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BRIEF ORIGINALS KURZORIGINALIA

The termiticidal properties of superhydrophobic wood surfaces treated with ZnO nanorods

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Abstract ZnO is a cost-effective and more environmentally friendly wood preservative than other metallic-based formulations. ZnO-stearate treatment imparts superhydrophobicity to wood surfaces, thereby providing triple protection to wood products, i.e., superhydrophobicity, inhibition to insects and microorganisms, and UV radiation protection. The objective of this study was to evaluate ZnO-stearate hydrophobic treatments of southern pine sapwood for resistance to Formosan subterranean termites. The data indicated that ZnO-stearate superhydrophobic treatment of southern pine wood samples received excellent mean visual ratings and mean weight loss values. The mean termite mortality was moderate. Unidentified fibril-like substances were found on the wood surfaces that were damaged by the termites.

Termitizide Eigenschaften superhydrophober Holzoberflächen, die mit ZnO-Nanopartikeln imprägniert wurden

Zusammenfassung ZnO ist ein kostengünstiges und umweltfreundlicheres Holzschutzmittel als viele andere Rezepturen auf Metallbasis. Eine Imprägnierung mit ZnO-Stearat verleiht der Holzoberfläche Superhydrophobizität mit Dreifachschutz, d.h. Superhydrophobizität, Wirkung gegen Insekten und Mikroorganismen sowie Schutz vor UV-Strahlung. Ziel dieser Studie war es, die Resistenz von mit ZnO-Stearat behandeltem Southern Pine Splintholz gegen die Formosan Bodentermiten zu untersuchen. Die Ergebnisse zeigten, dass der mittlere visuell festgestellte Zerstörungsgrad und der mittlere Masseverlust der mit ZnO-Stearat superhydrophobisch behandelten Southern Pine Splintholzproben sehr gering waren. Die mittlere Termitensterblichkeitsrate war mäßig. Auf den durch Termiten befallenen Holzoberflächen wurden unbekannte fibrillenartige Substanzen gefunden.

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1 Introduction

Novel and non-traditional methods to enhance wood durability of southern pine wood continues to be an important research topic. Proponents of these methods cite the lack of heavy metals in the treating process. Detractors of these methods indicate concern regarding reliable efficacy data. Clearly, there is an opportunity for a novel wood protection system. Nanometals have the potential to affect the wood preservation industry through the development of improved biocides with unique properties (Clausen et al. 2009).

The wood cell wall is comprised of celluloses, hemicelluloses, and lignin. All of these substances contain hydroxyl groups which link the three afore mentioned components of the wood cell wall to atmospheric moisture. Due to the inherent adsorptive nature of the hydroxyl groups, wood cell walls have the ability to remove water vapor from the atmospheric air until it is in equilibrium moisture with the air. Therefore, the chemical transformation of wood from hydrophilicity to hydrophobicity is always associated with the blockage, modification, or removal of the hydroxyl groups on cell walls, which serve to prevent adsorption of water from the environment (Wang et al. 2011).

The growth of fungi depends on suitable temperatures, moisture, and air (Clausen 2010). Serious decay occurs when the moisture content of the wood is over fiber saturation point. Therefore, the key to wood protection is to keep the wood dry. On a superhydrophobic wood surface, water droplets bead up and freely roll off the surface without leaving any trace of the beads, thereby keeping wood from contacting water. The moisture content of such a wood substrate is maintained below 20 percent, a safe threshold for the prevention of the growth of fungi that cause decay, even in a rainy climate.

Some of the previous areas of research that have been conducted on the chemical modification of wood for hydrophobicity, including acetylation (Lafuma and Quere 2003) metal oxides (Feng et al. 2002) the sol-gel process (Gao and Jiang 2004; Wu et al. 2005; Sun et al. 2005) and micro-emulsion techniques (Lee et al. 2004). These methods can be used to reduce or delay water and moisture sorption of the wood but cannot stop water from absorption into wood by direct contact. Most recently, more hydrophobic surfaces have been developed on fiber surfaces using polymer grafting, layer-by-layer (LbL) deposition, and plasma treatment (Li et al. 2007, 2008; Barthlott and Neinhuis 1997; Hou et al. 2007). However, only a few superhydrophobic surfaces have been developed on solid wood substrates (Neinhuis and Barthlott 1997; Nakajima et al. 2001; Artus et al. 2006).

