Improved Dimensional Stability of Nano-SiO_2/Wax Modified ACQ-treated Southern Pine

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Southern yellow pine (*Pinus* sp.) wood cubes were vacuum-pressure treated with nano-SiO_2 solution and different concentrations of amine copper quaternary (ACQ)/wax (0.5%, 2.5%, and 5.0% wax)-modified solutions. The effects of wax concentration and nano-SiO_2 addition on water absorption, air drying shrinkage, and moisture swelling stabilities were investigated. The results showed that during the whole process of water absorption and air drying shrinkage, better stability of nano-SiO_2 modified ACQ-treated wood could only be obtained with the ratio of wax addition equal to 2.5%. However, the best moisture swelling resistance was found in the samples modified with the highest wax addition (5.0%). Both wax and nano-SiO_2 could be useful for keeping the dimensional stability of the treated wood.

Keywords: Amine copper quaternary (ACQ); ACQ-treated wood; Nano-SiO_2; Wax; Dimensional stability

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INTRODUCTION

In recent years, ammoniacal copper quaternary (ACQ) wood preservative has become one of the most widely used water-borne wood preservatives in pressure treatment. Although ACQ-treated wood has effectively prolonged the service life of wood-based products, poor dimensional stability is still one of the most serious problems for outdoor application, which would seriously hurt the integrity of the structure and normal function of treated wood. However, this problem has not attracted more attention, and so relevant research is very limited. The processes of dimension change of treated wood is caused by diverse physicochemical factors during natural weathering (George *et al*. 2005). Photochemical degradation is manifested by an initial color change followed by loss of gloss, roughening, and checking (Chang *et al.* 1982; Evans *et al.* 2008).

The effective solutions to reduce the weathering of ACQ-treated wood involve water repellents and photoprotective additives. The most important water repellents used in wood preservation are waxes, particularly paraffin wax (Schultz *et al.* 2007). When wax emulsions are applied to wood by vacuum/pressure treatment, waxes penetrate beyond the zone affected by UV degradation. The wax is expected to perform throughout the life of the treated wood (Zahora 1991). Previous research shows that the ACQ/wax-treated wood exhibits better water resistance during the water soak process than non-treated wood. Samples with a higher percentage of wax have a higher resistance to water swelling and shrinkage. The samples with a lower percentage of wax addition had only a slight effect on the moisture swelling and shrinkage resistance (Yu *et al*. 2016a). The treatment of wood with a higher loading of wax reduces the moisture absorption by wood subjected to accelerated weathering and restricts the photodegradation of wood (Lesar *et al*. 2011).

However, wax treatments reduce the photodegradation only to a certain extent. Similar test results can be found in other studies that include water-repellent additives in preservative treatments. Use of the water repellent alone improves the physical performance of treated wood and minimizes the checking and splitting of said wood (Zahora 1991; Christy *et al.* 2005; Schauwecker *et al.* 2009), but it does not affect color change significantly. As a result, other additives are incorporated into aqueous wood preservatives with wax to modify the weathering stability of treated wood. The first emulsion additive to be developed consisted of a blend of wax, oil, and surfactants (Warburton *et al.* 1991). This additive is effective at increasing the water repellency and dimensional stability of chromated copper arsenate (CCA)-treated wood and reducing the checking of the treated wood when exposed outdoors. More stable water-repellent emulsion additives, based on either wax or light petroleum oil, have been developed as commercial wood preservatives (Fowlie *et al*. 1990; Greaves 1990). Both wax and oil emulsion additives are equally effective at reducing the checking of treated wood exposed to weathering and the water absorption and swelling of treated wood before weathering (Jin *et al.* 1992; Evans *et al*. 2009; Heräjärvi *et al.* 2014).

