

Enhancing Durability of Wood-Based Composites with Nanotechnology

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Abstract

Wood protection systems are needed for engineered composite products that are susceptible to moisture and bio-deterioration. Protection systems using nano-materials are being developed to enhance the durability of wood-based composites through improved resistance to biodeterioration, reduced environmental impact from chemical leaching, and improved resistance to ultraviolet (UV) degradation. Three approaches will be presented: (1) direct application of nano-metals to wood-based products, (2) slow release of biocides embedded in nano-polymer matrices, and (3) controlled delivery of biocides with a nano-carrier. In the first approach, wood was vacuum impregnated with nano-sized particles of metals commonly used in wood preservative formulations (e.g., zinc and copper). Nano-zinc oxide particles were shown to be leach resistant, protected against UV degradation, and acted as a termite toxicant when compared to soluble zinc, a key component of the wood preservative ammoniacal copper zinc arsenate and zinc borate. In the second approach, self-assembling hyperbranched nano-polymers were loaded with an organic biocide. The complex surface of the nano-polymer encapsulated the biocide until a change in the physical environment (i.e., elevated heat or moisture) triggered its release. Nano-polymer encapsulation could provide long-term protection of composites as a surface treatment. In the third approach, nano-tubules made from an inert material served as a carrier for organic biocides. Loaded nano-tubules released the biocide in a slow, controlled fashion and provided superior protection of heat-labile organic biocides during the fabrication process compared to treatment with the biocide alone. Loaded nano-tubules may be used for surface application, pressure impregnation, or as an additive to engineered products.

Introduction

Nano-materials often exhibit novel physical and physio-chemical properties that differ significantly from larger particles of the same material (Clausen 2007, Clausen and others 2011). Recent research looks at ways these properties can be exploited in the development of new preservative systems. Opportunities exist for using advances in nanotechnology to enhance the moisture tolerance of composites in traditional markets such as building materials. Embedding biocides in nano-polymer matrices or controlling delivery of biocides with nano-carriers is being evaluated to improve the durability of engineered composite products. The status

of research on nano-metals, nano-polymer matrices, and nano-carriers is presented and discussed.

Results and Discussion

Nano-Metals

Either used alone or in combination with existing biocides, nano-metals may play an important role in the next generation of wood protection products. Nano-metals are created 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). Nano-metal preparations of silver, zinc, copper, and other metals have high dispersion stability and low viscosity, allowing for more uniform particulate distribution over a surface (Clausen 2010, Kartal and others 2009).

Dispersion stability coupled with the controlled uniformity of pyrolyzed particles may greatly improve durability of solid and composite wood products in a number of applications: (1) preservative penetration in commercial lumber species, (2) treatability of refractory wood species that are of low commercial value, (3) organic treatments for engineered composites, (4) stability of finishes and coatings for aboveground applications, (5) nonleachable or hydrophobic treatments for both solid and composite materials, (6) photostability of treated wood, and (7) leach resistance of aqueous treatments.

In the presence of moisture, metals oxidize, which results in the release of metal ions. The ionic form of the metal is often the form that is responsible for microbial inhibition (Clausen 2010, Dorau and others 2004). Smaller particles having a higher surface area 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 and others 2009, Reddy and others 2007). Properties of nano-zinc oxide (nano-ZnO) particles were evaluated for their ability to alter physical and biological deterioration of southern pine.

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/m³ (Clausen and others 2010a). Unleached

