Comparison of Physical-mechanical and Mould-proof Properties of Furfurylated and DMDHEU-modified Wood

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In this study, 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) and furfuryl alcohol (FA) modification catalyzed by acrylic acid were comparatively studied. The effects on physical-mechanical properties and durability against mould of Masson pine and Camphor pine wood were investigated, including weight gain rate (WPG), moisture uptake, equilibrium moisture content (EMC), anti-swelling efficiency (ASE), parallel-to-grain compressive strength (CS), modulus of rupture (MOR), and mould resistance. The wood samples modified with DMDHEU closely retained their original color and texture, whereas the color of furfurylated wood became dark brown and the texture became clearer. The WPG of DMDHEU-treated wood ranged from 17.9% to 29.3%, which was lower than that of furfurylated wood that ranged from 36.7% to 39.3%. The equilibrium moisture content of DMDHEU-modified wood was slightly higher than the untreated wood, while furfurylation decreased the EMC of wood by approximately 50% compared with the untreated wood. The dimensional stability, parallel-to-grain compressive strength, and mildew resistance of Masson pine and Camphor pine improved after both modifications noticeably. It was concluded that acrylic acid can be utilized as a catalyst to perform wood furfurylation and DMDHEU modification.

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INTRODUCTION

Chemical modification has been recognized as an efficient strategy for dimensional stabilization of wood and protecting it from environmental damage (Xie *et al.* 2013). Wood chemical modification involves techniques where chemical and/or physical methods are applied to permanently alter the properties of wood cell walls through cell wall bulking, hydroxyl group deactivation, and/or filling the lumens with the chemicals to provide persistent protection to in-service wood (Hill 2006). The chemicals must have a small molecular size to penetrate wood micropores and be cured in wood cells (Klüppel and Mai 2013). Chemical modifications to wood, including heat-treatment, acetylation, modification with formaldehyde-based and N-methylol resins, and furfurylation, have been studied; some have been successfully applied in industrial production in recent decades (Xie *et al.* 2013). N-methylol compounds, such as 1,3-dimethylol-4,5-dihydroxyethylene-urea (DMDHEU), are widely used in the textile industry as finishing agents, and have successfully been used as wood modifying agents (Krause *et al.* 2003; Gérardin 2016; Emmerich *et al.* 2019; Kurt and Tomak 2019). Furfuryl alcohol is a low-molecular organic chemical with a strong polarity derived from corn cobs or sugar cane. It can be used to

improve several wood properties, including dimensional stability, hardness, modulus of rupture (MOR), modulus of elasticity (MOE), resistance to decay, and insect attacks (Epmeier *et al.* 2004; Lande *et al.* 2004; Hadi *et al.* 2005; Esteves *et al.* 2011; Li *et al.* 2015). Both DMDHEU and furfurylation are generally completed using acid-based catalysts and high-temperature treatment (Wewerka 1968; Barr and Wallon 1971; Krause *et al.* 2003; Xie *et al.* 2008).

Although an industrial process for wood furfurylation and modification based on DMDHEU has been developed and patented, investigations continue to be conducted on the use of furfuryl alcohol and DMDHEU for wood modification. Catalysts play a key role in the wood modification process. They should give the modifier formulation a long pot life, as well as ensure rapid polymerization when heated. Furthermore, the catalyst should have a small molecular weight, as well as similar affinity for wood substances and modifiers, as this ensures deep penetration into the wood cell wall without separation from the modifier. Both $AlCl_3 \cdot 6H_2O$ and tartaric acid were used for DMDHEU-modified Southern pine (Nicholas and Williams 1987). However, the catalyst led to the development of cracks in treated wood samples due to uneven distribution of DMDHEU, which resulted in the reduction of MOR. After that, magnesium chloride ($MgCl_2$), zinc nitrate ($Zn(NO_3)_2$), magnesium nitrate ($Mg(NO_3)_2$), and citric acid were used as catalysts to attempt to accelerate the cross-linking reaction of DMDHEU (Petrič *et al.* 2007; Xie *et al.* 2008; Yuan *et al.* 2013). Magnesium chloride ($MgCl_2$) has been found to be the most suitable catalyst for wood DMDHEU modification. However, some degree of strength loss of the treated wood is induced during the modification (Xie *et al.* 2007; Dieste *et al.* 2008; Emmerich *et al.* 2019). Similarly, the catalyst selection process for furfurylation of wood has gone through a long process. Zinc chloride was the initial catalyst used for wood furfurylation (Goldstein and Dreher 1960). However, zinc chloride easily separates from FA during penetration, with devastating effects on cellulose degradation and the long-term strength properties of treated wood (Anaya 1987). Schneider (1995) and Westin (1995) simultaneously developed alternative efficient catalysts using cyclic carboxylic for furfurylation of wood, citric acid, and maleic anhydride, which are the most studied catalysts in wood furfurylation (Lande *et al.* 2004, 2008; Venas and Rinnan 2008; Thygesen *et al.* 2010; Pfriem *et al.* 2012). Additionally, Baysal *et al.* (2004) reported that borates could be used as catalyst to perform furfurylation to improve the dimensional stabilization of wood. The authors have proposed a composite acidic catalyst for wood furfurylation in a previous study, which produced furfurylated wood with excellent mechanical and durable properties comparable to the widely used maleic anhydride, with less required FA and a lower cost (Li *et al.* 2015). Recently, Sejati *et al.* (2017) studied furfurylation of beech wood using five different catalysts; in addition to citric acid and maleic anhydride, maleic acid, itaconic acid, and tartaric acid were also studied. They indicated that tartaric acid can be considered as a new promising catalyst to perform wood furfurylation.

