INNOVATIONS IN WOOD PROTECTION IN THE AGE OF NANOTECHNOLOGY

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ABSTRACT

Advances in wood protection based on nanotechnology are being developed to improve resistance of wood products to biodeterioration, reduce environmental impacts from chemical leaching and resist UV degradation of in-service wood. A number of different approaches have been explored. First, the nanometals zinc oxide and copper oxide were evaluated as preservative treatments for wood. Both nanoZnO and nanoCuO were leach resistant. NanoZnO also inhibited decay fungi, acted as a termite toxicant, and provided photostability of wood against UV degradation. Second, self-assembling nanopolymer matrices were permeated with an organic biocide. The porous surface of the nanopolymer encapsulated and retained the biocide until a change in the physical environment, such as elevated temperature, triggered its release. Third, a nanocarrier system utilized inert nanotubules loaded with organic biocides for targeted delivery and slow, controlled release of biocide. Fourth, nanoentrapment assessed the ability of cellulose nanocrystals (CNC) to chemically bind and entrap soluble biocides within the wood structure without modifying the wood matrix. Merits of each approach will be discussed. The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service. This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain and not subject to copyright.

INTRODUCTION

Opportunities exist for utilizing nanomaterials to enhance the moisture tolerance and decay resistance of wood products and building materials due to their novel physical and physiochemical properties that differ significantly from larger particles of the same material (Clausen 2007; Clausen *et al*. 2011). Beyond the use of nanometals to inhibit biodeterioration, of particular interest are nanotechnologies that improve leach resistance in order to expand applications for soluble biocides. Soluble biocides might be embedded within nanopolymer matrices or encapsulated to offer slow-release and controlled delivery of biocides. Applications could range from new coatings to improved durability of engineered composite products that are particularly vulnerable to moisture.

Nanoparticles of metals that are already utilized by the wood preservation industry, i.e. copper or zinc, may play an important role in the next generation of wood protectants when they are either used alone or in combination with existing biocides. Nanometals are fabricated by altering particulate size either in the liquid phase (e.g. metal oxide sols, colloidal metals), gas phase (e.g. flame synthesis, plasma-based vapor phase synthesis) or solid phase (e.g. high energy ball milling) (Clausen 2007). Nanometal particles have high dispersion stability and low viscosity, allowing for more uniform particulate distribution over a surface (Clausen *et al*. 2009; Kartal *et al*. 2009). Dispersion stability coupled with a high surface area and controlled uniformity of pyrolyzed particles has the potential to improve durability of solid and composite wood products through a number of critical treatment criteria. Treatment criteria that could be improved include preservative penetration in commercial lumber species, treatability of refractory wood species that are of low commercial value, organic treatments for engineered composites, stability of finishes and coatings for above ground applications, non-leachable or hydrophobic treatments for both solid and composite materials, photostability of treated wood, and leach resistance of aqueous treatments.

When exposed to moisture, metals oxidize, resulting in the release of metal ions. The ionic form of the metal is often the form that is responsible for microbial inhibition (Clausen 2007, 2010; Dorau *et al*. 2004). Smaller particles have a higher surface area and result in a greater area available for oxidation. Particles with diameter less than 100 nm are required in order to have the necessary surface area to allow a continuous release of metal ions. The size of the metal particle has also been shown to affect microbial inhibition; the smaller the particle, the greater the antimicrobial activity (Nair *et al*. 2009; Reddy *et al*. 2007).

Nanopolymer matrices offer a sophisticated method for biocide encapsulation and controlled delivery. Self-assembling matrices, called hyperbranched fluoropolymer−poly(ethylene glycol) cross-linked networks (HBFP−PEG) were first created by melding two normally incompatible polymers and crosslinking the mixture (Bartels *et al*. 2007). The complex subsurface of the resulting hyperbranched nanopolymer has unusual tensile strength and provides nanoscale channels for the uptake and release of chemical molecules such as biocides. The size of the channels which has been likened to the holes in a sponge can be customized by the fabrication process to accommodate the chemical molecule of choice. The nanopolymer has been demonstrated to encapsulate and hold a chemical until a change in the physical environment (e.g. humidity, temperature, or pH) triggers its release. This technology has been successfully demonstrated for applications such as anti-fouling agents (Gudipati *et al*. 2005).

