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LEACHABILITY OF BORON FROM TRIMETHYL BORATE (TMB)/POPLAR WOOD COMPOSITES PREPARED BY SOL-GEL PROCESS

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ABSTRACT

To develop a novel wood preservative technique, trimethyl borate (TMB) was used with the sol-gel process to modify poplar wood with different initial moisture contents (MC). Microstructure morphology and boron retention of composites were studied. Scanning electron microscope images showed that wood with an initial MC of around 20 % exhibited a weight percent gain (WPG) of more than 30 % and deposited boron acid gels in cell lumens. X-ray diffraction indicated that the relative crystalline degree of wood cellulose in the composites slightly increased with increasing WPGs. Analysis of the crystalline structure of the composites showed that the wood crystalline region was not destroyed with sol-gel treatment as the characteristic diffraction peak of wood cellulose did not change. A boron characteristic diffraction peak at around 2 theta=27.5° caused by boron bonding was observed. Additionally boron retention after water leaching reached 2.46 kg·m^{-3} was in accordance with the threshold value of biotoxicity.

KEYWORDS: Trimethyl borate (TMB), wood preservative, crystal structure, leachability, sol-gel preparation.

INTRODUCTION

With standards of living and industry getting higher, environmentally friendly wood protective technology is becoming of increasing interest. Conventional wood preservatives such as CCA (Chromated copper arsenate, CCA), ACQ (Alkaline copper quaternary, ACQ) or CA (Copper azole, CA) which are chemical damaging to the environment and are harmful to human health, have been banned in many countries (Hill 2006). As an eco-friendly wood preservative, boron compounds such as boric acid (BA) and borax and trimethyl borate (TMB) have gained recent popularity as a wood preservative due to their low treatment cost, biological activity, easy application, and relatively low toxicity (Lyon et al. 2007, Thevenon et al. 2009). Several boron compound treatment technologies, including vapor-boron treatment to wood, have been developed (Tsunoda 1999), (Ergun and Mustafa 2005); however, their liability to leach from treated wood due to hydrophilicity and easy solubility in water has not yet be resolved. This feature limits the broader application of boron compounds in wood preservation. In our previous study, TiO_2/poplar wood composites were successfully prepared using a sol-gel process (Qin and Zhang 2012). The composites showed inorganic composition fixation and good antibacterial ability. Therefore, the sol-gel process appears to be an effective method to synthesize inorganic and organic composites. In this study, TMB was used as a precursor in the sol-gel process to modify poplar wood. The purpose of this study was to enhance the leaching resistance of borate-treated wood through the formation of a chemical complex of borate ester with water bound in wood cell walls during etherification to produce boron-cellulose polymers. The possible chemical reactions are:

$$B(CH_3O)_3 + 3H_2O \rightarrow H_3BO_3 + 3CH_3OH \tag{1}$$

$$Wood_{cellulose}\text{-}OH + H_3BO_3 \rightarrow Wood_{cellulose}\text{-}O\text{-}B(OH)_2 + H_2O \tag{2}$$

This study was designed to reveal the impregnation effectiveness and to enhance the leaching resistance of borate-treated wood basing on hydrolysis of TMB and subsequent polycondensation of hydrolysate by the sol-gel process. Their microstructure morphologies were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis, and the leachability of boron in water from composites was investigated.

MATERIAL AND METHODS

As an anisotropic porous material, wood has a better penetrating rate of liquid in the longitudinal direction. To encourage the sol solution to penetrate into the internal structure of the wood, specimens with a size of 20(R) × 20(T) × 3(L) mm (where, R is the radial direction, T is the tangential direction and L is the longitudinal direction) were obtained from fast-growing poplar wood (*Populus euramericana* cv.*´I-214´*). The specimens were selected and divided into three groups: H_1, H_2, and H_3. All specimens were then oven-dried and their weights (W_0) were measured. To provide an agent for the hydrolysis reaction of TMB, all specimens were moisture-conditioned in a humidity controller at a temperature of 25°C and relative humidity 60, 85, and 94 %, respectively. The specimens were moisture-conditioned for one month and reached an equilibrium moisture content of 10.98, 15.78 and 20.17 % for group H_1, group H_2 and group H_3, respectively. An additional group C was untreated as the control.

