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EFFECTS OF NANO-SiO_2/POLYETHYLENE GLYCOL ON THE DIMENSIONAL STABILITY MODIFIED ACQ TREATED SOUTHERN PINE

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ABSTRACT

Southern yellow pine (*Pinus* sp.) wood cubes were vacuum-pressure treated with nano-SiO2 solution and different concentrations of ACQ/polyethylene glycol (0.5%, 2.5% and 5.0%) modified solutions. The effects of polyethylene glycol concentrations and nano-SiO_2 addition on the water absorption, air drying shrinkage and moisture swelling stability of treated wood were investigated. The results showed that during the whole process of water absorption and air drying shrinkage, the better stability of nano-SiO_2 modified ACQ treated wood could only be obtained with the ratio of 2.5% polyethylene glycol addition. However, nano-SiO_2 and polyethylene glycol modification could take little effect on the moisture and water swelling resistance of treated wood with different treatments.

KEYWORDS: Amine copper quaternary (ACQ), ACQ treated wood, nano-SiO_2, polyethylene glycol, dimensional stability.

INTRODUCTION

Wood-based material is prone to be destroyed by microorganisms and pests when it is applied outdoors or indoors, such as white or brown fungus and termites. Nowadays, copper-amine has become an important constituent of several classical, novel, and proposed wood preservatives such as alkaline copper quat (ACQ) and copper azole (CA). Its importance is due to market restrictions on preservatives containing arsenic and chromium, for example, chromated copper arsenate (CCA), and the effectiveness of copper compounds against wood decay fungi (Humar et al. 2011). However, copper-amine preservative treated wood is easily deteriorated by a complex set of reactions induced by solar radiation, moisture, heat, oxygen, and environmental pollutants (Evans et al. 2008) and resulted in discoloration and deformation (Yu et al. 2011). Many researches have been performed to investigate how to improve the weathering stability of copper amine preservative treated wood. The effective solutions to reduce weathering of copper-amine treated wood involved water repellents and photoprotective additives (Yu et al. 2016a, Heräjärvi et al. 2014, Schultz et al. 2007). The other promising method involved the impregnation of cell wall with norganic nanocompounds, including silica (SiO_2), titanium dioxide (TiO_2), zinc oxide (ZnO) et al., which have been proved to enhance photostability, flame retardancy, water repellency and mechanical properties of the treated wood (Kong et al. 2017, Clausen et al. 2011, Mahltig et al. 2008).

In order to improve the dimensional stability of ACQ treated southern pine, nano-SiO_2 was introduced to the treated wood with seasonable dispersing agent in the water solution, then the polyethylene glycol as water repellent agent with different concentrations were added to ACQ solution to modify the dimensional stability of the treated wood in this study. This research will provide results that will be useful for enhancing the performance of ACQ-treated wood for outdoor applications.

MATERIAL AND METHODS

Samples

Sapwood of kiln-dried southern pine without any defect (*Pinus* sp.) was cut into small cubes with dimensions of 19.0×19.0 ×19.0 mm and stored in a conditioning room (50°C, 60% R.H.) to reach an equilibrium moisture content of 9-10%. The cubes were weighed, and selected the test samples with similar weight. 18 replicates per treatment were used to perform the dimensional stability and contact angle tests.

Nano-SiO_2 water solution

Nano-SiO_2 (hydrophilic type, analytically pure) was produced by Zhejiang Hongsheng Material Technology Co., Ltd., the average particle size was 20 nm and its purity was 99.5%. Because it is insoluble in the water, trisodium phosphate (analytically pure) produced by Tianjin Kemi Chemical Reagent Co., Ltd. was used to aid in its dissolution in the water solution. The reasonable ratio between nano-SiO_2 and trisodium phosphate were set to 1:10 as proved in our previous research (Liu et al. 2016, Yu et al. 2016b). 1.0 g nano-SiO_2 and 10.0 g trisodium phosphate were added into 100g deionized water, and the mixture solution was stirred using a magnetic stirrer for 1 h and then subjected to ultrasonic processing at 40°C for 30 min. If the solution was not clear, the mixture solution should be stirred in the magnetic stirrer again until the nano-SiO_2 and trisodium phosphate were dissolved completely.

