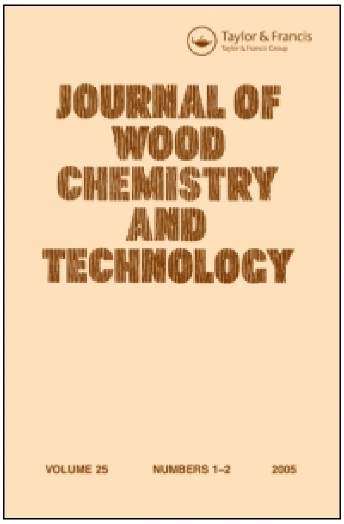

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Dimensional Stability and Flame Resistance of Silicate-Acetylated and -Propionylated Wood Composites

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DIMENSIONAL STABILITY AND FLAME RESISTANCE OF SILICATE-ACETYLATED AND -PROPIONYLATED WOOD COMPOSITES

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ABSTRACT

Silicate-acetylated wood (SAW) and silicate-propionylated wood (SPW) composites were prepared, and the dimensional stability and flame resistance of these composites were evaluated. The silicate gels had insignificant effects on the rate of acetylation or propionylation of wood. In the presence of silicate gels, the SAW and SPW composites showed slightly lower anti-swelling efficiency (ASE) during water or moisture absorption and a lower moisture excluding efficiency (MEE) than the corresponding acetylated wood and propionylated wood, but the SAW and SPW composites still retained fairly good dimensional stability. The oxygen indices (OIs) of the SAW and SPW composites were higher than those of untreated wood specimens and increased with an increase in the weight percent gains ($\mathrm{WPG_{si}}$s) of silicate gel fixation. The silicate gel fixation endowed the composites with flame resistance.

INTRODUCTION

Many treatments have been developed that improve the properties of wood and its usefulness as well as prolong its useful life. Acetylation of wood has been extensively studied by many researchers,[1-6] while the propionylation of wood has only been the subject of limited studies. It has been established that the acetylated wood, which retains the inherent advantages of wood, exhibits improved dimensional stability and biodegradation resistance.

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Methods of combination of wood and inorganic substances have been developed to enhance the properties, particularly the flame-resistance of wood.[7-13] Silicate compounds, which are cheap and negligibly harmful to the environment, are suggested to be promising chemical agents for impregnation and fixation in wood by forming gels.[14-15] But generally, wood-inorganic composites do not exhibit significant dimensional stability.[16]

In this study, silicate-acetylated wood (SAW) and silicate-propionylated wood (SPW) composites were prepared by combining acetylation or propionylation with silicate fixation in wood. The dimensional stability and the flame-resistance of the wood composites were then evaluated to assess the level of improvement.

MATERIALS AND METHODS

Wood Specimens

Sapwood of hinoki (*Chamaecyparis obtusa* Endl.) was used for producing the wood-based composites. The sizes of specimens were 30 (R) × 30 (T) × 5 (L) mm and 3.0 (R) × 6.5 (T) × 10 (L) mm. The specimens were extracted with a mixture of ethanol and benzene (1:2, vol) for 12h using a Soxhlet apparatus, and with acetone for another 12h. The extracted wood specimens were then dried at 105°C for 24h, weighed and measured. Three specimens were used for each reaction condition.

Chemical Agents

Sodium silicate (SiO_2/Na_2O=2.06~2.31), propionic anhydride [$(CH_3CH_2CO)_2O$], acetic anhydride [$(CH_3CO)_2O$], and all the other chemicals chemical grade (Wako Pure Chemical Industries, Ltd.).

Preparation of Wood-Silicate Composite

The water-saturated specimens were immersed in aqueous sodium silicate solutions of different concentrations and placed in a desiccator. The desiccator was evacuated for 30 min and then brought back to atmospheric pressure. The specimens were held in the desiccator for 12 h, immersed in 5% aqueous acetic acid for 24 h, leached in flowing water for 48 h, and oven-dried at 105°C for 24 h. The weights and sizes of the specimens were then determined.

Preparation of Silicate-Acetylated Wood (SAW) and Silicate-Propionylated Wood (SPW) Composites

The wood-silicate composites were impregnated with acetic anhydride (or propionic anhydride) at reduced pressure for 30 min. and then at atmospheric pressure for 24 h. The impregnated specimens were then wrapped with polyvinylidene chloride film and aluminum foil and placed in an oven to be acetylated (or propionylated) at 120°C for different times (1-8 h). After extraction with acetone for 12 h in a Soxhlet apparatus, the specimens were oven-dried at 105°C for 24 h, and their weights and sizes were measured.