ZnO is a cost-effective (Evans 2003), environmentally friendly preservative when compared with other metallic-based formulations. ZnO-stearate treated, superhydrophobic treatment provides triple protection to wood products, i.e., superhydrophobicity, decay resistance and insect repellency, and resistance to UV degradation. In a previous study, superhydrophobic films were developed by the growth of ZnO nanorods on wood substrates and subsequent self-assembling monolayers of stearic acid molecules (Wang et al. 2011). The objective of this study was to evaluate hydrophobic treatments of southern pine sapwood for resistance to Formosan subterranean termites (*Coptotermes formosanus*).

2 Materials and methods

The following chemical agents were obtained from Fisher Scientific or Sigma Aldrich companies: zinc nitrate hexahydrate ($Zn[NO_3]_2 \cdot 6H_2O$), ammonium chloride (NH_4Cl), urea ($[NH_2]_2CO$), ammonia hydroxide (NH_4OH), sodium hydroxide (NaOH), and stearic acid ($C_{17}H_{35}COOH$). All chemicals were reagent grade and were used as received.

Twenty southern pine (*Pinus* spp.) sapwood samples were used for the study. Ten samples (hereinafter referred to as Group A) were prepared so that a tangential surface of each sample contained completely early wood and the opposite tangential surface of the sample contained completely late wood. The remaining ten samples (hereinafter referred to as Group B) were prepared in the same way. Each sample in Groups A and B was 10 mm wide by 5 mm thick by 60 mm long. Prior to treatments, all of the samples were dried at 80 °C for 24 h. After drying, each sample was weighed.

All of the 10 samples in Group A were treated with zinc oxide. The synthesis reactions followed a procedure modified from that used by previous researchers (Tsuchida and Kitajima 1990; Ledwith et al. 2004; Wu et al. 2005; Wang et al. 2011). An aqueous solution was prepared in a polytetrafluoroethylene beaker containing 0.01 M $Zn(NO_3)_2$, 0.02 M NH_4Cl, 0.01 M urea, 0.025 M NaOH, and ammonia hydroxide. Group A samples were carefully suspended in the solution, which was then heated to 90 °C in 25 min. The system was stirred at the same temperature from 16 to 24 h. The pH of the solution was maintained at 10 ± 0.5. After the synthesis, the wood samples were washed with deionized water to remove the unreacted chemicals from the surfaces. The samples were then blown dry with nitrogen for 2 min. and were subsequently dried in an oven at 80 °C for 24 h. After drying, each sample was weighed the second time.

The self-assembling monolayer (SAM) coating reaction was followed in a polytetrafluoroethylene beaker. The treated samples were suspended in an *n*-hexane solution of stearic acid at room temperature for 48 h. After the SAMs reaction, the prepared films of each sample were then thoroughly washed with acetone, blown dry with nitrogen at room temperature, and then dried in an oven at 80 °C for 24 h. After drying, each sample was weighed the third time.

ZnO and stearic acid retentions for each of the five treated samples were estimated based on the initial and final weights of each of the ZnO and SAM treatments.

Prior to the termite test, the treated samples were reconditioned in a conditioning chamber for two weeks. Each was weighed after conditioning. The wettability of each sample was evaluated by the measurement of water contact angle at the sample surfaces using a goniometer (Hitachi, CA-A). The water contact angles of each sample were evaluated on the early wood and late wood surfaces.

Five of the treated Group A samples and five of the untreated Group B samples were randomly selected for the termite tests. The remaining samples in treated Group A (5) and untreated Group B (5) were oven-dried and were used to determine the moisture content of the treated samples in the two groups.

