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STUDY ON THE ANTI-LEACHING PROPERTY OF CHINESE FIR TREATED WITH BORATE MODIFIED BY PHENOL-FORMALDEHYDE RESIN

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ABSTRACT

In order to investigate the effect of phenol-formaldehyde (PF) resin on the anti-leaching property of disodium octaborate tetrahydrate $Na_2B_8O_{13}.4H_2O$ (DOT), one kind of inorganic borates, PF resins with three viscosities of 200, 1000, and 10000 mPa.s at 20°C which represent low, moderate, and high molecular weights respectively were prepared in laboratory and used in combination with DOT to treat the sapwood of Chinese fir (*Cunninghamia lanceolata* Hook.). The results showed that higher concentration of PF could fix boron better. Low molecular weight PF was favourable to improve the leaching resistance of boron because of its capability of penetrating into the wood cell wall. The optimal concentration of DOT was determined as 2 % BAE (boric acid equivalent) compared to 1 % BAE and 3 % BAE used in this study. The increased boron leaching at high concentration of DOT was considered to be caused by the limited capacity of PF to bond boron. SEM analysis showed that great amount of resin is accumulated in cell cavities or on the wood cell wall surface in wood treated with moderate or high molecular weight PF but little resin was found in the cell cavities of wood treated with low molecular weight PF. FITR analysis showed that low molecular weight PF would react with the wood components.

KEYWORDS: Phenol-formaldehyde (PF), borate, Chinese fir, anti-leaching.

INTRODUCTION

Water-borne wood preservatives are widely used in the field of wood protection. Considering the high concerns for threats from heavy metals such as arsenate and chromium, metal-free wood preservatives were thought to be potential alternatives. Borates, as one of this type, have been used in wood preservation to control against wood-decaying fungi and termites for long time, as indicated from the previous review by Carr (1959). They are usually easy to penetrate into wood (Lebow and Morell 1989), have relative fire retardance but little influence on appearance

(Hashim et al. 1994). Therefore, borates were widely used to treat engineered wood for indoor applications and recently explored to wood-based composites (Cavdar et al. 2008, Gentz et al. 2009, Yildiz et al. 2009, Namyslo and Kaufmann 2009, Gao et al. 2010). However, borates can not be used in outdoor applications without any additional protection because they are easy to leach out (Lloyd 1998, Polus-Ratajczak and Mazela 2004). Borates had shown to be toxic at high concentrations (Lloyd et al. 2003) and recently boron is classified as chemical of high concern due to it potential reproductive toxicity according to Global Harmonized System, although it was previously reported that they are not carcinogenic or mutagenic and humans are not at significant risk of reproductive failure due to borates from environmental sources (Fail et al. 1998). This controversy makes the boron fixation in treated wood more important.

In order to improve the leaching resistance of borates, researchers have tried many methods including:

(1) use monomers or polymers such as ethylene (Yalinkilic et al. 1998), methyl methacrylate (MMA), polyethylene glycol (PEG), glycerol, mannitol etc (Baysal et al. 2004),

(2) use some natural substances such as protein or tannin (Thévenon et al. 1999, Thévenon and Pizzi 2003, Mazela et al. 2007, Thévenon et al. 2009) or water repellents (Peylo and Willeitner 1995, Baysal et al. 2006),

(3) spray or brush the surface of treated wood by using varnish or alcohol ester paint (Homan and Militz 1995),

(4) use new processing technologies such as the vapor-phase boron treatment (Baysal and Yalinkilic 2005). Although the above methods improve the anti-leaching property of boron to different extents, there is still no satisfying method considering the cost, performance and the ease of processing.

