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ORIGINAL ARTICLE

Preparation of acetylated wood meal and polypropylene composites I: acetylation of wood meal by mechanochemical processing and its characteristics

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Abstract Wood meals of Sugi (*Cryptomeria japonica* D.Don) passing 2.0 mm and retained on 1.0 mm mesh screens were milled along with acetic anhydride (AA) and pyridine as a catalyst in a high-speed vibration rod mill at ambient temperature. The weight percent gain (WPG) of the chemically modified wood was calculated based on the yield after washing with deionized water. The effects of amounts of AA and catalyst added, pulverization time, and saponification of the acetylated wood on WPG were examined. In addition, FT-IR analysis, and water vapor adsorption and desorption tests were performed as functions of the WPG. Increases in WPG, the acetyl contents of the acetylated wood after saponification, changes in the FT-IR spectra after pulverization, and the water vapor sorption isotherms showed that the one-step acetylation systematically modified the hydroxyl groups of the wood into acetyl groups. Up to 38 % WPG was obtained at 100 phr AA and 15 phr catalyst, and 120 min pulverization. Pulverization time and the amounts of AA and catalyst added to the wood meals could be adjusted to obtain acetylated wood meal with the desired WPG. These demonstrated that the mechanochemical acetylation is a method to prepare acetylated wood meals with high WPG at less reaction time and required AA addition.

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Introduction

Wood–plastic composites (WPCs) are used in many outdoor products. Due to encapsulation of the wood meals by the plastic, 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]. Moisture intrusion in WPCs affects the behavior and durability of the composites [2].

The use of chemically modified wood through processes such as acetylation can improve the dimensional stability and biological durability of WPCs. The transformation of the hydroxyl groups in the wood into acetyl groups decreases the water absorbability of the wood meals and increases compatibility between the meals and plastic [4]. Ibach et al. [2] reported that acetylating the wood–polyethylene components in WPCs (50 % wood content) reduced moisture sorption and related performance losses such as decay and flexural property loss in laboratory tests. Mass losses in injection-molded polypropylene composites (50 % wood content) during a terrestrial microcosm (TMC) test, performed according to an expanded version of the European test standard NEV 807, significantly decreased compared with that of unmodified wood [5]. Furthermore, the stiffness of composites (50 % wood content) prepared from polylacetate-polymer and acetylated wood was maintained or slightly reduced even after the decay tests [6].

Acetylation of wood typically is performed using both liquid and vapor systems at elevated temperatures using acetic anhydride (AA) with or without a catalyst [7]. Recently, Matsunaga et al. [8] reported a novel wood

acetylation process using a system involving supercritical carbon dioxide. A weight percent gain (WPG) of 24–28 % was achieved upon reaction for 24 h. For WPC production, wood meal with a particle size less than 300 μm is usually used. Therefore, if acetylated wood meal could be used instead, the above-mentioned acetylation systems would apply to unmodified wood meal, or wood chips acetylated by the systems could be ground until the required size is reached.

Yefanov et al. [9] reported an acetylation of wood meal using a vibration mill. In the study, wood meals approximately 0.5–0.75 mm in diameter and AA with ammonium sulfate were pulverized at 25 °C for 30–180 min, to obtain a WPG of 12–36 %. Zhang et al. [10] prepared surface-acetylated cellulose powder through pan-milling using AA without a catalyst and applied them as fillers to enhance the reinforcement of natural rubber. These acetylation systems were effective for preparing acetylated wood meal in one step. However, application of the acetylated wood meal for WPCs has not been studied.

In our study, acetylated wood meals are prepared through a mechanochemical technique using a vibration rod mill in the presence of AA and pyridine as a catalyst, and the resulting chemically modified wood meals are used as materials for WPC production.

