Anti-Mildew Properties of Copper Cured Heat-Treated Wood

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The dimensional stability and resistance to degradation of wood can be improved using high temperature heat treatment under anaerobic conditions; however, mildew growth can have a deleterious impact on its appearance and commercial value. In this study, wood samples were impregnated in copper-containing solutions at high pressure before being recovered and cured at high temperatures to create treated wood samples with nano copper particles. This copper impregnated wood (up to 6.35% copper content) suppressed the growth of *Botryodiplodia theobromae* Pat. and *Aspergillus niger* van Tieghem with 100% efficiency, and *Penicillium citrinum* Thom with 75% efficiency. However, the growth of *Trichoderma viride* Pers was not suppressed. These results demonstrate that copper curing can be used to extend the scope, performance, and lifetime of heat-treated wood, enabling it to be used for a new range of applications.

Keywords: Copper-containing compounds; Heat treatment of wood; Anti-mildew; SEM; XRD; XPS; Nano copper particles

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INTRODUCTION

Heat-treated wood processed at 160 to 260 °C under a low oxygen atmosphere is a new environmentally friendly material that has been widely used for decorative wall paneling applications. This type of heat-treated wood can be divided into three categories, with wood being processed under an atmosphere of nitrogen, or *via* treatment with steam, or oil (Yan-Jun *et al.* 2002; Esteves *et al.* 2013). These treatments render the wood more visually appealing (Unsal *et al.* 2003; Johansson and Morén 2006), affording improved dimensional stability and degradation resistance properties after heat treatment (Dubey *et al.* 2012; Priadi and Hiziroglu 2013). However, its commercial quality is dramatically undermined, as mildew growth on wood is more likely to occur after it has undergone thermal treatment (Kun *et al.* 2010). Therefore, the identification of anti-mildew agents that can be applied to heat-treated wood would greatly increase its commercial applications.

The anti-mildew properties of heat-treated wood have been studied by many researchers, with Gu *et al.* (2010) reporting that *Botryodiplodia theobromae* Pat. caused less damage to heat-treated wood (185 and 205 °C for 1.5 h) from *Pinus sylvestris* var. *mongolica* and *Quercus mongolica* Fisch., even though mildew growth was not totally suppressed. Sivonen *et al.* (2003) analyzed damage to wood from *Pinus* spp. caused by *Coriolus versicolor* and concluded that good anti-mildew properties could only be achieved by heat-treating pine wood at temperatures above 220 °C. Theander *et al.* (1993) found that heat treatment resulted in accumulation of oligosaccharides at the surfaces of wood from *Pinus sylvestris* and *Picea asperata*, with the nitrogen content of these carbohydrates causing yellowing of the wood over time. The growth of *Penicillium brevicompactum* on wood is closely related to its nitrogen content and the amount of low molecular weight polysaccharides present, with the growth of mildew (like *Aspergillus* spp.) being suppressed by substances generated in reactions that occur during the heat treatment process. However, feasible solutions that can effectively suppress mildew growth on heat-treated wood still need to be developed to enable its commercial application to be broadened.

The characteristics of inorganic nano-materials (small size, large specific surface area, quantum size effects) means that they can potentially be used as environmentally friendly, antibacterial, and anti-mildew materials for coating heat treated wood (Kartal *et al.* 2009). They are an effective method for suppressing mildew growth, with cheap nano-copper particles widely used as effective anti-mildew agents, due to their inherent antifungal properties and low toxicity (Zhang *et al.* 2013; Yu *et al.* 2015). Initial methods developed to prepare nano copper particles were low yielding, energy-inefficient, and used toxic chemicals under non-aqueous conditions that required the presence of an inert atmosphere (Wu *et al.* 2006; Sastry *et al.* 2013). Consequently, new low-cost (Liu *et al.* 2012) liquid-phase reduction (Jain *et al.* 2015), and template methods (Yu *et al.* 2004) have been introduced for the cost-effective production of copper nanoparticles. For example, Khanna *et al.* (2007) prepared pure nano-copper particles using liquid-phase reduction conditions that used sodium formaldehyde sulfoxylate and sodium citrate (or tetradecanoic acid) as reagents. Heat treated wood has previously been cured by dipping in copper containing suspensions at high pressures and temperatures. This results in liquid-phase reduction conditions that generate nano copper particles *in situ* (Yang and Fan 2014), with the resultant copper cured wood samples exhibiting improved anti-mildew properties.

This study confirms that copper nanoparticles can be used as an effective anti-mildew treatment for protecting heat-treated wood against unwanted fungal growth.

EXPERIMENTAL

Materials

Wood was harvested from 25-year-old *Pinus massoniana* Lamb. that did not exhibit any signs of decay or mildew, with each test group consisting of six individual wood samples. Copper solutions were prepared by mixing copper hydroxide, diethylamine alcohol, polyethylene glycol 200, and water. Copper ammonia solutions were prepared by adding water to a stirred solution of copper hydroxide dissolved in diethanolamine. Other copper-containing solutions (designated as CuG) were prepared by adding polyethylene glycol 200 to copper ammonia solution.

Methods

Preparation of copper-containing wood samples

The dimensions of wood samples were 50 mm (longitudinal) × 20 mm × 5 mm. Samples were pre-heated in an oven at 60 °C until their weight remained constant. Samples were then submerged in a copper containing solution for 30 min at a vacuum pressure between 0.09 MPa and 1.5 MPa for 40 min. The wood samples were then recovered and dried at 60 °C until their weight remained constant.