Evaluation of Modified Wood Composites

Weight percent gain and bulking coefficient

The weight percent gains of the silicate-acetylated or propionylated wood composites (WPG_a or WPG_p) were calculated by the following formulas:

$$WPG_a = WPG_t - WPG_{si}$$

or

$$WPG_p = WPG_t - WPG_{si}$$

where WPG_a or WPG_p are the weight percent gain of the silicate-acetylated or silicate-propionylated wood composite from acetylation or propionylation, respectively; WPG_t is the total weight percent gain of silicate-acetylated or propionylated wood composite; and WPG_{si} is the weight percent gain of the corresponding wood-silicate composite.

Water Absorption and Leaching Test

The specimens were immersed in distilled water in a desiccator. The desiccator was evacuated 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) and antishrink efficiency (ASE_d) were calculated. In order to test the stability of the ASE_d and the leaching resistance of WPG_t, the specimens were subjected to the water-swelling and oven-drying procedure three more times.

Moisture Absorption Test

The specimens were placed in a desiccator containing saturated sodium chloride (75% relative humidity) at 23°C for 4 weeks. The weights and sizes of the specimens were measured and the moisture excluding efficiency (MEE) and the antiswelling efficiency (ASE_m) of specimens during moisture absorption were calculated.

Oxygen Index Test

The oxygen index method was applied to test the flame resistance of the composite specimens, according to the Japanese Industrial Standard JIS K 7201. The oven-dried specimens [3.0 (R) × 6.5 (T) × 10 (L) mm] were burned in an oxygen-nitrogen gas mixture, where the volume percent ratio was controlled. The critical oxygen index (OI) was the minimum volume percent concentration of oxygen that would just support the flaming combustion of the specimens.

RESULTS AND DISCUSSION

Dimensional Stability in Water Absorption

Weight Percent Gain

Figure 1 shows the relationship between the reaction time and weight

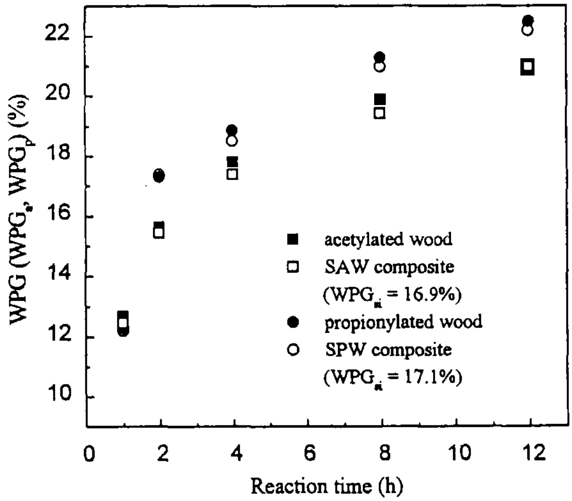

FIGURE 1. The relationship between reaction time and weight percent gain of silicate-acetylated or propionylated wood composite from acetylation or propionylation (WPG_a or WPG_p).

percent gain of silicate-impregnated wood for reaction with acetic (WPG_a) or propionic (WPG_p) anhydride. It is evident that the WPG_a and WPG_p increased with reaction time, and acquired values close to those of specimens free of silicate compounds.

Figure 2 shows the effect of weight percent gain of silicate gels (WPG_{si}) on the weight percent gain following acetylation or propionylation (WPG_a or WPG_p) in silicate-acetylated or propionylated wood (SAW or SPW) composite. There were no very obvious differences manifested in WPG_as and in WPG_ps with the change of WPG_{si} of SAW of SPW composite as compared with WPGs of the specimens free of silicate compounds (WPG_{si}=0%).

From Fig. 1 and Fig. 2, it is evident that the presence of silicate gels in wood has little or no effect on the rates of acetylation or propionylation of wood.