Both Masson pine (*Pinus massoniana* Lamb.) and Camphor pine (*Pinus sylvestris var. mongolica* Litv.) are the main tree species that need to be treated with preservatives before use in southern China. The aim of the study is to evaluate the feasibility of acrylic acid as a catalyst to perform wood furfurylation and DMDHEU modification of Masson pine and Camphor pine wood. Weight gain rate (WPG), moisture uptake, equilibrium moisture content (EMC), anti-swelling efficiency (ASE), parallel-to-grain compressive strength (CS), MOR, and mould resistance were selected as characterization parameters.

Furthermore, scanning electron microscopy (SEM) was used to investigate the effect of different modification on the wood's microstructure.

EXPERIMENTAL

Materials

Sapwood specimens of Masson pine (*Pinus massoniana* Lamb.) and Camphor pine (*Pinus sylvestris var. mongolica* Litv.) were bought from vendors in Guangdong Province of China. Wood samples were cut from sawn lumber with a thickness of 4 cm. They were dried at 103 °C until oven-dry state was achieved, weighed, then conditioned in 23 °C and 65% relative humidity for at least 30 days before the treatment. Wood samples were prepared according to GB/T 1928 (2009) (Table 1).

Table 1. Information of Wood Samples

Parameter	Sample Size (T × R × L)	Number of Samples / Groups
WPG	20 mm × 20 mm × 20 mm	10
ASE		
EMC	20 mm × 20 mm × 30 mm	10
CS		
MOR	10 mm × 10 mm × 160 mm	10
Mould test	20 mm × 5 mm × 50 mm	24

Methods
Solution preparation

Furfuryl alcohol (light yellow liquid, ≥ 98% purity) and DMDHEU were bought from Hongshuolin Company (Guangzhou, China). Buffering agents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Other chemicals that were used were of analytical grade, and all solutions were prepared with deionized water. The modification solution was prepared at room temperature, containing weight percentages of 50% DMDHEU (50 to 55% solid content) or FA and 5% acrylic acid as the catalyst. Water, buffering agents, catalyst, and DMDHEU or FA were added in that order.

Impregnation and polymerization

The samples and solutions were placed in a plastic box, and an iron gauze was used to press down the samples to prevent them from floating on the surface of the solution. The plastic box was placed in a tank and pressure treatment was applied. This process consisted of treatment in a vacuum for 15 min followed by 1.5 MPa of pressure for 30 min, then immersion in a modification solution for 16 h at normal pressure. The impregnated wood specimens were then wrapped in aluminum foil to avoid evaporation of the solution during the curing stage. The samples were cured at 95 °C for 3 h. After polymerization, the treated samples were further dried at 105 °C until an oven-dried state was achieved.

Physical and mechanical properties testing

The physical and mechanical properties of all the samples were tested according to Chinese National Standards GB/T 1931 (2009) and GB/T 1934.2 (2009).

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The WPG of modified wood was calculated using Eq. 1, which represents the weight changes caused by the modification,

$$\text{WPG (\%)} = \frac{M_1 - M_0}{M_0} \times 100 \tag{1}$$

where M_1 and M_0 are the oven-dry mass (g) of wood before and after modification, respectively.

To determine the wettability of treated and untreated wood, the treated and untreated wood blocks were weighed and soaked with deionized water in a glass container. They were then collected and weighed after 1, 5, 10, 15, 20, and 30 d. The water uptake (WU) was calculated according to Eq. 2,

$$\text{WU (\%)} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100 \tag{2}$$

where M_{wet} and M_{dry} are the weight (g) of wood after absorption of water and the oven-dried weight (g) of the wood samples, respectively.

The dimensional stability of wood was characterized by ASE. The dimensional stability of the dry and wet treated wood was measured. The tangential, radial, and longitudinal sizes were recorded. The ASE was calculated according to Eqs. 3 and 4,

$$\alpha \text{ (\%)} = \frac{V_{\text{wet}} - V_{\text{dry}}}{V_{\text{dry}}} \times 100 \tag{3}$$

$$\text{ASE (\%)} = \frac{\alpha_0 - \alpha_1}{\alpha_0} \times 100 \tag{4}$$

where V_{wet} and V_{dry} are the size (mm) of the modified wood samples in wet and dry states, respectively, and α_0 and α_1 represent the coefficient of wet expansion of the untreated and modified wood samples, respectively.