Heat treatment of wood samples

Wood samples were heat-treated using a custom-designed machine according to the following procedure. *Pinus massoniana* Lamb. wood samples that had been dipped in copper-containing solutions (and untreated controls) were placed on the iron wire net of a heating tank. The door of the heating chamber was closed, and the air pressure to the steam generator and carbonization unit set at 200 and 100 kPa, respectively, with oxygen being removed continuously from the heating tank over a period of 20 min. The steam carbonization process was then switched to an electrothermal carbonization process that was carried out at 220 °C for 3 h. After the heating process, the steam generator was turned on and the chamber allowed to cool *via* steam evacuation until the temperature decreased to 140 °C. The heat-treated samples were then retrieved from the heating tank.

Table 1. Curing Conditions Used for the Heat Treatment of *Pinus massoniana* Wood

Sample Number [1]	Parameters		
	CuG [2]	°C	*t*/h
CK	-	-	-
N	-	220	3
P1	4.38%	220	3
P2	5.35%	220	3
P3	6.35%	220	3
P4	7.70%	220	3
P5	8.70%	220	3

[1]Heat treated samples of untreated wood, heat treated wood and impregnated wood are designated as CK, N and P respectively;
[2]CuG represents the concentration of copper ion present in the dipping suspension.

Samples with dimensions of 50 mm × 20 mm × 5 mm were directly heat-treated to produce test samples for anti-mildew tests, with these treated wood samples then ground into a 40-60 mesh powder for subsequent SEM, EDS, XPS, and XRD analysis.

Anti-mildew tests and performance evaluation of wood samples

The dimensions of the wood samples used in the anti-mildew tests were 50 mm (along the texture length) by 20 mm by 5 mm. Each anti-mildew test was conducted on 6 identical wood samples, with individual samples being treated using the different conditions listed in Table 1. The anti-mildew properties of each sample were investigated by evaluating their ability to suppress the growth of four different mildews: *Botryodiplodia theobromae* Pat., *Aspergillus niger* van Tieghem, *Penicillium citrinum* Thom, and *Trichoderma viride* Pers. Antimildew tests were carried out according to the GB/T 18261 (2013) standard. A typical test involved the following steps: hot mildew medium containing 2% (w/w) maltose and 1.5% (w/w) agar was first poured into a sterilized glass culture dish. The mildew medium was cooled to room temperature and mildew spores inoculated into the medium. The glass medium dish was stored at 28 °C at a relative humidity of 85% for 1 week to allow the mildew to grow. Two sterilized glass rods were inserted into the mildew medium, and the sterilized wood samples placed on top of the glass rods. The samples were left for 1 month before their degree of infection was determined. The anti-mildew efficiency (E) of the wood samples was calculated according to Eq. 1,

$$E = \left(1 - \frac{D_1}{D_0}\right) \times 100\% \tag{1}$$

where D_1 and D_0 are the average degrees of infection of copper impregnated wood samples and wood controls respectively.

Color change ratings were divided into 4 classes: 0 indicated no mildew growth was present; 1 indicated that less than 25% surface area of the wood sample was covered by mildew; 2 indicated that 25 to 50% of the wood sample was covered by mildew; 3 indicated that 50 to 75% of the wood sample was covered by mildew; and 4 indicated that greater than 75% of the wood sample was covered by mildew.

Scanning electronic microscopy (SEM) and energy dispersive spectroscopy (EDS)

Two copper containing wood samples were ground into powders that were subsequently analyzed using SEM (Zeiss SUPRA 40, Oberkochen, Germany) and EDS (ZEISS SUPRA 40).

X-ray photoelectron spectroscopy (XPS)

A total of 20 mg of copper containing wood samples were ground into powders and their elemental composition and valence states analyzed using a Thermo Fisher Scientific Escalab 250Xi XPS machine (Waltham, MA, USA).

X-ray diffraction (XRD) analysis

A total of 100 mg of copper containing wood samples were ground into powders and the crystal structures and sizes of their metal particles analyzed using a Bruker D8 XRD analyzer (Karlsruhe, Germany). The crystal sizes of the particles were calculated according to the Scherrer equation (Eq. 2),

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{2}$$

where D is the crystal size, K is a constant; λ is the wavelength of the incident X-ray; β is the full width at half maximum (FWHM) of the diffraction peak; and θ is the recorded diffraction angle. The value of the constant K in the above equation is related to the definition of β, with K equal to 0.89 when β is referenced to the FWHM and equal to 1.0 when β is referenced to the integral breadth.

RESULTS AND DISCUSSION

Anti-mildew Properties of Copper Nanoparticle Treated *Pinus massoniana* Lamb Wood Samples

The ability of *Botryodiplodia theobromae* Pat., *Aspergillus niger* van Tieghem, *Penicillium citrinum* Thom, and *Trichoderma viride* Pers., to grow on control wood samples, heat-treated wood samples, and copper impregnated wood samples was investigated. Four control samples were used to verify the reliability of the assay conditions in each case, with samples that were completely covered with mildew assigned an anti-mildew efficiency score of 0 (Fig. 1). The anti-mildew properties of the controls and heat-treated samples were all scored as 0, indicating that untreated and heat-treated wood samples exhibited very poor anti-mildew properties (Du *et al.* 2016).

