Effect of Catalysts and Sodium Hydroxide on Glyoxal-treated Wood

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Treatment of poplar wood using glyoxal as a non-formaldehyde cross-linking reagent was investigated. Cross-linking occurred with glyoxal in the presence of the catalysts aluminum sulfate, magnesium chloride, zinc nitrate, maleic anhydride, ammonium dihydrogen phosphate, and ammonium persulfate. Ammonium persulfate was found to be the most effective single catalyst, which may be due to the synergistic catalytic effect of NH_4^+ and $S_2O_8^{2-}$, Further, catalyst combinations produced higher overall performance in comparison with the single one, and the optimal combination was maleic anhydride and ammonium persulfate. An increase in ammonium persulfate improved wood dimensional stability and anti-leaching properties, but weakened the hydrophobicity and deepened the colour of the modified wood. Considering the balance between anti-swelling efficiency, leachability, and water uptake, the optimum catalyst concentration was 2%. Although the addition of sodium hydroxide into a glyoxal solution can reduce wood discoloration, it may also reduce the modification efficiency.

INTRODUCTION

Cross-linking modification *via* the use of various cross-linking reagents with or without a catalyst at a high curing temperature is an effective way to improve wood properties, especially its dimensional stability (Yasuda *et al.* 1994; Yusuf 1996; Xiao *et al.* 2008, 2010). As a result, cross-links are formed between the hydroxyl groups in wood polymers (*i.e.*, cellulose, hemicellulose, and lignin) and the cross-linking reagent, thus blocking or substituting the hydrophilic hydroxyl groups and endowing wood with high dimensional stability (Weaver *et al.* 1960; Welch and Danna 1982; Yasuda *et al.* 1992). The reagent used in the modification must be efficient but nontoxic to humans in the final treated product and should be as nontoxic as possible during the treating stage (Rowell 2005). A catalyst, when required during the treatment stage, should also be nontoxic, effective, and cause little or no damage to the physical and mechanical properties of the wood.

Glyoxal, a low-volatile, non-toxic aldehyde, once was widely used in the textile industry as a finishing reagent (Frick and Harper 1982; Welch and Danna 1982; Xu *et al.* 2002). Recently, owing to environment requirements, it has been used to replace the toxic formaldehyde in the synthesis of environmental-friendly wood adhesives. Because of its two active merged aldehyde groups, it can be used to glyoxalate the lignin in the wood cell

wall or cross-link with hydroxyl groups in cellulosic materials *via* a hemi-acetal or acetal reaction with the presence of a catalyst (Ballerini *et al.* 2005; Lei *et al.* 2008; Mansouri *et al.* 2006; Moubarik *et al.* 2009; Navarrete *et al.* 2012, 2013; Yuan and Hu 2012). The reaction between dialdehydes and cellulose is usually catalyzed by an inorganic acid salt or weak organic acid, because a strong acid or base can extensively degrade the cellulose fabrics. The most frequently used catalysts in textile treatment include aluminum, magnesium, and zinc salts of inorganic acids (Choi *et al.* 1998; Kumar 1994; Lee and Kim 2004; Lee and Kim 2005; Nakano 1993; Welch 1984; Welch 1983; Welch and Danna 1982).

Considering its efficient use and environmental protection feature in durable press finishing of cellulosic fabrics and synthesis of wood adhesives, glyoxal has been successfully transferred into wood (also a cellulosic material) modification. To improve the dimensional stability, several wood species have been treated with glyoxal and glutaraldehyde under catalysis of zinc chloride, magnesium chloride, or pyridinium chloride (Weaver *et al.* 1960). The reaction of glyoxal and glycol with wood catalyzed by aluminum sulfate has also been studied (Nakano 1993). Aluminum sulfate has been shown to be the most active catalyst for the reaction between glyoxal and cellulose (Welch and Danna 1982).

Despite the improved dimensional stability and reduced moisture absorption after modification (Weaver *et al.* 1960; Yasuda *et al.* 1994; Yusuf 1996), the dimensional stabilizing effect is not satisfactory when glyoxal is applied to the dimensional stabilization of wood catalyzed by a strong mineral acid or inorganic acid salts. In addition, strong mineral acid or inorganic acid salts always cause hydrolysis of the polysaccharide moiety of wood, which may weaken the physical properties (Li *et al.* 2009).