The MOR and MOE of wood were tested according to the Chinese national standard GB/T 1936.1 (2009). The previously conditioned 10 mm × 160 mm × 10 mm (T × L × R) wood samples were tested in a three-point bending model using a universal mechanical testing machine (AGS-X plus-50 kN; Shimadzu, Tokyo, Japan). The machine was operated with a span of 120 mm and a displacement-controlled testing speed of 2 mm/min. The MOR and MOE were determined with Eqs. 5 and 6, respectively,

$$\text{MOR} = \frac{3P_{max}L}{2bh^2} \tag{5}$$

$$\text{MOE} = \frac{P_p L^3}{4\delta bh^3} \tag{6}$$

where P_{max} is the maximum load (N), L is the testing span of the samples (mm), b is the width of the samples (mm), h is the thickness of the samples (mm), P_{p} is the load difference (N) between the upper and lower boundary loads within the proportional limit, and σ is the mid-span deflection (mm) of the sample under P_{p}.

The parallel-to-grain compressive strength of wood was tested according to the Chinese national standard GB/T 1935 (2009). Samples with sizes of 20 mm × 30 mm × 20 mm (T × L × R) were loaded with a constant loading rate, and the maximum compressive load that the sample could withstand for more than 90 s without collapse was recorded.

Simple mould tests

Simple mould tests were performed in a climate chamber with controlled relative humidity (RH) and temperature, with a similar method used by Ahmed *et al.* (2013). Glass tubes were attached to the top of the chamber (Fig. 1). Each sample was hung from the supporting glass tubes. A 10-mm minimum gap was maintained between the two samples. *Aspergillus niger* V. Tiegh, *Penicillium citrinum* Thom, *Trichoderma viride* Pers. ex Fr., and *Botryodiplodia theobromae* Pat. were applied to infect the samples. The petri dish covered with molds was placed in the lower part of the climate chamber to infest the chamber with spores. The infected samples were kept for one month in the climate chamber. Mold growth on each sample was visually rated according to the criteria described in the Chinese National Standard GB/T 18261 (2013).
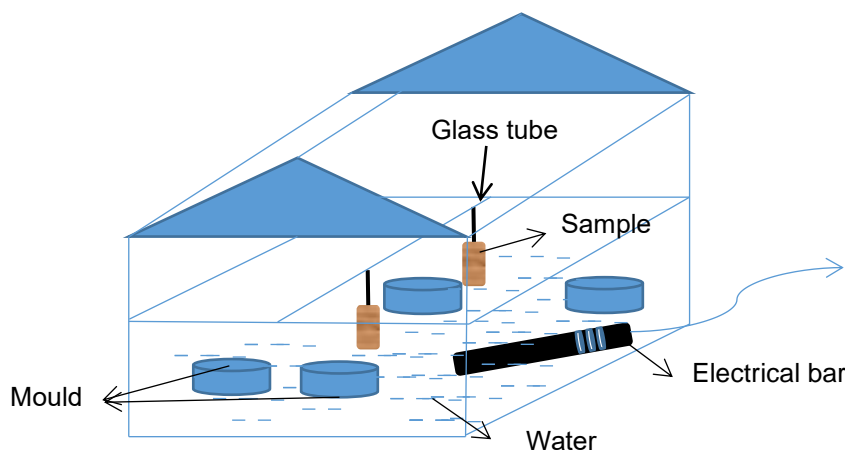

Fig. 1. Schematic of the climate chamber. An electrical bar was used to heat the water to maintain the temperature and humidity in the climate chamber

Scanning electron microscope (SEM) analysis of wood

Prior to SEM analysis, the specimens were coated in gold (Electron Microscopy China, Beijing, China). The cross and longitudinal sections of wood samples were scanned for macroscopic inspection. The samples were then examined using a scanning electron microscope (ZEISS SUPRA 40; Carl Zeiss, Jena, Germany) operating at an accelerating voltage of 30 kV.

RESULTS AND DISCUSSION

Physical Properties

The DMDHEU can form an interaction between hydroxyl groups and cross-link the wood cell wall (Gérardin 2016). Furfurylation of wood is based on *in situ* polymerization of furfuryl alcohol, which produces a branched polymer *via* connection of methylene groups and/or dimethylene ether groups (Barsberg and Thygesen 2009). No matter how different the modification mechanism, the penetration of modifiers in the cell wall is necessary to impart new properties on the treated wood. As shown in Fig. 2, the wood samples modified with DMDHEU almost retained their original color and texture, whereas the color of furfurylated wood became dark brown and the texture became clearer. After DMDHEU modification, $17 \pm 4\%$ and $29 \pm 3\%$ WPGs were observed for modified Masson