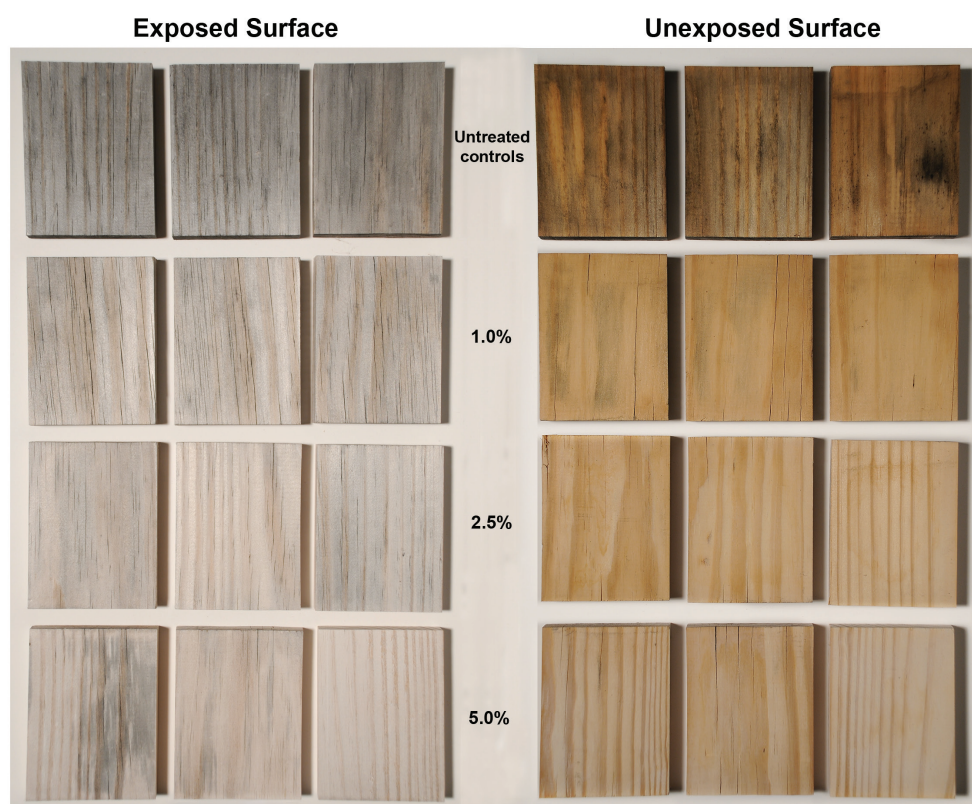


Figure 1. Weathering of nano-ZnO treated southern pine after 12 months of outdoor exposure. Unexposed surface (specimens on right) refers to the underside of the individual “exposed surface” specimens shown on the left.

samples were protected from UV damage after 12 months of outdoor exposure; photostability was visibly obvious on both exposed and unexposed surfaces compared with untreated controls (Fig. 1) (Clausen and others 2010b). Gray- ing 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 with untreated and unweathered southern pine. In laboratory tests against termites and decay fungi, zinc oxide (30 nm) caused moderate termite mortality in a no-choice bioassay but gave mixed results for inhibition of decay fungi (Kartal and others 2009, Clausen and others 2010b). A subsequent study on the effect of particle size compared 30-nm and 70-nm particles. Specimens were evaluated for leach resistance and termite mortality in laboratory tests (Clausen and others 2011). Results showed that there was no difference in leach resistance (<4%) or termite mortality (Fig. 2). Eastern subterranean termites consumed less than 10% of the leached nano-ZnO-treated wood, with 93% to 100% mortality in southern pine treated with both 30-nm and 70-nm ZnO particles.

Because engineered composites have a lower moisture tolerance than does solid wood, the unique properties of nano-ZnO (i.e., leach resistance, resistance to water absorption, photostability, and termite resistance) are characteristics that

could greatly improve the durability of engineered composites.

Nano-Polymer Matrices

Nano-polymer matrices offer a sophisticated method for biocide encapsulation and controlled delivery. Self-assembling nano-polymers, called hyperbranched fluoropolymer-poly(ethylene glycol) (HBFP-PEG) cross-linked networks, were first created by melding two normally incompatible polymers and crosslinking the mixture (Fig. 3) (Bartels and others 2007). The complex subsurface of the resulting hyperbranched nano-polymer has unusual tensile strength and provides nanoscale channels for the uptake and release of “guest” molecules such as biocides. The size of the channels, which have been likened to the holes in a sponge, can be customized to accommodate the guest molecule of choice. The nano-polymer is able 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 ranging from anti-fouling agents (Gudipati and others 2004) to fragrances.