In this paper, effects of amounts of AA and catalyst added, pulverization time, and saponification of the acetylated wood were examined. In addition, FT-IR analysis, and water vapor adsorption and desorption tests were performed as functions of the WPG. In the second part of this two-part paper, the mechanical properties in bending and tensile tests and water absorbability and swelling in 40 °C water of WPCs prepared from the acetylated wood meals will be 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 (amount of ethanol–benzene solubles (1:2 [v/v]) was 0.7 %). Special grade AA and pyridine were used as the reaction reagent and catalyst, respectively, for acetylation.

Acetylation using vibration rod mill

Acetylation of the wood meals was performed using a high-speed vibration rod mill (CMT, TI-100 type, Tokyo, Japan) equipped with two closed stainless-steel vessels (10 ml, CMT, Type H2, Tokyo, Japan). Oven-dried wood meal (5.0 g), AA (1.25–6.25 g), pyridine (0.025–0.938 g), and an A-type of rod (CMT, Tokyo, Japan) were placed into each vessel. The composition was based on parts per hundred of the wood meal (phr) in weight ratio (Table 1). The two vessels were then set on the mill and run for 5–180 min under mechanical pulverization. Liberated thermal energy inside the vessel was not controlled during the mechanochemical acetylation. After reaction, the treated wood meal was diluted with deionized water and filtered using a glass-fiber filter (Toyo, GA-100, pore size 1.0 μm). The wood meal retained on the filter was washed until the filtrate became neutral and then was dried to constant weight at 105 °C. The weight percentage gain (WPG) was calculated using Eq. 1:

$$\mathrm{WPG}\ (\%) = (W_a - W_s)/W_s \times 100 \quad (1)$$

where W_a is weight (g) of acetylated wood meal and W_s is weight (g) of the wood sample before acetylation.

It was possible that the WPG of the acetylated wood meals could increase due to abrasive substances between the rod and vessel. However, no difference was found in the ash content of acetylated wood meal after 120 min pulverization and the untreated wood meal; both had ash content less than 0.3 wt %.

Table 1 Composition of acetylation mixture (phr by weight)

No.	Wood meal	Acetic anhydride	Pyridine	Pyridine/acetic anhydride
1	100	50	0	0
2	100	50	0.5	0.01
3	100	50	5	0.10
4	100	50	7.5	0.15
5	100	25	3.75	0.15
6	100	40	6.0	0.15
7	100	75	11.25	0.15
8	100	100	15.0	0.15
9	100	110	16.5	0.15
10	100	125	18.75	0.15

FT-IR analysis

FT-IR spectra were obtained using a FT/IR-620 instrument (Jasco Corporation, Tokyo, Japan). The test specimens were dried at 105 °C and prepared using the KBr-disk method. Each spectrum was obtained with 4 cm^{-1} resolution at 60 times accumulation. Wood meal pulverized for 40 min without AA and catalyst was used as an unmodified wood meal control.

Saponification of acetylated wood meal

Acetyl content of the acetylated wood meals was determined by saponification of the samples. Modification of a previously published method was used [11]. Oven-dried wood meal (about 0.3 g) with 25 mL of 0.4 N KOH ethanol solution was left for 24 h at room temperature, and 25.5 mL of 0.4 N sulfuric acid was added. After acidification for 40 min, the mixture was titrated with 0.1 N NaOH to the equivalence point as indicated by a pH meter. The acetyl content was calculated using Eq. 2:

$$\text{Acetyl content (mol/g)} = (A - B) \times 0.1 \times N/W - C \quad (2)$$

where A is the volume (mL) of NaOH solution after acidification of acetylated wood meal, B is the volume (mL) of the blank solution, N is the normality of the NaOH solution, W is the weight (g) of acetylated wood meal, and C is the acetyl content (mol/g) of unmodified wood meal.