However, heat-treated copper containing wood samples effectively suppressed the growth of *Botryodiplodia theobromae* and *Aspergillus niger*, with 100% inhibition of these fungi being observed when relatively high concentrations of copper were present in the dipping solution. It is likely that the micro/nano scale copper particles and oxides generated during the reduction of copper ions by polyethylene glycol 200 and the presence of reducing sugars and other reducing agents combine to suppress the growth of these mildew (Kamdem *et al.* 1998; Zhang *et al.* 2013; Yang and Fan 2014). There was 75% inhibition of the growth of *Penicillium citrinum* on impregnated wood samples treated with 6.35% copper-containing solutions, but no anti-mildew effect was observed for *Trichoderma viride*, reflecting the difficulty of preventing heat-treated wood being colonized by these aggressive fungi (Salem *et al.* 2016).

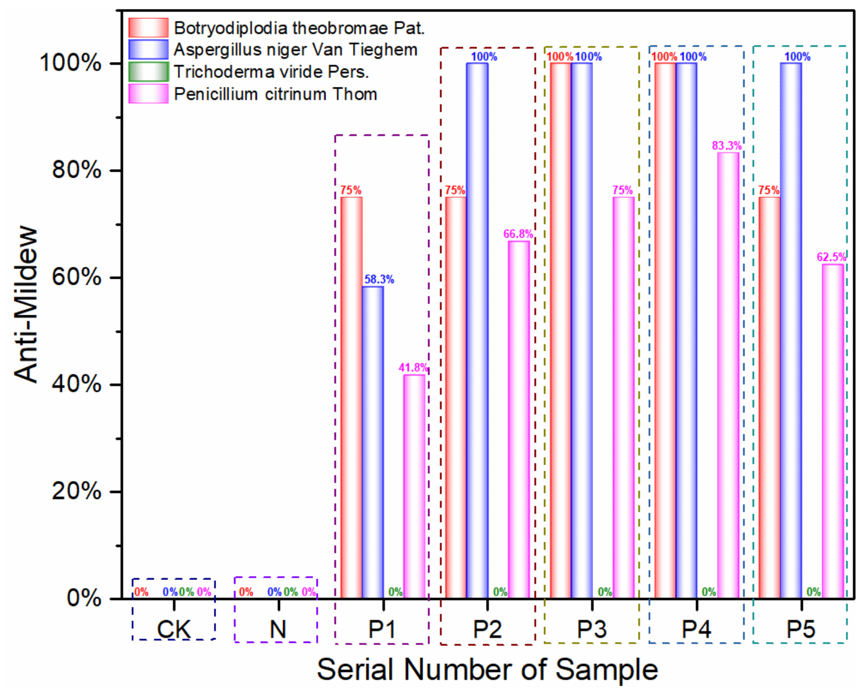


Fig. 1. Prevention of mildew growth on different types of *Pinus massoniana* wood samples

Exploration of the Anti-mildew Mechanism of Heat-treated Copper-containing Wood

Curing copper containing wood samples at 220 °C for 3 h effectively suppressed the growth of certain types of mildew; therefore, the structural morphology of these wood samples was investigated to elucidate how this treatment process might suppress fungal growth.

SEM and EDS Analysis of Heat-treated Copper-containing Wood

Heat-treated copper-containing wood samples that exhibited anti-mildew properties were analyzed using SEM and EDS. Figure 2 shows the SEM images and corresponding EDS results for copper-containing wood samples treated at 220 °C for 3 h. The SEM images show that particles adhered to the surface of the wood sample, with EDS analysis confirming the presence of copper. The EDS analysis in Fig. 2 also shows that the O/C ratio varied from 0.63 to 0.48 depending on the temperature and length of treatment time. In this respect, it is likely that dehydration byproducts are generated when wood is heat-treated, leading to a decrease in its oxygen content (Inari *et al.* 2006).