Sulfur dioxide (SO_2), an excellent catalyst for formalization, has been applied in the treatment of wood with glutaraldehyde and glyoxal, and the dimensional stability, acoustic properties, and mechanical strength of the treated wood were compared with those obtained from formaldehyde treatment (Minato and Yano 1990; Yasuda *et al.* 1994). Because SO_2 is a gas, however, it is difficult to control in wood treatment when compared to an aqueous system, and this may limit its use. In addition, the acidity of the modifying reagent solution will greatly affect the reaction rate and efficiency of the treatment, and a strong acid can cause extensive degradation. Therefore, it is necessary to find a new and effective catalyst for wood modification by glyoxal and to clarify the effects of sodium hydroxide on the properties of modified woods. In addition, glycol was found to be very effective to reduce or prevent the yellowing of glycol-treated cotton fabrics (Choi and Kim 2001; Lee and Kim 2004; Welch and Danna 1982), therefore, it was used as an additive in this study together with the glyoxal.

In this study, a new catalyst, together with five other catalysts commonly used in durable press finishing or wood modification, was incorporated into the treatment of wood by glyoxal. Further, the combination of the optimized catalyst with different acidity and alkalinity catalysts was also applied. The effects of catalyst type, dosage of ammonium persulfate, and dosage of sodium hydroxide on the physical properties of wood, and leachability of modified wood after five leaching tests were also investigated. Finally, the weight percent gain (WPG), anti-swelling efficiency (ASE), and leachability of modified woods were calculated to evaluate the catalytic efficiency.

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EXPERIMENTAL

Materials

Chemicals

Glyoxal (40% aqueous solution) was used as a cross-linking reagent. Magnesium chloride hexahydrate (MgCl$_2$·6H$_2$O), aluminum sulfate hexadecahydrate (Al$_2$(SO$_4$)$_3$·16H$_2$O), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), maleic anhydride, ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$), ammonium persulfate ((NH$_4$)$_2$S$_2$O$_8$), hexamethylenetetramine (HMT), sodium tetraborate (Na$_2$B$_4$O$_7$), and sodium bisulfate (NaHSO$_3$) were used as catalysts. Sodium hydroxide (NaOH) was used as a 30% aqueous solution. All the chemical reagents were of analytical purity and purchased from Beijing Chemical Works (China).

Sample preparation

Samples were cut from the sapwood of poplar (*Populus tomentosa* Carr.) for the evaluation of dimensional stability, and eight matched samples with dimensions of 20 mm (tangential) × 20 mm (radial) × 20 mm (longitudinal) were prepared.

Methods

Treatment conditions

Before impregnation, all samples were oven-dried at 103 ± 2 °C for 12 h to a constant weight (*i.e.,* when the average weight change of the samples was less than 0.01 g over 2 h); the initial oven-dried weights and sizes were measured. Then, the samples were impregnated with the modified solution containing glyoxal (20% aqueous solution), catalysts (0 to 2 wt% final concentration), and glycol/glyoxal (molar ratio 0.5) using a vacuum oven (0.1 bar, 30 min) and ambient pressure (10 min). To investigate the effect of NaOH on modification, the acidity of the solutions was adjusted before impregnation with various concentrations of NaOH (0.1 to 1.0 wt%) to varying pH values in the range of 2.5 to 5. After impregnation, the excess solution was blotted off with tissue paper and the samples were placed into an oven for curing. The samples were gradually heated to 120 °C (10 °C min^{-1}), cured for 4 h, and finally oven-dried at 103 ± 2 °C to constant weight. The final weight and size of the samples were measured. The WPG due to chemical load was calculated as follows,

$$\text{WPG(\%)} = [(W_t - W_u)/W_U] \times 100 \qquad (1)$$

where W_u and W_t are the oven-dried weight (g) of a wood sample before and after treatment, respectively.

The bulking effect (BE) of a sample is calculated as follows,

$$\text{BE(\%)} = [(V_t - V_u)/V_u] \times 100 \qquad (2)$$

where V_u and V_t are the oven-dried volume of a wood sample before and after treatment, respectively.

Dimensional stability and water uptake

To measure the water absorption ability of untreated or treated samples, blocks were immersed in distilled water for 24 h, the surface water was removed by tissue paper,

and the mass was measured. The dimensions of the blocks were also measured with a digital micrometer ($\pm$ 0.01 mm) following immersion.