The WPG of the acetylated wood usually was calculated using Eq. 1. In addition, the acetyl content determined by saponification could also be used to calculate WPG (WPG_{sapo}) using Eq. 3:

$$WPG_{sapo}(\%) = \text{Acetyl content} \times 43 / 100 \quad (3)$$

Water vapor adsorption and desorption tests

Equilibrium moisture content (EMC) of the acetylated wood meals was measured over a range of relative humidities at 25 °C. The RHs were controlled by the use of saturated-salt solutions. Salts used were LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, NaBr, NaCl, KCl, and K_2SO_4, giving RHs of 11.3, 22.5, 32.8, 43.2, 57.6, 75.3, 84.2, and 97.3 %, respectively.

For adsorption tests, the acetylated wood meals were dried under vacuum at 60 °C for 48 h before the test. About 0.3 g of the sample was placed on a platform one of the saturated-salt solutions in a glass tube (100 mL) with a screw-top lid. Three specimens were tested for each condition. Three weeks were required that the mass changes of less than 0.2 mg before and after the measurements. In contrast, for desorption tests, samples reaching equilibrium were immediately moved to the glass tubes with a lower RH and run until the mass changes were less than 0.2 mg. EMC at various RHs were calculated using Eq. 4:

$$\text{EMC}\ (\%) = (W_e - W_{vd})/W_{vd} \times 100 \quad (4)$$

where W_e is the weight (g) of acetylated wood meal at equilibrium and W_{vd} is the weight (g) of vacuum-dried acetylated wood meal.

Particle size analysis of acetylated wood meal

Particle size distribution of acetylated and unmodified wood meals was performed by sieve analysis using three mesh size sieves: 106, 212, and 300 μm.

Results and discussion

Effect of catalyst amount on acetylation

To determine the reactivity of the wood meal, the time dependence of WPG was studied and the results are shown in Fig. 1. For the study, 50 phr of AA and 0–7.5 phr of catalyst were used. When wood meal was pulverized with AA only (control), WPG increased gradually after 20 min and reached 11.5 % at 80 min pulverization. The addition of 0.5 phr catalyst to AA resulted in significant increases in WPG compared with that at the same pulverization time without catalyst. Although further addition of catalyst increased WPG within 60 min, no differences were found in WPG values between 5.0 and 7.5 phr addition at the same pulverization time.

A maximum WPG of approximately 19 % was found after 40 min pulverization, when 5.0 and 7.5 phr of catalyst were used. The number of moles of AA used in this study was 0.0245 mol. If all of the acetyl groups replaced the hydrogen atoms of the hydroxyl groups of the wood, a value of 20.6 % WPG would be obtained. Therefore, the results of the acetylation behavior showing maximum and constant WPG demonstrate that most of the AA reacted with the hydroxyl groups of the wood.

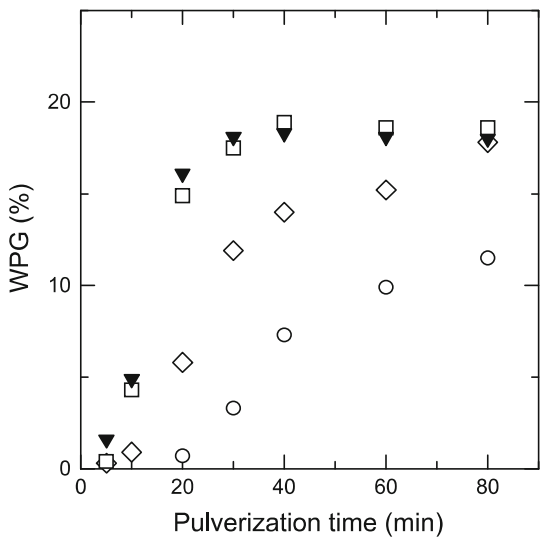

Fig. 1 Time-course of WPG changes during acetylation. Amount of catalyst (phr): *open circle* 0 (control), *open diamond* 0.5, *filled inverted triangle* 5.0, *open square* 7.5, wood meal/AA = 100/50 (phr)

Zhang et al. [10] reported that the size reduction of solid cellulose and activation of its specific surface area during mechanochemical milling are accompanied by chemical bond distorting and bond length extending due to the imposed stress, when the imposed stress is beyond the chemical bonding energy. In the mechanochemical processing shown in Fig. 1, the same size reduction and activation possibly took place and the activated functional groups would be replaced by the acetyl groups even at ambient temperature.