pine and Camphor pine wood, respectively. This result suggested that the use of acrylic acid as a catalyst can perform the reaction of DMDHEU in wood, but the amount of catalyst that is used needs to be further optimized. Furthermore, whether there are amounts of monomeric acrylic acid in the treated wood needs to be considered. A previous study suggested that DMDHEU and acrylic acid could be used to synthesize the DMDHEU-AA products for cotton fabrics treatment, and the crosslinking between cellulose and the –COOH of the DMDHEU-AA was confirmed (Chen *et al.* 2001). Therefore, the presence of unreacted monomers probably could be avoided. The WPG was slightly lower than has been previously reported in systems catalyzed by other catalysts. Mamiński *et al.* (2016) observed 36 ± 4% and 22 ± 6% WPGs for modified oil palm (*Elaeis guineensis* Jacq.) waste trunk, with 34% and 17% DMDHEU, respectively, containing 5 wt% p-toluenesulfonic acid (p-TSA) used as the catalyst. Dieste *et al.* (2008) modified *Betula* sp. and *Fagus sylvatica* plywood with 0.8 M to 2.3 M DMDHEU using 4% magnesium nitrate as the catalyst, gaining the WPG of treated wood was between 6% and 35%. The material they modified was not solid wood, which is one of the factors to consider. In contrast, higher WPGs appeared in furfurylation of Masson pine and Camphor pine wood, ranging between 20.9% to 35.9% and 37.9% to 44.4% with averages of 25.2% and 39.2%, respectively. Esteves *et al.* (2011) treated *Pinus pinaster* with a 70% FA mixture and found an average WPG of 38%. Sejati *et al.* (2017) reported that the WPG of European beech (*Fagus sylvatia* L.) furfurylated with 50% FA and 5% tartaric acid catalyst was 40.7% for larger samples. The result indicated that acrylic acid can also perform the reaction of furfuryl alcohol in wood and obtain comparable results.
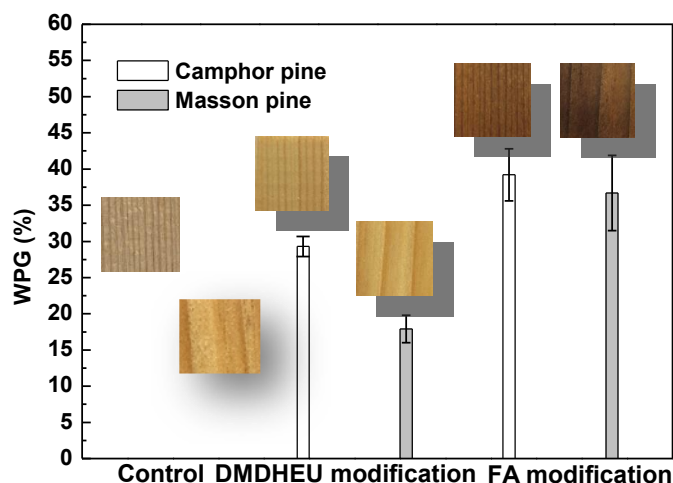

Fig. 2. The WPG of modified Masson pine and Camphor pine wood

The equilibrium moisture content (EMC) of untreated and modified wood is shown in Fig. 3, for which the measurements were done after conditioning in a controlled environment at 20 °C and 65% relative humidity for 30 days. The EMC of furfurylated Masson pine and Camphor pine wood decreased 44% from 8.5% to 4.8%. These results showed a clear decrease in EMC that was consistent with the results of other researchers (Epmeier *et al.* 2007; Esteves *et al.* 2011). In contrast, the EMC of DMDHEU-modified wood did not decrease, but it presented a higher EMC than those of untreated Masson pine

and Camphor pine wood. This meant DMDHEU-modified wood absorbed more moisture than the control wood. According to most previous studies, DMDHEU modification can also remarkably reduce the EMC of wood. For example, the EMC of Scots pine and European beech wood treated with 30% DMDHEU (catalyst $MgCl_2$) was reduced 3% to 4% (Schaffert *et al.* 2006). This phenomenon can be attributed to the unreasonable amount of catalyst used for DMDHEU modification. The DMDHEU molecule itself is a hygroscopic substance, with a molecular weight composed of up to 39% of OH groups. The reactions of DMDHEU monomers, approved for wood, cause cross-linking of the hydroxyl groups of (-OH) of cellulose and hemicellulose through the reactive functional groups, and polymerization (auto-condensation), which produce molecules that consist of 26% and 24% OH groups, respectively (Emmerich *et al.* 2019).
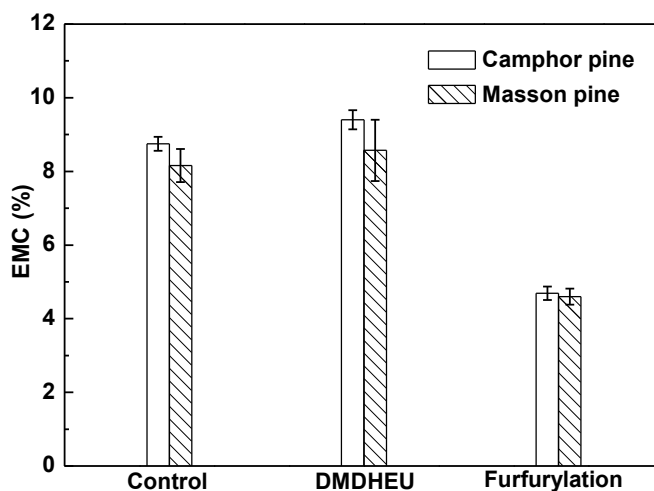

