

EFFECT AND MECHANISM OF NANOSIZE COPPER OXIDE ON SOME PHYSICAL AND MECHANICAL PROPERTIES OF FLAKEBOARDS

Wei Gao^{1,2}, Jinzhen Cao¹, D. Pascal Kamdem³

ABSTRACT

The effects of nanosize copper oxide and basic copper carbonate on the physical and mechanical properties of flakeboards were investigated according to ASTM Standard D-1037, and the curing process of phenol formaldehyde (PF) resin containing copper compounds was further investigated using dynamic differential scanning calorimetry (DSC). The results showed that nanosize copper oxide had no or slightly beneficial effects on the mechanical properties and dimensional stability of the flakeboards. While basic copper carbonate increased thickness swelling and water absorption to some extent, the difference was not statistically significant. The DSC results indicated that the comparable activation energy and reaction enthalpy, obtained from nanosize copper oxide treated samples, contributed to the higher degree of conversion of PF resin and undiminished bonding strength of flakeboards, which is probably related to the acceleration of the addition reactions taking place among small molecules in PF resin and the enhancement of heat transfer of composite mat caused by nanosize copper oxide.

Keywords: nanosize copper oxide, basic copper carbonate, flakeboard, physical and mechanical properties, differential scanning calorimetry (DSC).

INTRODUCTION

Development of oriented strand board (OSB) has been limited to indoor utilizations where biological deterioration is not critical. Protection against biological degrading agents may promote its outdoor applications. One proposed strategy for achieving this is the use of naturally durable wood species as the raw material to produce OSB. However, those wood species have limited availability and inconsistent decay resistance which varies from sapwood to heartwood within the same log, within species, with the silvicultural practices and the provenance of the log (Amusant *et al.* 2009). A more practical way for improving biological performance is to use preservatives in OSB (Sean *et al.* 1999, Goroyias and Hale 2004, Donath *et al.* 2008). They used inorganic and organic formulations containing copper, borate or zinc. Cheney *et al.* (2009) found that the copper based preservatives (Cu ammonium acetate, Cu diammine acetate, Cu diammine carbonate, basic Cu carbonate) reduced weight losses of aspen strandboards caused by brown-rot fungus *G. trabeum* or white-rot fungus *T. versicolor* to below 10%. Copper is a well established fungicide and recently it was used in its copper carbonate micronized form in combination with an organic biocides to protect wood (Barnes *et al.* 2008, Cookson *et al.* 2008). Stirling *et al.* (2008) reported that wood treated with micronized copper quat (MCQ) is also resistant to soft rot decay fungi. This resistance is likely due to the soluble copper released in the cell wall of treated wood. Barnes *et al.* (2008) noted that the mechanical properties of micronized copper preservative systems treated southern pine were not affected. Although micronized copper has been widely used to treat solid wood and their efficacy on the biological resistance and/or strength properties was well established, their applications in wood composites are still limited (Vidrine *et al.* 2008, Vidrine *et al.* 2009). The reason was partly due to the adverse effect of preservatives on physical and mechanical properties of wood composites because their potential interaction or interference with adhesive.

¹College of Material Science & Technology, Beijing Forestry University, Qinghua Eastroad 35, Haidian, Beijing, China, 100083.

²Faculty of Material Engineering, Southwest Forestry University, Kunming City, Yunnan Province, P. R. China, 650224.

³Department of Forestry, Michigan State University, East Lansing, MI 48824, USA.

Received: 14.10.2010 Accepted: 07.04.2011

Corresponding author: caoj@bjfu.edu.cn

This study examines the feasibility of incorporating solid copper oxide (CuO) nanoparticles in the adhesive mix during the laboratory manufacture of flakeboard, and then evaluates the mechanical and physical properties as indication of compatibility. To achieve this objective, several loading levels of nanosize copper oxide were added in a commercial PF adhesive and the properties of the so-made flakeboards were compared to that of commercial origin made with similar glue and flakes. DSC was used to investigate the effect of CuO nanoparticles on the curing process of phenol formaldehyde (PF) resin.