The cross-linked HBFP-PEG45 nano-polymer was loaded with an experimental multi-component biocide formulation containing carvone as an indicator molecule.

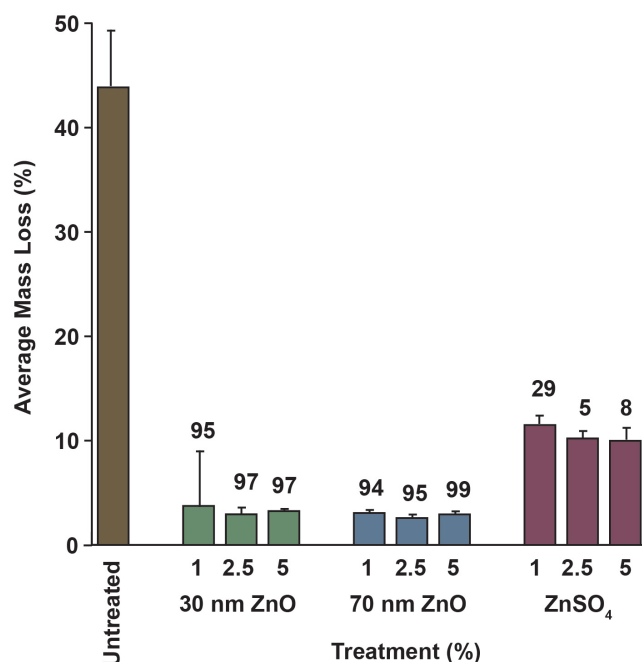


Figure 2. Eastern subterranean termite resistance to southern pine treated with nano-zinc oxide and soluble zinc sulphate indicated by mass loss, i.e., wood consumption. The number above each column represents the average percent termite mortality for that treatment group.

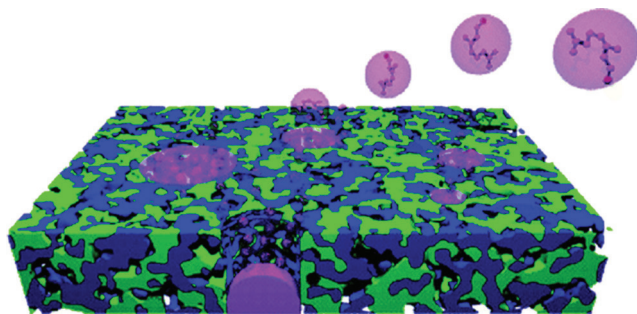


Figure 3. Self-assembling nano-polymer networks act like the holes in a sponge to hold biocides (depicted in purple) until changes in the environment trigger their release (Brown and others 2005, Bartels and others 2007).

The loaded polymer matrix was evaluated for controlled release of the biocide over a range of temperatures from 25 to 75 °C. Gravimetric changes in the loaded nano-polymer following an 8-h exposure to 25, 40, or 75 °C are shown in Table 1. Following isothermal release, the nano-polymer matrices were extracted in methylene chloride and quantitatively analyzed with GC-MS for residual carvone (Table 1).

Results showed that as temperature increased, more of the volatile indicator molecule was released from the matrix with isothermal weight loss reaching 100% after exposure to 75 °C. Quantitative results from the GC-MS analysis suggested that isothermal weight loss alone could not reliably

Table 1—Carvone analysis of loaded HBFP–PEG45 following isothermal release at varying temperatures

Temperature (°C)	Carvone loaded (µg)	Isothermal weight loss (%)	Carvone extracted (µg)
Control	—	0	0
25	297	35.5	101
40	348	95.4	48.5
75	303	100	20.9

predict release of the biocide above 25 °C. Biocides encapsulated in customized nano-polymer networks could provide prolonged protection as surface treatments for engineered composites.