Phenol-formaldehyde (PF) resin is formed by phenol and aldehyde under certain catalyst. In alkaline circumstance, addition reaction between phenol and aldehyde first happen to generate hydroxymethyl phenol. If the hydroxymethyl phenol stops polymerization before its gelling point, it will become resol-type PF (Bruze 1985), which is water soluable and has the ability of self-polymerization. Furuno et al. (2004) used low concentration PF with low molecular weight to impregnate wood and found that PF entered the wood cell wall successfully and improved the corrosion resistance and dimensional stability. The molecular weight of PF was very important and affected by many factors such as the time and temperature of reaction, catalyst, molar ratio of phenol to aldehyde, etc. It is difficult to determine in practice, so usually the viscosity is used to represent the molecular weight instead. According to mark-houwink equan, the relationship between viscosity and molecular weight can be shown in Eq. (1) (Reisner and Rowe 1969).

$$\eta=k(M)^{\alpha} \tag{1}$$

where: η represents the viscosity (mPa.s), (M) is viscous average molecular weight, k and α are coefficients. At same temperature and concentration conditions, the molecular weight of PF is proportional to its viscosity.

Boric acid, borax ($Na_2B_4O_7 \cdot 10\ H_2O$), and disodium octaborate tetrahydrate($Na_2B_8O_{13} \cdot 4\ H_2O$) are three most widely used borates in wood protection. DOT has better soluability at room temperature than borax and boric acid. Grace et al. (2000, 2006) studied the outdoor termite resistance of wood treated with DOT and summarized that DOT could effectively protect underground wood structure from being attacked by termites over a long period. Yu and Cao (2009) used high concentration PF to modify the above-mentioned three borates to improve the resistance of boron leaching and found that borax and DOT exhibited better results than boric acid. However, the effect of PF concentrations and molecular weights on boron fixation of DOT in treated wood has not been investigated yet. Therefore, this study proposed to investigate the influence of three variables including the concentration of DOT, the concentration and the molecular weight PF on boron leaching by using orthogonal experiment. Scanning electron microscope (SEM) and Fourier transform infrared spectrum (FTIR) tests were also performed for further explanation.

MATERIAL AND METHODS

Material

19 mm cubic samples were made from the sapwood of Chinese fir (*Cunninghamia lanceolata* Hook.) from Sichuan province, China. The selected samples have average annual ring of around 3 mm and are free of visible defects. They were placed in a humidity chamber with temperature and relative humidity setting at 20°C and 50 ±2 % until reaching equilibrium moisture content of 9~10 %. Then, they were weighed and classified into 12 groups. Six replicates were used in each group.

The reagents used in this study included formaldehyde (between 37 % and 40 %), nitric acid (65 %), perchloric acid (70 %), phenol, sodium hydroxide, DOT, and potassium bromide (KBr), which were all bought from market.

Laboratory preparation of resol-type PF

Secondary synthesis process was used to prepare three different molecular weight PF solutions with molar ratio of phenol to formaldehyde at 2.

Preparation of low molecular weight PF: Firstly phenol was melted below 50°C, and then slowly poured in reactor together with NaOH (30 %). After heating up to 45°C in 10 min, formaldehyde, about four-fifths of the whole was added into reactor for the first time. The reactor needed to be heated up to 80°C within 20 min and reacted for another 1 h. While temperature went down to 70°C, the rest formaldehyde was added. Also, the reactor needed to be heated up to 80°C and reacted for 2 h. After cooling down to below 40°C, the production was poured out and tested with Brookfield at 20. The viscosity of obtained PF was 200 mPa.s at 20°C.

Preparation of moderate molecular weight PF: the procedure is as same as the preparation of low molecular weight PF until the addition of formaldehyde for the first time. Then the reactor was heated up to 90°C within 40~50min and kept for 20 min, and then cooled down to 80°C to add the rest formaldehyde. After heating up to 90°Cand reacting for 105 min, the production was cooled down. The viscosity of obtained PF was 1000 mPa.s at 20°C.

Preparation of high molecular weight PF: reaction was referred to preparation of moderate molecular weight PF by only changing temperature to 95°C and time to 1 h. The viscosity of obtained PF was 10000 mPa.s at 20°C.

Experiment design

A $L9(3^3)$ orthogonal experiment was designed by using the concentration of DOT, concentration and molecular weight of PF as its variables, as shown in Tab. 1. The performed tests were labeled as DP1~DP9, as listed in Tab. 2.

Tab.1: Variables and levels used in the orthogonal experiment of DOT modified by PF.

