WOOD RESEARCH
64 (6): 2019
965-974

DIMENSIONAL STABILITY OF NANO-SIO_2/EMULSIFIED WAX MODIFIED CuAz-TREATED WOOD AFTER ONE YEAR OUTDOOR EXPOSURE TEST

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(Received December 2018)

ABSTRACT

Samples were vacuum-pressure treated with nano-SiO_2 water solutions with BET specific surface area of 60,150, 200, 380 respectively, and then impregnated with copper azole (CuAz) preservatives or emulsified wax modified CuAz preservatives. The effects of emulsified wax and nano-SiO2 on the dimensional stability were investigated according to standard GB/T 1934 (2009) after one year outdoor exposure test. The results showed that the addition of nano-SiO_2 or/and emulsified wax could reduce the water absorption rate of treated wood, and the best water repellent was observed in the samples treated with BET specific surface area of 60 $m^{2} \cdot g^{-1}$. The addition of wax into nano-SiO_2 modified wood was essential to improve the radial and tangential swelling and shrinkage stability of nano-SiO_2 treated wood. The bigger BET specific surface area of nano-SiO_2 would be adversely affected the dimensional stability of the treated wood.

KEYWORDS: Copper azole, nano-SiO_2, wax, dimensional stability, outdoor exposure.

INTRODUCTION

In order to improve the biological efficiency of wood, it is necessary to perform suitable preservative treatment (Pang et al. 2012). In recent years, CuAz preservative has become one of the most widely used water-borne wood preservatives in wood preservation market because of the better corrosion resistance and free of arsenic, chromium and other persistent organic

pollutants or volatile organic compounds (Tang et al. 2013, Xi et al. 2015). Although CuAz treated wood has been proved to prolong the service life of wood and other wooden products, a lot of weathering resistance problems have emerged apparently during its service life, such as the poor dimensional stability, color change, et al. (Long et al. 2017) as the result of the shortage of weathering resistance ingredients in the formulas.

Many researchers have paid more attentions to explore new measurements to improve the weathering resistance of wood. Among of them, heat treatment was applied to reduce the water absorption of wood by changing its physical properties, such as fiber molecular chains, and prevent the erosion of bacteria and insects (Jiang et al 2013, Xie et al. 2014). Wang et al. (2019) showed that the wood shape stability was improved by medium-low hydrothermal treatment, and the moisture migration and wood permeability were also improved at the same time. Many chemical modification methods such as resin impregnation, acetylation and painting were also been performed to improve the dimensional and color stability of wood. The most economical and effective method to improve the dimensional stability has been proved to be treated with the mixed system of emulsified wax (Zhong et al. 2014, Wang et al. 2014). Qian et al. (2019) showed that the dimensional stability of the treated wood impregnated with wax and dimethylsilicone oil mixture could be improved significantly with suitable treatment conditions. Nano-particles of various elements may have great potential for improve the weathering resistance of the traditional preservative treated wood (Blee and Matisons 2008, Kartal et al. 2009). Among different available nano-particle, silica nanoparticles (SiO_2) are more useful for the modification of wood because of their lower toxicity and better solubility (Mo 2011, Wang 2012). Nano-SiO_2 addicted into coatings can provide shielding effect for coatings to ensure the durability of paint color and dimensional stability (Qing et al. 2011, Mo et al. 2012). Wood modified by nano-SiO_2 had obvious improvement in strength, hardness and wear resistance, as well as the flame retardancy, anticorrosion and dimensional stability (Yu et al. 2017). Tang et al. (2018) showed that the dimensional stability of ACQ treated wood could be improved with the ratio of 2.5% polyethylene glycol and 1% nano-SiO_2 addition.

In this experiment, nano-SiO_2 and emulsified wax were introduced to modify CuAz treated wood. The actual dimensional stability performance of nano-SiO_2 and emulsified wax modified CuAz treated wood was evaluated by the outdoor exposure experiment for one year. The research results are aimed to provide some useful information to the industrial design of producing more seasonable schedules for CuAz treated wood.

MATERIAL AND METHODS

Samples

Sapwood of kiln-dried southern pine without any defect (*Pinus* sp.) was cut into small cubes with dimensions of 30 × 20 × 10 mm (length × width × height) and stored in a conditioning room (50°C, 60% R.H.) to reach an equilibrium moisture content of 9-10%. Test samples were selected with similar weight and 6 replicates were used in each group.