Nano-Carriers

Several nano-carrier systems are recognized that may find an application in the field of wood protection, particularly for increased durability of engineered composites (e.g., oriented strandboard (OSB)). For example, a patented nano-carrier system uses 100-nm plastic beads embedded with biocide (Laks and Heiden 2004). Based on the type of polymer comprising the bead, pore size in the bead, biocide viscosity and solubility, biocide-embedded nanoparticles can be designed for slow, controlled release of the biocide. Other cylindrical, tubule-shaped materials (i.e., nano-tubules) made from ceramics, clay, metal, or lipids that have been used as carriers in various medical and industrial applications are now being evaluated for use in engineered composites. Some properties of nano-carriers that would benefit the field of wood protection include

- delivery and placement of biocide,
- slow release of a biocide, and
- release of the biocide upon exposure to certain environmental conditions, such as high humidity.

Protection of heat-labile organic biocides during panel fabrication has greatly limited the applications of newly developed biocides and the number of treatment options for engineered composites.

When developing controlled-release nano-tubules for biocide delivery in composites, a considerable number of variables must be optimized prior to proof of concept. How to precisely control release of a biocide, whether the nano-tubules are compatible with resin used to fabricate the composite, whether the resin itself may be a barrier to release of the biocide, and calculating and regulating actual release rate were examined in the preliminary stage of this project. Methodology was developed for analyzing the thermal stability of nano-tubules loaded with a commercial biocide over a range of temperatures from 170 to 190 °C and time. Release rate of the biocide was based on leach resistance, and residual efficacy was evaluated following leaching using two microbial assays that measured the zone of fungal