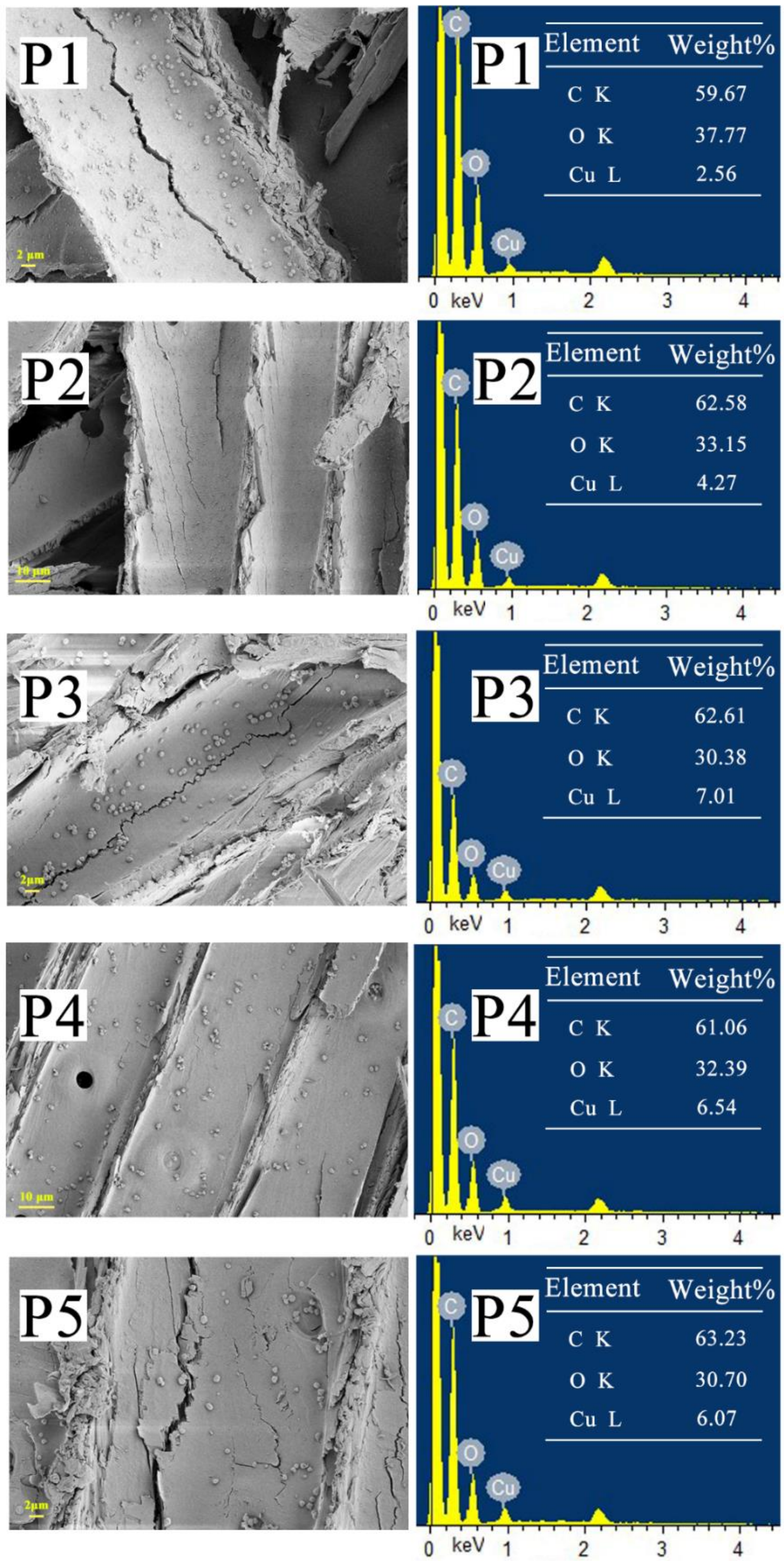


Fig. 2. SEM and EDS results for heat-treated wood samples dipped in suspensions containing different concentrations of copper

Figure 1 reveals that the amount of *Penicillium citrinum* that grew on the heat-treated copper-containing wood samples initially decreased with increasing concentrations of CuG in the dipping solution, but then it increased again at higher levels of CuG. After reaching a peak level, the conversion rate for reduction of Cu^{2+} to Cu^0 and Cu^+ decreased as the concentration of Cu^{2+} increased. Further investigations will be required to gain a better understanding of the reaction pathways that are occurring.

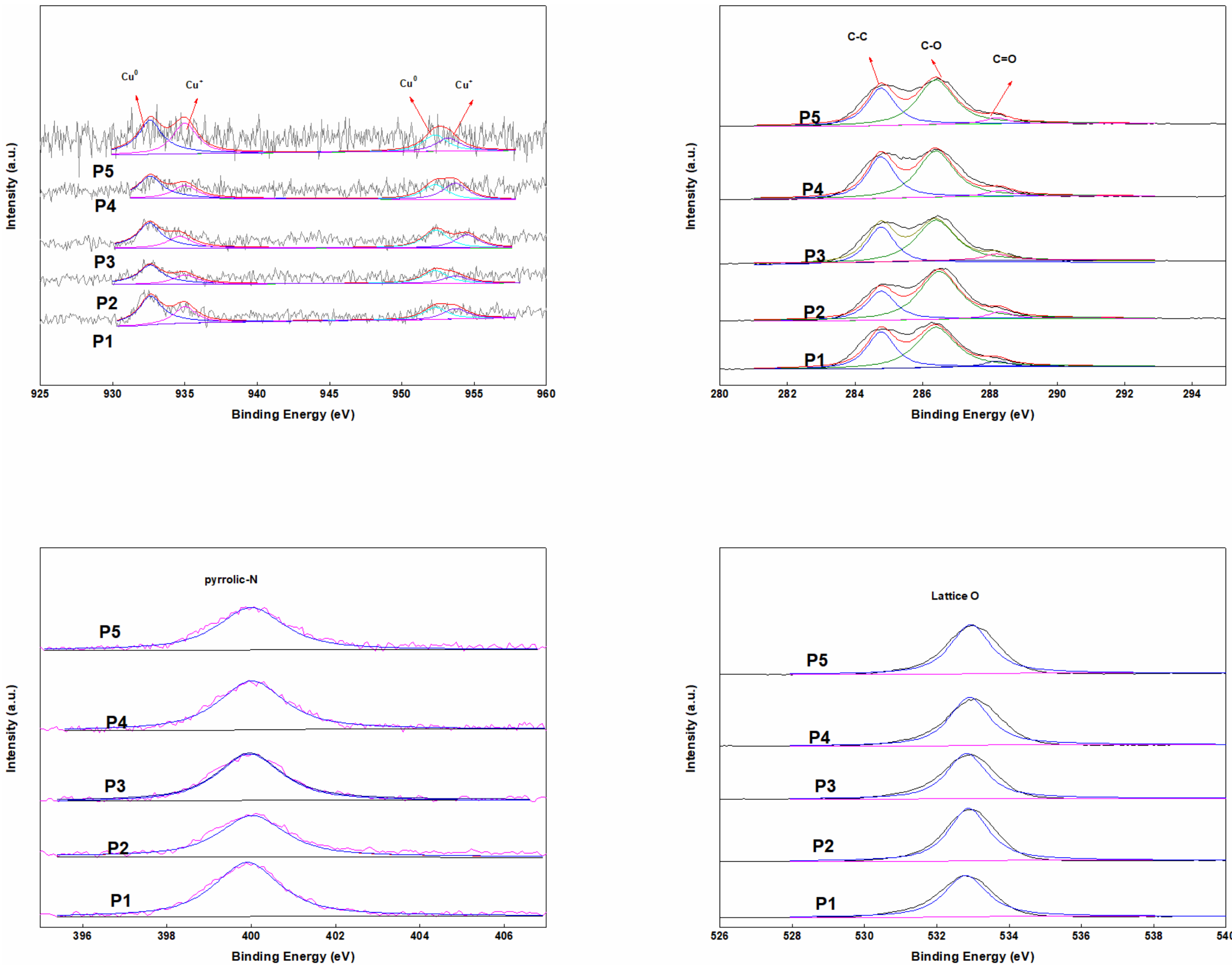
XPS Analysis of Heat-treated Copper-containing Wood Samples