MATERIALS AND METHODS

Panel Manufacturing and Testing

The flakes used in this study were composed of mixed wood species (aspen 55%, pine 20%, soft maple 20%, and hard maple 5%), which were obtained from Weyerhaeuser plant located in Grayling, Michigan, USA. The average size of the flakes was 0.5 ± 0.1 mm in thickness, 15 ± 5 mm in width and 100 ± 10 mm in length along the direction parallel to grain. Aqueous phenol formaldehyde (PF) resin GP 70CR66 (Georgia-Pacific Resins, Inc.) with 54% solid content was also obtained from Weyerhaeuser, which is the resin used routinely to manufacture commercial OSB. Nanoparticle size copper (cupric) oxide (CuO) was obtained from Johnson Mathey Company. It was a 23-37 nm particle size Aps (air plasma spray) powder with a nominal specific surface area of 25 to 40 m²/g. Basic copper (cupric) carbonate ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) labeled as BCC, was purchased from Aldrich Chemical Company and used as received for comparative purposes.

Nanosize CuO was mixed with PF resin at three loadings of 0.12, 0.25, and 0.49% (w/w, based on flakes), respectively and BCC was at 0.68% (equivalent to 0.49% CuO). Moisture content of the flakes was about $3 \pm 0.5\%$. The resin was sprayed on flakes at a ratio of 3.5% w:w of solid resin. Adhesive coated flakes were removed from the rotary blender and used to hand form a mat of flakes with random orientations to achieve a target density after pressing and curing at temperature of 204°C at 4.8 Mpa for 300s. Five panels were made for each treatment group. An untreated control was also prepared for comparison. Panels with nominal size of 9.8 by 406 by 406 mm with target density of 650 kg/m³ were trimmed by removing the edges to $8 \times 300 \times 300$ mm panels to avoid low density edges. Samples were conditioned at $22 \pm 2^\circ\text{C}$ and $70 \pm 2\%$ relative humidity (RH) to constant weight before testing their physical and mechanical properties, which were thickness swelling at edge (TS), water absorption (WA), internal bond strength (IB), modulus of rupture (MOR), and modulus of elasticity (MOE) (bending flatwise) were assessed using ASTM D1037 (ASTM 1999).

The effects of nanosize CuO and/or copper carbonate were established by evaluating the differences between properties of treatments and the control groups using one-way ANOVA analysis at 95% confidence level with SPSS 16.0 (SPSS Inc., Chicago, Illinois, USA).

Dynamic DSC Scanning and Calculation

DSC60 (Shimadzu, Japan) equipped with a TA-60 thermal analysis system was used to monitor the effect of the addition of copper oxide nanoparticles and copper carbonate on the curing of the commercial phenol formaldehyde OSB grade resin used in this work. The temperature and heat calibrations of DSC were performed by using standards of indium, tin, lead and zinc. PF sample of 10 ± 2 mg was placed in a sealable aluminum capsule with vapor pressure limit at 4.9 MPa. The weight of the sealed samples was taken before and after DSC testing to monitor weight loss during the testing. Nitrogen gas at 10ml/min was used at temperature of 40 to 250°C with heating rates of 5, 10 and 20°C/min. Three replicates were scanned for each condition. The total area under the exothermal curve, based on the extrapolated baseline was used to calculate the reaction enthalpy of curing using TA-60 thermal analysis software (Shimadzu Inc., Kyoto, Japan), and the standard method ASTM E698-01 (ASTM 2001) to estimate the activation energy E_{698} as well.

RESULTS AND DISCUSSION

Physical and Mechanical Properties

The properties of flakeboards laboratory manufactured with nanosize copper oxide nanoparticles or copper carbonate added in the glue mix and the oriented strand board from commercial source at PF ratio of 3.5% are listed in table 1.

Table 1. Physical and mechanical properties of flakeboards made with copper oxide nanoparticles or basic copper carbonate added in the glue mix.

