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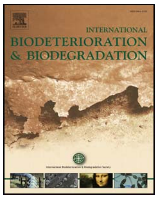

Resistance to fungal decay of paraffin wax emulsion/copper azole compound system treated wood

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ABSTRACT

Poplar (*Populus cathayana*) is susceptible to fungal infection with white-rot fungus (*Trametes versicolor* (L.) Murrill.). The effects of paraffin wax emulsion and Copper Azole (CA) preservative treatment were studied in regard to the fungal resistance. A full-cell process was used to treat the samples with varying paraffin wax emulsion concentrations (0.5%, 1.0%, and 2.0%), CA concentrations (0.3% and 0.5%), and their six compound systems. The highest observed mass loss of decay was 64% for untreated wood. Paraffin wax emulsions played an important role in resisting the white-rot fungi. The CA preservative effectively improved the decay resistance of the wood, which obtained a mass loss between 1.1% and 3.2%. The compound systems showed a higher mass loss, compared to the CA treated wood. This was caused by the high concentration of paraffin wax emulsion, which inhibited the impregnation of CA in the compound system. The paraffin wax concentration increased, resulting in a decreased mass loss of compound systems treated wood. The white-rot fungi decay caused the wood cells to separate and serious degradation of the lignin, the hemicellulose occurred, as well as a slight degradation of the cellulose.

1. Introduction

Wood is a poplar natural material with many applications. When wood is used outdoors, it is subjected to temperature and humidity. Non-natural durable wood is susceptible to infection by microorganisms, which results in observable color changes and structural damage at the cell wall level (Yang et al., 2017; Meyer-Veltrup et al., 2017). As a result, the physical and the mechanical properties of the decayed wood are reduced. The service life of wood is extended by treating wood with preservatives. Water-borne preservatives are poplar because they are inexpensive and maintain a good permeability (Cao et al., 2010). In the past 80 years, copper chromium arsenate (CCA) has been extensively used worldwide. However, due to its toxicity to the environment and to humans, CCA has been banned in half of Europe since the 1980s and 90s. As replacements, copper-based preservatives like ACQ (alkaline copper quaternary) and CA (copper azole) have been developed and utilized (Zhong et al., 2014). Copper plays an important role in wood preservatives (Gascon-Garrido et al., 2016), because it improves decay resistance effectively with minimal toxicity to animals and humans. However, wood treated with water-borne preservatives may suffer from poor dimensional stability, due to ineffective water resistance (Thybring, 2017). The efficacy of the wood treatments would be improved by increasing the water resistance of the preservative-modified wood (Meyer and Brischke, 2015). Paraffin wax is an inexpensive by-product of petroleum refining, which is primarily composed of normal alkanes with carbon numbers ranging from C18 to C50 (Wang et al., 2010). In its solid form, paraffin wax has widespread application in waterproofing wood and wood products, as it provides a good barrier coating and is non-toxic. Paraffin wax is directly mixed with the wood fibers through a hot-grinding process that results in fiberboard. When modifying wood, it would be more effective to utilize paraffin wax emulsion by impregnation (Lesar et al., 2010; Brischke and Melcher, 2015; Humar et al., 2016). Studies found that the wax could slow water vapor diffusion and improve the dimensional stability of wood (Lesar et al., 2010; Kaldum et al., 2016). The wax enhances the decay resistance, as well as the durability of the wood (Lesar and Humar, 2011; Humar et al., 2016).

Previous research has attempted to mix the waterproofing agents and wood preservatives. Hickson, an American company, added a waterproofing agent to CCA (Zhong et al., 2014). Chen et al. (2009) added paraffin wax emulsion into CCA, ACQ preservatives and investigated the water absorption, hygroscopicity of compound system treated

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wood. The study found that the compound systems improved water resistance of treated wood while the paraffin wax emulsion hindered the impregnation of the preservatives slightly. In our previous work, a compound system of paraffin wax emulsion and CA was developed, which exhibited high stability. The treated wood performed well in waterproofing, anti-mold, anti-blue stain, and metal corrosion resistance tests (Wang et al., 2014, 2015, 2016; Zhong et al., 2014). In addition, the interaction among the paraffin wax emulsion, CA and wood was investigated by the stress relaxation approach (Liao et al., 2016). The waterproofness of paraffin wax emulsion could enhance the decay resistance of wood, while it also had a weak adverse effect on impregnation of preservative. However, the decay resistance of wood treated with compound system is not clear. Therefore, this study aims to explore the white-rot fungus decay resistance performance of wood treated with the CA/paraffin wax emulsion compound system and clarify the impact of paraffin wax emulsion on decay resistance of compound system treated wood.