XPS analysis of the surface of particles present in the heat-treated copper-containing wood sample (220 °C for 3 h) revealed the presence of peaks for Cu^+ at 934.9 eV and 954.4 eV, with Cu^0 peaks being detected at 932.9 eV and 952.6 eV, respectively (Fig. 3). These XPS results confirmed the presence of nano-copper and nano-cuprous oxide particles in these copper-impregnated wood samples. Only one peak was observed in the O 1s region, which was assigned to the presence of C-O bonds (Inari *et al.* 2006; Nzokou and Kamdem 2010). Three peaks were present in the C 1s region, corresponding to the presence of C-C, C-O, and C=O bonds. The O/C ratio of pure cellulose is 0.83 and the O/C ratio of pure lignin is 0.33 (Inari *et al.* 2006; Nzokou and Kamdem 2010). The O/C ratio for the heat-treated copper-containing wood samples was between 0.42 and 0.48, suggesting that hydrothermal carbonization occurs during the steam treatment process at 220 °C, resulting in decomposition of the more labile hemicellulose component (Huang *et al.* 2010, 2013). This results in a decrease in the amount of accessible sugar feedstocks that are available for mildew growth, which also leads to a relative increase in lignin content, which is known to increase the ability of wood to suppress mildew growth.

XRD Analysis of Dipped and Heat-Treated Wood Samples

Figure 4 shows the different diffraction peaks that were detected for copper-treated wood samples at 43.3°, 50.4°, and 74.1°. These peaks match known crystal data for (111), (200), and (220) planes of cubic crystalline structures (Usman *et al.* 2013) for elemental copper, with no evidence of any cuprous oxide being present in the treated wood samples. Ding *et al.* (2013) reported on the potential leaching of nano copper particles (10, 50 nm, and ACQ) from treated wood samples, describing that micro/nano-scale copper particles with sizes of 50 nm exhibited the best resistance to leaching. In accord with the Scherrer equation and the XRD results, the average size of the nano copper particles present in the treated wood samples in this study was 100 nm, which is likely to result in good anti-leaching properties. Therefore, the excellent anti-mildew properties of the heat-treated copper-containing wood samples are attributable to the presence of elemental copper in micro/nano scale form that are resistant to leaching (Xu 2013).

The *in situ* process used to generate the micro/nano scale copper particles represents an eco-friendly coating method (Sedighi *et al*. 2014; Dobrovolný *et al*. 2015) that minimizes exposure of the user to potentially toxic nanoparticles (Raffi *et al*. 2010). Micro/nano scale copper particles in the heat treated wood adhere to and disrupt the cytoderm of mildew through a series of electrostatic interactions with the cell wall that serve to inhibit fungal growth (Mondal and Mani 2012; Civardi *et al*. 2015). Future work in this area will be directed towards determining the mechanism of action of the anti-mildew properties of these copper micro/nano scale particles, with the aim of identifying new treatments that can effectively suppress the growth of recalcitrant fungi (such as *Trichoderma viride*) on heat-treated wood.


Cu0
Cu+
Cu0
Cu+
P5
P4
P3
P2
P1
Intensity (a.u.)
925
930
935
940
945
950
955
960
Binding Energy (eV)
C-C
C-O
C=O
P5
P4
P3
P2
P1
Intensity (a.u.)
280
282
284
286
288
290
292
294
Binding Energy (eV)
pyrrolic-N
P5
P4
P3
P2
P1
Intensity (a.u.)
396
398
400
402
404
406
Binding Energy (eV)
Lattice O
P5
P4
P3
P2
P1
Intensity (a.u.)
526
528
530
532
534
536
538
540
Binding Energy (eV)