The other promising additives that have attracted considerable interest from the scientific community during the last decade are formed by the impregnation of the cell wall with inorganic nanocompounds, including silica (SiO_2), titanium dioxide (TiO_2), zinc oxide (ZnO), and others. These additives enhance the photostability, flame retardancy, water repellency, and mechanical properties of treated wood (Mahltig *et al*. 2008; Clausen *et al*. 2011; Kong *et al*. 2017). Nano-particles of various elements could be important in the development of the next generation of wood preservation chemicals, as they may show better protection against deterioration by various factors as well as better physical properties, such as water absorption and dimensional stability (Blee and Matisons 2008; Kartal *et al*. 2009). Of the different available nano-particles, silica nanoparticles (SiO_2) are most useful for the modification of wood preservatives due to their lower toxicity and better solubility. Hosseini *et al.* (2014) showed that lignocellulosic waste material along with mineral fillers, like nano-SiO_2, can be successfully utilized to make fiber reinforced composites (FRCs) with useful physical and mechanical properties. Higher nano-SiO_2 content generally improves the mechanical properties of all the composites reinforced by lignocellulosic material, (Shi *et al*. 2007). Employing nano-SiO_2 for improving wood properties enhances the dimensional stability, hardness, and flame resistance of the treated samples.

The aim of this study was to evaluate the effects of nano-SiO_2 and wax concentration on the dimensional stability of ACQ-treated southern pine, and to determine the optimum formulations in the modification solutions.

EXPERIMENTAL

Material and Methods

Wood samples

Sapwood of kiln-dried southern pine without any defects (*Pinus* sp.) was cut into small cubes with dimensions of 19.0 mm × 19.0 mm × 19.0 mm and stored in a conditioning room (50 °C, 60% relative humidity (RH)) to reach an equilibrium moisture content of 9% to 10%. The cubes were weighed, and those with similar weights were selected to be the test samples.

Nano-SiO₂ water solution

Nano-SiO_2 (hydrophilic type, analytically pure) was produced by Zhejiang Hongsheng Material Technology Co., Ltd. (Hangzhou, China). The average particle size was 20 nm, and its purity was 99.5%. Due to its insolubility in water, trisodium phosphate (analytically pure) produced by Tianjin Kemi Chemical Reagent Co., Ltd. (Tianjin, China) was used to aid in the dissolution of nano-SiO_2 in the water solution. A reasonable ratio between nano-SiO_2 and trisodium phosphate is 1:10 (Liu *et al*. 2016; Yu *et al*. 2016b). 1.0 g of nano-SiO_2 and 10.0 g of trisodium phosphate were added into 100 g of deionized water, which was then stirred using a magnetic stirrer for 1 h and subjected to ultrasonic processing at 40 °C for 30 min. The solution was stirred in the magnetic stirrer until the nano-SiO_2 and trisodium phosphate were dissolved completely and the mixture was clear.

ACQ/wax modification preservatives

The mass fraction of the active components (33.3% dodecyl dimethyl benzyl ammonium chloride, 66.7% copper oxide) in the ACQ preservative was 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 either 0.5%, 2.5%, or 5.0% paraffin wax (melting point: 58 °C to 60 °C, purity: 40%) emulsion. Both the concentrations of ACQ and wax were the concentrations in the final formulation of the mixture preservatives.

Sample impregnation treatment

Vacuum-pressure impregnation was performed on the samples with nano-SiO_2 water solution and oven dried at 60 °C to achieve a constant weight. The samples were then vacuum-pressure impregnated with different ACQ or ACQ/wax modification solutions. First, samples were placed into the pressure chamber, and the vacuum was set to -0.1 MPa for 1 h to remove the air in the chamber and in the wood samples, then the solution was admitted into the samples. The vacuum was released, and the pressure was elevated to 0.8 MPa for another 1 h to promote more solution permeating into the samples. Then the pressure was released and the samples were removed from the pressure chamber. The treated samples were post-treated at 70 °C for 10 h with hot air circulation to accelerate the fixation process of copper in the treated wood and then oven dried at 60 °C to achieve a constant weight. After drying, the dimensional stability tests including water absorption test, wood air drying shrinkage test and wood moisture absorption swelling test were performed according to standard GB/T 1934 (2009), and six replicates in each test group.

