease in stiffness of the acetylated wood meals. However, further studies are required to understand the relation between WPG and bending properties of WPCs.

Tensile properties

The tensile strength of WPCs is shown in Fig. 2. No large differences were found in the density of the samples with different WGP and MAPP levels (data not shown).

In samples with and without MAPP, no clear relations were found between WPG and tensile strength, as shown in the bending strength. The average value of samples without MAPP was 20.3 MPa, and that of 24.6 MPa was found in samples with MAPP. These are decreased by 24 and 31 %, respectively, comparing to those of unmodified wood meal. When MAPP was used in WPCs, greater tensile strength was found at all WPG levels. However, the decrease ratio in tensile strength was greater than that in bending strength as compared to the values of WPC with unmodified wood meal.

Dimensional stability

The water absorbability and thickness swelling of WPCs soaked in 40 °C water for 8 weeks are shown in Fig. 3. The WA decreased significantly from about 8 to 4 % and TS decreased from about 3 to 1 %, with an increase in WPG. In our previous paper [6], equilibrium moisture content (EMC) of acetylated wood meals significantly decreased with the increasing WPG. Therefore, a decrease in accessible hydroxyl groups clearly decreased the WA and the TS of WPCs.

No large differences in WA and TS were found between samples with and without MAPP at each WPG. In general, the use of a compatibilizing agent not only increased mechanical strength, but also decreased water adsorption due to polymer–wood adhesion and dispersion [8]. Therefore, the samples with MAPP containing unmodified wood (0 % WPG) showed lower WA and TS. However, in this study, no effect of MAPP on dimensional stability was found for WPCs containing acetylated wood meals.

Figure 4 is the effects of soaking time on WA and TS of WPCs without MAPP. WPCs with acetylated wood meal of 35.5 % WPG are lacking in certain data after 12 weeks. However, the other data showed large increases in WA and TS up to 4 weeks, and very slowly increases at times beyond 4 weeks. The acetylated wood meals with more than 18 % should be used as materials for WPC production to make an improvement in dimensional stability.

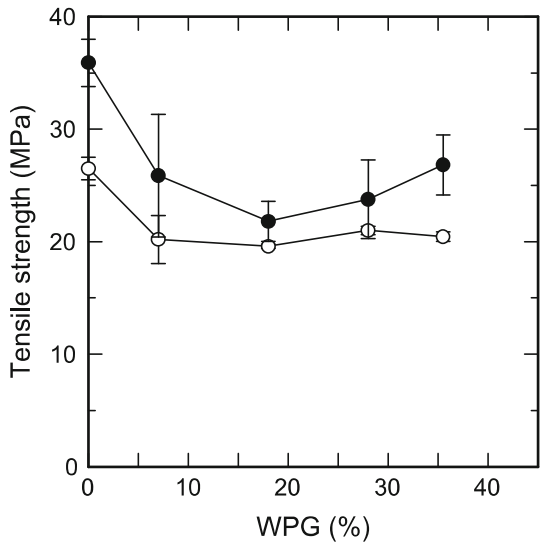

Fig. 2 Influence of WPG on tensile strength of WPCs. *closed circle* with MAPP, *open circle* without MAPP. Note: The *plotted values* are means of three replicates and the *error bars* indicate ranges of standard deviations

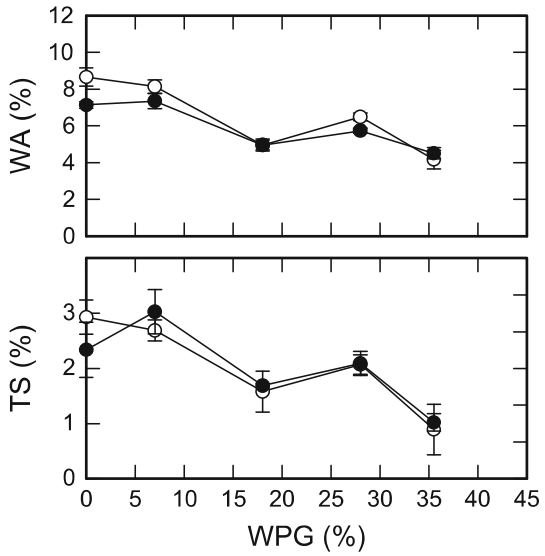

Fig. 3 Influences of WPG on water absorbability (WA) and thickness swelling (TS) of WPCs. *closed circle* with MAPP, *open circle* without MAPP. Note: The *plotted values* are means of three replicates and the *error bars* indicate ranges of standard deviations

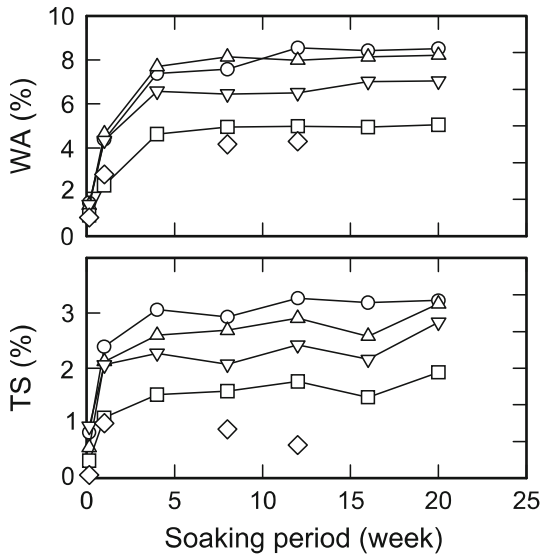

Fig. 4 Influence of soaking period on water absorbability (WA) and thickness swelling (TS) of WPCs without MAPP. WPG: *open circle* unmodified, *open triangle* 7.0 %, *open square* 18.0 %, *open inverted triangle* 28.0 %, *open diamond* 35.5 %

Conclusions

Acetylated wood meals with 7.0–35.5 % WPG were prepared through mechanochemical processing using a high-speed vibration rod mill. WPCs containing 50 % acetylated wood meals were produced by an injection molding technique. For mechanical properties, no large differences were found in the bending and tensile strength of WPCs without MAPP at all WPG levels, where decreases by 19 % bending strength and 24 % tensile strength were found compared to the values of untreated composites. The use of MAPP increased the bending strength by 36 % and tensile strength by 21 %, but no effect on bending modulus was found. An increase in WPG significantly decreased the water absorbability and thickness swelling of WPCs as measured by soaking tests in 40 °C water. In the tests, greater increases in WA and TS were found up to 4 weeks. Lowest WA and TS were observed in the sample with 35.5 % WPG.

On the subject of use of acetylated wood, the mechanochemical processing was a promising technique for preparing WPC materials with improved dimensional stability. However, inhibitions of reducing mechanical properties of the WPCs are desirable.

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