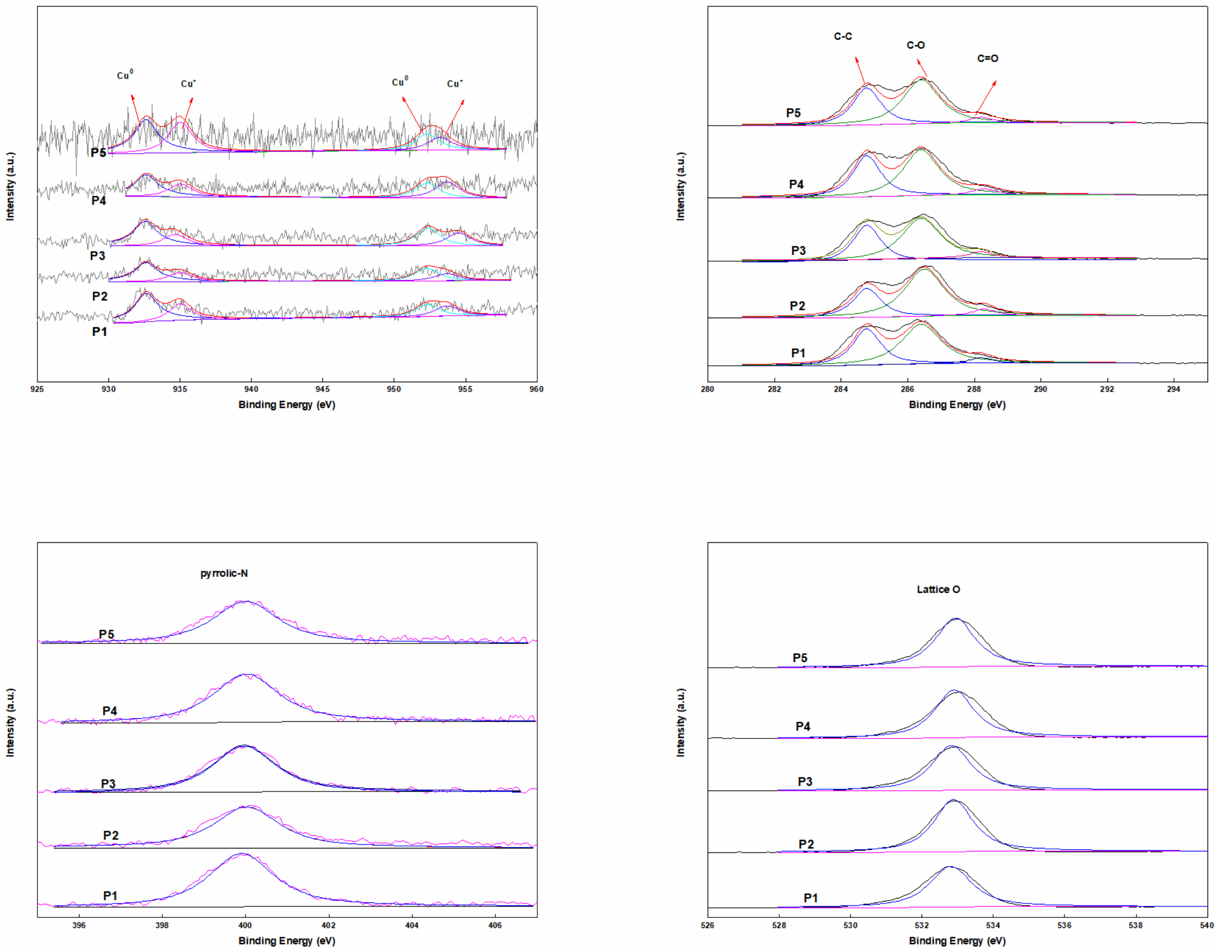


Fig. 3. XPS analysis of heat-treated wood samples dipped in solutions containing different concentrations of copper

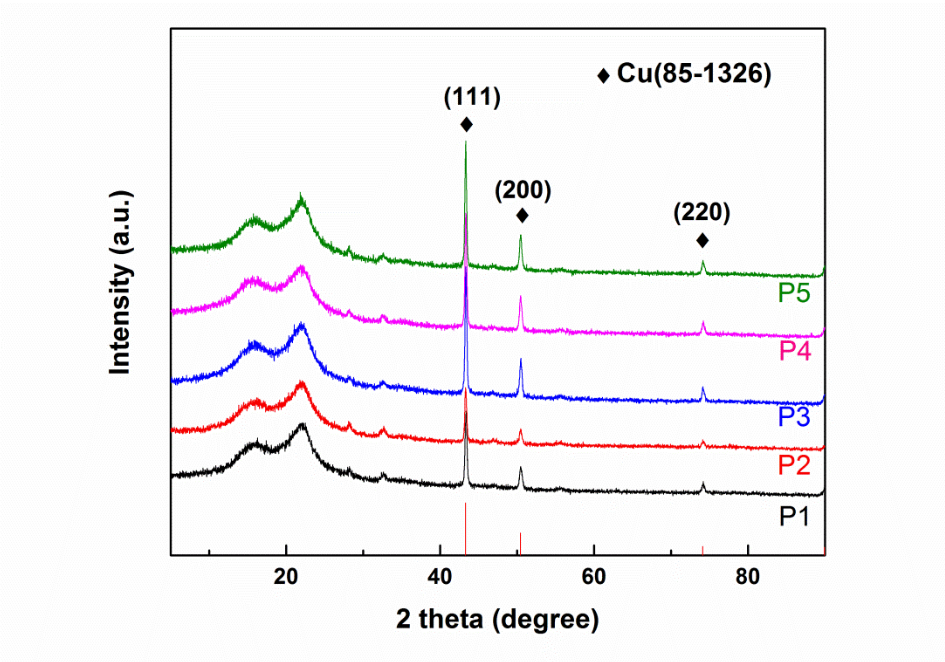


Fig. 4. XRD analysis of heat-treated wood samples dipped in suspensions containing different concentrations of copper