Nano-SiO_2 water solution

Hydrophilic nano-SiO_2 (analytically pure) with BET specific surface area of 60, 150, 200, 380 $m^2 \cdot g^{-1}$, was produced by Zhejiang Hongsheng Material Technology Co., Ltd., and its purity was 99.5%. In order to increase the water-solubility of nano-SiO_2, trisodium phosphate (analytically pure) produced by Tianjin Kemi Chemical Reagent Co., Ltd. was introduce into the water solution. The reasonable ratio between nano-SiO_2 and trisodium phosphate were

set to 1:10 as proved in our previous researches (Yu et al. 2016). 1.0g nano-SiO_2 and 10.0 g trisodium phosphate were added into 100 g 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. Wood samples were performed vacuum-pressure impregnation with different nano-SiO_2 water solutions respectively and post-treated at 70°C, R.H. 80% for 10 h with hot air circulation and then oven dried at 60°C to achieve constant weight. Repeat the cycle of the impregnation and drying treatments for one more time to achieve the maximum nano-SiO_2 retention. 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 1 h to remove the air in the chamber and wood samples, the solution was introduced into the samples. Then release the vacuum, and elevate the pressure to 0.8 MPa for another 1 h to promote more solution permeating into the samples. At the end, release the pressure and remove the samples from the pressure chamber.

CuAz / and emulsified wax modification preservative treatment

Ten sets of nano-SiO_2 treated wood samples were vacuum-pressure impregnated with different solutions as listed in Tab. 1. Mass fraction in the active components (3.9% tebuconazole, 96.1% copper) of 15% CuAz preservative was diluted to 0.6%, and mixed with 2.5% paraffin wax (melting point 58 to 60°C, purity 40%) emulsion. Both the concentrations of CuAz and wax were the concentrations in the final formulation of the mixture preservatives. The treated samples were post-treated at 70°C, R.H. 80% for 10 h with hot air circulation and then oven dried at 60°C to achieve constant weight.

Outdoor exposure test

In order to test the effects of weathering conditions on the actual dimensional stability performance of modified CuAz treated wood with different treatments, samples were placed outdoor on the roof of China Wood Testing Centre in Beijing for one year (May 2017 - May 2018). After exposure test, the treated samples were dried at 50°C, 80% R.H. for 10 h with hot air circulation and then oven dried at 60°C to achieve constant weight.

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

Treatment	Nano-SiO_2		CuAz (%)	Wax (%)
	BET specific surface area ($m^2 \cdot g^{-1}$)	Maximum solubility (g/100g)		
T1	60	0.6	0.6	0
T2	150	0.8		
T3	200	1.3		
T4	380	1.9		
T5	60	0.6		2.5
T6	150	0.8		
T7	200	1.3		
T8	380	1.9		
T9	0	0		
T10	0	0		0

Dimensional stability test

Water absorption measurement

The water absorption measurements were taken according to standard GB/T 1934.1 (2009) as described detailed in the literature of Yu et al. (2016). The percents of water absorption (WA)

and water repellent (RWA) by the samples were computed using Eq. 1 and Eq. 2 respectively:

$$WA = \frac{W_1 - W}{W} \times 100\% \quad (1)$$

$$RWA = \frac{WA_C - WA_T}{WA_C} \times 100\% \quad (2)$$

where: W, W_1 - weights of each specimen before and after water absorption measurement (g), WA_C, WA_T - percentage of water absorption of the untreated samples and the treated samples (%).

Wood swelling measurement

The percentages of tangential air drying shrinkage (ATS) by the samples were computed using Eqs. 2. The wood swelling measurement is according to standard GB/T 1934.2 (2009) as described in the literature of Yu et al. (2016). The percents of the tangential and radial moisture absorption swelling (MTS and MRS) by the samples were computed using Eq. 3 and Eq. 4:

$$MTS = \frac{TS_2 - TS_1}{TS_1} \times 100\% \quad (3)$$

$$MRS = \frac{RS_2 - RS_1}{RS_1} \times 100\% \quad (4)$$

where: TS_1 and TS_2 - tangential dimensions of each specimen before and after the moisture absorption swelling measurement (mm),
RS_1 and RS_2 - radial dimensions of each specimen before and after the water moisture swelling measurement (mm).

The percents of the tangential and radial water absorption swelling (WTS and WRS) of the samples were found using Eq. 5 and Eq. 6:

$$WTS = \frac{TS_3 - TS_1}{TS_1} \times 100\% \quad (5)$$

$$WRS = \frac{RS_3 - RS_1}{RS_1} \times 100\% \quad (6)$$

where: TS_1 and TS_3 - tangential dimensions of each specimen before and after the water absorption swelling measurement (mm),
RS_1 and RS_3 - radial dimensions of each specimen before and after the water absorption swelling measurement (mm).