Table 1. Treatment Conditions for Samples Used in Different Experiments

Experiment	Nano-SiO_2 Treatment	ACQ Concentration (%)	Wax Concentration (%)
T1	N	0.6	0
T2	Y		0
T3			0.5
T4			2.5
T5			5.0

Note: Y, with the treatment; N, without the treatment.

Dimensional Stability Test

Water absorption measurement

All 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 they were tested. The water absorption measurements were taken according to standard GB/T 1934.1 (2009) (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 W_1 and W_2 are the weights of each specimen before and after the water absorption measurement, respectively.

Wood air drying shrinkage measurement

All treated and untreated specimens were immersed into 20 ± 2 °C deionized water to reach stable dimensions before air drying. Then shrinkage measurement was recorded according to standard GB/T 1932 (2009) (Yu *et al* 2016a).

The tangential dimensions of all samples were recorded to an accuracy of ± 0.01 mm (TL_2). The percentages of tangential air drying shrinkage (ATS) by the samples were computed using Eq. 2,

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

where TL_1 and TL_2 are the tangential dimensions of each specimen before and after the air drying shrinkage measurement, respectively.

Wood moisture absorption swelling measurement

The wood swelling measurement is according to standard GB/T 1934.2 (2009), (Yu *et al* 2016a). The percentages of the tangential moisture absorption swelling (*MTS*) by the samples were computed using Eq. 3,

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

where $\mathrm{T}S_1$ and TS_2 are the tangential dimensions of each specimen before and after the water moisture swelling measurement, respectively.

Statistical analysis

The effects of wax 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 P-value was calculated and compared with the critical value 0.05. $P < 0.05$ means the factor has a significant effect on the experimental result.

Yu *et al*. (2017). “SiO₂/wax ACQ-treated wood,” ***BioResources*** 12(4), 7515-7524. 7518

RESULTS AND DISCUSSION

Water Absorption Analysis

The percentage of water absorption as a function of water soaking duration is presented in Fig. 1. The water absorption test was carried out for about 45 d. Water absorption was very fast in the initial 10 d. The only nano-SiO_2 modified ACQ-treated wood (T2) had the best water resistance performance, while the nano-SiO_2 modified ACQ-treated wood with higher wax additions (T4 and T5) resulted in a higher water absorption compared with the ACQ-treated wood (T1). In this initial stage, water was likely mainly absorbed by the surface of the treated wood. Compared with wax, nano-SiO_2 modified ACQ-treated wood exhibited better hydrophobicity because nano-SiO_2 could block the interspace of the treated wood so that water could not have a path into the wood. However, the soluble wax was prone to leach out from the surface of the treated wood and could not block the water path in the wood surface effectively. As the duration increased, the water absorption rates were reduced in groups T4 and T5, while the water absorption rates increased in the other three groups. At the stable stage, samples in T4 group achieved the least water absorption. In this final stage, water was mainly been absorbed by the inside of the treated wood. This is because inside the wood, wax has a better water leaching resistance and could play an effective role in blocking the water path. Moreover, greater hydrophobicity was obtained only with a reasonable ratio between wax and ACQ solution. This result was consistent with previous research showing that during water absorption, the percentage of absorbed water in the ACQ-treated wood with a reasonable ratio of wax was lower than the percentage in the ACQ-treated wood (Yu *et al*. 2016a).