Levels	**Variables**		
	A	**B**	**C**
	Concentration of DOT BAE* (%)	**Concentration of PF (%)**	**Molecular weight levels of PF**
1	1	5	low
2	2	10	moderate
3	3	20	high

- BAE represents boric acid equivalent concentration.

Treatment of wood samples

Samples were pressure treated in a full cell process. First, the samples were vacuum treated at 0.01 MPa for 30 min and then the treating solution was let in to completely submerge the samples. After pressurized at 2 MPa for 60 min, samples were taken out and dried in an oven at 60°C for 6 h and further at 110°C for 8 h.

Besides, 3 control groups (D1, D2, D3) treated with different concentrations of DOT (1, 2, and 3 % BAE, respectively) were also prepared by using the same full-cell process. The control samples were also dried for further tests.

Leaching test

Leaching test was performed according to AWPA E11-07 standard (2007). Each group of 6 samples was immersed in deionized water for 14 days. Deionized water was changed after 6, 24 and 48 h and thereafter at 48 h intervals. When the leaching test finished, the samples were dried at 40°C for 24 h, then separately grounded into powder to pass a 20-mesh sieve and dried at 105°C for 24 h. 0.5 g powder was weighed to a precision of 0.001 g for each group to perform acid digestion. The contents of boron in the digested liquids were tested by inductively coupled plasma atomic emission spectrometry (ICP-OES) (Perkin 5300V, USA). Then the leaching rate of boron was calculated according to Eq. (2):

$$LAB=(1-\frac{B}{A})x\ 100\quad(\%) \tag{2}$$

where: LAB is the leaching rate of boron in each sample %, A and B represent the boron retentions in samples before and after leaching test kg.m^{-3} respectively.

Scanning electron microscope (SEM) analysis

The morphology structure of treated wood was investigated by a Philips (Hitachi S-3400, Japan) scanning electron microscope (SEM) with an acceleration voltage of 3 kV. The samples used for SEM analysis with a dimension of 5×5×1mm were cut from the centre of the treated wood along radial section and attached to loading films at 800 amplification.

Fourier transform infrared spectrum (FTIR) analysis

FTIR analysis was carried out on a Tensor 27 spectrometer and potassium bromide (KBr) was used to collect the background. Air-dried powder, passed through a 100-mesh sieve, was mixed with KBr in a weight ratio of 1:100 before spectrum collection. All spectra were displayed in wavelengths raging from 600 to 1800.cm^{-1}.

RESULTS AND DISCUSSION

Leaching rate of boron

The leaching rates of boron in the wood treated with different combinations of DOT and PF were listed in Tab. 2. The results of intuitive analysis and variance analysis were shown in Fig. 1 and Tab. 3.

From Tab. 2, it is clear that the boron in the control groups treated only with DOT had nearly depleted after leaching test, which is consistent to previous investigations (Yalinkilic et al. 1998, Kartal and Green 2003, Lloyd et al. 2003, Baysal et al. 2004). While after modification by PF resin, most of the groups showed obvious reduction on boron leaching except the groups using 5 % PF with moderate or high molecular weight (DP4, DP7). DP6, which used 20 % PF with low molecular weight to combine with 2 % BAE DOT, obtained the best anti-leaching effect by reducing the leaching rate to 18.39 %. In previous study, the researchers reported almost a complete fixation by using 20 % PF with low molecular weight to combine with 0.5 % BAE DOT (Yu and Cao 2009). The difference was considered to be related to the different concentration of DOT, which will be further discussed later.

Tab. 2: Leaching rates of boron in the treated wood.

Groups	Labels	Variables			B_2O_3 retention in unleached wood (kg.m^{-3})	B_2O_3 retention in leached wood (kg.m^{-3})	Average leaching rates of boron (%)
		A	B	C			
Control groups	D1	1	-	-	6.074	0.313	94.84(0.91)*
	D2	2	-	-	8.590	0.297	96.26(0.77)
	D3	3	-	-	16.631	0.450	93.70(0.69)
Groups of DOT modified by PF	DP1	1	5	low	6.506	0.661	89.84(0.33)
	DP2	1	10	moderate	6.644	1.618	75.60(1.33)
	DP3	1	20	high	6.273	2.354	62.47(1.53)
	DP4	2	5	moderate	10.402	0.626	93.98(0.74)
	DP5	2	10	high	12.308	1.858	84.89(1.60)
	DP6	2	20	low	9.951	8.116	18.39(2.85)
	DP7	3	5	high	16.251	0.819	94.94(0.87)
	DP8	3	10	low	19.465	6.029	69.00(1.24)
	DP9	3	20	moderate	18.674	4.630	75.20(0.59)

* Values in brackets represent standard deviations of six replicates.

