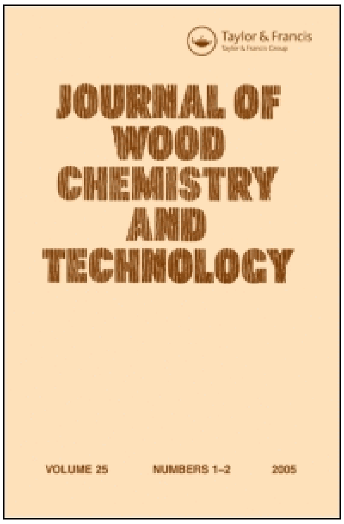

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Properties of Colloidal Silica-Fixed and Propionylated Wood Composites (I): Preparation and Dimensional Stability of the Composites

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Abstract: Colloidal silica-fixed and propionylated dual-treated wood (CSPW) composites were prepared and their dimensional stability evaluated. The results indicated that: (1) colloidal silica only–treated wood composites had minimal dimensional stability improvement, and they could be propionylated similarly to untreated wood specimens and (2) CSPW composites had a high antiswelling efficiency (ASE) during liquid water or moisture vapor absorption relative to propionylated only–treated wood, and a lower moisture excluding efficiency (MEE) during the moisture vapor absorption than propionylated wood.

Keywords: Colloidal silica, CSPW composite, dimensional stability

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INTRODUCTION

Chemical modification of the renewable natural raw material wood is an effective method for improving its dimensional stability, decay resistance, and other properties, providing new opportunities for wood to compete with synthetic materials, metals, and inorganic building materials. Acetylation of wood gives good dimensional stability and durability, and thus has been extensively studied by many researchers[1–7] who found that acetylated wood retained almost all the inherent advantages of wood. Surprisingly, the propionylation of wood has been the subject of only a few studies.[8–10]

Our previous studies on uncatalyzed propionylation and acetylation of wood established that propionylation using propionic anhydride at high temperature can give much greater dimensional stability than acetylation using acetic anhydride at the same temperature.[10]

Another wood modification process is the combination of wood and inorganic substances to enhance the wood properties, particularly the flame-resistance and decay-resistance.[11–17] Silicate compounds are promising chemical agents for wood treatment because they are cheap and environmentally benign.[18,19] In previous studies we found that the impregnation and fixation of water glass in wood, to make silicate compound–wood composites, negatively affected the dimensional stability.[20,21] Recently, a study reported that silicic acid compounds impregnated in wood as colloidal silica, could partially stabilize wood and were non-leachable.[19] It was also found that the wood–silica composites, prepared using a colloidal silica-boric acid system, showed good decay, termite, and fire-resistance properties.[22–24]

Surprisingly, little work has been done on propionylated wood, especially propionylation of wood–inorganic substance composites. Colloidal silica-fixed and propionylated dual-treated wood (CSPW) composites were prepared, and their dimensional stability, flame resistance, and decay resistance were examined. In this article we report on the results of the study of the dimensional stability of the CSPW composites.

MATERIALS AND METHODS

Wood Specimens

Sapwoods of sugi (*Cryptomeria japonica* D. Don) with a size of 30 (R) × 30 (T) × 5 (L) mm, were used for producing the CSPW composites. The specimens were extracted with ethanol-benzene (1 : 2, vol) for 12 h using a Soxhlet apparatus, and with acetone for another 12 h. The extracted specimens were then dried at 105°C for 24 h. The oven-dried weights and sizes of specimens were subsequently measured. Five specimens were used for each reaction condition.

Chemical Agents

Colloidal silica (Snowtex 30, 30.4% silicic acid anhydride) was of industrial grade from Nissan Chemical Industries, Ltd., Japan. Propionic anhydride [$(CH_3CH_2CO)_2O$] and all the other chemicals used were of chemical grade from Wako Pure Chemical Industries, Ltd., Japan.

Preparation of Colloidal Silica-Fixed Wood (CSW) Composites

The specimens were immersed in colloidal silica suspensions of different concentrations that were neutralized with 5% aqueous acetic acid to bring the pH to 7.0–7.2. Each specimen container was placed in a vacuum oven that was evacuated for 30 min and then brought back to atmospheric pressure for 12 h. After impregnation, the specimens were oven-dried at 105°C for 24 h, and the weights and sizes of the specimens were subsequently measured.