Antiswelling Efficiency

The relationship between the weight percent gain of the wood-silicate

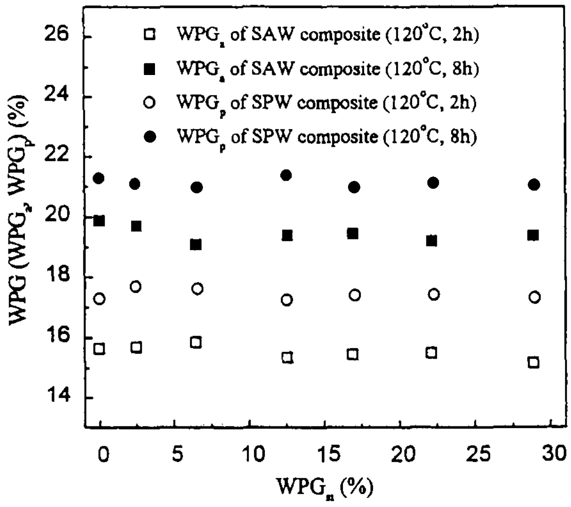

FIGURE 2. The effect of weight percent gain of silicate gels (WPG_{si}) on weight percent gain from acetylation of propionylation (WPG_a or WPG_p) in silicate-acetylated or propionylated wood (SWA or SWP) composite.

composites (WPG_{si}) and the antiswelling efficiency (ASE_w) of SAW and SPW composites during water absorption is shown in Fig. 3.

The ASE_ws of SAW and SPW composites were lower than those of the corresponding acetylated wood and propionylated wood specimens (WPG_{si}=0%), and they decreased slightly in proportion to the loading of silicate gels. The ASE_ws of SAW and SPW composites indicate that the silicate gels mainly exist in the cell lumina. Thus, the silicate gels would not be expected to contribute to the dimensional stabilization of the composites. It was thought[12] that shrinkage of the silicate gels in SAW or SPW composites resulted when the specimens was dried, resulting in lower values of ASE_ws of SAW of SPW composite in comparison with the corresponding acetylated wood or propionylated wood. Although the ASE_ws of both the SAW and SPW composites decreased with an increase in the loading of silicate gels, the decrease in the ASE_w was quite small and the composites still retained a high level of ASE_w values, as is obvious from Fig. 3.

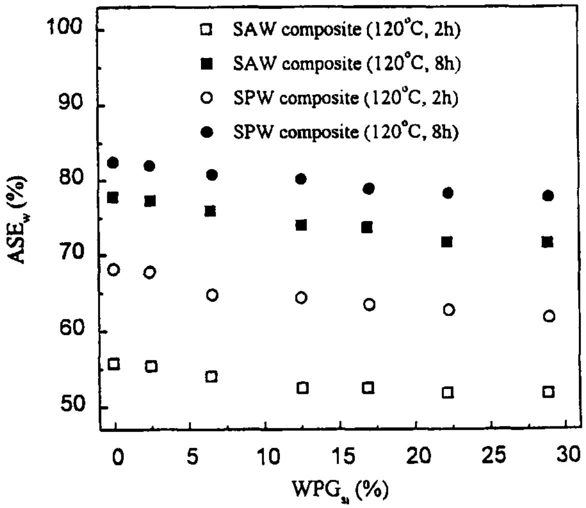

FIGURE 3. The relationship between weight percent gain of wood-silicate composite (WPG$_{si}$) and antiswelling efficiency (ASE$_w$) of SWA and SWP composites during water absorption.

Resistance to Water Leaching of SAW and SPW Composites

The changes in the anti-shrink efficiency (ASE$_d$) and the total weight percent gain (WPG$_t$) in the SAW and SPW composites with the wet-dry cycles are shown in Fig. 4. The WPG$_t$s of the SAW and SPW composites decreased only slightly after the leaching test of four wet-dry cycles. Also, there were little or no changes of ASE$_d$s in the SAW and SPW composites after the leaching test. This suggests that not only the acetylated or propionylated wood, where the acetyl (propionyl) groups were bonded to wood components, had a high resistance to leaching, but also that the silicate gels existing in wood possessed a high resistance to leaching by water.