Based on the swelling difference between the treated and untreated samples, the ASE was calculated as follows,

$$ASE(\%) = [(S_u - S_t)/S_u] \times 100 \tag{3}$$

where S_u and S_t are the volumetric swelling of an untreated and a treated wood sample respectively.

Water uptake (WU) of a sample as an index of water repellency efficiency from the initial and final wet weights after water saturation was calculated as follows,

$$WU(\%) = [(W_w - W_d)/W_d] \times 100 \tag{4}$$

where W_w and W_d are the wet weight of a sample after and before saturation with water, respectively.

Leaching test

After calculation of the WU, all the samples were oven-dried at 103 $\pm$ 2 °C to a constant weight. The samples were immersed in distilled water at 25 °C for 24 h and then oven-dried at 103 $\pm$ 2 °C to a constant weight. This process was repeated five times and, at the end of each circle (term given to each process) the water was replaced. The leaching rate (L) due to water immersion was calculated as follows,

$$L(\%) = [(W_{iw} - W_{fw})/W_{iw}] \times 100 \tag{5}$$

where W_{iw} and W_{fw} are the WPGs of a treated wood sample before and after immersion, respectively.

RESULTS AND DISCUSSION

Effects of Six Different Catalysts

The type of catalyst will greatly affect cross-linking, and a properly selected catalyst may lead to high reaction efficiency between glyoxal and wood components. The physical properties of woods treated with six catalysts are shown in Table 1. Clearly, the effects on wood properties differed among these catalysts. The ASE was more than 50% in all treated woods with addition of 2 wt% of catalyst, and was up to 49% even in the sample treated with glyoxal without catalyst, demonstrating the high efficiency of glyoxal in wood modification. According to Table 1, ASE was the highest in $(NH_4)_2S_2O_8$, followed by maleic anhydride, $NH_4H_2PO_4$, $Al_2(SO_4)_3 \cdot 16H_2O$, $MgCl_2 \cdot 6H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$. These results were different from a finding that $Al_2(SO_4)_3 \cdot 16H_2O$ had the greatest catalytic activity in the reaction of glyoxal with cellulose (Welch and Danna 1982). The WUs also greatly decreased after modification, with the smallest effect (29.2%) with $Zn(NO_3)_2 \cdot 6H_2O$ and the largest effect (64.9%) with $(NH_4)_2S_2O_8$, which indicated the improvement of hydrophobicity. After five leaching tests, all the samples displayed high leachability, even after catalysis by $(NH_4)_2S_2O_8$ (54.6%). Thus, it can be generally concluded that despite the high leachability, $(NH_4)_2S_2O_8$ was the most efficient among the six catalysts in improving

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wood dimensional stability and water resistance; therefore, it has an advantage in wood modification compared with inorganic acid salts. Moreover, the treatment with the inorganic acid salts $Zn(NO_3)_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ had no obvious effect on the modification compared with the control group.

Table 1. Effects of Catalyst Type on Properties of Glyoxal-treated Woods[a]

Catalyst (wt %)	WPG (%)	BE (%)	ASE (%)	WU (%)	Leachability (%)
Untreated	——	——	——	110.3 ± 6.5	——
Control*	42.2 ± 2.2	8.5 ± 0.3	49.3 ± 2.8	68.8 ± 5.1	82.5 ± 1.3
$MgCl_2 \cdot 6H_2O$	42.1 ± 4.0	9.1 ± 0.3	52.9 ± 4.4	68.7 ± 3.3	80.3 ± 3.9
$Al_2(SO_4)_3 \cdot 16H_2O$	41.7 ± 2.2	9.5 ± 0.8	56.0 ± 4.9	54.2 ± 5.0	66.9 ± 3.1
$Zn(NO_3)_2 \cdot 6H_2O$	37.1 ± 2.0	9.4 ± 0.5	50.9 ± 6.7	78.1 ± 6.6	84.2 ± 3.5
Maleic anhydride	47.5 ± 2.0	10.6 ± 0.4	61.7 ± 1.5	62.0 ± 5.3	78.5 ± 1.7
$NH_4H_2PO_4$	41.1 ± 4.8	8.6 ± 0.6	58.2 ± 6.3	53.4 ± 4.4	67.0 ± 2.7
$(NH_4)_2S_2O_8$	44.4 ± 3.3	9.6 ± 0.7	72.5 ± 3.7	38.7 ± 2.1	54.6 ± 3.8
[a] Values are expressed as the means of eight replicates ± standard deviation					
* treated without catalyst					