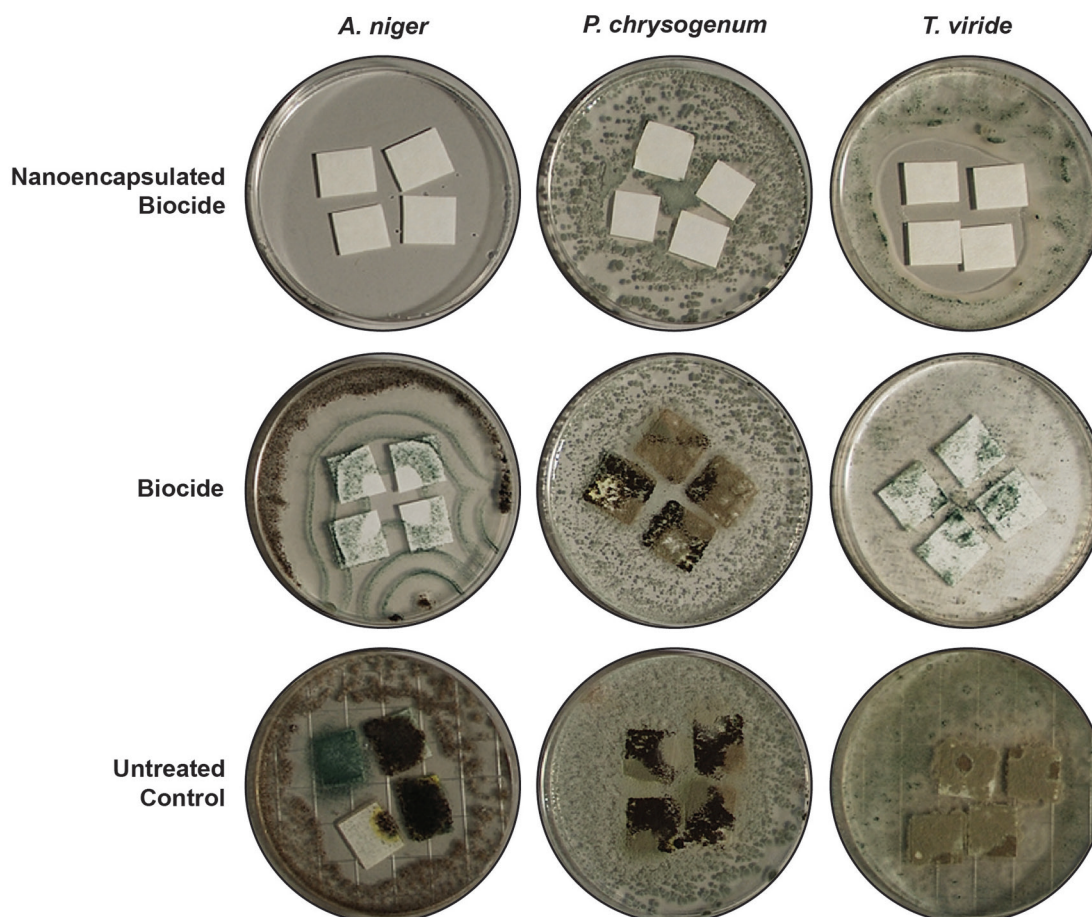


Figure 4. Paper samples treated with biocide-loaded nano-tubules, biocide alone, and untreated controls challenged with three mold fungi.

inhibition in a Petri plate and fungal resistance in a simulated environmental chamber.

Biocide-loaded nano-tubules were incorporated into OSB, medium density fiberboard (MDF), and paper. Samples of nano-treated OSB were tested for modulus of rupture (MOR), modulus of elasticity (MOE), density, moisture swelling, and antifungal resistance in laboratory tests. Preliminary studies on engineered composites demonstrated thermal protection, slow release, and enhanced mold inhibition for the biocide loaded into nano-tubules compared to controls that incorporated either biocide alone or nano-tubules alone. Figure 4 shows the results of paper treated with biocide-loaded nano-tubules and exposed to three mold fungi, *Aspergillus niger*, *Penicillium chrysogenum*, and *Trichoderma viride*. Controls are untreated paper and paper treated with the biocide. Not only are the mold fungi completely inhibited on the surface of samples treated with loaded nano-tubules, but the clearing zone surrounding the samples demonstrates the release of biocide from the nano-tubules. Improved protection of paper treated with biocide-loaded nano-tubules is obvious compared to paper treated with the biocide alone or to untreated paper controls.

Similar results were seen for OSB and MDF that were treated with biocide-loaded nano-tubules compared with untreated controls (Fig. 5). Treated and untreated specimens were placed on Petri dishes of malt extract agar, sprayed with a suspension of *Aspergillus niger* mold spores, and incubated for 4 weeks according to the ASTM D 4445–10 standard laboratory test for controlling sapstain and mold fungi on unseasoned lumber (ASTM 2010). Mold growth occurred on the agar surface and on the surface of untreated test specimens, but mold growth was completely inhibited on specimens treated with biocide-loaded nano-tubules. Release of biocide from the nano-tubules is also evident from the clearing zone surrounding test specimens on agar plates.

Conclusions

Advances in the development of nanotechnology for improved durability of engineered composites are in progress. Unique properties such as photostability, leach resistance, and biocide behavior against biodeteriorating organisms have been identified for select nano-metals. Such properties are desirable for development of new preservative systems. Encapsulating biocides in designer nano-polymer matrices