Effect of AA amount on acetylation

The time-dependency of WPG after acetylation using different AA amounts was examined (Fig. 2a). The ratio of catalyst to AA was kept constant at 15 wt %. When 25 phr of AA was used, WPG increased with pulverization time to produce a value of approximately 8 % WPG at 20 min. At times beyond 20 min, the WPG value remained constant up to 60 min. Further additions of AA increased WPG. When 40 phr AA and 20 min pulverization, and 75 phr AA and 80 min pulverization were used, about 15 and 29 % WPG were obtained, respectively. Even upon addition of 100 phr AA, about 38 % of WPG was achieved after 120 min. In general, the level of substitution of solid wood rarely exceeds 25 % WPG because of the limited diffusion of AA. However, mechanochemical acetylation in this study achieved a greater WPG value in less pulverization time. Yefanov et al. [9] have also achieved 36 % WPG using a vibration mill after 60 min pulverization. Therefore, a decrease in the crystal region of cellulose due to the imposed stress may be one of the reasons of the greater WPG value. However, further studies are necessary to understand the effects of mechanochemical pulverization on the crystal region of cellulose.

Two reaction rates for WPG were found (Fig. 2b). One rate was found up to 20 min pulverization ($Y = 0.11X^{1.65}$), and another from 30 to 120 min ($Y = 5.84X^{0.39}$). The reactivity of AA on cell wall components occurred in the order lignin > hemicellulose > cellulose [12]. Therefore, the former and latter reaction rates could be attributed to the acetylation of lignin and hemicellulose, and cellulose, respectively.

The composition of Sugi wood is 30.6 % lignin, 46.0 % cellulose, 16.5 % hexosan, and 6.9 % pentosan [13]. The number of moles of accessible hydroxyl groups can be calculated according to [14]:

$$(0.306 \times 1)/180 + (1 - 0.55)(0.460 \times 3)/162 + (0.165 \times 3)/162 + (0.069 \times 2)/132 = 0.00963,$$

(55 % of crystal region of cellulose was used).

A factor 0.00963 represents the number of mole of hydroxyl groups per gram of wood obtained. If the accessible hydroxyl groups could be replaced by acetyl groups, 40.5 % WPG would be obtained. On the other hand, theoretical values of WPG after acetylation under mechanochemical pulverization can be calculated from the numbers of moles of AA used.

Figure 3 shows the relation between the theoretical and experimental values of WPG. The measured value was the maximum WPG at each acetylation condition indicated in Fig. 2 and those obtained from further AA additions (data

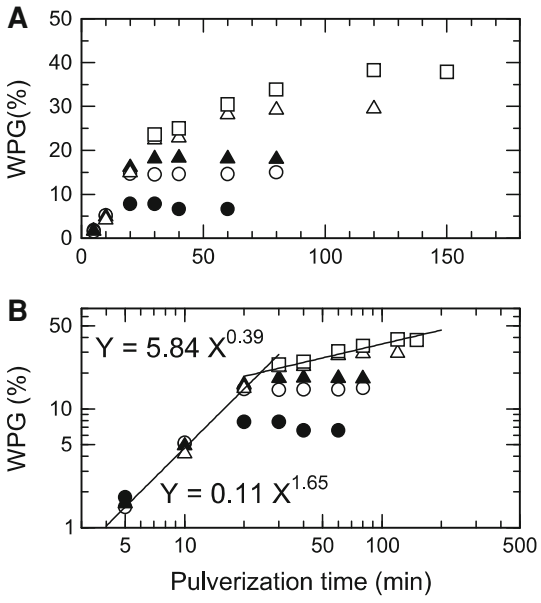

Fig. 2 **a** Time-course of WPG changes during acetylation; **b** double logarithmic plot of the same data. Amount of AA (phr): *filled circle* 25, *open circle* 40, *filled triangle* 50; *open triangle* 75, *open square* 100, pyridine/AA = 0.15