Fig. 3. The EMC of modified Masson pine and Camphor pine wood

Overall, both modifications reduced the rate and amount of water uptake of Masson pine and Camphor pine wood (Fig. 4). A comparative look at the difference in water absorption between Masson pine and Camphor pine wood shows that the former had a lower water uptake than that of the latter after the same soaking time. This difference can be related to structural differences in the different species. Both untreated Masson pine and Camphor pine wood showed a more rapid water uptake than that of modified wood after the same submersion times, except the DMDHEU-modified Camphor pine wood showed quicker water uptake in the first 9 days compared to the untreated wood. Furfurylation caused a greater reduction in water uptake than the DMDHEU modification. The reduction effect of furfurylation was also shown by Treu *et al.* (2009) and Bastani *et al.* (2015). Additionally, they found that furfurylated wood with a higher uptake of FA caused a slightly greater reduction in water uptake. The improvement of furfurylated wood hydrophobicity was mainly due to the polymerization of small but polar FA monomers in the wood cell walls. The formed hydrophobic FA resin causes the cell wall to become bulkier and reduces its ability to swell upon water absorption (Dong *et al.* 2015; Kong *et al.* 2018). As previously reported, DMDHEU modification also can reduce the water absorption of wood. Coated Scots pine (*Pinus silvestris* L.) sapwood panels pre-treated with DMDHEU resulted in lower uptake in periodical submersion tests (Xie *et al.* 2008). Mamiński *et al.* (2016) reported that 34% and 17% DMDHEU-modified palm trunk

reduced water absorption 48% and 25% after 24 h of soaking, respectively. The lower water uptake of the DMDHEU-treated wood is explained by the penetration of DMDHEU into the cell walls and the resulting cell wall bulking, which reduces the number of sites in the cell wall that are available to absorb water molecules (Xie *et al.* 2008). Furthermore, DMDHEU modification reduces the fibre saturation point by filling micropores that are available for water sorption in the cell walls of untreated wood (Yasuda *et al.* 1994; Dieste *et al.* 2008). The DMDHEU fills some of the larger pores, leaving less space for water adsorption; this implies that the control wood absorbs more water than modified wood (Dieste *et al.* 2009). The phenomena that DMDHEU-modified Camphor pine wood soaked up more water than untreated wood in the first 9 days can be explained by the hygroscopic character of the DMDHEU monomer, which provides additional adsorption sites after modification (Emmerich *et al.* 2019).
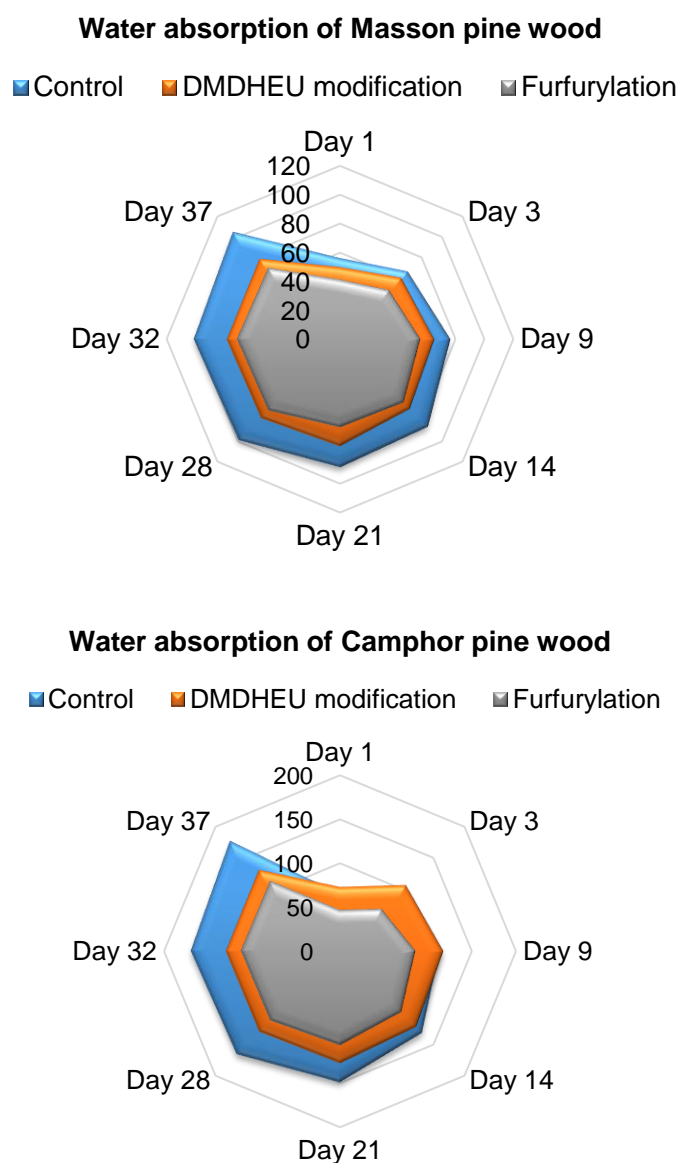