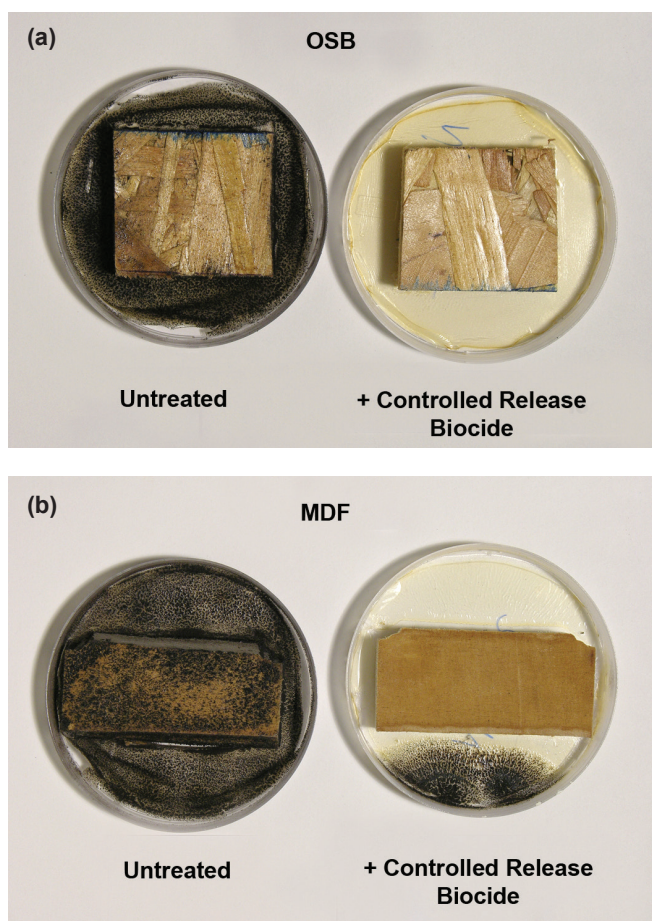


Figure 5. Oriented strandboard (OSB) (top) and medium density fiberboard (MDF) (bottom) either untreated or treated with biocide-loaded nano-tubules were challenged with the mold fungus, *Aspergillus niger*.

are promising delivery systems that release the biocide when triggered by a specific change in the environment. Nano-polymer matrices are ideal for surface treatments of solid and composite wood products. Nano-carriers, such as nano-tubules, can be loaded with organic biocides for targeted delivery that is protected from heat during the fabrication process. Loaded nano-tubules undergo controlled release of biocide to provide prolonged protection of composites from fungal growth.

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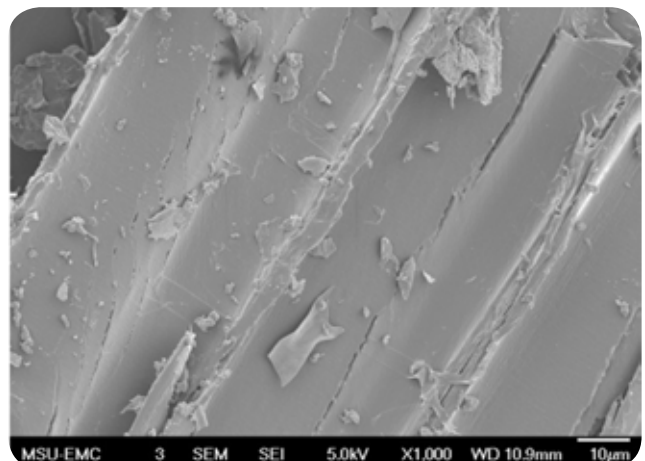
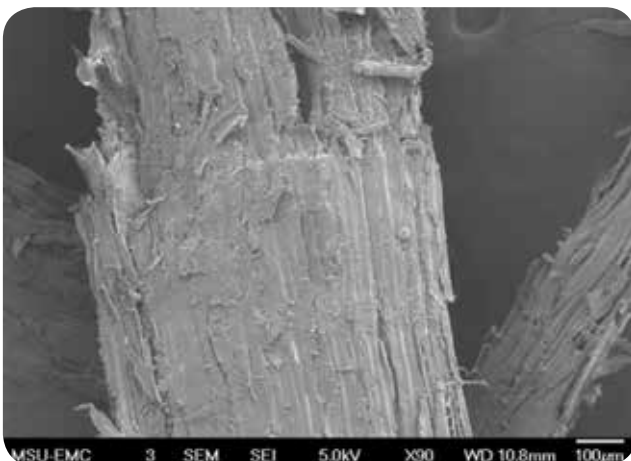
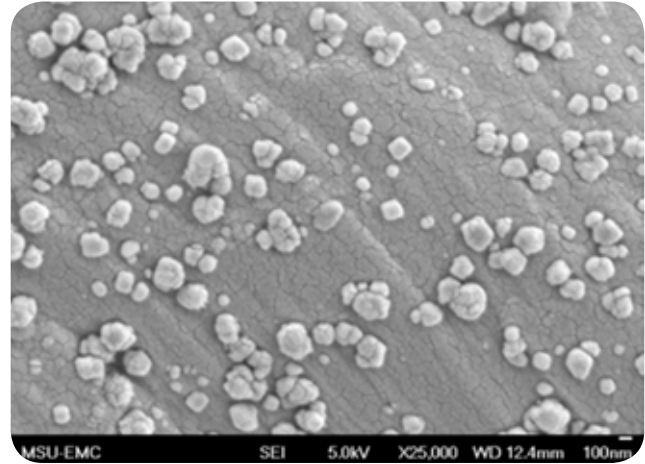
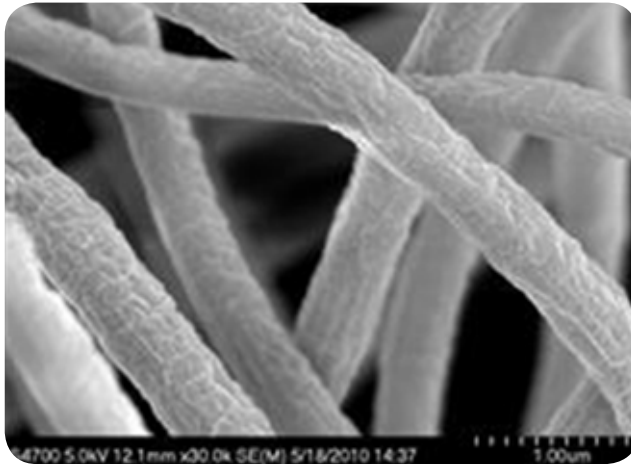
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Nanocelluloses: Potential Materials for Advanced Forest Products