Treatment	Average Density (kg/m ³)	IB (MPa)	MOR (MPa)	MOE (GPa)	Water absorption (%)		Thickness swelling (%)	
					2h	24h	2h	24h
PF Control	678 (24)	0.33 (0.08) ab	28.6 (5.0) a	3.89 (0.84) a	46.3 (4.6) ab	60.5 (2.4) a	24.9 (2.9) a	28.6 (3.4) a
PF+CuO 0.12%	680 (36)	0.33 (0.06) ab	36.7 (7.7) a	4.29 (0.67) a	45.9 (5.4) ab	59.1 (4.7) a	22.9 (3.7) a	27.4 (4.1) a
PF+CuO 0.25%	663 (39)	0.33 (0.08) ab	29.0 (5.1) a	3.81 (0.66) a	46.4 (6.5) ab	57.6 (4.1) a	22.5 (2.6) a	26.0 (3.0) a
PF+CuO 0.49%	669 (24)	0.37 (0.07) bc	33.2 (6.2) a	4.46 (0.70) a	49.0 (6.4) ab	59.4 (4.8) a	23.2 (3.0) a	26.1 (4.3) a
PF+BCC 0.68%	686 (19)	0.27 (0.05) ab	29.9 (6.2) a	4.20 (0.66) a	52.2 (4.0) b	62.4 (3.2) a	25.6 (3.5) a	29.5 (5.1) a
Weyerhaeuser	675 (19)	0.20 (0.06) a	34.1 (2.9) a	4.33 (0.75) a	40.5 (5.0) a	72.6 (2.7) b	14.2 (5.7) b	28.2 (5.7) a
			16.6 [⊥] (1.5) b	1.41 [⊥] (0.24) b				

Values represent means of 5 replicates per treatment, while figures in parentheses are the standard deviations. Within columns, means with the same letters indicate that the difference is statistically insignificant using Tukey's Studentized Range Test ($\alpha = 0.05$).

The superscripts of "^{||}" and "[⊥]" represent the flexural strengths measured along the parallel and perpendicular directions of oriented flakes, respectively.

The average IB for panels made with unmodified PF was 0.33 MPa. For those panels containing lower loading levels of copper oxide nanoparticles, the IB of the panels were unchanged, while increasing the loading of copper oxide nanoparticles to 0.49%, the IB of the panel increased to 0.37 MPa. However, the difference was insignificant compared to the unmodified PF control was insignificant at 95% interval of confidence as revealed by ANOVA test. The introduction of 0.68% BCC to panels caused a decrease in IB from 0.33 MPa to 0.27 MPa, but again this difference was not significant. The lowest IB value was obtained from the commercial OSB board, which may be explained by the different process variables between industrial and laboratory manufacture such as pressure level and duration.

The average values of flexural MOR and MOE mostly increased after adding copper oxide nanoparticles or BBC to PF adhesive compared with unmodified control, suggesting that the incorporation of copper in the adhesive had little influence on the flexural properties of flakeboards, which is consistent with previous reports on the effect of micronized copper oxide on aspen flakeboards using PF resin as a binder (Vidrine *et al.* 2008).

The dimensional stability which includes the values of WA and TS after 2 and 24 hours' immersion in distilled water at $20\pm 1^\circ\text{C}$ was shown in table 1 and figure 3. No significant difference was detected among groups of boards made in the laboratory by using unmodified PF or PF modified with either of the copper compounds. While compared to the commercially made boards, the difference is significant in some cases, for example, the WA after 24 h and the TA after 2 h. Although the WA after 2 h of laboratory made flakeboards with PF modified with CuO nanoparticles showed no significant difference with commercial OSB due to the wide standard deviation, the average values of WA after 2 h were consistently trend of higher than that of commercial OSB. However, the WA after 24 h showed the reserves result; namely, the WA of laboratory made flakeboards was lower than that of commercial OSB. The reason was considered to be related with the addition of wax in the formulation of commercial OSB, which would hinder water absorption at first but then be overcome by continued soaking. The lower WA after 24 h of laboratory made flakeboards suggested that both CuO nanoparticles and BCC had an effect on reducing water sorption after long duration. Correspondingly, the TA was also lower after 2 h for commercial OSB but after 24 h there was no significant difference between all groups. This trend was similar to the results in a previous report (Jusoh *et al.* 2005). Compared the average WA and TS values of CuO nanoparticles (0.49%) with BCC (0.68%) at the same copper concentration, it can be clearly found that the values of the boards containing CuO nanoparticles are slightly lower than that of the boards with BCC without statistical significance.

From the above discussion, we can draw the conclusion that nanosize CuO and basic copper carbonate can be incorporated in the glue mix at levels used in this work with no significant negative effect on the mechanical properties and even with some slight improvement in dimensional stability of flakeboard. The mechanism to explain the performance was further investigated by using DSC to clarify the curing process of PF adhesive containing copper oxide nanoparticles and BCC.