Sol solutions were prepared using TMB as the precursor, ethanol as the solvent and acetic acid as the catalyst (TMB/ethanol=2:1 in volume ratio, TMB/acetic acid=1:0.01 in mole ratio). The specimens of groups H_1, H_2, and H_3 were impregnated in the prepared sol solution at 25°C for 24 hours under vacuum conditions with a pressure of -0.095MPa. After impregnation, specimens were placed in an oven at 40°C for 48 hours and then 65°C and 105°C for 24 hours, respectively, to ensure the sols were aged and boric acid/poplar wood composites were prepared. Oven-dried weights (W) of the composites were then measured as weight percent gains (WPG) after the sol-gel process treatment, which was calculated according to:

$$WPG= (W-W_0)/ W_0 \times 100 \qquad (\%) \qquad (3)$$

where: W_0 - the oven-dried weight (g) before treatment,
W - the oven-dried weight (g) via sol-gel treatment, respectively.

The microstructure morphologies of the composites were characterized by SEM (S-3400N, Shimazu Japan) and their crystal structures were analyzed by XRD (XRD-6000, Shimazu Japan) using CuK_{α} radiation. Leachability tests were conducted according to AWPA Standard E11-06 as water leaching. Leaching was done in deionized water stirred by a magnetic stirrer (400-500 rpm/min) at 25°C for 8, 24 and afterward for each 48 h deionized water change consecutively for 14 d. After leaching, the leachate was analysed by an ion chromatograph (IC 500P, Yokogawa-Hokushin Electric, Tokyo) equipped with ion exclusion column. Boron retention in the specimens was detected as ionic boron by IC before and after water leaching. A total of three replicates were performed in each group.

RESULTS AND DISCUSSION

The prepared precursor solutions were transparent, yellow or light brown colored, with viscosities of 1.6~2.4 mPa·s, and particle sizes in the solutions ranged from 0.2 to 5 nm depending on alkoxide concentration and hydrolysis degree. According to chemical Eqs. 1 and 2, the sols were solidified as boric acid gels upon further etherification reactions to form boric acid gels within the cell wall. Therefore, bound water associated with cell wall substances was critical as the initiator for the chemical reactions. The relationship between WPGs and initial moisture contents is shown in Fig. 1.

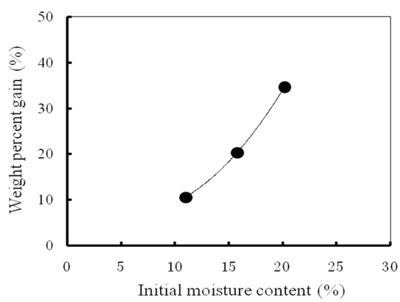

Fig. 1: Relationship between WPGs and initial moisture contents of humidity-conditioned poplar wood specimens.

With the increase in MC, the WPGs exhibited an increased linear trend. The WPGs were 10.6~34.67 % corresponding to initial moisture contents of 10.98~20.17 %, respectively. The wood specimen with higher initial moisture content resulted in higher WPG of 34.67 at the MC level of 20.17 %. When the MC of the specimen was relatively high, the etherification reactions were carried through in the cell lumens of the wood. The sols adequately reacted with water to form gels, which formed stable chemical combinations with the wood cell walls according to Eq. 2. Additionally, the WPGs exceeding 30 % for specimens in group H_3 showed that part of the gels of boric acid bound with wood cell substances according to 43.7~50.99 % in percentage of cell wall area an annual ring of poplar wood.

Composite morphologies are shown in Fig. 2. The SEM images demonstrate that boric acid gels were deposited in the cell lumens of the wood. It is clear that the gel particles adhered to the cell lumen of the wood. Gels with a particle size of 2-30 μm increased with increased initial moisture content, indicating the sols penetrated readily into the wood cell lumens under vacuum conditions, and boric acid gels formed during the aging stage after sols impregnated into the wood. Inorganic substances deposited in the cell lumens would enhance the functionality of composites such as fire-retarding and anti-termites properties corresponding to characteristic of boron compounds.

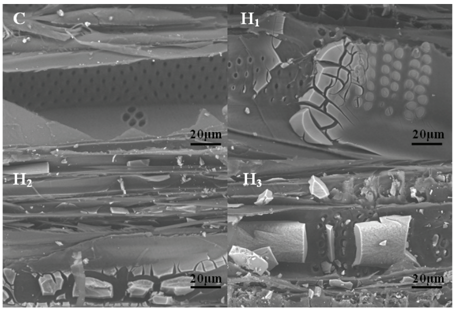

Fig. 2: Radial section SEM photographs of TMB sol-gelled poplar wood (SEM×1200).