Formosan subterranean termites (*Coptotermes formosanus*) were collected in New Orleans, Louisiana. Prior to test, the termites were stored in an incubator for a week. The termite weight average was 0.00334 g. Termite tests were performed in accordance with American Wood Protection Association (AWPA) standard E1-09 (AWPA 2009). The single choice method was used. The tests were conducted in ten testing jars. Five jars were used for the test of treated wood (Group A), and five jars were used for the test of the untreated controls (Group B). Each testing jar contained 150 g of autoclaved sand and 30 ml of distilled water. A treated or control sample was placed in each jar on top of the sand on an aluminum foil barrier to prevent any chemical leaching. Four hundred termites were added to the opposite side of each jar from the test sample. The jar tops were then replaced loosely. Immediately following the 28-day test, the samples were placed in the conditioning chamber for two weeks to determine mass. Each sample was evaluated visually and rated using the AWPA E1-09 scale of 10 to 0, beginning with 10 (no attack) and 0 (failure). The number of dead termites in each jar was also determined and is reported as the mortality (%) based on the initial number of live termites.

The damaged wood surfaces and the crystal structure and morphology of the prepared ZnO film on the surface of the wood substrates were characterized using a scanning electron microscope (SEM, Hitachi TM-1000) before and after the termite tests.

The data obtained were analyzed for resistance with means and standard deviations determined by Statistical Package for the Social Sciences (SPSS 2006). The Least Significant Difference (LSD) mean separation test procedure was used (Steel and Torrie 1980).

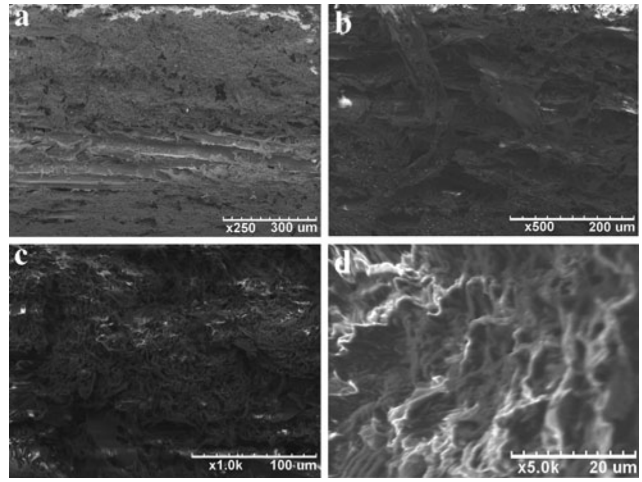

Fig. 1 Scanning electron microscope images of untreated southern pine samples that were damaged by subterranean termites

Abb. 1 REM-Aufnahmen von unbehandelten, durch Bodentermiten geschädigte Southern Pine Proben

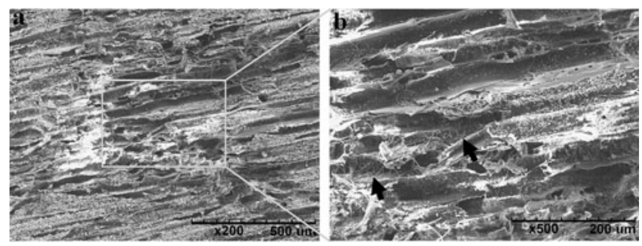

Fig. 2 Scanning electron microscope images of ZnO-stearate superhydrophobically treated southern pine samples that were damaged by subterranean termites

Abb. 2 REM-Aufnahmen von mit ZnO-Stearat superhydrophobisch behandelten und durch Bodentermiten geschädigte Southern Pine Proben

3 Results and discussion

Figure 1 shows SEM images of an untreated southern pine control sample exposed to Formosan termites. In the center of Fig. 1a, about five cell lumens were less damaged by the termites. Thus, the walls and lumens of the cells can be identified from the image. The remaining surfaces were cluttered with fragmented, fibril-like cell wall pieces and debris. Figure 1b displays some larger cell wall pieces lying across the cell lumens. They were removed by the termites from the samples. More debris was found in the corner areas of Fig. 1b. Unknown small particles that are white in color were also found at the left down corner of the picture.