Dynamic DSC Analysis

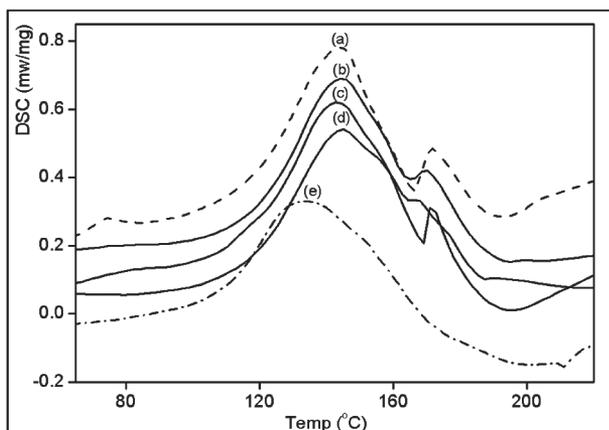


Figure 1. Dynamic DSC curves of PF control (a), PF with nanosize copper oxide at loading levels of 0.12% (b), 0.25% (c), and 0.49% (d), and PF with basic copper carbonate 0.68% (e) at a heating rate of $10^\circ\text{C}/\text{min}$.

Figure 1 demonstrates the dynamic scanning calorimeter (DSC) curves of PF control and PF resin containing CuO nanoparticles and BCC at a heating rate of 10 °C/min. The major exothermic peak for PF control appeared at 144.5°C, followed by another peak at about 171.7 °C. The onset curing temperature was close to 108.5°C. With the addition of nanosize CuO, the first peak temperature similar to the exothermic peak of PF control did not change, but the other peak initially at 171.7 °C for PF control shifted slightly to 170.0 °C. However, the addition of 0.68% BCC to the PF adhesive resulted in a shift of the exothermic peak to 133.7 °C without an observable second peak. More detailed DSC tests were run at different heating rates to elucidate the effect of the addition of CuO nanoparticles and BCC as represented in figure 2.

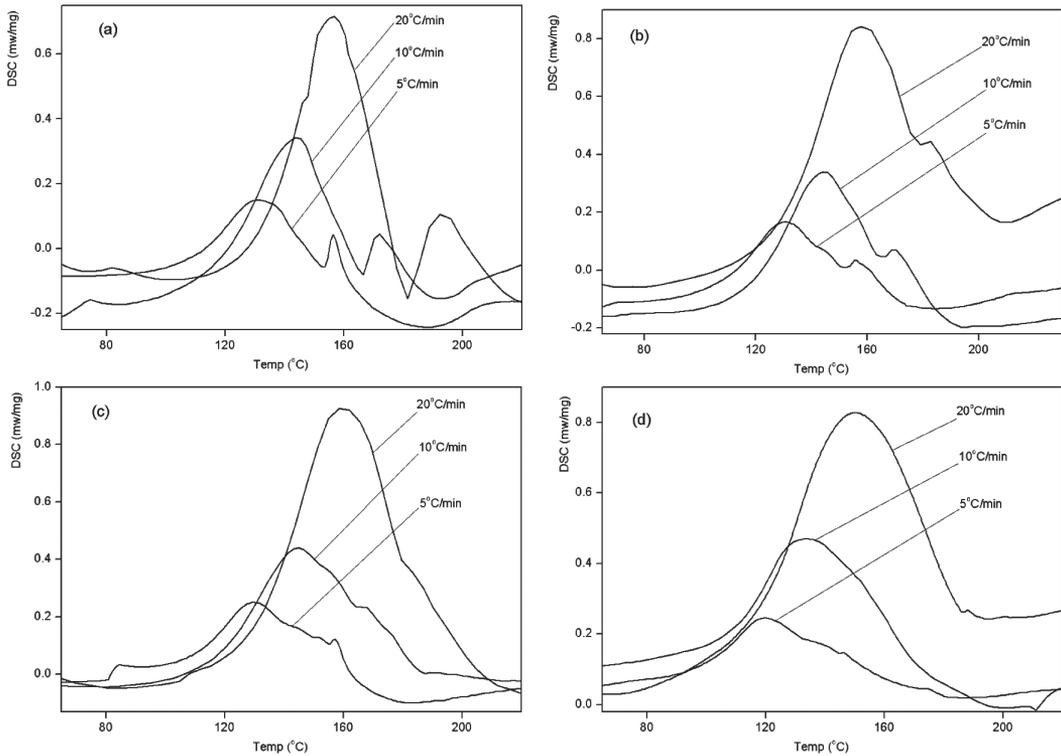


Figure 2. Dynamic DSC curves of control PF resin (a) and PF resin with nanosize copper oxide at concentration of 0.12% (b), 0.49% (c), and basic copper carbonate 0.68% (d) at heating rate of 5, 10 and 20 °C /min respectively.