Antiswelling Efficiency (ASE$_m$) and Moisture Excluding Efficiency (MEE)

The relationship between the weight percent gain of the wood-silicate composite (WPG$_{si}$) and the antiswelling efficiency (ASE$_m$) of the SAW and SPW

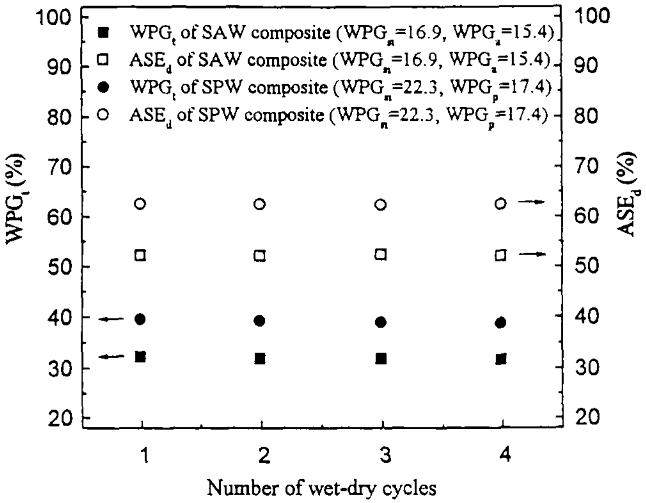

FIGURE 4. The changes of antishrink efficiency (ASE_d) and the total weight percent gain (WPG_t) in the SWA and SWP composites with the wet-dry cycles.

composites toward moisture absorption is shown in Fig. 5. The trend of the ASE_ms , a very slight decrease with increasing WPG_{si}, was similar to that of the ASE_ws of the SAW and SPW composites (Fig. 3), probably for the same reason.

Figure 6 shows the relationship between the weight percent gain of wood-silicate composite (WPG_{si}) and the moisture excluding efficiency (MEE) of SAW and SPW composites during moisture absorption. It is evident that the MEE decreased with increasing WPG_{si} because of the high hygroscopicity of the silicate gels. Probably when SAW and SPW composites are used for construction, it will be advantageous to control the relative humidity of the surrounding environment, in the same way as for untreated wood to maintain dimensional stability.

Oxygen Index

The oxygen index (OI) test with the advantages of good repeatability and very small specimen size is a good test method for evaluating the effectiveness of

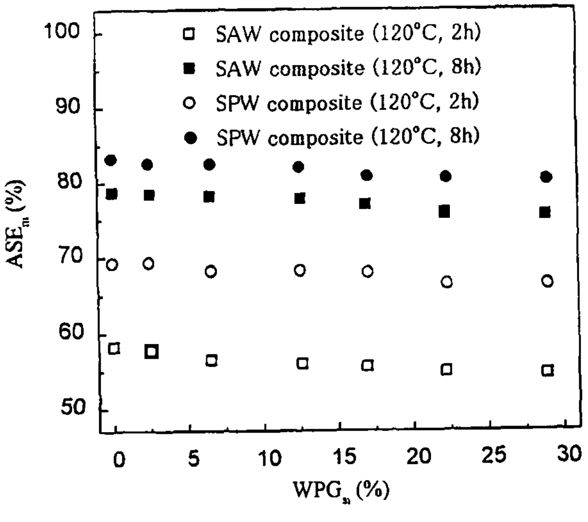

FIGURE 5. The relationship between weight percent gain of wood-silicate composite (WPG$_{si}$) and the antiswelling efficiency (ASE$_m$) of SWA and SWP composites during moisture absorption.

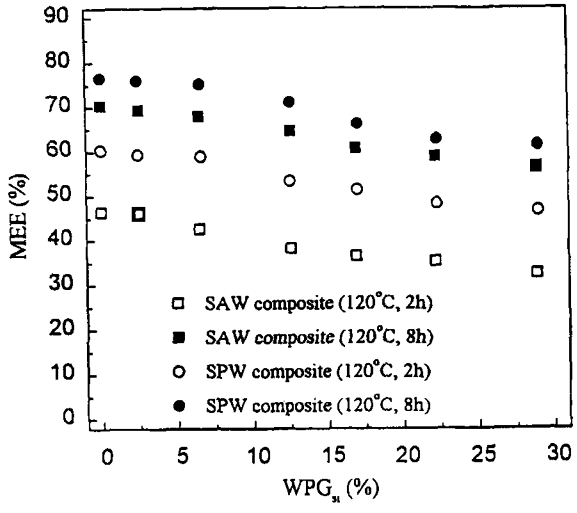

FIGURE 6. The relationship between weight percent gain of wood-silicate composite (WPG$_{si}$) and the moisture excluding efficiency (MEE) of SWA and SWP composites during moisture absorption.

