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RESEARCH ARTICLE

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Improvement of wood properties by urea-formaldehyde resin and nano-SiO_2

Abstract In order to improve wood properties of triploid clones of *Populus tomentosa*, urea-formaldehyde (UF) resin was compounded with nano-SiO_2, coupling agents and flame retardants in different ways to prepare five kinds of modifiers. The poplar wood samples were impregnated with the modifiers and heated to prepare UF-SiO_2-wood composites. The antiswelling efficiency, resistance of water absorption, oxygen index and hardness of the composites were measured. Results show that all of the modifiers reduced water absorption of poplar wood and enhanced flame resistance and hardness. Nano-SiO_2 showed a marked effect in improving the hardness of wood. In addition, all of the modifiers, except UF-C-SiO_2-polymer, improved the dimensional stability of poplar wood. The UF resin and nano-SiO_2 compound improved general properties of poplar wood.

Keywords wood modification, UF resin, nano-SiO_2, triploid clones of *Populus tomentosa*

1 Introduction

It has been recognized in many countries that it is important to improve wood properties, especially those of inferior wood, to make good use of inferior wood and to enhance the utilization-rate of wood resources (He and Wu, 2002). Triploid clones of *Populus tomentosa* is one of the most abundant species of fast-growing trees in China. To relieve the crisis of the lack of wood resources in China, it will be important to improve the properties of triploid clones of *P. tomentosa* wood. Among the many ways to arrive at this goal, wood modification technology is one feasible method (Wang et al., 2001).

Wood modification has been emphasized and studied by many researchers. Saka et al. (1992, 1993a, 1993b, 1994, 1996a, 1996b) reported to have prepared wood-based inorganic composites by sol–gel processes, which possessed comparatively high dimensional stability and flame resistance. Takeshi et al. (1991, 1992, 1993), taking sodium silicate as a main reagent, improved the flame resistance, decay resistance and dimensional stability of wood, but compromised the mechanical strength and anti-hygroscopicity. Yamaguchi (1994a, 1994b) treated wood samples with silica sol, in which phosphoric acid was added to adjust its pH value and enhanced the bending strength and dimensional stability of wood. Fumie et al. (1998) prepared wood-based inorganic composites, which were highly antibacterial, by applying an antibacterial reagent during sol–gel processes. Li et al. (2001) studied the preparation of acetylated and propionylated wood-silicate composites with fairly good dimensional stability and fire-resistance. It was also reported (Qian et al., 2001) that impregnating fir wood with urea-formaldehyde resin followed by hot-pressing could improve its mechanical strength. Shen et al. (2005) modified fir wood with natural organic compounds and enhanced its hardness and abrasion resistance. Applying phenol-formaldehyde resin, Fang et al. (1999) and Furuno et al. (2004) respectively treated poplar wood and Japanese cedar wood, enhancing the dimensional stability and mechanical strength of poplar wood and the dimensional stability and decay resistance of cedar wood. In addition, wood-SiO_2 composites with comparatively high dimensional stability were prepared by Wang et al. (1996, 1998) and Sun et al. (1998). It was also reported that tetraethyl orthosilicate (TEOS) and tetrabutyl titanate ($Ti(OBu)_4$) could be used to improve the permeability and hardness of wood (Xu et al., 2005).

However, almost all of the previous studies emphasized only on the modification of part of the properties of wood rather than all of them; some treatments even impaired some good performances of wood.

Nano-materials and nano-technology have been successfully utilized in many fields. For instance, some nano-oxides markedly enhanced the abrasion resistance and self-cleaning function of some paints. It was reported that nano-SiO_2 was beneficial in improving the bonding strength of UF adhesive

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and abate its free formaldehyde emission (Lin et al., 2005). Therefore, it could be expected that nano-materials could be applied to modify the properties of inferior wood as well (Shi et al., 2004).

In this study, nano-SiO_2, coupling agents, flame retardants and urea-formaldehyde resin were applied to treated triploid clones of *P. tomentosa* wood. Antiswelling efficiency, resistance of water absorption, oxygen index and hardness of the treated wood specimens were measured to evaluate their general properties.

2 Materials and methods

2.1 Materials

Wood specimens: sapwoods of triploid clones of *P. tomentosa* (10 years old; the dimensions are shown in Table 1), urea (industrial production), formaldehyde solution (37%), nano-SiO_2 (Nanjing High Technology Nano Co. Ltd, Style: HT Si01), ammonium chloride (analytically pure), hexamine (chemically pure), coupling agent (KH550 analytically pure), flame retardant (our own preparation), hydrochloric acid solution (1 mol/L, our own preparation), acetic acid solution (36%, analytically pure), ammonia (25%) and sodium hydroxide solution (30%, both of our own preparation).