CONCLUSIONS

1. Wood samples were dipped in copper-containing solutions and then heat-treated at 220 °C for 3 h to create copper-impregnated heat-treated wood samples. XPS and XRD analysis revealed that the surfaces of these treated wood samples contained significant amounts of nano copper particles.
2. Heat-treated wood samples containing a copper content of 6.35% suppressed the growth of *Botryodiplodia theobromae* Pat. (100% suppression), *Aspergillus niger* van Tieghem (100% suppression), and *Penicillium citrinum* Thom (75% suppression) on heat-treated wood.

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REFERENCES CITED

Civardi, C., Schwarze, F. W., and Wick, P. (2015). "Micronized copper wood preservatives: An efficiency and potential health risk assessment for copper-based nanoparticles," *Environ. Pollut.* 200, 126-132. DOI: 10.1016/j.envpol.2015.02.018

Ding, X., Meneses, M. B., Albukhari, S. M., Richter, D. L., Matuana, L. M., and Heiden, P. A. (2013). "Comparing leaching of different copper oxide nanoparticles and ammoniacal copper salt from wood," *Macromol. Mater. Eng.* 298(12), 1335-1343. DOI: 10.1002/mame.201200439

Dobrovolný, K., Ulbrich, P., Švecová, M., and Bartůněk, V. (2015). "Affordable, green, and facile synthesis of copper nanoparticles stabilized by environmentally friendly surfactants," *Metall. Mater. Trans. B* 46(6), 2529-2533. DOI: 10.1007/s11663-015-0424-9

Du, X., Liu, Y., and Lian, K. (2016). "Mechanism and properties of antibacterial activity of core/shell copper carbon nanocomposite," in: *Antibacterial Science and Technology Forum 2016*, Su Zhou, Jiang Su, China.

Dubey, M. K., Pang, S., and Walker, J. (2012). "Oil uptake by wood during heat-treatment and post-treatment cooling, and effects on wood dimensional stability," *Eur. J. Wood Wood Prod.* 70(1-3), 183-190. DOI: 10.1007/s00107-011-0535-1

Esteves, B., Marques, A. V., Domingos, I., and Pereira, H. (2013). "Chemical changes of heat treated pine and eucalypt wood monitored by FTIR," *Maderas. Ciencia y Tecnologia* 15(2), 245-258. DOI: 10.4067/S0718-221X2013005000020

GB/T 18261 (2013). "Test method for anti-mildew agents in controlling wood mould and stain fungi," Chinese National Standardization Management Committee, Beijing, China.

Gu, L., Ding, T., Lu, B., and Zhu, K. (2010). "Study on biological durability of pressurized steam-treated wood," *China For. Prod. Ind.* 37(5), 6-9.

Huang, R. F., Lü, J.-X., Cao, Y.-J., Zhao, X., Zhao, Y. K., Z. Y.-D., and Wu Y.-Z. (2010). "Impact of heat treatment on chemical composition of Chinese white poplar wood," *J. Beijing For. Univ.* 32(3), 155-160.

Huang Y., Yuan X.-Z., Li, H., Huajun, H., and Z., G. (2013). "Study on hydrothermal carbonization of rice straw," *Chinese J. Environ. Eng.* 7(5), 1963-1968.

Inari, G. N., Petrissans, M., Lambert, J., Ehrhardt, J. J., and Gérardin, P. (2006). "XPS characterization of wood chemical composition after heat treatment," *Surf. Interface Anal.* 38(10), 1336-1342. DOI: 10.1002/sia.2455

Jain, S., Jain, A., Kachhawah, P., and Devra, V. (2015). "Synthesis and size control of copper nanoparticles and their catalytic application," *T. Nonferr. Metals Soc. China* 25(12), 3995-4000. DOI: 10.1016/S1003-6326(15)64048-1

Johansson, D., and Morén, T. (2006). "The potential of colour measurement for strength prediction of thermally treated wood," *Holz als Roh- und Werkstoff* 64(2), 104-110. DOI: 10.1007/s00107-005-0082-8

Kamdem, D. P., Zhang, J., and Freeman, M. H. (1998). "The effect of post-streaming on copper naphthenate-treated southern pine," *Wood Fiber Sci.* 30(2), 210-217.

Kartal, S. N., Green, F. III, and Clausen, C. A. (2009). "Do the unique properties of nanometals affect leachability or efficacy against fungi and termites?," *Int. Biodeter. Biodegr.* 63(4), 490-495. DOI: 10.1016/j.ibiod.2009.01.007

Khanna, P. K., Gaikwad, S., Adhyapak, P. V., Singh, N., and Marimuthu, R. (2007). "Synthesis and characterization of copper nanoparticles," *Mater. Lett.* 61(25), 4711-4714. DOI: 10.1016/j.matlet.2007.03.014

Kun, Z., Hua, C. K., Hui-Ming, L., Wang, C. R., and Ping, S. Y. (2010). "Mold inhibition of heat-treated lumber," *China Wood Ind.* 24(1), 42-44.