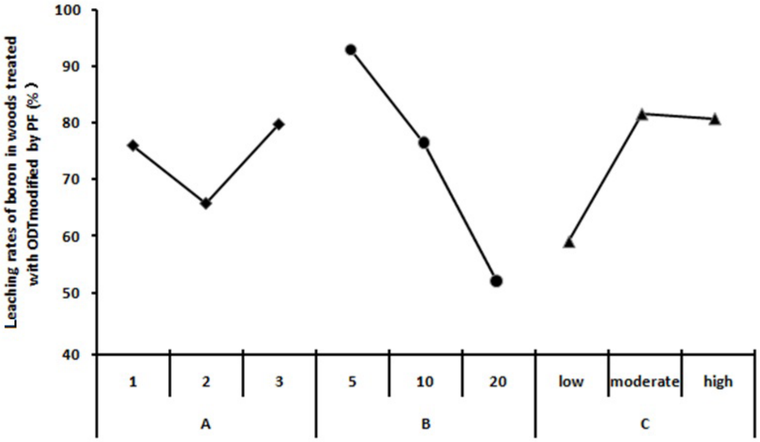


Fig. 1: Intuitive analysis of boron leaching rates in wood treated with DOT modified by PF.

Tab. 3: Variance analysis of boron leaching rates in wood treated with DOT modified by PF.

Factors	Deviance	Ratio of F	TLV of F	Significance
A	313.27	0.665	4.320	
B	2541.64	5.399		*
C	978.14	2.078		

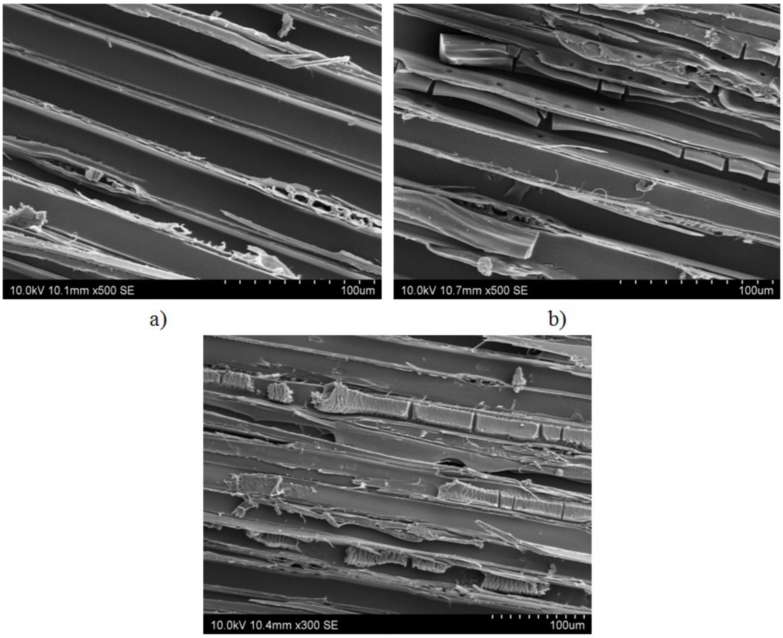
According to the results of intuitive analysis and variance analysis, the leaching rates of boron were affected by the concentration of DOT, the concentration and the molecular weight of PF. The concentration of PF was the significant influencing factor. The leaching rates decreased with the increasing PF concentration. In average, the leaching rate was about 50 % at a PF concentration of 20 %; however if PF concentration was lowered to 5 %, the leaching rate would reach 93 %, which suggested higher concentration of PF fixed boron better.