It has been reported that glyoxal can chelate with metal ions easily (Welch and Danna 1982). When the inorganic acid salts ($MgCl_2 \cdot 6H_2O$, $Al_2(SO_4)_3 \cdot 16H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$) were used as catalyst, the metal ions in the solution could form five-member ring chelating monomer and react with the hydroxyl groups in wood cells by an acetal or semi-acetal reaction in the presence of heat (Meyer *et al.* 1976; Welch and Danna 1982; Yang and Chen 2000). This was the reason that the modification catalyzed by the inorganic acid salt could yield a relatively improved performance. For $(NH_4)_2S_2O_8$, an ammonium and persulfide salt that is an efficient initiator is widely used in polymerization (Bokias *et al.* 1998; Ebdon *et al.* 1994; Furuzono *et al.* 1999; Masere *et al.* 2000). Its catalytic mechanism of the reaction between glyoxal and cellulose may be different from that of the ionic metal salt. The persulfate ion ($S_2O_8^{2-}$) can produce free radicals and initiate polymerization, which may strengthen the cross-linking between glyoxal and wood cellulose and thus contribute to the modification. In addition, the ammonium ion (NH_4^+) is an efficient catalyst for liquid-phase reactions of carbonyl compounds (including glyoxal) and thus produces abundant oligomeric species by acid-catalyzed acetal formation and subsequent oligomerization, where NH_4^+ acts as a Bronsted acid and activates the glyoxal by protonation (Liggio *et al.* 2005; Nozière *et al.* 2010; Noziere and Cordova 2008; Noziere *et al.* 2008). Therefore, the combined effect of NH_4^+ and $S_2O_8^{2-}$ contributed to the highest catalytic activity and the highest modification performance, indicating the greater effect than the inorganic acid salts.

The WPGs of modified wood treated by different catalysts after each leaching test are shown in Fig. 1. Clearly, the WPGs of all woods treated by different catalysts markedly decreased after the five leaching tests. In addition, the loss of WPG was highest after the first leaching test and then decreased gradually with the increased number of leaching tests. The WGP did not change much after three leaching tests. The loss of WPG was partly due to the unreacted chemicals in the wood and to the hydrolysis of the bond formed during repeated immersion and curing. The wood treated with $(NH_4)_2S_2O_8$ displayed the greatest WPG after five leaching tests, which indicates the higher anti-leachability of $(NH_4)_2S_2O_8$ in wood modification with glyoxal because of its effective catalysis in cross-linking between glyoxal and wood components.
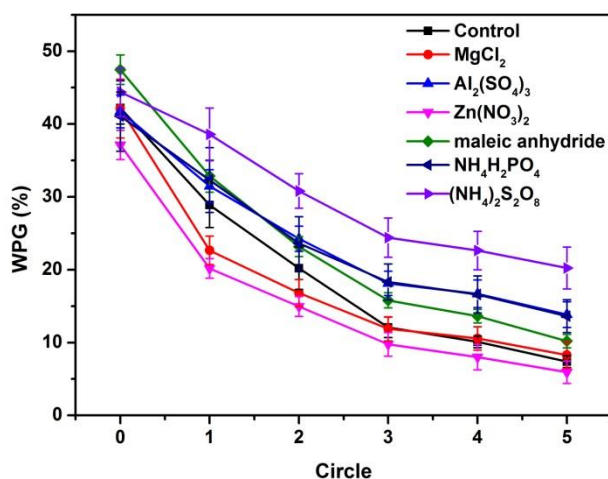
Fig. 1. WPG of treated wood after each leaching test. Glyoxal concentration was 20%, catalyst dosage was 2 wt% (final solution), glycol to glyoxal ratio was 1:2, and curing temperature was 120 °C