Table 1 Dimensions of wood specimens

Application	Sizes (R × T × L) /mm
Antiswelling efficiency, resistance of water absorption, leaching efficiency	30 × 30 × 5
Hardness*	6 × 100 × 100
Oxygen index	2 × 6.5 × 150

*The dimensions of the specimens used for hardness measurements were different from the regulations of GB1941-80 but made no differences in the contrasts of the properties between the groups.

2.2 Method

2.2.1 Preparation of UF resin

UF resin was prepared according to the conventional alkali–acid–alkali process (urea:formaldehyde = 1:1.15, mol/mol).

Performances: viscosity = 16.5 MPa·s; solid content = 56.4%; gel time = 150 s; pH = 7.1; free formaldehyde content = 0.10%; appearance was opalescent liquid.

2.2.2 Preparation of UF-C-SiO_2-polymer

Nano-SiO_2 was treated, at first, with a coupling agent (nano-SiO_2: coupling agent = 1:0.15, weight/weight, high-speed stirring) and was then added to the reacting system of the UF resin mentioned above during the acid process (urea: formaldehyde:nano-SiO2 = 1:1.15:0.13, mol/mol/mol).

Performances: viscosity = 15.0 MPa·s; solid content = 41.8%; gel time = 105 s; pH = 7.3; free formaldehyde content = 0.12%; appearance was opalescent liquid.

2.2.3 Preparation of UF-C-SiO_2-compound

The conventional UF resin and treated nano-SiO_2, as mentioned above, were mixed together under high-speed stirring for 10 min (UF: nano-SiO_2 = 100:0.5, weight/weight).

2.2.4 Preparation of UF-SiO_2-compound

The conventional UF resin and untreated nano-SiO_2 were mixed together under high-speed stirring for 10 min (UF: nano-SiO_2 = 100:0.5, weight/weight).

2.2.5 Preparation of UF-R-SiO_2-compound

Flame retardant was added to the conventional UF resin and the compound was stirred until it became homogeneous (UF:flame retardant = 100:20, weight/weight).

2.2.6 Treatments of wood specimens

Five groups of wood specimens (five specimens were used for each group) were separately immersed in the different reagents, into which ammonium chloride (1% of the solid weight of UF resin) had been added as hardener, at reduced pressure (0.02 MPa) for 30 min and then at atmospheric pressure for 6 h. The process was then repeated once. The superfluous reagents on the surface of the specimens were wiped away. Then, the specimens were oven-dried at 120°C for 30 min and their weights and dimensions subsequently measured.

2.2.7 Measurements of treated wood specimens

The treated specimens were immersed in water and the pressure was reduced to 0.02 MPa for 30 min, then resumed at atmospheric pressure for 24 h at room temperature. The dimensions of the water-absorbed specimens were measured. After that, the specimens were oven-dried at 105°C for 24 h and the dimensions and weight measured.

1) Weight percent gain (WPG) was calculated using the following formula (1).

$$WPG = \frac{G_2 - G_1}{G_1} \times 100\% \tag{1}$$

where G_1 was the weight of oven-dried wood specimens before treatment (g) and G_2 the weight of oven-dried wood specimens after treatment (g).

2) The antiswelling efficiency (ASE) was calculated using the following formula (2):

$$ASE = \frac{\Delta V_0 - \Delta V}{\Delta V_0} \times 100\% \tag{2}$$

where ΔV_0 is the volumetric swelling coefficient of untreated wood specimens (%), $\Delta V_0 = [(V' - V_0)/V_0] \times 100\%$, ΔV the volumetric swelling coefficient of treated wood specimens

(%), $\Delta V = [(V_3 - V_2)/V_2] \times 100\%$. V_2 is the volume of oven-dried treated wood specimens (mm^3), V_3 the volume of treated wood specimens after water saturation (mm^3), V_0 the volume of oven-dried untreated wood specimens (mm^3) and V' is the volume of untreated wood specimens after water saturation (mm^3).

3) The bulking coefficient (B) was calculated as follows:

$$B = \frac{V_2 - V_1}{V_1} \times 100\% \tag{3}$$

where V_1 is the volume of oven-dried wood before treatment (mm^3).

4) The leaching efficiency (L) was calculated using the following formula (4).

$$L = \frac{G_2 - G_4}{G_2 - G_1} \times 100\% \tag{4}$$

where G_4 is the weight of oven-dried treated wood after leaching (g).