ACQ/polyethylene glycol modification preservatives

The mass fraction in the active components (33.3% Dodecyl Dimethyl Benzyl ammonium Chloride, 66.7% copper oxide) of ACQ preservative is 15%. Two sets of ACQ solutions were used for impregnation. The first set contained 0.6% ACQ preservative, and the second set contained 0.6% ACQ preservative mixed with 0.5%, 2.5%, or 5.0% polyethylene glycol emulsion. Both the concentrations of ACQ and polyethylene glycol were the concentrations in the final formulation of the mixture preservatives.

Sample impregnation treatment

Samples were performed vacuum-pressure impregnation with nano-SiO_2 water solution and oven dried at 60°C to achieve constant weight as shown in Tab. 1. Then the samples were vacuum-pressure impregnated with different ACQ or ACQ/wax modification solutions. The vacuum-pressure treatment was set as follows: The samples were put into the pressure chamber and the vacuum was set to -0.1 MPa for 1h to remove the air in the chamber and in the wood samples, the the solution was admitted into the samples.

Tab 1: Treatment conditions for samples used in different experiments.

Experiment	Nano-SiO_2	ACQ concentration (%)	Polyethylene glycol (%)
T1	N	0.6	0
T2			
Y		0	
T3			0.5
T4			2.5
T5			5.0

Note: Y, perform the treatment; N, not perform the treatment.

Release the vacuum was released, and elevate the pressure to 0.8 MPa for another 1h to promote more solution permeating into the samples, then release the pressure and remove the samples from the pressure chamber. The treated samples were post-treated at 70°C for 10 h with hot air circulation and then oven dried at 60°C to achieve constant weight. After drying, the dimensional stability tests were performed according to standard GB/T 1934 (2009).

Dimensional stability test

Water absorption measurement

All the treated and untreated specimens were conditioned in an oven set at 60 ± 2°C for 24 h and cooled over anhydrous cupric sulfate in a desiccator before test. The water absorption measurements were taken according to standard GB/T 1934.1 (2009) as described in the literature of Yu et al (2016a). The percent of water absorption (WA) by the samples was computed using Eq. 1,

$$WA = \frac{W_2 - W_1}{W_1} \times 100\% \tag{1}$$

where W1 and W2 are the weights of each specimen before and after the water absorption measurement.

Wood air drying shrinkage measurement

All the treated and untreated specimens were immersed into 20 ± 2°C deionized water to reach stable dimensions before air drying shrinkage measurement was recorded according to standard GB/T 1932 (2009) as described in the literature of Yu et al (2016). The tangential dimensions of all samples were recorded to an accuracy of ± 0.01 mm (TL2). The percentages of tangential air drying shrinkage (ATS) by the samples were computed using Eq. 2,

$$ATS = \frac{TL_1 - TL_2}{TL_1} \times 100\% \tag{2}$$

In Eq. 2, TL_1 and TL_2 are the tangential dimensions of each specimen before and after air drying shrinkage measurement.

Wood moisture and water absorption swelling measurement

The wood swelling measurement is according to standard GB/T 1934.2 (2009) as described in the literature of Yu et al (2016). The percentages of the tangential moisture (MTS) and water absorption (WTS) swelling by the samples were computed using Eqs. 3 and 4,

$$MTS = \frac{TS_2 - TS_1}{TS_1} \times 100\% \tag{3}$$

In Eq. 3, TS_1 and TS_2 are the tangential dimensions of each specimen before and after the water moisture swelling measurement.

$$WTS = \frac{TS_3 - TS_1}{TS_1} \times 100\% \tag{4}$$

In Eq. 4, TS_1 and TS_3 are the tangential dimensions of each specimen before and after the water absorption swelling measurement.