Liu, Q.-M., Zhou, D.-B., Yamamoto, Y.-Y., Kuruda, K., and Okido, M. (2012). "Effects of reaction parameters on preparation of Cu nanoparticles via aqueous solution reduction method with $NaBH_4$," *T. Nonferr. Metals Soc. China* 22(12), 2991-2996.

Mondal, K. K., and Mani, C. (2012). "Investigation of the antibacterial properties of nanocopper against *Xanthomonas axonopodis* pv. *punicae*, the incitant of pomegranate bacterial blight," *Ann. Microbiol.* 62(2), 889-893. DOI: 10.1007/s13213-011-0382-7

Nzokou, P., and Kamdem, D. P. (2010). "X-ray photoelectron spectroscopy study of red oak- (*Quercus rubra*), black cherry- (*Prunus serotina*) and red pine- (*Pinus resinosa*) extracted wood surfaces," *Surf. Interface Anal.* 37(8), 689-694. DOI: 10.1002/sia.2064

Priadi, T., and Hiziroglu, S. (2013). "Characterization of heat treated wood species," *Mater. Des.* 49, 575-582. DOI: 10.1016/j.matdes.2012.12.067

Raffi, M., Mehrwan, S., Bhatti, T. M., Akhter, J. I., Hameed, A., Yawar, W., and ul Hasan, M. M. (2010). "Investigations into the antibacterial behavior of copper nanoparticles against *Escherichia coli*," *Ann. Microbiol.* 60(1), 75-80.

Salem, M. Z. M., Zidan Y. E., Mansour M. M. A., El Hadidi N. M. N., and Elgat, W. A. A. A. (2016). "Antifungal activities of two essential oils used in the treatment of three commercial woods deteriorated by five common mold fungi," *Int. Biodeter. Biodegr.* 106, 88-96. DOI: 10.1016/j.ibiod.2015.10.010

Sastry, A. B. S., Aamanchi, R. B. K., Prasad C. S. R. L., and Murty, B. S. (2013). "Large-scale green synthesis of Cu nanoparticles," *Environ. Chem. Lett.* 11(2), 183-187. DOI: 10.1007/s10311-012-0395-x

Sedighi, A., Montazer, M., and Hemmatinejad, N. (2014). "Copper nanoparticles on bleached cotton fabric: *in situ* synthesis and characterization," *Cellulose* 21(3), 2119-2132. DOI: 10.1007/s10570-014-0215-5

Sivonen, H., Nuopponen, M., Maunu, S. L., Sundholm, F., and Vuorinen, T. (2003). "Carbon-thirteen cross-polarization magic angle spinning nuclear magnetic resonance and Fourier transform infrared studies of thermally modified wood exposed to brown and soft rot fungi," *Appl. Spectrosc.* 57(3), 266-273. DOI: 10.1366/000370203321558164

Theander, O., Bjurman, J., and Boutelje, J. B. (1993). "Increase in the content of low-molecular carbohydrates at lumber surfaces during drying and correlations with nitrogen content, yellowing and mould growth," *Wood Sci. Technol.* 27(5), 381-389. DOI: 10.1007/BF00192224

Unsal, O., Korkut, S., and Atik, C. (2003). "The effect of heat treatment on some properties and colour in eucalyptus (*Eucalyptus camaldulensis* Dehnh.) wood," *Maderas. Ciencia y Tecnologia* 5(2), 145-152. DOI: 10.4067/S0718-221X2003000200006

Usman, M. S., El Zowalaty, M. E., Shameli, K., Zainuddin, N., Salama, M., and Ibrahim, N. A. (2013). "Synthesis, characterization, and antimicrobial properties of copper nanoparticles," *Int. J. Nanomed.* 2013(1), 4467-4478.

Wu, C., Mosher, B. P., and Zeng, T.. (2006). "One-step green route to narrowly dispersed copper nanocrystals," *J. Nanopart. Res.* 8(6), 965-969. DOI: 10.1007/s11051-005-9065-2

Yan-Jun, X., Yi-Xing, L., and Yao-Xing, S. (2002). "Heat-treated wood and its development in Europe," *J. For. Res.* 13(3), 224-230. DOI: 10.1007/BF02871703

Xu, X. (2013). *Study on the Preparation and Antibacterial Property of Nano-copper and Curdlan Composite*, Master's Thesis, Wuhan University of Technology, Wuhan, China.

Yang, R., and Fan, J. (2014). "Synthesis of copper nanoparticles by thermal decomposition in polyethylene glycol system," *Mater. Rev.* B, 28(7), 88-94.

Yu, H., Sun, F., Wang, X., Chen, R. and Zhang, Y. (2015). "Copper and cuprous oxide nanomaterials prepared by solution-synthesis under low temperature," *Nat. Sci. J. Harbin Normal Univ.* 31(5), 73-75.

Yu, Y., Du, F.-P, Yu, J. C., Zhuang, Y.-Y., and Wong, P.-K. (2004). "One-dimensional shape-controlled preparation of porous Cu_2O nano-whiskers by using CTAB as a template," *J. Solid State Chem.* 177(12), 4640-4647. DOI: 10.1016/j.jssc.2004.10.025

Zhang, W. F., Yan, X. Q., Wang, Z. H., Sun, L., Zhao, Y. B., and Zhang, Z. J. (2013). "Synthesis and antimicrobial properties of flowerlike copper nanomaterials," *J. Func. Mater.* 44 (15), 2156-2161.

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