Preparation of Colloidal Silica-Fixed and Propionylated Wood (CSPW) Composites

The colloidal silica-fixed wood (CSW) composites were impregnated with propionic anhydride at reduced pressure for 30 min and then at atmospheric pressure for 24 h. The impregnated specimens were wrapped with polyvinylidene chloride film and aluminum foil and then placed in an oven to be propionylated at 120°C for different times (1, 2, 4, and 8 h). After extraction with acetone for 12 h in a Soxhlet apparatus, the specimens were oven-dried at 105°C for 24 h, and the weights and sizes were then measured and their weight percent gain (WPG) was determined.

Evaluation of the Modified Wood Composites

Weight Percent Gain

The weight percent gains of propionylation (WPG_p) in colloidal silica-fixed and propionylated wood (CSPW) composites were calculated by Equation (1):

$$WPG_p = WPG_t - WPG_{csi} \qquad (1)$$

where WPG_t is the total weight percent gain of the colloidal silica-fixed and propionylated wood (CSPW) composites, and WPG_{csi} is the weight percent gain of colloidal silica gel in the composite.

Liquid Water Absorption and Leaching Test

The specimens were immersed in distilled water in a vacuum oven, and the pressure was reduced for 30 min and then returned to atmospheric pressure for 24 h at room temperature. After this treatment, the dimensions of the water-swollen specimens were measured. The specimens were then oven-dried at 105°C for 24 h, and the dimensions were again measured. From the changes in volumetric dimensions, the antiswelling efficiency (ASE_w) was calculated according to Equation (2):

$$ASE = \frac{Su - St}{Su} \times 100 \tag{2}$$

where ASE is the antiswelling efficiency, Su is the untreated volumetric swelling coefficient, and St is the treated volumetric swelling coefficient.

The volumetric swelling coefficient was calculated by Equation (3):

$$S = \frac{V1 - V0}{V0} \times 100 \tag{3}$$

where S is the volumetric swelling coefficient, V1 is the volume of wood after liquid water absorption, and V0 is the volume of oven-dried wood.

From the changes in weights, the reduction in the water absorptivity (RWA) was calculated from Equation (4):

$$RWA = \frac{Nu - Nt}{Nu} \times 100 \tag{4}$$

where RWA is the reduction in the liquid water absorptivity, Nu is the water regain of the untreated wood, and Nt is the water regain of the treated wood.

The water regain was calculated by Equation (5):

$$N = \frac{W1 - W0}{W0} \times 100 \tag{5}$$

where N is the water regain, W1 is the weight of the wood after liquid water absorption, and W0 is the weight of the oven-dried wood.

In order to examine the effect of adding silica to wood on the RWA, the Nt in Equation (4) was calculated from Equation (6), and the RWA′ was calculated according to Equation (4):

$$Nt = \frac{W1 - Wt}{W0} \times 100 \tag{6}$$

where Nt is the water regain of the treated specimen, W1 is the weight of the treated specimen after liquid water absorption, Wt is the weight of the oven-dried treated specimen, and W0 is the weight of the oven-dried specimen before treatment.

For testing the leaching resistance of WPG_t and investigating the change of ASE_w, the specimens were subjected to the water-swelling and oven-drying procedure three more times.

Moisture Vapor Absorption Test

The specimens were placed in a desiccator in which the relative humidity (about 75%) was controlled by a saturated sodium chloride solution at about 23°C for 4 weeks. The weights and dimensions of the specimens were measured and the moisture excluding efficiency (MEE) and the antiswelling efficiency of the specimens during the moisture absorption (ASE_m) were calculated using Equations (2) and (7).

$$\mathrm{MEE} = \frac{\mathrm{Mu} - \mathrm{Mt}}{\mathrm{Mu}} \times 100 \tag{7}$$

where MEE is the moisture excluding efficiency, Mu is the untreated moisture regain, and Mt is the treated moisture regain.

The moisture regain was calculated by Equation (8):

$$\mathrm{M} = \frac{\mathrm{W1} - \mathrm{W0}}{\mathrm{W0}} \times 100 \tag{8}$$

where M is the moisture regain, W1 is the weight of wood after moisture vapor absorption, and W0 is the weight of oven-dried wood.

In order to examine the effect of adding silica to wood on MEE, the Mt in Equation (7) was calculated from Equation (9), and the MEE′ was calculated according to Equation (7):

$$\mathrm{Mt} = \frac{\mathrm{W1} - \mathrm{Wt}}{\mathrm{W0}} \times 100 \tag{9}$$

where Mt is the moisture regain of the treated specimen, W1 is the weight of the treated specimen after moisture vapor absorption, Wt is the weight of the oven-dried treated specimen, and W0 is the weight of the oven-dried specimen before treatment.