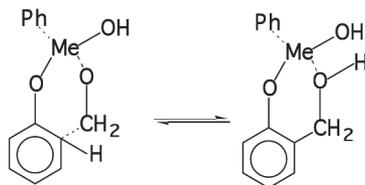
It is clear from figure 2 that CuO nanoparticles and BCC have different effects on the thermal behavior of PF during curing from room temperature to 200 °C. Table 2 lists the DSC parameters of PF control, PF with different loadings of nanosize copper oxide, and PF with BCC computed from DSC curves according to ASTM E698-01 (ASTM 2001). The energy of activation (E_{698}), illustrating the chemical reactivity of the curing reactions, was obtained from the exothermic peak from the DSC curves at three heating rates (Figure 2).

Table 2. DSC parameters of PF control, PF+CuO, and PF+BCC.

Sample	ΔH (J/g)	E_{698} (KJ/mol)	T_P (°C)		
			5 (°C/min)	10 (°C/min)	20 (°C/min)
PF Control	135.67 (35.47)a	72.10	130.99	144.36	156.19
PF+CuO 0.12%	138.72 (41.55)a	66.00	130.44	144.58	157.90
PF+CuO 0.25%	148.26 (20.38)b	65.97	130.01	143.00	157.70
PF+CuO 0.49%	150.60 (22.06)b	65.90	130.90	144.90	158.48
PF+BCC 0.68%	125.68 (26.01)c	55.77	119.66	133.73	150.26

Values represent means of 3 replicates per treatment, while figures in parentheses are the standard deviations. In a same column the same followed alphabets represent that the difference is statistically insignificant using Tukey's Studentized Range Test ($\alpha = 0.05$).

In general, the activation energy of modified PF is lower than that of PF control. Further more, the addition of 0.68% copper carbonate caused greater reduction on activation energy than 0.49% nanosize CuO. It indicated that both copper compounds improved the cure reactions of PF resin. The probable reason is that copper oxide is a Lewis base, which may accelerate the addition reactions taking place among small molecules in PF resin. It is characterized by the formation of chelates as transient compounds according to the following formula (Pizzi 1979 a,b,c):



As the cure reactions of PF resin are typically exothermic, it can be confirmed that the reaction enthalpy, or in the other words, the amount of heat released in the reaction, is proportional to the degree of conversion during the curing process or the cross-linking created in the adhesive self-condensation (Vázquez *et al.* 2006). The DSC results from table 2 illustrated that the reaction enthalpy increased obviously with the addition of nanosize copper oxide in the curing system. Moreover, the highest reaction enthalpy value of 152.40 J/g was obtained by the sample of PF with 0.49% copper oxide. This indicates that the final degree of conversion of the curing reaction for PF with nanosize CuO is higher than that of PF control. This is also evidence for the similar or slightly improved dimensional stability of the corresponding flakeboards (Table 1). The reason was considered to be related to the increased thermal conductivity of flakeboard mat caused by the addition of nanosize copper oxide since the reported data showed that the thermal conductivity of CuO particle is 20 W/Mk (Kwak and Kim 2005), while the air dried wood was between 0.070 to 0.407 W/Mk (Yin 1996). Therefore, both heat transfer of the flakeboard mat and the curing process of PF resin were enhanced, and the final mechanical properties of flake board were sometimes slightly improved as well.

CONCLUSIONS

Nanosize copper oxide had no or slightly beneficial effects on the mechanical properties and dimensional stability of flakeboard. While basic copper carbonate increased thickness swelling and water absorption to some extent, the difference was not statistically significant. The DSC results indicated that the activation energy of PF cure decreased significantly with the addition of 0.68% basic copper carbonate, and the reaction enthalpy reduced at the same time, which resulted in the relatively lower bond strength of for treated flakeboards. However, comparable activation energy and reaction enthalpy were obtained from PF resin control and nanosize copper oxide treated samples, indicating that application of nanosize copper oxide resulted in the higher degree of conversion of PF resin and undiminished bond strength. The biological resistance of nanosize copper oxide and basic copper carbonate treated flakeboards will be examined in further study.