Wood shrinkage measurement

The wood shrinkage measurement is according to standard GB/T 1934.2 (2009) as described in the literature of Yu et al. (2016). The percents of tangential and radial air drying shrinkage (ATS and ARS) by the samples were computed using Eq. 7 and Eq. 8:

$$ATS = \frac{TL_1 - TL_2}{TL_1} \times 100\% \quad (7)$$

$$ARS = \frac{RL_1 - RL_2}{RL_1} \times 100\% \quad (8)$$

where: TL_1 and TL_2 - tangential dimensions of each specimen before and after air drying shrinkage measurement (mm),
RL_1 and RL_2 - radial dimensions of each specimen before and after air drying shrinkage measurement (mm).

The tangential and radial wood shrinkage (OTS and ORS) was computed by Eq. 9 and Eq. 10, respectively:

$$OTS = \frac{TL_1 - TL_3}{TL_1} \times 100\% \quad (9)$$

$$ORS = \frac{RL_1 - RL_3}{RL_1} \times 100\% \quad (10)$$

where: TL_1 and TL_3 - tangential dimensions of each specimen before and after oven drying shrinkage measurement (mm),
RL_1 and RL_3 - radial dimensions of each specimen before and after oven drying shrinkage measurement (mm).

RESULTS AND DISCUSSION

Water absorption analysis

Percents of water repellent (RWA) of different CuAz treated wood after one year outdoor exposure were shown in Fig. 1. Compared to untreated samples (T10), both nano-SiO_2 and wax modification could improve the water repellent of the treated wood. The reasons can be attributed to that the nano-SiO_2 particles and wax can block the entrance path of water, which have been proved by many related researches (Hazarika et al. 2014, Yu et al. 2016). Among the samples only treated with nano-SiO_2 (T1-T4), the effect of nano-SiO_2 on RWA was obvious, in which the best water repellent was observed in the samples only treated with BET specific surface area of 60 $m^2 \cdot g^{-1}$. The result was likely to be caused by the stabilization of different types of nano-SiO_2 in treated wood during outdoor exposure. It has been proved that the combination of nano-SiO_2 and wax (T5-T8) could not exert synergistic effect of water repellent on the treated wood compared to be used singly (T1-T4, T9). The most likely reason for this result was that the combinations among nano-SiO_2, wax and wood continents were very weak and were easily destroyed during outdoor exposure, which was the most urgent problem need to be solved in the future.

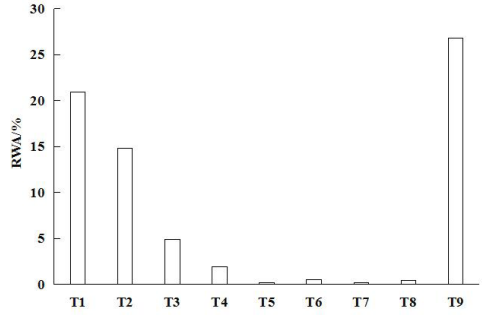

Fig. 1: Percents of water repellent (RWA) of CuAz-treated wood with different treatments.

Swelling analysis

Tangential and radial swelling results (as a percent) for the CuAz treated wood during moisture and water absorption process with different treatments are presented in Tab. 2.

Tab. 2: Tangential/radial moisture and water swelling of different CuAz-treated wood.

Treatment	Moisture swelling (%)		Water swelling (%)	
	MRS	*MTS*	*WRS*	*WTS*
T1	0.58(0.36)	0.71(0.21)	5.21(0.36)	7.01(0.30)
T2	0.14(0.14)	0.64(0.23)	4.67(0.29)	6.93(0.68)
T3	0.81(0.03)	1.05(0.07)	5.35(0.75)	8.42(0.38)
T4	0.47(0.24)	0.91(0.17)	5.61(0.61)	8.27(0.71)
T5	0.48(0.10)	0.58(0.07)	5.34(0.30)	6.46(0.22)
T6	0.38(0.19)	0.27(0.32)	5.83(0.31)	6.11(0.61)
T7	0.29(0.01)	0.88(0.02)	4.56(0.11)	7.34(0.33)
T8	0.95(0.04)	1.18(0.20)	5.92(0.44)	7.89(0.74)
T9	0.66(0.15)	0.61(0.18)	6.28(0.66)	6.87(0.41)
T10	0.77(0.05)	0.62(0.22)	5.43(0.35)	6.17(0.31)