Effects of Different Combinations of Catalysts

In this part of the study three kinds of alkaline catalysts [$NaHSO_3$, HMT, and $Na_2B_4O_7$] and three kinds of acidic catalysts [$Al_2(SO_4)_3 \cdot 16H_2O$, maleic anhydride, and $NH_4H_2PO_4$] were added to the $(NH_4)_2S_2O_8$ catalyzed solution, respectively. The effects of the combined catalysts on the properties of the treated woods are shown in Table 2. Clearly, when $NaHSO_3$, HMT, and $Na_2B_4O_7$ were combined separately with $(NH_4)_2S_2O_8$ at the weight percentage of 1:1, the ASEs decreased while the WUs increased compared to the wood treated only with $(NH_4)_2S_2O_8$. This may be due to the weakened acidity after the addition of an alkaline catalyst, which may adversely affect the catalytic reaction. Although the ASEs of the treated woods were not improved after the addition of $Al_2(SO_4)_3 \cdot 16H_2O$, maleic anhydride, or $NH_4H_2PO_4$, the hydrophobicity was greatly improved. This may be attributed to both the synergistic effect and the increased acidity (since the three chemicals are acidic and may contribute to the cross-linking).

Table 2. Effects of Combined Catalysts on Properties of Modified Woods Treated by Glyoxal[b]

| Catalyst (wt %)	WPG (%)	BE (%)	ASE (%)	WU (%)	Leachability (%)
$NaHSO_3$ + $(NH_4)_2S_2O_8$ (1:1) [*]	42.1 ± 1.7	9.8±0.6	57.8± 1.8	73.8 ± 5.2	86.1 ±3.2
HMT + $(NH_4)_2S_2O_8$ (1:1)	38.7 ± 1.7	9.6 ± 1.0	59.4 ± 3.5	76.8 ± 1.2	79.0 ± 2.7
$Na_2B_4O_7$ + $(NH_4)_2S_2O_8$ (1:1)	40.5 ± 2.9	9.5 ± 0.7	53.6 ± 2.9	74.9 ± 3.3	71.6 ± 6.0
$Al_2(SO_4)_3 \cdot 16H_2O$+$(NH_4)_2S_2O_8$(1:1)	40.0 ± 1.7	9.8 ± 1.0	65.0 ± 3.5	16.5 ± 1.2	41.3 ± 2.7
Maleic anhydride+$(NH_4)_2S_2O_8$(1:1)	46.1 ± 3.5	10.6 ± 0.5	67.4 ± 2.7	15.8 ± 3.0	40.1 ± 7.4
$NH_4H_2PO_4$ + $(NH_4)_2S_2O_8$ (1:1)	46.6 ± 1.2	9.8 ± 1.1	64.0 ± 2.2	29.0 ± 4.7	42.6 ± 6.7
$(NH_4)_2S_2O_8$	44.4 ± 3.3	9.6 ± 0.7	72.5 ± 3.7	38.7 ± 2.1	54.6 ± 3.8
[b] Values are expressed as means of eight replicates ± standard deviation [*] Ratio of weight percentage					
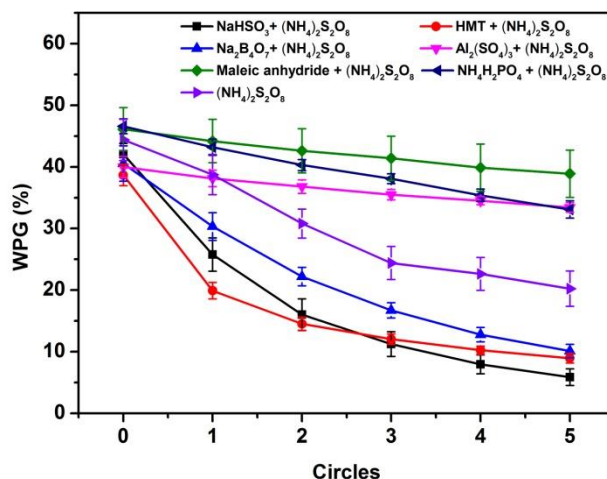
Fig. 2. WPG of treated wood after each leaching test. Glyoxal concentration is 20%, catalyst dosage is 2 wt% (final solution), glycol to glyoxal ratio is 1:2, and curing temperature is 120 °C

The WPGs of the modified wood treated by the combined catalysts after each leaching test are shown in Fig. 2. Clearly, all the WPGs with $NaHSO_3$, HMT, and $Na_2B_4O_7$ were reduced with an increase in the number of leaching tests, while the WPGs with $Al_2(SO_4)_3 \cdot 16H_2O$, maleic anhydride, or $NH_4H_2PO_4$ did not result in obvious change. This phenomenon indicated that the combination of $Al_2(SO_4)_3 \cdot 16H_2O$, maleic anhydride, or $NH_4H_2PO_4$ with $(NH_4)_2S_2O_8$ enhanced the modification effect, probably due to a synergistic effect and the increase in acidity.