5) The resistance of water absorption (RWA) is calculated by formula (5):

$$RWA = \frac{\Delta G_0 - \Delta G}{\Delta G_0} \times 100\% \tag{5}$$

where G_0 is the weight of oven-dried untreated wood specimen (g), $\Delta G_0 = [(G' - G_0)/G_0] \times 100\%$, $\Delta G = [(G_3 - G_2)/G_2] \times 100\%$, G_3 is the weight of treated wood specimens after water saturation (g) and G' the weight of untreated wood specimens after water saturation (g).

6) Measurement of hardness

The hardness of treated wood specimens and control specimens were measured according to GB1941-1991.

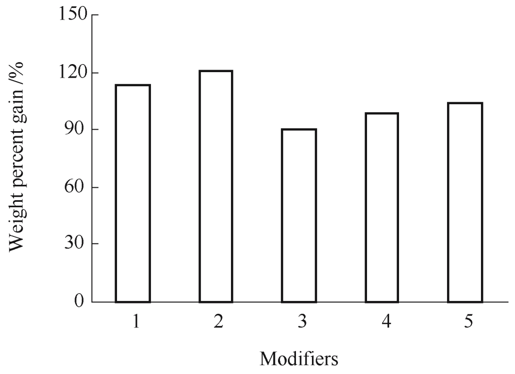
7) Measurement of oxygen index

The oxygen indices were measured according to the GB7911.6-87.

3 Results and discussion

3.1 Weight percent gain (*WPG*)

The effects of different modifiers on *WPG*s of wood specimens are shown in Fig. 1. In contrast with the *WPG*s of specimens treated with UF resin, the *WPG*s of other groups, to which nano-SiO$_2$ was added, did not fluctuate widely, which indicated that small amounts of nano-SiO$_2$ applied in this study did not markedly affect the impregnation of UF resin into wood.

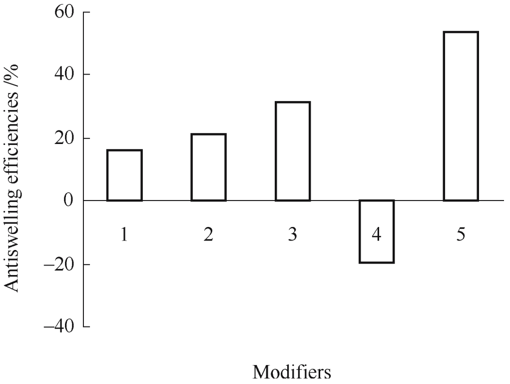


1: UF resin; 2: UF-SiO$_2$-compound; 3: UF-C-SiO$_2$-compound; 4: UF-C-SiO$_2$-polymer; 5: UF-R-SiO$_2$-compound.

Fig. 1 Effects of modifiers on weight percent gain of the specimens

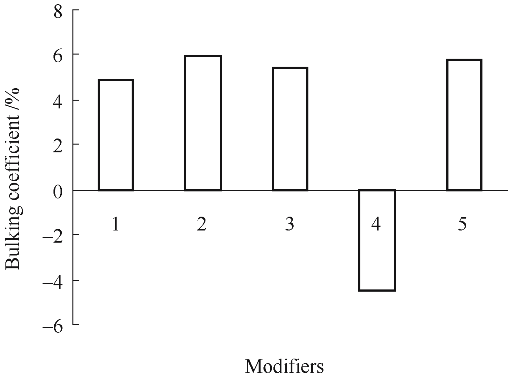
3.2 Dimensional stability and bulking coefficient

In this study, *ASE* was used to reflect the dimensional stability of treated wood; the higher the *ASE*, the better the dimensional stability. The effects of the modifiers on the bulking coefficient and *ASE* of wood specimens are shown in Figs. 2 and 3. Apart from the UF-C-SiO$_2$-polymer, the other four modifiers all enhanced the *ASE* and volume of wood specimens, which should be attributed to the molecules of the



1: UF resin; 2: UF-SiO$_2$-compound; 3: UF-C-SiO$_2$-compound; 4: UF-C-SiO$_2$-polymer; 5: UF-R-SiO$_2$-compound.