Proceedings of Nanotechnology in Wood Composites Symposium

Zhiyong Cai
Kristina Oksman Niska



Abstract

This report provides a summary of technical papers presented at the Nanotechnology in Wood Composites Symposium held at the USDA Forest Products Laboratory in Madison, Wisconsin, May 18, 2011. Papers in this report included the oral presentations and posters that explore the adaptability and applicability of using nanocellulose as a potential resource to create value-added commodities and innovative bio-based composites. Presenters from around the world reviewed nanotechnology applications in developing and improving forest products in the past, present, and future. A variety of nanomaterials are obtained from wood, including nanofibrils, nanocrystals, lignin particles, and extractives. Most research efforts focus on developing continuous, high-performance composite reinforcement from cellulose nanofibrils; improving performance and value-added features of existing wood-based composites; developing coatings and additives for improved durability of wood composites; and developing films and membranes with tailored mechanical and barrier properties, sensing capabilities, and biodegradability.

Keywords: nanocellulose, nanofibril, nanocrystal, biocomposite, wood product

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Contents

Executive Summary	1
Presenters	1
Nanotechnology Applications in Forest Products—Past, Present, and Future	3
Transparent Polymer Composites Reinforced by Nanocrystalline Cellulose	5
Enhancing Durability of Wood-Based Composites with Nanotechnology	8
Artificial Ligaments/Tendons Based on Cellulose Nanofibers	13
Nanocellulose/Conducting Polymer Nanocomposite Films Based on Bacterial Cellulose	18
Eucalyptus Micro and Nanofibres for Reinforcement of Polymeric Nanocomposites	22
Impact Properties and Characteristic Impact Resistance Model of Cellulose Nanofibril-Filled Polypropylene Composites	25
Synthesis of Hybrid Porous Cellulose/Metal Nanocomposites	45
An Investigation into the Mechanical Behaviour of Surface-Modified Fibrillated Cellulose Reinforced Composites	50
Production and Characterization of Nano-Structured Carbons from Pine Chips	54
An Investigation of Fabrication Thermal Insulation Wood-Based Composite Using Nanotechnology	64
Mechanical and Thermal Properties of Microcrystalline Cellulose/Nanoclay/Polypropylene	70