ACKNOWLEDGEMENT

The authors wish to acknowledge the International Research Group on Wood Protection (IRG-WP) for a Travel Award that allowed Mr. Wei Gao to complete the experiment of this work in Michigan State University. We also thank Weyerhaeuser for providing flakes and adhesive to this research.

REFERENCES

- Amusant, N.; Arnould, O.; Pizzi, A.; Depres, A.; Mansouris, R. H.; Bardet, S.; Baudasse, C. 2009.** Biological properties of an OSB eco-product manufactured from a mixture of durable and non durable species and natural resins. *European Journal of Wood and Wood Products* 67(4): 439-447.
- ASTM. 1999.** Standard test method for evaluating properties of wood-based fiber and particle panel material. D1037-99. ASTM International. West Conshohocken, USA.
- ASTM. 2001.** Standard test method for arrhenius kinetic constants for thermally unstable materials. ASTM E698-01. ASTM International. West Conshohocken, USA.
- Barnes, H. M.; Lindsey, G. B.; Hill, J.; Pompeo, M.; Hodge, R. 2008.** Bending properties of southern pine treated with micronized preservative systems. The 39th Annual Meeting of International Research Group on Wood Preservation, Istanbul, Turkey.
- Cookson, L. J.; Creffield, J. W.; McCarthy, K. J.; Scown, D. K. 2008.** Australian trials on the efficacy of micronized copper. The 39th Annual Meeting of International Research Group on Wood Preservation, Istanbul, Turkey.
- Donath, S.; Spetmann, P.; Jaetsch, T.; Zahlmann, T. 2008.** Protection of OSB against termites by incorporation of different actives via glue line treatment. The 39th Annual Meeting of International Research Group on Wood Preservation, Istanbul, Turkey.
- Goroyias, G. J.; Hale, M. D. 2004.** The mechanical and physical properties of strand boards treated with preservatives at different stages of manufacture. *Wood Science and Technology* 38(2): 93-107.
- Jusoh, I. B.; Nzokou, P.; Kamdem, P. 2005.** The effect of silicone on some properties of flakeboard. *Holz Als Roh-Und Werkstoff* 63(4): 266-271.

Kwak, K.; Kim, C. 2005. Viscosity and thermal conductivity of copper oxide nanofluid dispersed in ethylene glycol. *Korea-Australia Rheology Journal* 17(2): 35-40.

Pizzi, A. 1979(a). Phenolic resins by reactions of coordinated metal ligands. *Journal of Polymer Science: Polymer Letters Edition* 17(8): 489-492.

Pizzi, A. 1979(b). Phenol and tannin-based adhesive resins by reactions of coordinated metal ligands, Part I: phenolic chelates. *Journal of Polymer Science* 24(5): 1247-1256

Pizzi, A. 1979(c). Phenol and tannin-based adhesive resins by reactions of coordinated metal ligands, Part II: Tannin adhesives preparation, characteristics and application. *Journal of Polymer Science* 24(5): 1257-1268.

Sean, T.; Brunette, G.; Côté, F. 1999. Protection of oriented strandboard with borate. *Forest Products Journal* 49(6): 47-51.

Stirling, R.; Drummond, J.; Zhang, J.; Ziobro, R. J. 2008. Micro-distribution of micronized copper in southern pine. The 39th Annual Meeting of International Research Group on Wood Preservation, Istanbul, Turkey.

Vázquez, G.; González-Álvarez, J.; Antorrena, G. 2006. Curing kinetics of phenol formaldehyde resin and wood-resin interactions in the presence of wood substrates. *J. Therm. Anal. Calorim* 84(3): 651-654.

Vidrine, C.; Kamke, F.; Preston, A.; Morrell, J. J. 2009. The effects of copper-based preservative technologies on the resistance of aspen strandboards to biological degradation. *Wood and Fiber Science* 41(3): 211-219.

Vidrine, C.; Kamke, F. A.; Morrell, J.; Preston, A. 2008. Preserving panels by furnish addition of copper compounds: Effects on panel properties. American wood protection association.

Yin, S. 1996. *Wood science*. China Forestry Press. Beijing, China.