Fig. 2 Effect of modifiers on the antiswelling efficiency of the specimens



1: UF resin; 2: UF-SiO$_2$-compound; 3: UF-C-SiO$_2$-compound; 4: UF-C-SiO$_2$-polymer; 5: UF-R-SiO$_2$-compound

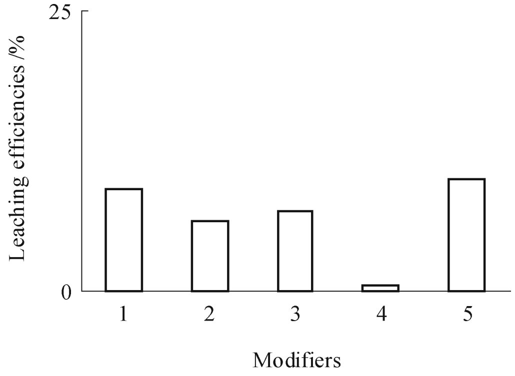
Fig. 3 Effect of modifiers on the bulking coefficient of the specimens modifiers that penetrated into and swelled the cell walls of wood. Thus, the swelling efficiency of the treated specimens caused by water absorption was low. Such “volume effect” was a significant factor contributing to the enhancement of the dimensional stability of wood (Li et al., 2003).

Some researchers are of the opinion that the molecular weight of resin greatly affect its penetration efficiency into wood and thus determine, to some extent, the dimensional stability of treated wood (Ryu et al., 1993; Imamura, 1998). It was also reported that, comparatively, resins with low molecular weights easily penetrated into the wood cell walls; however, the resins with much higher molecular weights tended only to reach the wood cell lumen instead of the cell walls, which hardly affected the dimensional stability of wood (Furuno and Goto, 1978, 1979; Imamura et al., 1983; Kajita and Imamura, 1991). Therefore, we can infer that UF-C-SiO_2-polymer, which resulted in a decrease of dimensional stability of wood, hardly reached the wood cell walls but mainly located in the cell lumen, because the high molecular weight of the UF-C-SiO_2-polymer resulted from the high reactivity of nano-SiO_2.

Wood specimens treated with the UF-R-SiO_2-compound showed a higher dimensional stability than others. That should be due to the flame retardant. First, the fire retardant was polar and water-soluble and therefore easily penetrated into wood cell walls and swelled them. Secondly, the flame retardant contained borax; thus boric acid (H_3BO_3) could be produced, which reacted with the hydroxyls in cell walls of wood in the following manner: on the one hand, fibrils were grafted together, on the other hand, the number of hydrophilic groups was reduced. Therefore, the antiswelling efficiency of the specimens treated with the reagent containing the flame retardant was very high, reflecting a high dimensional stability.

3.3 Leaching efficiency (*L*)

From Fig. 4, it is apparent that the leaching efficiency of the modifiers was all very low. However, the little weight loss revealed that a small amount of reagents with low molecular weight was not involved in the reaction with other reagents or wood components. The UF-C-SiO_2-polymer showed the least leaching efficiency; this can confirm that nano-SiO_2 with high reactivity improved the reaction of the polymer, resulting in fewer remnants of small molecules.

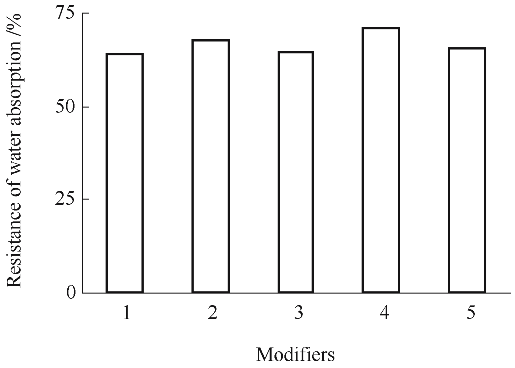


1: UF resin; 2: UF-SiO_2-compound; 3: UF-C-SiO_2-compound; 4: UF-C-SiO_2-polymer; 5: UF-R-SiO_2-compound.

Fig. 4 Effect of modifiers on the leaching coefficient of the modifiers

3.4 Resistance of water absorption (*RWA*)

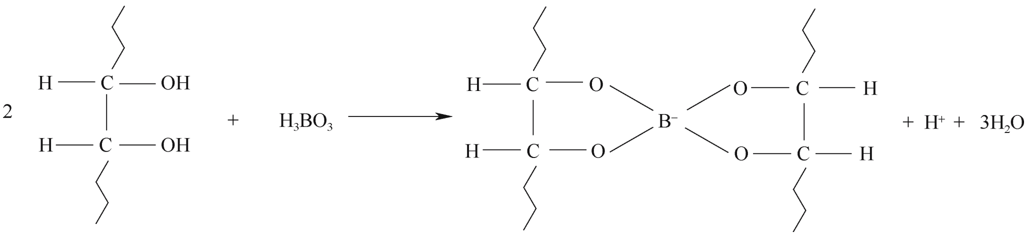
*RWA*s of treated wood specimens are shown in Fig. 5. All the specimens strongly resisted water absorption. One reason was that the capillaries in wood were obstructed by modifiers and thus water lost its main channel. The other reason was that many hydrophilic groups on cell walls of wood were replaced by many functional groups of modifiers and water-absorption spots decreased greatly.