Fig. 4. The water uptake of untreated and modified Masson pine and Camphor pine wood

Figure 5 summarizes findings that both DMDHEU modification and furfurylation improved the dimensional stability of Masson pine and Camphor pine wood. The ASE in the tangential (T-ASE), radial (R-ASE), and volume (V-ASE) of furfurylated Masson pine on average was 48.2%, 40.4%, and 39.3%, respectively, and those of furfurylated Camphor pine on average were 45%, 20%, and 26.4%, respectively. Several previous studies have reported that furfurylation can greatly enhance the dimensional stability of wood. Epmeier *et al.* (2004) and Esteves *et al.* (2011) reported the ASE of furfurylated Scots pine and *Pinus pinaster* ranged from 45% to 50% when catalyzed by maleic anhydride. In the authors' previous study, the ASE of furfurylated Masson pine wood catalyzed with a composite organic acid catalyst increased on average 47.6%, 61.45%, 66.41%, and 53.87% in the tangential, radial, and longitudinal directions, and volumetric, respectively (Li *et al.* 2015). The average values for the T-ASE, R-ASE, and V-ASE for the Masson pine treated with DMDHEU were 56%, 29%, and 47.8%, respectively, those of DMDHEU-treated Camphor pine were 56.1%, 31.6%, and 51.2%, respectively. In contrast, the ASE of DMDHEU-modified wood was higher than that of furfurylated wood. This was explained by the modification mechanism. The dimensional stability increased to a great extent when modification took place in the wood cell walls rather than in cell cavities.
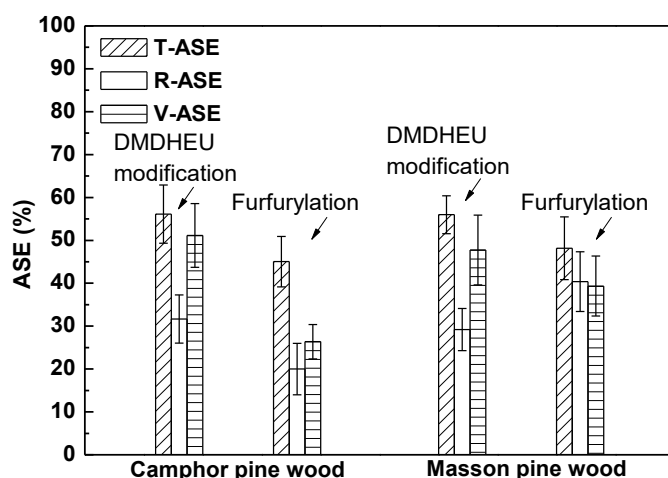

Fig. 5. The ASE of untreated and modified Masson pine and Camphor pine wood

Mechanical Properties

The compressive tests revealed that the DMDHEU modification and furfurylation had a positive effect on the parallel-to-grain CS, as shown in Fig. 6a. The CS of modified Camphor pine wood increased 50% relative to the control. For the DMDHEU-modified and furfurylated Masson pine wood, the CS increased 21% and 51% relative to the control. Winandy and Rowell (2005) reported that beech wood treated with DMDHEU catalyzed by $MgCl_2$ exhibited an increase in compression strength of up to 65%.

Figure 6b shows the effect of modification on the MOR of Masson pine and Camphor pine wood. The MOR of furfurylated Camphor pine and Masson pine wood increased 12.9% and 25.7% relative to the untreated wood, respectively. The MOR of DMDHEU-modified Masson pine was only increased 2.8% relative to the untreated wood, while that of DMDHEU-modified Camphor pine wood decreased 25% relative to the control. Nicholas and Williams (1987) modified Southern pine with 10% DMDHEU catalyzed by 0.5% $AlCl_3·6H_2O$ and 0.5% tartaric acid and found a reduction of the MOR