Several types of nanocarrier systems are recognized that may have application in the field of wood protection, particularly for increased durability of engineered composites (i.e. oriented strandboard). One example, a patented nanocarrier system utilizes 100 nanometer plastic beads embedded with biocide (Laks and Heiden 2004). Biocide-embedded nanoparticles can be designed for slow, controlled release of the biocide depending on the type of polymer comprising the bead, pore size in the bead, biocide viscosity and solubility. Other cylindrical, tubule-shaped materials (i.e. nanotubules) made from ceramics, clay, metal or lipids have been used as carriers in various medical and industrial applications. They are now being evaluated for use as a nanocarrier of biocides to improve protection of engineered composites from biodeterioration. Some properties of nanocarriers that would benefit the field of wood protection include precise delivery and placement of biocides, slow release of a biocide, or **r**elease of the biocide upon exposure to certain environmental conditions, such as moisture or high humidity.

When developing controlled release nanotubules for biocide delivery in composites, a considerable number of variables must be optimized prior to proof of concept. How can you precisely control the release of a biocide? Are the nanotubules compatible with the resin used to fabricate the composite? Will the resin itself be a barrier to release of the biocide? To answer these questions, methodology was developed for analyzing the thermal stability of nanotubules loaded with a commercial biocide over a range of temperatures (170°C–190°C) and time. The release rate of the biocide from nanotubules was based on the rate of biocide leaching. Residual efficacy was evaluated by microbial assays that measured fungal resistance following leaching.

Nanoentrapment by creating a simple physical barrier to limit leaching of soluble biocides from wood may be possible with cellulose nanocrystals (CNC). CNC are created by breaking down wood through acid hydrolysis. High-yield CNC production has been achieved on a scalable level by Wang and others (2012). The resulting CNC are uniformly dispersible and the sulfate ester groups created during acid hydrolysis are suitable for ionic binding with cationic compounds. Dispersion stability of CNC coupled with the controlled uniformity results in a nanomaterial that can penetrate wood in an aqueous dispersion. The question was posed "If wood were vacuum-treated with CNC followed immediately by vacuum-treatment with an otherwise soluble cationic biocide, would ionic binding occur within the wood and prevent leaching of the biocide?" Preliminary results from tests in progress suggest it is possible. Complete results will be published separately at a later date.

MATERIALS AND METHODS

Nanometals: Detailed methods describing vacuum treatment of wood with nanometals and evaluation methods for resistance to fungi, termites, leaching and UV were published in Clausen *et al*. (2009, 2010a, 2011) and Kartal *et al*. (2009).

Nanopolymer matrices: Detailed materials and methods for matrix fabrication were published by Bartels *et al*. (2007). Clausen (2012) described the analytical method used to determine biocide release.

Nanocarrier systems: Clausen (2012) detailed methods for evaluating wood and paper products treated with biocide-loaded nanotubules for resistance to mould fungi and biocide leaching.

RESULTS AND DISCUSSION

Nanometals: Initial studies showed that nanoparticles of copper oxide and zinc oxide were resistant to leaching compared to metal oxide controls (Kartal *et al.* 2009). Nanocopper inhibited *Gloeophyllum trabeum* and *Trametes versicolor*, but not the copper tolerant brown-rot fungus *Fibroporia radiculosa*. Different size particles of nanozinc oxide (nano ZnO) were further evaluated for their ability to alter physical and biological deterioration of southern pine (Clausen *et al*. 2011). When southern pine sapwood was vacuum impregnated with 30 nm particles of zinc oxide, virtually no leaching occurred in a laboratory leach test, even at the highest retention of 13 kg/m^3. Unleached nanoZnO-treated samples were protected from