Statistical analysis

The effects of polyethylene glycol addition on the dimensional results of the treated wood was evaluated by one-way analysis of variance and S-N-K(S) test calculated in the SPSS software. In the variance analysis, the significant value P was calculated and compared with the critical value 0.05. P<0.05 means: the factor has a significant effect on the experimental result.

RESULTS AND DISCUSSION

Water absorption analysis

Percentages of water absorption of ACQ treated wood with different treatments are presented in Fig. 1. The water absorption test was carried out for about 45 d and the moisture content in the wood was increased from near 0 to the saturation moisture content. As observed from Fig. 1, the curves of the treated wood during water absorption process could be divided into two different stages.

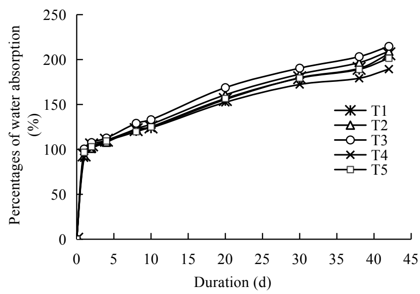


Fig. 1: Water absorption of ACQ treated wood with different treatments.

In the early stage (0-1d), the moisture content increased quickly because of the higher hygroscopicity of microstructure (intercellular space and cell lumen), major chemical components (cellulose, hemi-cellulose, and lignin) and the ingredients of wood preservative lack of hydrophobic constituents (Qing et al. 2017). In the late stage (1-45d), all the rates of water absorption into the treated wood became more slowly to reach the saturation stage, which corresponded to the water saturation in the wood space and wood cell wall. During these two different stages, compared to ACQ treated wood (T1), the other ACQ treated wood modified with nano-SiO_2 and different concentrations of polyethylene glycol showed different water absorption performance. As showed in Fig. 1, the minimum moisture content in the ACQ treated wood was observed in ACQ treated wood modified with nano-SiO_2 and 2.5% polyethylene glycol (T4), while in other modified ACQ treated wood, the water absorption rate was close to ACQ treated wood (T1). It seems that nano-SiO_2 and polyethylene glycol modification would decrease the water absorption hygroscopicity of ACQ treated wood only with seasonable proportion of polyethylene glycol. The better water repellent results have been also proved by other researches. Hosseini et al. (2014) showed that lignocellulosic waste material along with nano-SiO_2, can be successfully utilized to make fiber reinforced composites (FRCs) with useful water repellent property. Employing nano-SiO_2 for improving wood properties enhances the dimensional stability, hardness, and flame resistance of the treated samples (Shi et al. 2007).

Air drying shrinkage analysis

Percentages of tangential air drying shrinkage of ACQ treated wood with different treatments are presented in Fig. 2.

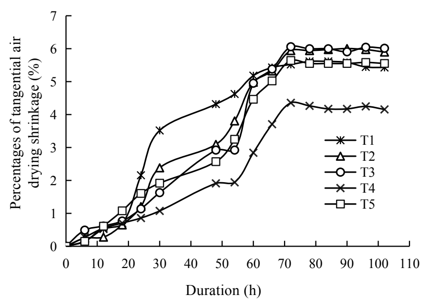
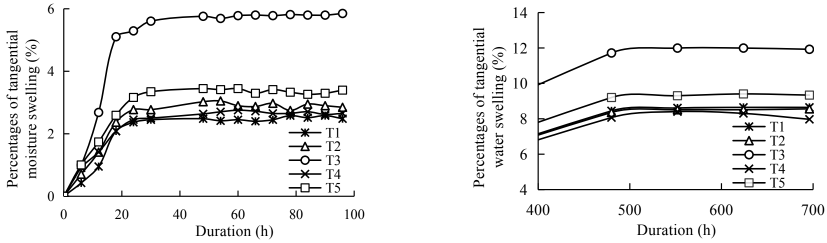


Fig. 2: Tangential air drying shrinkage of ACQ treated wood with different treatments.