Effects of $(NH_4)_2S_2O_8$ Dosage

The relationship between the catalyst dosage and the properties of the modified woods is shown in Table 3. The WPG increased with the addition of $(NH_4)_2S_2O_8$, which indicates that more glyoxal was incorporated in the wood. The ASE increased in a trend similar to WPG with an increase of catalyst. However, when more than 2% of $(NH_4)_2S_2O_8$ was added, the ASE did not change much.

Table 3. Effects of $(NH_4)_2S_2O_8$ Dosage on Properties of Glyoxal-Treated Woods[c]

$(NH_4)_2S_2O_8$ dosage (wt %)	WPG (%)	BE (%)	ASE (%)	WU (%)	Leachability (%)
0	41.6 ± 3.6	8.2 ± 0.8	49.0 ± 2.6	68.9 ± 4.6	79.5 ± 5.0
0.5	37.3 ± 2.5	9.1 ± 0.6	51.9 ± 3.7	46.0 ± 7.7	65.3 ± 6.7
1.0	40.6 ± 3.7	8.9 ± 0.8	66.1 ± 4.8	30.0 ± 1.9	53.4 ± 4.0
2.0	44.4 ± 3.3	9.6 ± 0.7	72.5 ± 3.7	38.7 ± 2.1	54.6 ± 3.8
4.0	46.8 ± 3.0	9.5 ± 0.5	72.4 ± 1.7	47.6 ± 4.6	46.0 ± 1.9
[c] Values are expressed as means of eight replicates ± standard deviation					

The catalyst dosage obviously affected WU. When no catalyst was added, the WU increased to 68.9%, but when 1% catalyst was added, the WU sharply decreased to 30%. In addition, the leachability after five leaching tests decreased markedly from 79.5% (without catalyst) to 46.0% (with 4% catalyst), which indicates the improved anti-leaching

ability. All of the improved properties may be due to the more complete reaction of glyoxal in the wood, which resulted from the increase in NH_4^+ content and acidity in the solution. However, the increased addition of catalyst deepened the discoloration of modified wood (Fig. 3), probably due to the increased degradation of cellulose and lignin in a much more acid solution (Xiao *et al.* 2012).
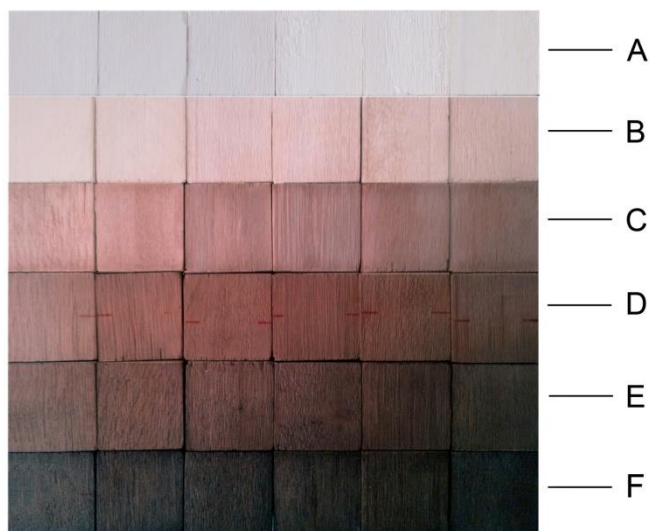

Fig. 3. Color of the modified wood with varying catalyst dosages. (A) untreated wood, (B) treated with 0 wt%, (C) 0.5 wt%, (D) 1 wt%, (E) 2 wt%, and (F) 4 wt% $(NH_4)_2S_2O_8$. Glyoxal concentration is 20%, glycol to glyoxal ratio is 1:2, and curing temperature is 120 °C

Effects of NaOH Dosage

Because cross-linking occurs after the addition of an acidic catalyst or inorganic acid salt (Dieste *et al.* 2008; Nakano 1993; Weaver *et al.* 1960; Xiao *et al.* 2012), the addition of NaOH can change the acidity of the modifying solution and further affect the catalytic efficiency of modification. The effects of NaOH dosage on properties of glyoxal-treated woods are shown in Table 4. Obviously, ASE decreased with an increase of NaOH, while both WU and total leachability increased which caused a decline in performance of the modified wood. The addition of more NaOH resulted in an additional decline in performance. For instance, when 1% NaOH was added, the ASE decreased by 17.3% while the WU increased by 51.3% and leachability by 70.4%.