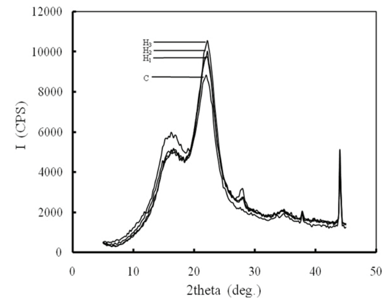

Fig. 3: X-ray diffraction patterns of TMB modified wood specimens (H_1: WPG=10.6 %, H_2: WPG=20.35 %, H_3: WPG=34.67 % and C: Control).

Crystalline structures of composites were also analyzed by XRD, as shown in Fig. 3. The degree of crystalline increased with increasing WPGs. TMB which undergoes rapid hydrolysis with moisture containing in wood cell wall would chemically react with hydroxyl groups of wood substances (Ahmed et al. 2004). As shown in Fig. 3 diffraction intensities increased at 2Θ=22.5° with increases of initial moisture content of wood confirmed that relative contents of cellulose crystalline are increased and there are covalent links between boron acid and hydroxyl groups in wood cell wall. Increases in the relative content of cellulose crystalline were most likely the result of crystalline B_2O_3 existing in the composites (Meder et al. 1999). Furthermore, diffraction intensities at 22.5° indicated that the crystalline structure of the wood was not destroyed by sol-gel treatment. It is worth mentioning that the diffraction peaks at 2Θ=27.5° indicated characteristic peaks of boric acid or/and B_2O_3•$3H_2O$, as the diffraction data were in good agreement with the CAS card for boron oxide (CAS No. 76-1655). The results indicated that boric acid gels formed stable chemical bonds with wood substances in composites. The results also implied that this was an effective method to increase the water leaching resistance of borated-treated wood using the sol-gel process.

The leachability of boron from TMB/poplar wood composites prepared by the sol-gel process based on the AWPA Standard E11-06 of water leaching is shown in Tab. 1. Each evaluation was carried out in triplicate and the values obtained were averaged to produce the final data.

Tab. 1: Retention rates of boron in TMB modified poplar wood with different WPGs (%).

Sample	WPG (%)	Boron in sample ($kg \cdot m^{-3}$)	Boron in sample after leaching ($kg \cdot m^{-3}$)	Boron retention rate (%)
H1	10.6	16.92	0.56	3.31
H2	20.35	33.40	1.85	5.54
H3	34.67	38.91	2.46	6.32

It is clear that B_2O_3 was retained and TMB/wood composites had a maximum boron-loading of 38.91 $kg \cdot m^{-3}$ for H_3, with boron retention after leaching of 2.46 $kg \cdot m^{-3}$. As an insecticide, boron has a biotoxicity threshold value of 2.5 $kg \cdot m^{-3}$ in wood when being used as wood preservative (Tsunoda 1999). Boron retention after leaching had a minimum of 0.56 $kg \cdot m^{-3}$. Toxic threshold values determined for solid wood were 0.9, 1.8 and 1.8 $kg \cdot m^{-3}$ BAE (boric acid equivalent) respectively, against the white-rot fungus *Trametes versicolor* (L.: Fr.) Pilat, the brown-rot fungus *Fomitopsis palustris* (Berk. et Curt.), and the subterranean termite *Coptotermes formosanus* Shiraki (Tsunoda 1999, Ahmed et al. 2011). In this study, TMB/modified poplar wood with an initial moisture content of 20 % was prepared by the sol-gel process. Boron retention was 0.56 - 2.46 $kg \cdot m^{-3}$ and was in accordance with the threshold value of biotoxicity.

CONCLUSIONS

To develop novel wood preservative technology, trimethyl borate was used with the sol-gel process to modify poplar wood with different initial moisture contents. Their microstructures were investigated by SEM and XRD to confirm the treatment effectiveness. Boric acid is precipitated in the lumens and partly in the wood cell wall. Boric acid retention was detected as ionic boron by IC after water leaching. Results showed that water leaching resistance was effectively increased through sol-gel process based on possible reactions. Boric acid with a characteristic crystalline diffraction peak at 27.5° of 2Θ, showed that boric acid gels formed stable chemical bonds with wood substances in the TMB/poplar wood composites. Based on characteristics of boron, the composites obtained are promising for applications such as fungi and termite resistance and flame retardation.

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