Figures 1c and 1d are higher magnification micrographs to illustrate the damage on wood surfaces following termite attack. As can be seen from the two figures, the fiber-like pieces are from 100 to 400 µm in length and about 1µm (1000 nm) in diameter. For a typical cell of southern pine juvenile wood, the cell wall thickness is 4.5 µm for early wood and 9.5 µm for late wood (Larson et al. 2001). Therefore, it is reasonable to believe that these substances were microfibrils from the cell walls removed by the termites along the fibril orientation of the S2 layer. If this is the case, then it is not clear why the cell wall components were piled up, discarded, and left unconsumed by the termites. It also demonstrates the capability of termites to deconstruct cell walls of wood fibers into microfibrils. Further research is therefore warranted to understand the destructive process of wooden materials by termites for the purposes of termite control or deconstruction of wood materials.

Figure 2 shows SEM images of a ZnO-stearate treated southern pine sample exposed to Formosan termites. The area in the center of Fig. 2a was believed to be attacked by the termites. In this area, the ZnO nanocrystal layer on cell wall surfaces was removed, exposing the untreated cell walls. In addition, as being pointed by the arrows in Fig. 2b, fiber-like pieces were found that were similar in diameter and length to the ones found on the surfaces of termite-damaged, untreated southern pine wood (Fig. 1d). Compared to the untreated wood, termite attacks to the ZnO-

Table 1 Formosan subterranean termite efficacy data of the experimental and control treatment groups
Tab. 1 Mittlere Sterblichkeitsrate, mittlerer Masseverlust und mittlerer visuell festgestellter Zerstörungsgrad der Versuchs- und Kontrollgruppen

Treatment group	Mean mortality (%)	Mean mass loss (%)	Mean visual rating
Untreated	6.5 A[a]	41.4 A	0.0 A
ZnO-stearate treated	29.6 B	1.0 B	9.4 B

[a]Mean values with similar letters were not statistically different at alpha = 0.05 using the LSD mean separation test. Note: comparisons were made vertically within a column.

stearate treated wood were substantially restrained because of the protection of ZnO nanorods on the surfaces.

ZnO retention of the 10 samples was from 1.6% to 8.6%. The ZnO retention average of the 10 samples was 3.9%. It was observed that ZnO nanocrystals grew only on the surfaces of the treated samples. Few ZnO nanorods were found below the surfaces. Therefore, ZnO retention can also be calculated as retention per unit area of the sample surface. Of the 10 treated samples, the area retention was from 13.7 to 59.9 g/m^2. The area retention average was 31.9 g/m^2. It is noted, however, that the weight or area retention was calculated based on samples' weights before and after the treatment. During the growth of ZnO nanorods in solutions for an extended period of time, water-soluble extractives may be dissolved in hot water (90 °C) and removed from the sample. According to a study by Choong et al. (1998), hot-water extractives in southern pine sapwood were about 1%. In this study, the weight losses caused by the removal of extractives in the solution may have been compensated by the gain of ZnO nanocrystals in the wood. Therefore, the ZnO weight and area retention averages were about 4.9% and 40.1 g/m^2, respectively, when hot-water extractives were taken into account.

The retention of steric acid in the wood was minimal. The measured weight of most samples after the stearate treatment was less than the measured weight of the samples before the treatment. More extractives may be dissolved in the hexane solution during the stearate treatment and removed from the wood samples. It is reported that the yield of extractable material from ponderosa pine stumps by hexane is up to 27%, most of which are rosin, pine oil, and turpentine (Joye et al. 1969). However, stearic acid molecules covered the ZnO nano rod surface by molecular layers through SAM reactions (Wu et al. 2005; Wang et al. 2011). Therefore, the retention of stearic acid should be less than 1%.