RESULTS AND DISCUSSION

Dimensional Stability of Colloidal Silica-Fixed Wood (CSW) Composites in both Liquid Water and Moisture Vapor Absorption

Figure 1 shows the effects of the weight percent gain of the colloidal silica fixation (WPG_{csi}) in the colloidal silica-fixed wood (CSW) composites on antiswelling efficiency (ASE_w) and reduction in water absorptivity (RWA) during the liquid water absorption, antiswelling efficiency (ASE_m), and

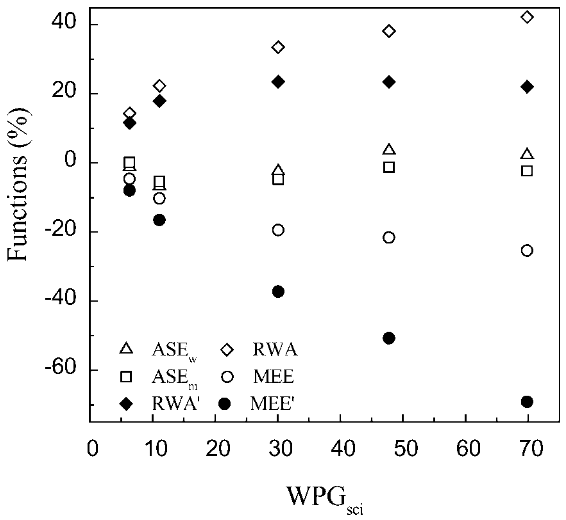

Figure 1. Dimensional stability of colloidal silica-fixed wood (CSW) composites during liquid water and moisture vapor exposure.

moisture excluding efficiency (MEE) during the moisture vapor absorption of CSW composites.

As shown in Figure 1, the values of both the ASE_w and ASE_m of the CSW composites were approximate zero (less than 10%) and had essentially no dependence on the WPG_{csi} of the composites. This suggested that colloidal silica fixing in wood gave little dimensional stability. The RWA and RWA′ of the CSW composites showed positive values due to the silica gel reducing the opening space in wood and keeping wood from absorbing much more liquid water. The MEE and MEE′ showed negative values and decreased as the WPG_{csi} of CSW composites increased because of the high hygroscopicity of silica gels.

Dimensional Stability of Dual-Treated CSPW Composites in Water Absorption

Weight Percent Gain of CSPW Composites

Figure 2 shows the relationship between the reaction time and the weight percent gains on propionylation of the CSPW composites and the propionylated-only treated woods. The results indicated that the WPG on propionylation in the CSPW composites were similar to those in the propionylated woods, which showed rather high values (more than 18%) even at a 120°C–2 h reaction and increased with an increase in propionylation time.

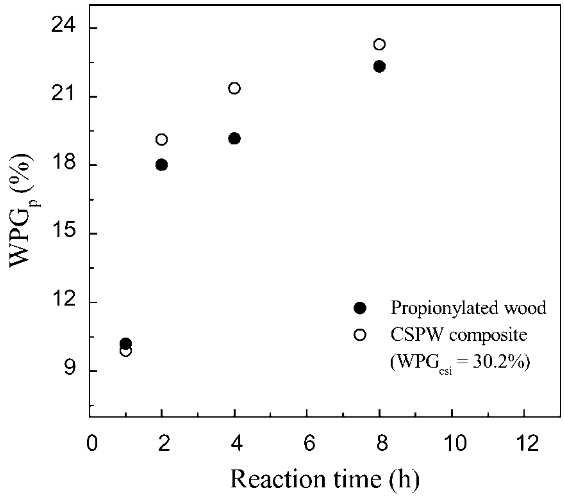

Figure 2. The relationship between reaction time and weight percent gain on propionylation (WPG_p) of the CSPW composite and the wood.

Nevertheless, the CSPW composites showed a little higher WPG value of propionylation than the propionylated woods. This is probably due to sodium oxide in the colloidal silica solution that can react with propionic acid, the resultant sodium propionate being an effective catalyst to wood propionylation.[25]

Table 1 shows the effect of the weight percent gain of colloidal silica (WPG_{csi}) on the weight percent gain of propionylation (WPG_p) in the CSPW composites. The composites fixed with colloidal silica could get a little higher weight gain of propionylation than those free of colloidal silica gels ($WPG_{csi} = 0$) because of the reason mentioned earlier; sodium propionate can catalyze wood propionylation. But there were little obvious differences in WPG_ps with the change of WPG_{csi} in CSPW composite even for the reaction times of 2 h and 8 h.