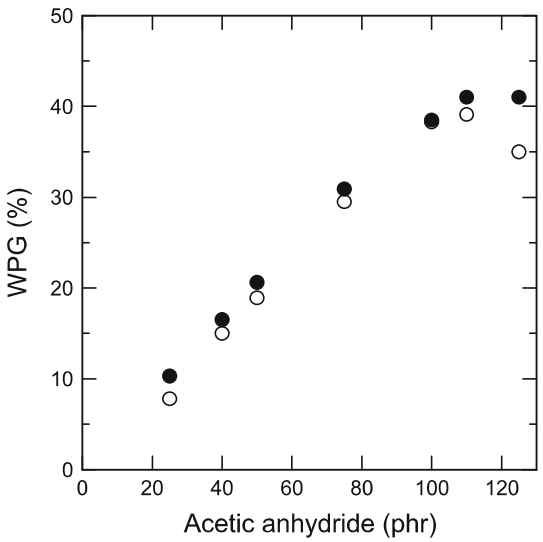

Fig. 3 Relation between theoretical WPG (*filled circle*) and measured maximum WPG (*open circle*) during acetylation

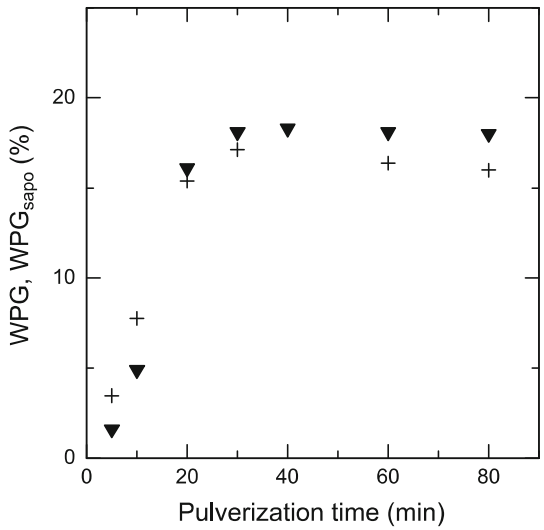

Fig. 4 Time-course of changes in WPG (*filled inverted triangle*) and WPG_{sapo} (+) during acetylation. WPG_{meso} was calculated from acetyl content after saponification

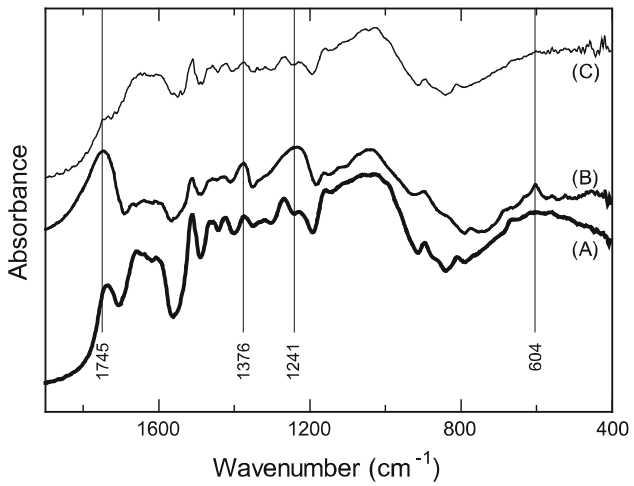

Fig. 5 FTIR spectra of **a** unmodified wood meal, **b** acetylated wood meal (37.9 % WPG), and **c** acetylated wood meal after saponification

not shown). The measured WPG values were in close agreement with the theoretical WPG values from 40 to 110 phr AA, indicating more than 90 % of the AA was consumed during the mechanochemical pulverization.