in bending of 37%. Beech wood treated with DMDHEU catalyzed by $MgCl_2$ exhibited only a slight decrease of MOR in bending (Winandy and Rowell 2005). Additionally, Dieste *et al.* (2008) also reported that the plywood produced with *Betula* sp. and *F. sylvatica* and modified with DMDHEU presented no remarkable reduction of bending strength. This can be partly explained by the modified wood's different EMC. Furthermore, acidic modifier solutions will inevitably remove some number of hemicelluloses from wood, which will cause more negative effects on the bending properties. The experimental results showed that the wood samples treated by different modifiers exhibited different failure modes after the bending test. The samples treated by DMDHEU exhibited a regular fractured surface with some fragments and had a certain degree of embrittlement. The failure of the furfurylated wood samples exhibited a similar fracture pattern as that of untreated wood. Xie *et al.* (2013) found that resin modification can reduce the impact property of wood and increase its brittleness.
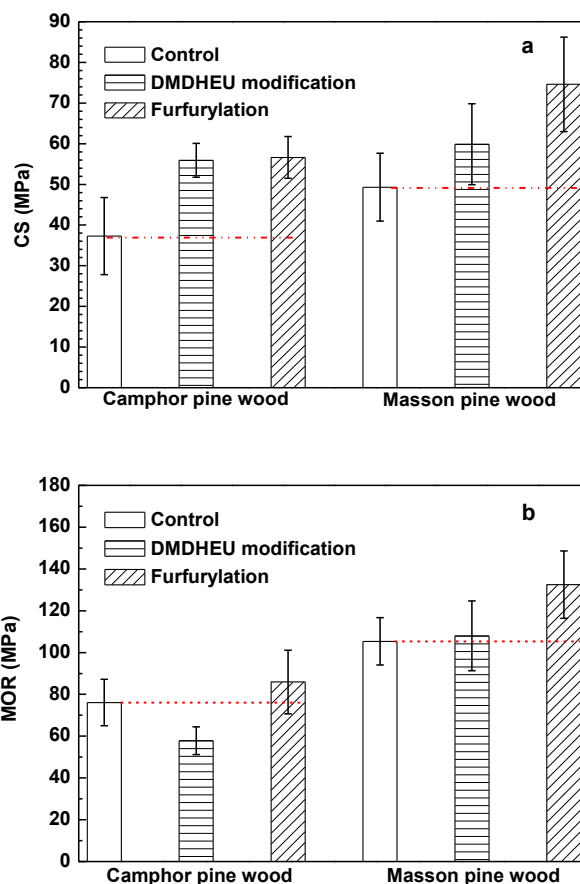

Fig. 6. The effect of modification on the CS and MOR of Masson pine and Camphor pine wood

Figure 7 displays the SEM images of the cross and vertical sections for untreated and modified wood samples. For the cross-section, the natural cellular structure of Masson pine and Camphor pine wood with irregular cell shapes can be observed from the untreated samples. Compared to the untreated wood samples, part of the wood cells with filled lumen and cell walls can be observed from DMDHEU- and furfuryl alcohol-modified wood samples (shown by the arrow in Fig. 7 $b_1/c_1/e_1/f_1$). These results suggested that the wood

structure could be permanently filled with resins through the chemical reaction. Moreover, the cell inwall of the furfurylated wood samples was smoother and full, which indicated that the furfuryl alcohol modifier penetrated the cell walls more easily. Another important finding was that the cell wall of the DMDHEU-modified wood samples exhibited slight cracks (shown by the arrow in Fig. 7b$_1$ and e$_1$), and many resins were scattered in the lumens. This phenomenon could have been due to the morphology of DMDHEU resins. Compared to the untreated samples, substances were noticeably adhered to the vertical structure of all modified wood samples, which resulted in the smooth lining of the cells and the raised pits' edges. Part of the pits of the modified wood samples were filled with resins. This filling could block the entry of water into the wood, so that the water-induced dimensional change of the wood could be decreased. Furthermore, in DMDHEU-modified wood samples, the intercellular layer exhibited a bulk type with a brittle, ruptured surface (arrow in Fig. 7b$_2$). This may explain why the MOR of DMDHEU-modified Camphor pine wood decreased.
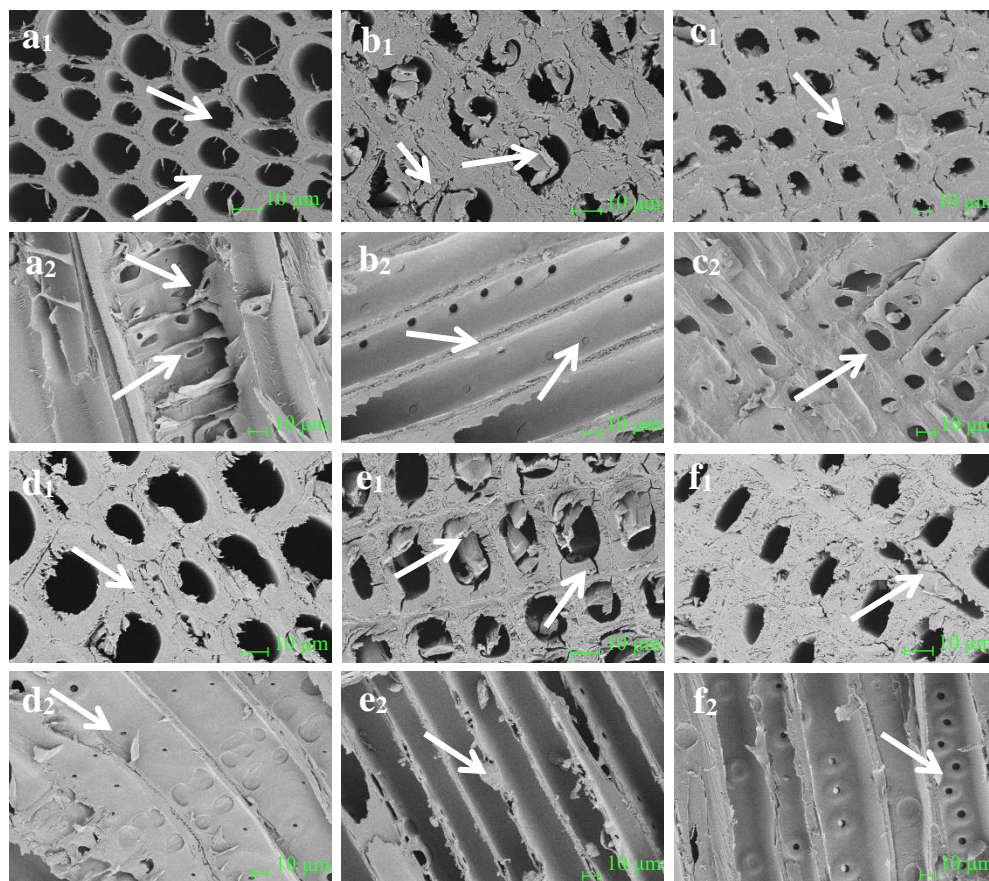