Table 4. Effect of NaOH Dosage on Properties of Glyoxal-Treated Woods[d]

NaOH dosage (wt %)	WPG (%)	BE (%)	ASE (%)	WU (%)	Leachability (%)
0	42.6 ± 4.0	9.7 ± 0.9	69.3 ± 2.8	49.9 ± 9.2	25.3 ± 1.3
0.1	38.5 ± 5.1	9.3 ± 0.8	64.4 ± 2.3	61.5 ± 3.4	25.3 ± 2.4
0.2	36.5 ± 3.8	8.8 ± 0.4	60.6 ± 3.7	60.5 ± 4.9	27.7 ± 2.3
0.4	36.9 ± 4.2	8.8 ± 0.5	60.9 ± 2.7	61.7 ± 4.7	30.1 ± 2.9
0.6	41.5 ± 4.1	9.6 ± 0.8	57.6 ± 3.0	62.1 ± 4.0	30.1 ± 4.1
1.0	44.9 ± 2.1	9.9 ± 0.4	57.3 ± 4.0	75.5 ± 8.9	43.1 ± 2.2
[d] Values are expressed as mean of eight replicates ± standard deviation					

The decreased performance of modified wood can be primarily attributed to the decreased acidity of the solution due to the addition of NaOH. Therefore, it is easy to infer that when the solution was highly acidic, the catalyst had a higher catalytic efficiency and endowed wood with a better performance. Thus, it can further explain the curves in Fig. 2 owing to the addition of various acidic and alkaline catalysts in the solution.

Fig. 4. Color of the modified wood with different dosages of NaOH. (A) untreated wood, (B) treated with 1 wt%, (C) 0.6 wt%, (D) 0.4 wt%, (E) 0.2 wt%, (F) 0.1 wt%, and (G) 0 wt% NaOH. Glyoxal concentration is 20%, $(NH_4)_2S_2O_8$ dosage is 2 wt% (final solution), glycol to glyoxal ratio is 1:2, and curing temperature is 120 °C

The acidity of the solution may also affect the strength and color of the wood. Despite the improved performance, higher acidity also led to degradation of wood components and dark wood color, which are unfavorable for subsequent applications. The color of the modified wood with different amounts of NaOH is shown in Fig. 4. Clearly, with the addition of NaOH, the color of the modified wood blocks became increasingly lighter and closer to the color of the untreated blocks. In conclusion, proper addition of NaOH may contribute to successful modification, although the ASE may decrease slightly.

CONCLUSIONS

1. Glyoxal was confirmed to be an efficient wood modification reagent that greatly improved the dimensional stability and reduced the water uptake. The wood treated by glyoxal without catalyst had an ASE of about 49%, and the water uptake was reduced by 37.6% in comparison with the untreated one.

2. The type of catalyst can greatly affect wood modification, with $(NH_4)_2S_2O_8$ the most efficient catalyst, as it endowed wood with high dimensional stability, low water uptake, and low leaching efficiency. This may be due to both the catalytic effect of NH_4^+ (which can produce abundant oligomeric species by acid-catalyzed acetal formation and subsequent oligomerization) and the catalysis of $S_2O_8^{2-}$ (which can produce free radicals and initiate polymerization reaction), thus promoting the cross-linking between wood components and glyoxal. In addition, combination of different kinds of catalysts also had a great effect on the modification. Maleic anhydride and

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ammonium persulfate were shown to be the optimal combination, which may be attributed to both the synergistic effect of the two kinds of catalysts and the increased acidity.

3. Both the addition of catalyst and NaOH greatly affected the physical properties of the modified wood. Although the increased usage of $(NH_4)_2S_2O_8$ improved the dimensional stability and anti-leaching property of modified woods, it reduced the hydrophobic property and deepened the colour of the wood. Considering the balance between anti-swelling efficiency, leachability, and water uptake, the optimum catalyst concentration was 2%. The addition of NaOH alleviated the decolorization of wood, but also weakened the modification effect. Thus, proper usage of catalyst and NaOH will contribute to better modification.

ACKNOWLEDGMENTS

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