The mean mortality, mass loss, and visual rating of the experimental samples from this experiment are summarized in Table 1. The weight losses of the five untreated southern pine samples ranged from 31.0% to 46.0%, while the mortality of the five untreated southern pine samples ranged from 8.5% to 11.8%. The weight loss and mortality data from the untreated southern pine wood group indicates the termites had high vigor. The weight losses of the five ZnO-stearate treated southern pine samples were from 0.7% to 2.2%, while the mortality of the five ZnO-stearate treated southern pine samples were from 19.5% to 38.3%. The mean weight losses of the untreated and ZnO-stearate treated southern pine samples were 39% and 1.4%, respectively; the mean mortality of the untreated and ZnO-stearate treated southern pine samples were 10.4% and 29.9%, respectively. The mean weight loss of the untreated southern pine samples was significantly higher than the mean weight loss of the ZnO-stearate treated southern pine samples ($p < 0.0001$), and the mean mortality of the untreated southern pine samples was significantly lower when compared to the mean mortality of the ZnO-stearate treated southern pine samples ($p = 0.00032$). This result is consistent with previous findings by Kartal et al. (2009) and Clausen et al. (2009). Both studies found that nanozinc inhibited termite feeding and caused moderate termite mortality among other positive attributes. In a related study, Green and Arango (2007) reported that 0.5% nanozinc with and without silver inhibited termite feeding and caused 70–76% mortality.

After termite attacks, two of five ZnO-stearate treated samples were sound and were rated 10 out of a possible 10. The remaining samples were slightly attacked by the termites and rated 9. The mean rating of the ZnO-stearate treated samples was 9.4. The untreated samples were severely damaged by termites. All of the untreated control samples were rated zero.

Figure 3 displays the weight losses and mortality in relation to the water contact angles (hydrophobicity) of ZnO-stearate treated southern pine samples. Of the five treated samples, the contact angles of an early wood surface of one sample and both early wood and late wood surfaces of another sample were over or equal to 150°, which indicates that these surfaces were superhydrophobic. Of the five treated samples, the contact angle averages of the early wood and late-wood were 127° and 139°, respectively. As being shown in Fig. 3, sample weight losses increased with an increase of water contact angles. Since weight losses of the treated samples were very small, the relationship between weight losses and water contact angles needs further verification. However, the termite mortality was found not to relate with the water contact angles of the sample surfaces (Fig. 3).

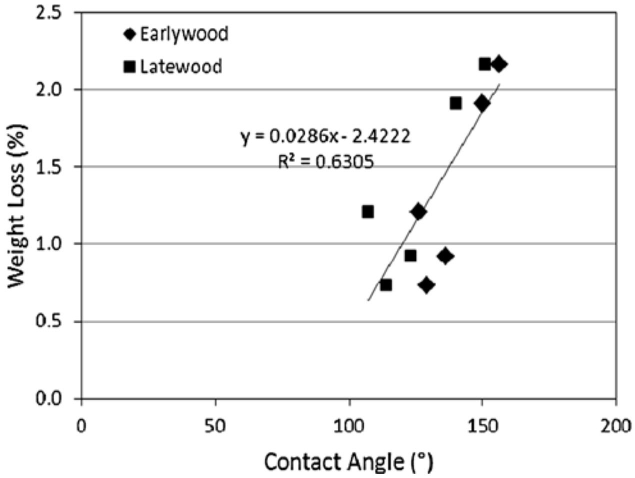

Fig. 3 Weight loss in relation to water contact angles of southern pine samples treated with ZnO-stearate superhydrophobic treatments
Abb. 3 Zusammenhang zwischen Masseverlust und Kontaktwinkel von Wasser der Southern Pine Proben, die mit ZnO-Stearat superhydrophobisch imprägniert wurden

4 Conclusion

ZnO-stearate treated, superhydrophobic southern pine samples were subjected to Formosan termite attack. Compared to no treatment, ZnO-stearate superhydrophobic treatment restrained the termite damages. The ZnO-stearate treated wood led to a moderate mortality. The mean weight losses and mortality of the ZnO-stearate treated southern pine samples were 1.4% and 29.9%, respectively, while the mean weight losses and mortality of the untreated southern pine samples were 39.0% and 10.4%, respectively. The mean rating of the ZnO-stearate treated samples was 9.4, whereas the mean rating of the untreated samples was zero (failure). Water contact angles of the ZnO-stearate treated sample surfaces were found not to relate with termite mortality. Unidentified, fibril-like pieces and debris were observed on the surfaces of the untreated and ZnO-stearate treated samples following termite attack.

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