It was observed that during moisture absorption process the effect of nano-SiO_2 or/and wax modification on tangential/radial swelling were quite different. Compared to untreated samples (T10), the dimensional stability of samples only with wax modification (T9) could be improved to some extent, especially for the radial direction, which demonstrated that wax can provide permanent prevention of moisture into wood during outdoor exposure. Among the samples treated with different types of nano-SiO_2 and/or wax, the radial dimensional stability was a little better than that in the tangential direction but not obvious. The swelling ratio was bigger in the samples of T1-T4 compared to T5-T8, which was caused by the addition of hygroskopicity nano-SiO_2. It seemed that wax was essential to reduce the hygroskopicity of the treated wood. Overall, the combination of nano-SiO_2 and wax was effective to improve the tangential and radial moisture swelling stability of the treated wood, which was likely caused by the excellent prevention of moisture into the treated wood. During water absorption process, it was obviously showed that the dimensional stability in all samples were more better in tangential direction than in radial direction. The effect of different types of nano-SiO_2 on the moisture and water swelling dimensional stability of the treated samples was obvious, which seemed that the bigger BET specific surface area would be adversely affected the dimensional stability and the worst result was also observed in the samples modified by nano-SiO_2 with BET specific surface area of 380 $m^2 \cdot g^{-1}$.

Shrinkage analysis

Percents of tangential/radial air and oven drying shrinkage of treated and untreated southern pine are presented in Tab. 3. It was also observed that the radial dimensional stability was a little better than that in the tangential direction of all the samples. During air and oven drying shrinkage processes, both the ratios of tangential and radial shrinkage in the samples of T9 were the lowest, and the dimensional stability was better in T5-T8 than that in T1-T4, which demonstrated that the addition of wax could improve the radial and tangential dimensional stability of nano-SiO_2 treated wood. Compared to T10, the dimensional stabilization of the samples with nano-SiO_2 or/and wax modification would have a little poorer after one year

outdoor exposure, although the increase ratio of shrinkage was no more than 2%. The reason was likely attributed to the photo degradation of lignin and extractive in the samples of T9 and T10 without nano-SiO_2 modification during outdoor exposure, which would increase the dimensional stability of the treated wood. The effect of different types of nano-SiO_2 on the shrinkage dimensional stability of the treated samples was similar with the swelling result that the bigger BET specific surface area would be adversely affected the dimensional stability.

Tab 3: Tangential/radial air and oven drying shrinkage of different CuAz-treated wood.

Treatment	Air drying shrinkage (%)		Oven drying shrinkage (%)	
	ARL	*ATL*	*ORL*	*OTL*
T1	5.18 (0.96)	6.11 (0.11)	6.24(0.64)	7.62(0.27)
T2	5.85 (0.37)	6.58 (0.40)	7.38(0.56)	8.12(0.34)
T3	5.80(0.72)	6.93 (0.28)	7.39(0.31)	8.56(0.20)
T4	6.90 (0.55)	6.92 (0.11)	8.41(0.72)	8.58(0.27)
T5	5.56(0.46)	4.96(0.60)	7.53(0.81)	7.10(0.56)
T6	4.43(0.60)	5.89(0.11)	6.21(0.24)	7.02(0.25)
T7	4.94(0.70)	6.25(0.43)	6.97(0.78)	7.53(0.58)
T8	5.90(0.02)	6.64(0.01)	7.70(0.21)	8.44(0.02)
T9	4.23(0.92)	5.45(0.01)	4.69(1.08)	6.97(0.10)
T10	4.26(0.34)	5.50(0.50)	5.35(0.33)	7.00(0.57)

CONCLUSIONS

1. Both nano-SiO_2 and wax modification could improve the water repellent of the treated wood, and the best water repellent was observed in the samples treated with BET specific surface area of 60 $m^2 \cdot g^{-1}$. The combination of nano-SiO_2 and wax (T5-T8) could not exert synergistic effect of water repellent on the treated wood compared to be used singly during outdoor exposure.
2. For swelling and shrinkage performance, the addition of wax into nano-SiO_2 modified wood was essential to reduce the hygroskopicity and improve the radial and tangential dimensional stability of nano-SiO_2 treated wood.
3. The effects of different types of nano-SiO_2 on the water repellent, swelling and shrinkage stability of the treated samples were similar that the bigger BET specific surface area would be adversely affected the dimensional stability and the worst result was observed in the samples modified by nano-SiO_2 with BET specific surface area of 380 $m^2 \cdot g^{-1}$.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support of the Subjects of National Natural Science Foundation of China (NSFC No. 31400499), the National College Students Innovation and entrepreneurship training program (201910057047), and the Scientific Research Project of Tianjin Education Commission (2017KJ032).

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