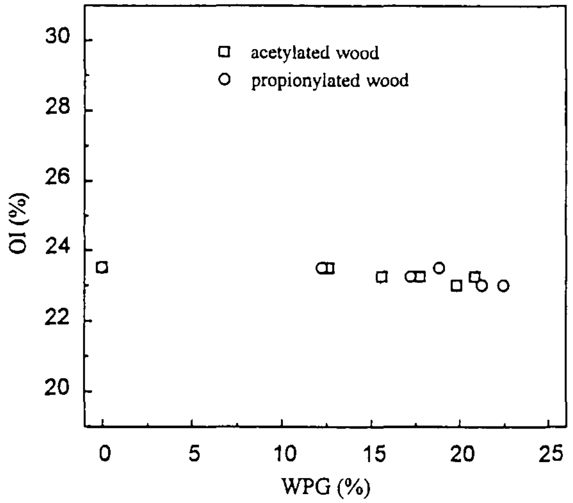

FIGURE 7. The relationships between oxygen index (OI) and WPG of acetylated wood and propionylated wood.

fire retardants on materials. It was originally developed for polymers, but it can be also used for wood, in particular fire retardant-treated wood.[17-19] The relationships between the oxygen index (OI) and WPG of acetylated and propionylated wood are shown in Fig. 7. The acetylated wood and the propionylated wood showed little or not change of OI compared with the untreated specimens. This indicates that wood is not endowed with flame resistance through the agency of acetylation or propionylation.

Fig. 8 shows the effect of the weight percent gain of silicate gel (WPG_{si}) on the oxygen index (OI) of SAW and SPW composites. The SAW and SPW composites showed a fairly good flame resistance, and the OI increased with an increase in WPG_{si}. This shows clearly that the silicate gel can effectively reduce the combustibility of wood, thus acting as a fire retardant.

The mechanism of silicate gel as a fire retardant may be explained by a barrier theory.[20] The fire-retardant chemicals prevent the escape of volatile

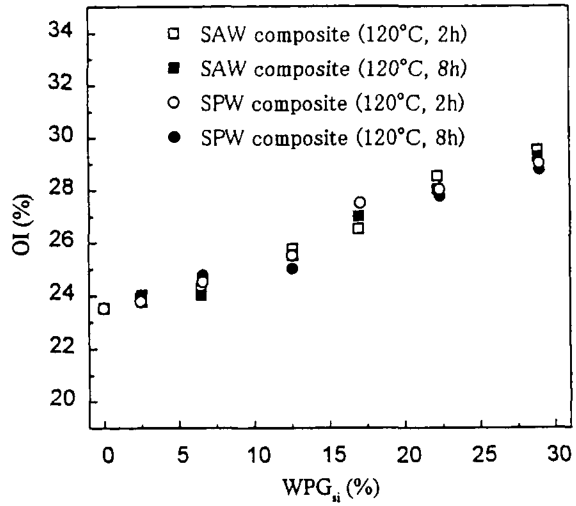

FIGURE 8. The effect of weight percent gain of silicate gels (WPG$_{si}$) on oxygen index (OI) of SWA and SWP composites.

products by forming a glassy barrier. At the same time the barrier also prevents oxygen from reaching the substrate and insulates the wood surface from high temperatures.

CONCLUSIONS

Silicate-acetylated wood (SAW) and the silicate-propionylated wood (SPW) composites could be prepared by combining the fixation of silicate gels with acetylation or propionylation of the wood.

Although the of ASE$_w$, ASE$_m$, and MEE values of the SAW (or SPW) composite were slightly less than those of the corresponding acetylated or propionylated wood and decreased with increasing silicate gel content, the SAW and SPW composites still retained fairly good dimensional stability. The OI of these composites increased with increasing silicate gel content, indicating a reduction in the flammability of the wood.

ABBREVIATIONS

SAW: silicate-acetylated wood

SPW: silicate-propionylated wood

$\mathrm{ASE_w}$: antiswelling efficiency during water absorption

$\mathrm{ASE_m}$: antiswelling efficiency during moisture absorption

$\mathrm{ASE_d}$: antishrink efficiency

MEE: moisture excluding efficiency

OI: oxygen index

$\mathrm{WPG_a}$: weight percent gain of silicate-acetylated wood composite from acetylation

$\mathrm{WPG_p}$: weight percent gain of silicate-propionylated wood composite from propionylation

$\mathrm{WPG_{si}}$: weight percent gain of silicate gel fixation in wood composite

$\mathrm{WPG_t}$: total weight percent gain of silicate-acetylated or propionylated wood composite

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