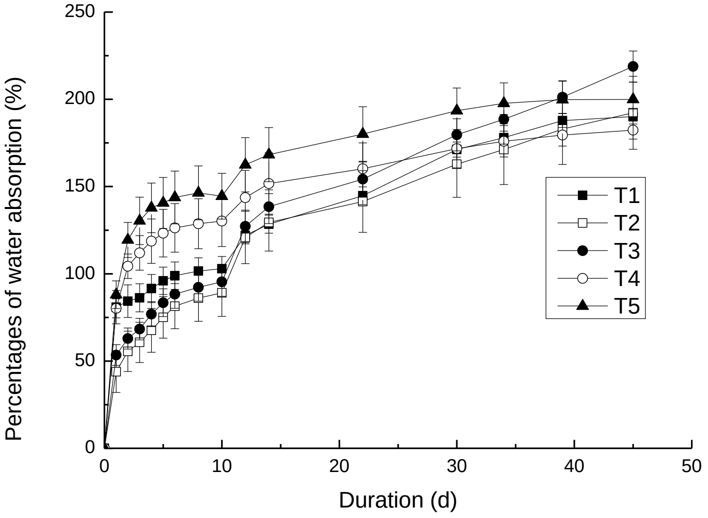

Fig. 1. Water absorption of treated and untreated southern pine

Air Drying Shrinkage Analysis

The percentages of tangential air drying shrinkage of treated and untreated southern pine testing for 120 h are presented in Fig. 2. Other than T4, all groups showed different trends at the initial and stable stages. At the fast air drying shrinkage stage (0 h to 60 h), compared to the samples without any modification (T1), samples with a higher wax content in the nano-SiO_2 modified ACQ-treated wood (T5) were more likely to shrink quickly in the air drying condition. However, the only nano-SiO_2 modified ACQ-treated wood (T2) showed greater tangential air drying shrinkage stability. This result was attributed to a higher moisture content in that stage, so the water-soluble wax could not take an effective role in preventing dimension change. At the stable stage (60 h to 120 h), compared to T1, as the water content in the treated wood got closer to the lower air drying water content, wax in the treated groups (T3, T4, T5) began to deposit into the wood void space, playing an effective role in preventing dimension change, which was more obvious in the treated groups with more wax addition (T4, T5). During the whole air drying shrinkage stage, samples in the T4 group with 2.5% wax and nano-SiO_2 modified ACQ-treated wood exhibited the best stability, and the tangential air drying shrinkage was only about 2%. However, samples in groups T2 and T3 had higher shrinkage percentages. These test results also demonstrated that a reasonable proportion of wax is critical for ACQ-treated wood to prevent air drying shrinkage.