During air drying, in which period the treated wood turned from water saturation state to air drying stage, the tangential shrinkage increased quickly in the initial 70 h, which corresponded to the moisture content from moisture saturation point to near air drying moisture content, and then the rates began to slow down and reach the air drying state after 102 h test. As showed in Fig. 2, compared to T1 (ACQ treated), the rates of tangential shrinkage in the other treated wood with different concentrations of polyethylene glycol and nano-SiO_2 were lower in the initial 70 h, and became very similar in the late stage, except for T4 group (nano-SiO_2 and 2.5% polyethylene glycol modified), in which the shrinkage rate could be reduced obviously. It also demonstrated that nano-SiO_2 and polyethylene glycol modification would decrease the air drying shrinkage of ACQ treated wood with seasonable proportion of polyethylene glycol. These results were also consistent with our previous results that samples with seasonable percentage of water repellent and nano-SiO_2 addition had obvious effect on the moisture swelling and shrinkage resistance (Yu et al. 2017).

Moisture and water swelling analysis

Percentages of tangential moisture and water swelling of ACQ treated wood with different treatments are presented in Fig. 3a and 3b.



(a) moisture swelling (b) water swelling

Fig. 3: Tangential moisture and water swelling of ACQ treated wood with different treatments.

As observed from Fig. 3a, the rates of tangential moisture swelling in the other treated wood with different concentrations of polyethylene glycol and nano-SiO_2 modified were close or slight higher compared to T1(ACQ treated). The similar results could be also found in the rates of tangential water swelling in ACQ treated wood with different treatments. The promising water swelling result is only found in the T4 group. These results demonstrated that nano-SiO_2 and polyethylene glycol modification could take little effect on the moisture and water swelling resistance.

The one-way analysis of variance for the treated southern pine in different treatments was shown in Tab. 2.

Tab. 2: One-way analysis of variance for the treated southern pine in different treatments by SPSS.

Dimensional Test	Group	Mean (%)	SD	Quadratic sum	df	F	Significant
Water absorption	T1	206.40	4.27	11.56	29	8467.35	0.00
	T2	209.22	9.90				
	T3	214.68	8.89				
	T4	189.33	5.18				
	T5	201.44	9.84				
Tangential moisture swelling	T1	2.48	0.16	76.46	29	21.09	0.00
	T2	2.85	0.13				
	T3	5.85	0.79				
	T4	2.65	0.22				
	T5	3.40	0.06				
Tangential air drying shrinkage	T1	5.43	0.12	3149.60	29	85.11	0.00
	T2	5.90	0.56				
	T3	6.01	0.36				
	T4	4.16	0.74				
	T5	5.55	0.76				

It was noted that polyethylene glycol/nano-SiO_2 modified ACQ-treated wood played significant effects on the water absorption, tangential moisture swelling and tangential air drying shrinkage. The results has proved that southern pine treated with polyethylene glycol/nano-SiO_2 modified preservatives was promising for its safe outdoor application.

CONCLUSIONS

1. During the whole process of water absorption, the better hydrophobicity of nano-SiO_2 modified ACQ treated wood was obtained with the ratio of 2.5% polyethylene glycol, and both polyethylene glycol and nano-SiO_2 could block the water absorbed into the treated wood.
2. Except T4 group (nano-SiO_2 and 2.5% polyethylene glycol modified), the other treated wood with polyethylene glycol and nano-SiO_2 modified has slight shrinkage change in the initial stage and became very similar with T1 group (ACQ treated) in the late stage. The shrinkage rate of treated wood in T4 group (nano-SiO_2 and 2.5% polyethylene glycol modified) could be reduced obviously.
3. Nano-SiO_2 and polyethylene glycol modification could take little effect on the moisture and water swelling resistance of treated wood with different treatments.

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