From the experimental results, we can conclude that the woods fixed by silica gels prepared from colloidal silica suspension can propionylate much

Table 1. The effect of the weight percent gain of colloidal silica (WPG_{csi}) on the weight percent gain on propionylation (WPG_p) of the CSPW composites

WPG_{csi} (%)	0.00	6.34	11.14	30.06	47.80	69.88
WPG_p (%) (120°C, 2 h)	18.01	19.32	19.01	19.13	19.17	18.46
WPG_p (%) (120°C, 8 h)	22.32	22.67	22.67	23.29	22.61	23.32

the same as the untreated controls. In addition, the silica gels have no negative effect on the propionylation of the wood and, rather, may have a minor promotional effect, or that some silica hydroxyl groups were propionylated.

Antiswelling Efficiency of CSPW Composites

In previous studies, it was established that impregnation and fixation of water glass in wood or propionylated wood composites showed a negative effect on the dimensional stability of wood.[20,21] However, CSPW composites showed antiswelling efficiency (ASE_w) values approximately equal to the propionylated woods ($WPG_{csi} = 0$) and, rather, a minimal higher value. This fact indicated that colloidal silica gave wood a slight dimensional stability. This result is consistent with Yamaguchi and Furuno's studies.[18,19,22]

Generally, high treatment temperature affects the dimensional stability of wood. In our experiments, however, we found a negligible effect of treatment temperature on dimensional stability.

Although colloidal silica treatment provided little dimensional stabilization, a subsequent propionylation treatment endowed silica-fixed wood with striking ASE_w values.

Resistance to Water Leaching of CSPW Composites

For testing water leaching resistance of CSPW composites, the treated specimens were subjected to the water-swelling and oven-drying procedure 4 times. The CSPW composites showed little decrease in WPG_ts and ASE_ws after the 4 wet-dry cycles. This suggests that not only the propionyl groups but also the silica gels had good resistance to water leaching. This coincides with Yamaguchi and Furuno's results, that the silica gels were stable and insoluble.[18,22]

Antiswelling Efficiency (ASE_m) during Vapor Moisture Absorption and Moisture Excluding Efficiency (MEE) of CSPW Composites

The ASE_m values showed a similar trend to the ASE_w values of the CSPW composites, and colloidal silica showed a slight positive effect on the ASE_m values (Figure 1).

The effects of the weight percent gain of colloidal silica fixation (WPG_{csi}) on the moisture excluding efficiency (MEE) of the CSPW composites during the moisture absorption are shown in Figure 3. The MEE values of the CSPW composites decreased with increasing WPG_{csi} because of the high hygroscopicity of colloidal silica gels. Probably when CSPW composites are used as an indoor material such as floorboard or other interior decoration products, this will be advantageous for conditioning the relative humidity of the surrounding

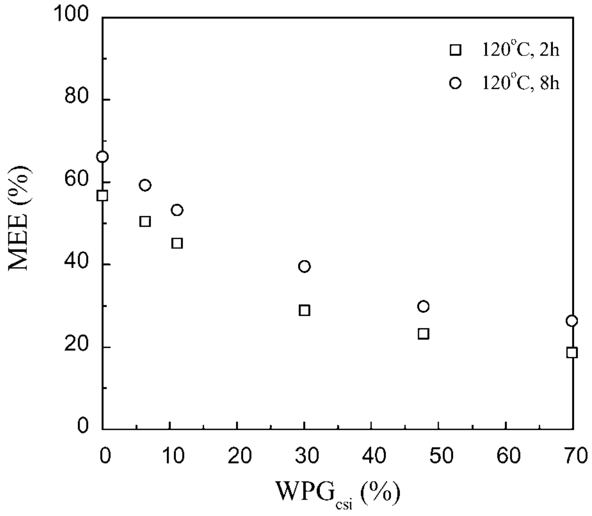

Figure 3. The effect of the weight percent gain on colloidal silica fixation (WPG$_{csi}$) on the moisture excluding efficiency (MEE) of CSPW composites during the moisture absorption.

atmosphere by absorbing or releasing the moisture in a manner similar to untreated wood while keeping the wood dimensionally stabile.

CONCLUSIONS

The colloidal silica–fixed wood composites could be propionylated to the same extent as the untreated wood. The values of ASE$_w$ and ASE$_m$of the CSPW composite were very high and close to those of the propionylated-only treated wood, indicating great dimensional stability of the treated wood, and changed only slightly with increasing WPG$_{csi}$. On the other hand, the CSPW composites showed lower MEE values than the propionylated woods and the MEE decreased with increasing WPG$_{csi}$, showing a better moisture absorption capability.

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