2. Materials and methods

2.1. Materials

Poplar (*Populus cathayana*) samples were purchased from Shanmu Company in Baoding, Hebei province, China. Five-year-old poplar samples had an air-dry density of 0.38 g/cm^3 and an average growth ring width of 0.6 cm. A non-durable sapwood without tension was used for testing. The samples were cut 20 mm (L) × 20 mm (R) × 10 mm (T) sections. The samples were free of knots and did not have visible evidence of infection by mold, stain, fungi. The CA wood preservative was purchased from the Guangzhou Xingyue Wood Preservative Limited Company in China. The CA had a mass fraction of two effective components of copper and triazole at 9.98% and 0.42%, as well as an assistant solvent of ammonium hydroxide at 12.48%. The paraffin wax emulsion was prepared in the laboratory together with the natural surfactants of the alkyl glycoside and combined until it reached solid content of 26%, as determined previously (Wang et al., 2014). *Trametes versicolor* (L.) Murrill. FP-101664 SS1 purchased from the Chinese Academy of Sciences was used for testing decay resistance. This is a common white-rot fungus in China and suitable for hardwood according to Chinese standard GB/T13942.1–1992 (Yu et al., 2008; Cao et al., 2010).

2.2. Wood treatment

Two concentrations of CA (0.3% and 0.5%) were used to obtain the corresponding minimal retention levels, in accordance with category UC3 and UC4A (American Wood Protection Association Standard, 2003). Three concentrations of paraffin wax emulsions were used (0.5%, 1.0%, and 2.0%). This resulted in six uniform and stable compound systems prepared by physically mixing CA, paraffin wax, and deionized water, according to previous literature protocol (Wang et al., 2014). This mixture was then used to impregnate the wood samples using a full-cell process. The samples were exposed to a vacuum condition at −0.01 MPa for 30 min, and then submerged into a treated liquid under a pressure of 0.5 MPa for 1 h. The pressure was released and the samples were collected for incubation for 30 min at atmosphere pressure, to ensure full saturation of the samples. The treated samples were placed in open air for one week. They were then dried in an oven at 103 ± 2 °C until a constant weight was reached. The sample grouping and the weight percent gain for each group were determined, see Table 1 for details.

2.3. Laboratory fungal test

The laboratory fungal test was performed in accordance with the Chinese standard GB/T13942.1–2009 (2009). A 300 ml cylindrical culture bottle, with a plastic screw lid, was used as the decay chamber. 150 g of sand was screened through an U.S. No.6 ~ No.8 sieve to remove impurities. 7.5 g of wood powder, 4.3 g of corn flour, and 0.5 g of brown sugar were uniformly mixed and added into the bottle. Two feeder strips (25 mm × 25 mm × 3 mm) of poplar were placed on top of the mixture. 50 ml of water containing 0.8% malt extract was added to the mixture. The culture bottles were sterilized in an autoclave at 121 °C for 60 min. After cooling to room temperature, a piece of white-rot fungus inoculum was cut equivalent to approximately 5 mm square from near the leading edge of mycelium in cultures and section of inoculum was placed in contact with an edge of the feeder strip on the mixture. The entire mixture was incubated at 25 °C, 60%–80% relative humidity (RH) for 2 weeks. When the hypha covered the feeder strip, the test blocks, after being sterilized for 30 min, were placed in the culture bottles. Each bottle contained two test blocks. The bottles were placed in the incubation room and incubated at 25 °C, 60%–80% RH for 12 weeks. The mass loss of the six replicates was calculated based on the oven-dried weight of the samples before and after the fungal test. Average values and the standard deviations were applied to analyze the data. There were four durability classes determined according to mass loss. A mass loss of 0–10% corresponded to very durable, 11–24% corresponded to durable, 25%–44% corresponded to slightly durable, and more than 45% corresponded to no durability.

2.4. Morphology analysis

The samples surfaces were sputter-coated with gold and characterized with a scanning electron microscope (SEM, Hitachi S-3400, Japan) in the low vacuum mode with a SE detector. The acceleration voltage was set to 5 kV, with a working distance of 10 mm.

2.5. FTIR spectral measurement

The chemical changes of the samples were monitored by a Fourier transform infrared FTIR spectrometer (Bruker, Vertex 70v, Germany). Potassium bromide (KBr) was used to collect the background. Air-dried powder was passed through a 100-mesh sieve. The sieved powder was then mixed with KBr, at a weight ratio of 1:100, before spectrum collection. The Omnic Macros Basic was used to analyze the data of the FTIR. All spectra were displayed at wavelengths ranging from 400 cm^{-1} to 4000 cm^{-1}.

2.6. XRD analysis

The wood samples were crushed to 60–80 mesh and characterized with XRD at an angle of scanning of 5°–40° (2θ). The scanning speed was 4°/min. The XRD results reflected the crystallinity index, which was dependent on the empirical formulas provided by Bragg (Howell et al., 2011).

3. Results

3.1. Mass loss

The mass loss and durability classes of the wood samples are listed in Table 1. The highest mass loss (64%) occurred when the UAD (Untreated after decay) sample was exposed to white-rot fungus for 12 weeks incubation, suggesting the *Trametes versicolor* was active. The Chinese standard states that a mass loss higher than 45% demonstrates the effectiveness of the fungal tests. The mass losses of the three paraffin wax emulsion-treated groups were reduced to 62%, 61% and 58%. This was caused by an increase in paraffin wax emulsion concentration from 0.5% to 2.0%. The mass losses of the two CA treatment groups with concentrations of 0.3%, and 0.5% were 3.2% and 1.1%. The mass losses of the compound systems were 14.7% and 14.2%, for the 0.3% and the 0.5% CA with the 0.5% paraffin wax emulsion. These values

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