Saponification and FT-IR analysis of acetylated wood meals

The reaction between hydroxyl groups of wood and AA by mechanochemical pulverization was confirmed by analyzing the samples through saponification and FT-IR spectroscopy.

Figure 4 shows the change in WPG value with time during acetylation at a wood meal/acetic anhydride/pyridine ratio of 100/50/7.5 (phr). The WPG_{sapo} value was calculated using the acetyl content after saponification of the acetylated woods. As shown in Fig. 4, no large differences were found between the WPG and the WPG_{sapo} values at the same pulverization time ($WPG_{sapo} = 0.90WPG$, $R = 0.98$), indicating that a similar number of acetyl groups substituted during mechanochemical pulverization were recovered after saponification. In addition, FT-IR spectra of acetylated wood meal before and after saponification are shown in Fig. 5. Emergence of a strong absorption peak at 1745 cm^{-1} due to carbonyl stretching vibration was found in the spectrum of acetylated wood, compared with that of unmodified wood. Increases in the intensity of absorption bands at 604 cm^{-1} (CH_3), 1241 cm^{-1} (C–O), and 1376 cm^{-1} (CH_3) were also recognized [15]. Therefore, the disappearance or weakening of the peaks after saponification indirectly support the reaction between the hydroxyl groups of the wood and AA through mechanochemical pulverization.

Sieve analysis of acetylated wood meals

The average WPG values for acetylated wood meals used for water vapor adsorption and desorption tests were 7.0, 18.0, 28.0, and 35.5 %. These acetylated wood meals were prepared with AA amounts of 25, 50, 75, and 100 phr for 30, 40, 90, and 120 min pulverization, respectively (Fig. 2). Unmodified wood meal was pulverized for 40 min.

The particle sizes of acetylated and unmodified wood meals differed by pulverization time and/or AA amount used. Clumps of wood meal due to plasticization were found in acetylated wood meals with more than 28 % WPG when they were subjected to elevated temperatures and pressures due to frictional heat and impact strength. Therefore, acetylated wood meals with 28.0 and 35.5 % WPG were crushed for 10 s using a crush mill (WDL-1, Osaka Chemical Co. Ltd., Osaka) before test.

Figure 6 shows particle size distributions of acetylated and unmodified wood meals. The acetylated wood meals with less than 18 % WPG were mainly composed of particle sizes less than 300 μm. In constant, acetylated wood meals with WPG values greater than 28.0 % were more common at particle sizes larger than 300 μm even after the milling.

Adsorption and desorption isotherms for acetylated wood meals

Adsorption and desorption isotherms for acetylated and unmodified wood meals are shown in Fig. 7. For both of the isotherms, acetylated wood meal with 18.0 % WPG had a lower EMC value compared with that of unmodified wood meal, where approximately half of the EMC value

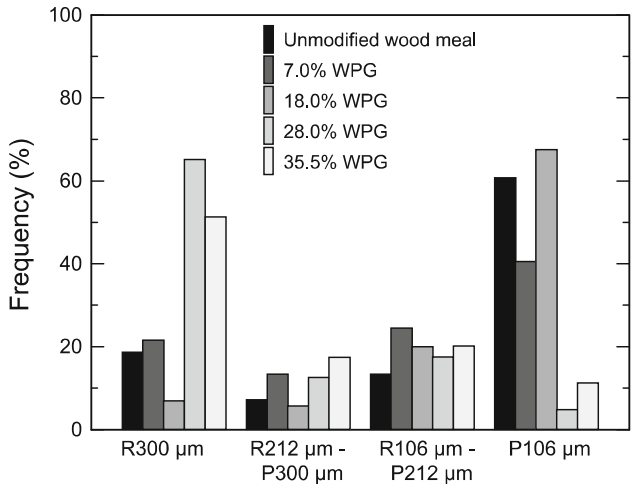

Fig. 6 Particle size distributions of unmodified and acetylated wood meals. *R* retained on a mesh size sieve, *P* passed through a mesh size sieve