Fig. 7. The SEM morphology of untreated and modified wood samples. Picture a$_1$a$_2$ (d$_1$d$_2$) is from untreated Masson pine and Camphor pine wood; Picture b$_1$b$_2$ (e$_1$e$_2$) is from Masson pine and Camphor pine wood treated by DMDHEU resin; Picture c$_1$c$_2$ (f$_1$f$_2$) is from Masson pine and Camphor pine wood treated by FA resin.

Mould-proof Properties

Mould tests were performed in a climate chamber with controlled 95% RH and a temperature of 25 °C. The results of the mould evaluation of modified Masson pine and

Camphor pine wood with DMDHEU and furfurylation are summarized in Table 2. The untreated Masson pine and Camphor pine wood showed little resistance to mould exposure and became rapidly covered with mould after one week. After 4 weeks of exposure, the DMDHEU-modified and furfurylated wood showed some excellent resistance to mould growth compared to the untreated samples. After one month of testing, the untreated wood samples were almost covered by *Aspergillus niger* and *Botryodiplodia theobromae*. According to the criteria in the Chinese National Standard GB/T 18261 (2013), the mould resistance level reached 4. In contrast, there was a small amount of hypha infection on the surface of the DMDHEU-modified wood samples and little infection on the surface of the furfurylated wood samples. The mould resistance rating value after four weeks of testing of untreated DMDHEU-modified and furfurylated Masson pine and (Camphor pine wood) was 4 (3.6), 0.96 (0.4), and 0.05 (0), respectively. The improvement of mold resistance by both modifications can be attributed to multiple factors. First, the entry channel of mold into the wood was blocked (Xie *et al.* 2008). Second, the reduction in moisture adsorption inhibited fungi growth on the surface of furfurylated wood (Ringman *et al.* 2014). Furthermore, the introduction of an acidic catalyst during the modification process changed the pH value of the wood surface and made it unsuitable for mold growth (Wu and Weng 2000).

Table 2. Results of Mould-proof of Untreated and Modified Masson Pine and Camphor Pine Wood

Samples	Treatment	Average Mildew Grade	Resistance Effectiveness (%)
Masson Pine	Control	4	0
	DMDHEU modification	0.96	76
	Furfurylation	0.05	98
Camphor Pine	Control	3.6	10
	DMDHEU modification	0.4	90
	Furfurylation	0	100

In the present study, acrylic acid can be used successfully as a catalyst to perform the reaction of DMDHEU and furfuryl alcohol in wood. However, more measurements and experiments should be conducted to demonstrate that the modification is harmless to human health and environmentally friendly. For example, the formaldehyde emissions should be considered due to DMDHEU monomers are synthesized from urea, glyoxal and formaldehyde (Emmerich *et al.* 2019). Studies have shown that formaldehyde emissions were affected by curing conditions, reagent concentration and type of reagent (Schaffert *et al*. 2005; Krause 2006; Bollmus 2011). The relevant investigations are being conducted to optimize catalyst content and curing condition of DMDHEU modification.

CONCLUSIONS

1. Both DMDHEU modification and furfurylation remarkably improved the physical and mechanical properties and mildew resistance of Masson pine and Camphor pine wood.

The results showed that acrylic acid can be used successfully as a catalyst to perform the reaction of DMDHEU and furfuryl alcohol in wood.

2. DMDHEU modification almost retained the wood samples' original color and texture, whereas the color of furfurylated wood became dark brown and the texture became clearer. Both modification had a positive effect on the dimensional stability and the parallel-to-grain CS of wood, and the modified wood showed excellent resistance to mould compared to the untreated samples with the more than 76% resistance effectiveness.

3. There were significant differences in the effects of the two modification methods on EMC and WU of wood. For example, the EMC of furfurylated wood was reduced 50%, while that of DMDHEU-modified wood was slightly higher than the untreated wood. The results indicated that the use of acrylic acid as a catalyst needs to be further optimized for DMDHEU modification.

ACKNOWLEDGMENTS

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