Within the experiment range, 2 % BAE DOT obtained better leaching resistance of boron compared to 1 % BAE and 3 % BAE DOT. The drop at higher concentration might be caused by the limited capacity of PF to bond boron in DOT. This conforms to the fact that almost complete fixation was obtained in previous study by using 20 % PF with low molecular weight to combine with 0.5 % BAE DOT (Yu and Cao 2009).

As for the molecular weight of PF, low molecular weight PF performed much better than the moderate and high molecular weight PF resins. It is easy to understand since the higher degrees of polymerization would hinder the penetration into wood cell wall. On average, the leaching rate of boron in wood treated with DOT combined with low molecular weight PF was 59.1 % but increased to 81.0 % while treated with DOT combined with moderate or the high molecular weight PF.

SEM analysis

The results of SEM analysis were shown in Fig. 2. As shown in Fig. 2, the low molecular weight PF can penetrate into wood cell wall, which was demonstrated by a clean surface of cell wall. However, in wood samples treated with moderate and high molecular weight PF resins, it clearly shows a large amount of resins accumulated in cell cavities or on the surface of wood cell wall. This further confirms the reason why low molecular weight PF obtained the greatest improvement on boron fixation.



a) b)

c)

Fig. 2: SEM graphs of wood treated with DOT modified by PF with different levels of molecular weight (800 x) a) low molecular weight PF, b) moderate molecular weight PF, c) high molecular weight PF.

FTIR analysis

Fig. 3 shows the results of FTIR analysis for untreated Chinese fir and the treated group with best fixation effect.

The new bonds appeared at 715.cm^{-1} and 1212.cm^{-1} for treated wood should be assigned to the vibration absorption of benzene ring and the vibration absorption of phenolic hydroxyl groups, respectively, which are the characteristic bonds of PF (Pendey and Pitman 2003). The bond at 3350.cm^{-1} assigned to the vibration of hydroxyl groups and the bond at 1645.cm^{-1} to adsorbed water were both reduced, suggesting reactions between hydroxyl groups and PF or steric hindrance because of PF. The bond at 1735.cm^{-1} assigned to carboxyl stretching vibration in carboxylic acid groups in hemicelluloses, the bond at 1510.cm^{-1} assigned to aromatic skeletal vibration in lignin, and the stretching absorption C-H bond at 2900.cm^{-1} and C=O stretching vibration at 1606.cm^{-1} characteristic for cellulose all decreased, showing that PF in wood cell wall reacted with wood main components including cellulose, hemicelluloses and lignin.

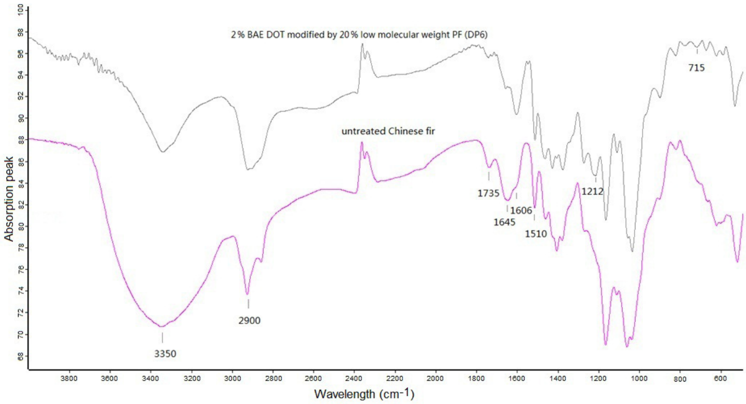


Fig. 3: FTIR spectrums of untreated wood and wood treated with 2 % BAE DOT modified by 20 % low molecular weight PF (DP6).

CONCLUSIONS

Low molecular weight PF has significant effect on reducing boron leaching from DOT treated wood due to its capability of penetrating into the wood cell wall and reacting with the wood components including cellulose, hemicelluloses and lignin. It should be noted that if the concentration of DOT is very high then high concentration of PF would be required to fix the boron included. In this study, the optimized modifier for 2 % BAE DOT was determined as 20 % PF with low molecular weight.

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