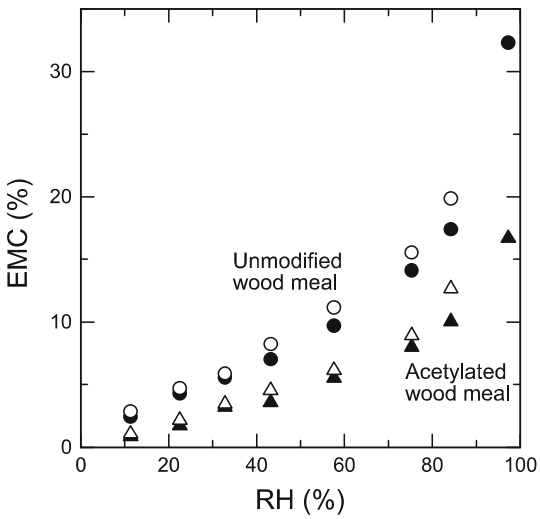

Fig. 7 Adsorption and desorption ithotherms for unmodified wood meal and acetylated wood meal (18.0 % WPG). adsorption: *filled circle* and *filled triangle*; desorption: *open circle* and *open triangle*

was obtained at the same RH. Next, effects of WPG on EMC are shown in Fig. 8. Increases in WPG decreased EMC at the same RH. Thus, the degree of substitution of the hydroxyl groups significantly affected the EMC of acetylated wood meals. For 35.5 % WPG, about 87 % of the accessible hydroxyl groups should be replaced by the acetyl groups. An EMC value of 8.4 % was obtained at 97.3 % RH. Therefore, even if the WPG of acetylated wood meal achieved 40.5 %, the theoretical value, some EMC percentages would be expected at higher RH values. Rowell et al. [16] reported EMC values of acetylated pine and aspen at several levels of acetylation (6.0–20.4 % WPG) and three levels of RH (30, 65 and 90 %) at 27 °C. Although the equilibrium temperature was different, the

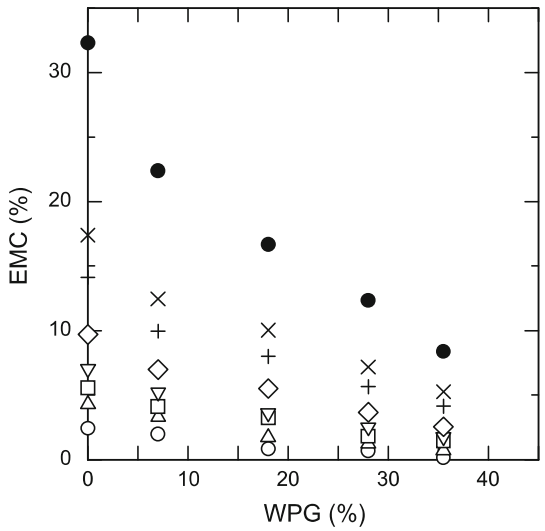

Fig. 8 EMC of unmodified wood meal and acetylated wood meals at different WPG during adsorption testing. RH: *open circle* 11.3 %, *open triangle* 22.5 %, *open square* 32.8 %, *open inverted triangle* 43.2 %, *open diamond* 57.6 %, *plus symbol* 75.3 %, *multi symbol* 84.2 %, *filled circle* 97.3 %

results reported here showed similar or lower EMC levels compared to the literature.

Conclusions

Acetylated wood meals were prepared successfully by mechanochemical processing using a high-speed vibration rod mill. Pulverization time and the amounts of AA and catalyst added to the unmodified wood meals could be adjusted to obtain acetylated wood meal with the desired WPG. In this study, up to 38 % WPG was obtained at 100 phr AA and 15 phr catalyst, and 120 min pulverization. Modification of the hydroxyl groups of the wood to acetyl groups was confirmed by the acetyl content of the acetylated wood meals after saponification, by changes in the FT-IR spectra before and after pulverization, and by the water vapor sorption isotherms.

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