1: UF resin; 2: UF-SiO_2-compound; 3: UF-C-SiO_2-compound; 4: UF-C-SiO_2-polymer; 5: UF-R-SiO_2-compound.

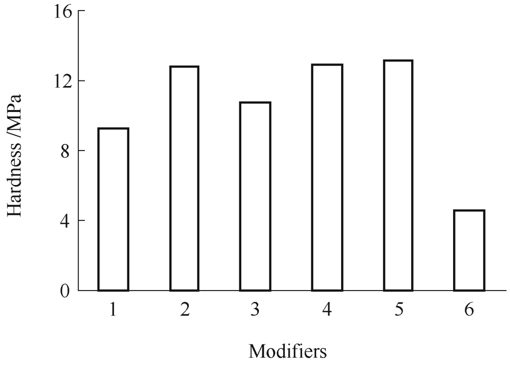
Fig. 5 Effect of modifiers on the resistance of water absorption of the specimens

$$H_3BO_3 + H_2O \longrightarrow B(OH)_4^- + H^+$$



3.5 Hardness

From Fig. 6, we can see that, in contrast with the control specimens, all of the treated specimens had higher hardness. Modifiers which were hardened during the heating process served, to some extent, as fillings in cavities of the wood and therefore enhanced its hardness. It was also clear that the specimens treated with the modifiers that contained nano-SiO_2, had higher hardness than those treated with UF resin without nano-SiO_2. That should naturally be due to nano-SiO_2, which is well-known for its high hardness and stability, as a result of its special structure of three-dimensional networks (Liu and Hao, 2002). Therefore, nano-SiO_2 endowed treated wood with a remarkably high hardness.

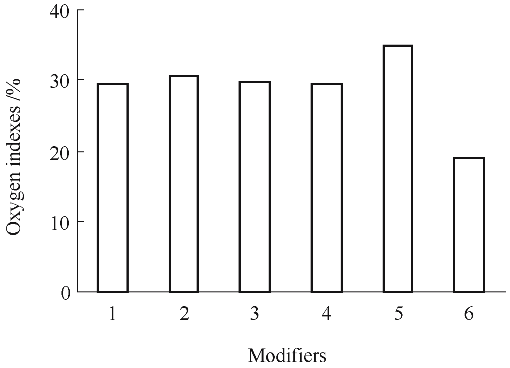


1: UF resin; 2: UF-SiO_2-compound; 3: UF-C-SiO_2-compound; 4: UF-C-SiO_2-polymer; 5: UF-R-SiO_2-compound; 6: control wood specimens.

Fig. 6 Effect of modifiers on the hardness of the specimens

3.6 Flame resistance

An oxygen index was established to reflect the flame resistance of treated wood in this study. The higher the oxygen index, the better the flame resistance. The oxygen indices of wood specimens are shown in Fig. 7. Clearly, all treated wood specimens had much better fire resistance than the control specimens. There was much nitrogen in the UF resin and the flame retardant was rich in boron and phosphorus, all of which played important roles in enhancing the flame resistance of wood. When the flame retardant was heated to a certain degree, polyphosphoric acid, an effective dehydrating agent, was produced and resulted in the carbonification of the wood surface. The layer of the carbonified wood had a low rate of heat transfer and inhibited heat decomposition of the inner wood. On the other hand, the borides contained in the flame retardant were melted and covered the surface of wood and thus wood was insulated from heat and oxygen.



1: UF resin; 2: UF-SiO_2-compound; 3: UF-C-SiO_2-compound; 4: UF-C-SiO_2-polymer; 5: UF-R-SiO_2-compound; 6: control wood specimens.

Fig. 7 Effect of modifiers on the oxygen index of the specimens

4 Conclusions

1) In this study, all of the five modifiers improved the flame resistance of triploid clones of *P. tomentosa* wood. With the exception of UF-C-SiO_2-polymer, the other four modifiers improved the dimensional stability of triploid clones of *P. tomentosa* wood.

2) Nano-SiO_2 is markedly beneficial in enhancing the hardness of triploid clones of *P. tomentosa* wood.

3) Taking into account all the properties together of triploid clones of *P. tomentosa* wood, the wood specimens treated with UF-R-SiO_2-compound had the best general performances.

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