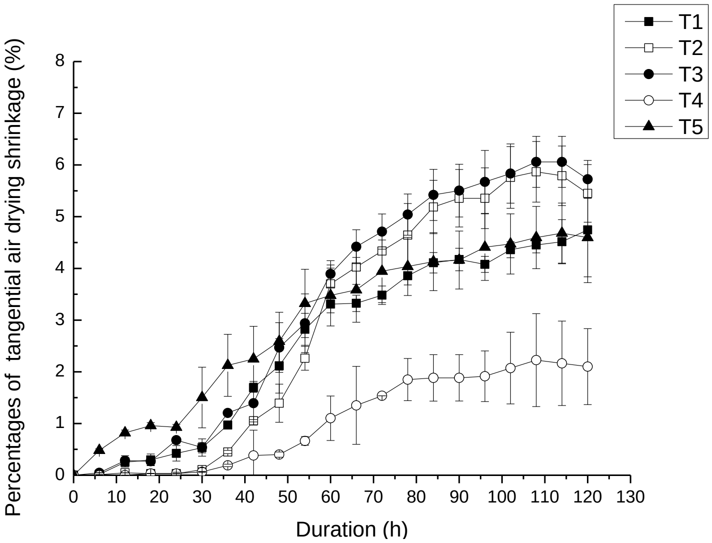

Fig. 2. Tangential air drying shrinkage of treated and untreated southern pine

Moisture Swelling Analysis

The percentages of tangential moisture swelling of treated and untreated southern pine testing for 96 d are presented in Fig. 3. Compared with the samples without any modification (T1), samples with a higher wax content in the nano-SiO_2 modified ACQ-treated wood exhibited better moisture swelling resistance. For group T5, which had the highest wax proportion, the percentage of moisture swelling was only less than 1%. It looks like in all the samples (T1 to T4), except T5, the process of tangential moisture swelling could be divided into two different phases. At the initial stage of the process (0 to 50 d), the percentages of tangential moisture swelling of treated and untreated southern pine increased sharply, and almost totally realized slight change in the initial 50 days. At the final stage of the process (50 to 96 d), the change of tangential moisture swelling in all the samples were very small. During the whole process of tangential moisture swelling, the nano-SiO_2 modified and the wax/nano-SiO_2 modified ACQ-treated wood presented better moisture swelling resistance than group T1. Thus, both wax and nano-SiO_2 could be useful for preventing moistening of treated wood.

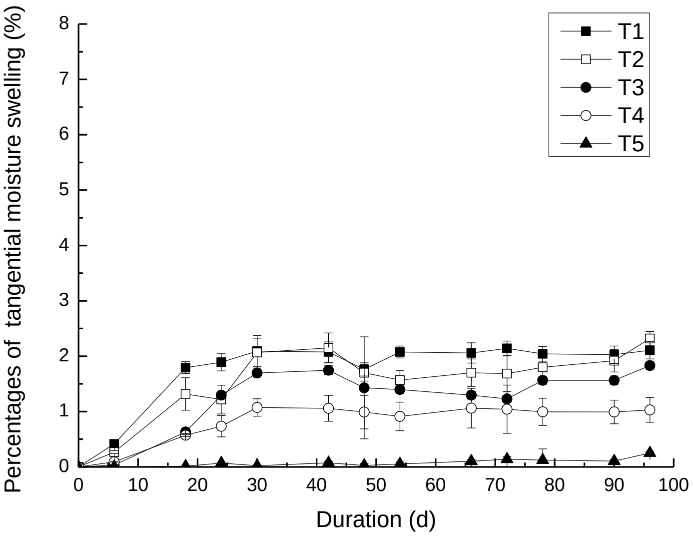

Fig. 3. Tangential moisture swelling of treated and untreated southern pine

The one-way analysis of variance for the treated southern pine in different treatments was shown in Table 2. It was noted that wax/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 wax/nano-SiO_2 modified preservatives was necessary for its safe outdoor application.

Table 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	Significance
Water Absorption	T1	190.11	4.27	17.65	29	11115.99	0.00
	T2	192.29	9.90				
	T3	218.81	8.89				
	T4	182.35	5.18				
	T5	199.95	9.84				
Tangential Moisture Swelling	T1	2.11	0.16	50.51	29	388.29	0.00
	T2	2.32	0.13				
	T3	1.83	0.79				
	T4	1.03	0.22				
	T5	0.25	0.06				
Tangential Air Drying Shrinkage	T1	4.74	0.12	5280.68	29	95.18	0.00
	T2	5.45	0.56				
	T3	5.72	0.36				
	T4	2.10	0.74				
	T5	4.60	0.76				

CONCLUSIONS

1. During water absorption, the greatest hydrophobicity of nano-SiO_2 modified ACQ-treated wood was obtained with the ratio of wax addition equal to 2.5%. Moreover, both wax and nano-SiO_2 could block the water absorbed into the treated wood.
2. The highest shrinkage resistance was found in samples with a higher percentage of wax addition (2.5%) in the nano-SiO_2 modified ACQ-treated wood. The tangential air drying shrinkage at this percentage of wax addition was only about 2%, which also demonstrated that wax with reasonable proportion is critical for ACQ-treated wood to prevent air drying shrinkage.
3. During tangential moisture swelling, the only nano-SiO_2 modified and the wax and nano-SiO_2 modified ACQ-treated wood presented better moisture swelling resistance. This result demonstrated that both wax and nano-SiO_2 could be useful for preventing moisture in treated wood.

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