UV damage after 12 months of outdoor exposure; photostability was visibly obvious on both exposed and unexposed surfaces compared to untreated controls (Clausen *et al*. 2010a). Graying was markedly diminished, although checking occurred in all specimens. Nano-ZnO treatment at a concentration of 2.5% or greater also provided substantial resistance to water absorption following 12 months of outdoor exposure compared to untreated and unweathered southern pine. In laboratory tests against termites and decay fungi, unleached southern pine treated with 30 nm zinc oxide particles caused moderate termite mortality in a no-choice bioassay, but gave mixed results for inhibition of decay fungi (Kartal *et al*. 2009; Clausen *et al*. 2009). A subsequent study examined the effect of particle size on southern pine treated with dispersions of 30 nm or 70 nm ZnO. Specimens were evaluated for leach resistance and termite mortality in laboratory tests (Clausen *et al*. 2011). Results showed that there was no difference between leach resistance (<4%) or termite mortality. Eastern subterranean termites consumed less than ten percent of the leached nano-ZnO-treated wood which resulted in 93 – 100 percent termite mortality in southern pine treated with either 30 nm or 70 nm ZnO particles.

Nanopolymer matrices: A sample of cross-linked HBFP-PEG45 nanopolymer was loaded with an experimental multi-component biocide formulation developed by Clausen and others (Clausen *et al*. 2010) that was augmented with carvone as an indicator molecule. The loaded polymer matrix was evaluated for controlled release of the biocide over a range of temperatures from 25°C to 75°C. Gravimetric changes in the loaded nano-polymer following an 8 hr exposure to 25°C, 40°C, or 75°C were tracked following isothermal release by extracting the nanopolymer matrices in methylene chloride. Extracts were quantitatively analyzed with GC-MS for residual carvone (Clausen 2012). Results showed that as temperature increased, more of the carvone was released from the matrix with isothermal weight loss reaching 100% after exposure to 75°C.

Nanocarrier systems: Biocide-loaded nano-tubules were incorporated into oriented strandboard (OSB), medium density fiberboard (MDF) and paper (Clausen 2012). Samples of nanotubule-treated OSB were tested for MOR, MOE, density, moisture swelling and antifungal resistance in laboratory tests. Preliminary studies on engineered composites demonstrated thermal protection, slow release and enhanced mould inhibition for the biocide loaded into nano-tubules compared to controls which incorporated either biocide alone or nano-tubules alone. Biocide-loaded nano-tubules were incorporated into paper and exposed to spores from three mould fungi, *Aspergillus niger, Penicillium chrysogenum* and *Trichoderma atraviride*. Controls consisted of untreated paper and paper treated with the biocide alone; untreated samples showed copious growth of test fungi and samples treated with biocide alone showed little or no inhibition of mould growth on the samples. Not only were the mould fungi completely inhibited on the surface of samples treated with loaded nano-tubules, but a clearing zone surrounding the samples demonstrated release of biocide from the nanotubules. Similar results were seen for OSB and MDF that were treated with biocide-loaded nanotubules compared with untreated controls. Treated and untreated specimens were placed on Petri dishes of malt extract agar, sprayed with a suspension of *Aspergillus niger* mould spores and incubated for 4 wk according to the ASTM D4445-10 standard laboratory test for controlling sapstain and mould fungi on unseasoned lumber (ASTM 2010). Mould growth occurred on the agar surface and on the surface of untreated test specimens, but mould growth was completely inhibited on specimens treated with biocide-loaded nanotubules. Release of biocide from the nanotubules was also evident from the clearing zone surrounding test specimens on agar plates. **Nanoentrapment**: Initial results suggest that cellulose nanocrystals bind cationic biocides. Through a dual treatment process, the resulting CNC/biocide hybrid can entrap otherwise soluble biocides within the wood structure. Details on the methods and results of the CNC/biocide hybrid treatment process will be published separately.

CONCLUSIONS

The unique properties of nanomaterials enable endless innovative improvements in the field of wood protection for surface treatments, pressure treatments, or as direct additives to furnish (i.e. wood flakes or particles) for engineered wood composites. Select nanometals such as ZnO have desirable preservative properties, namely leach resistance, photostability, and termite toxicity, and could be used alone or in combination with other biocides to formulate new preservatives. Biocides encapsulated in customized nanopolymer networks could provide prolonged protection as surface treatments for solid and composite wood products. Production of nanotubules loaded with biocide has been scaled up for commercial treatment of building products that are susceptible to mould growth.

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