Use of Nanoparticles for Controlled Release of Biocides in Solid Wood

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Received 16 May 1997; Accepted 4 June 1997

ABSTRACT: The fungicides tebuconazole and chlorothalonil were successfully incorporated into polymeric nanoparticles with median particle diameters of 100–250 nm. Polyvinylpyridine (PVPy) and polyvinylpyridine-co-styrene (10% styrene and 30% styrene) were employed as the polymer matrix. The size of the nanoparticle increased with increased styrene content. The biocide also affected particle size, with chlorothalonil consistently yielding larger nanoparticles than tebuconazole. The release of the biocides from the polymeric nanoparticles was studied by suspending them in water. The release rate of both tebuconazole and chlorothalonil decreased with increased styrene content in the matrix, and chlorothalonil consistently released more slowly from the polymeric nanoparticles than did tebuconazole. It was found that biocides were successfully introduced into solid wood by incorporating them within polymeric nanoparticles, suspending the nanoparticles in water, and using the suspension to treat the wood with conventional pressure treatments. Once in the wood, the polymer matrix serves as a reservoir for the biocide and controls its release rate into the wood. Southern pine sapwood samples were treated with biocide-containing nanoparticles suspended in water, then exposed to the wood decay fungus *Gloeophyllum trabeum* using a simple wafer test. Samples exhibited fungal resistance at appropriate levels of biocide incorporation. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 458–465, 2001

Key words: nanoparticle; controlled release; wood preservative; tebuconazole; chlorothalonil

INTRODUCTION

In recent years, research on wood preservation has focused on development of environmentally benign wood preservatives and methods to introduce these preservatives into wood. The driving force behind this research has been the perceived environmental and worker hazards associated with the major conventional wood preservatives—CCA (Chromated Copper Arsenate), creosote, and pentachlorophenol. Newer wood preservative formulations commonly involve the use of organic biocides that are dissolved in organic solvents and suspended in water using emulsifiers, often in combination with copper.[1] The solvent-containing emulsion is incorporated into the wood under pressure and the solvent then dissipates during drying and use. The primary objectives of the work described here were to determine if polymeric nanoparticles (solid polymer particles with a diameter between 10 and 1000 nm) could be prepared in a manner that might be suitable for use with wood products, if nanoparticles could be used to carry the biocides into wood, to determine if the biocides had biological efficacy in wood, and if altering the hydrophobicity of the polymer ma-

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Contract grant sponsor: U.S. Department of Agriculture and Michigan Technological University

Journal of Applied Polymer Science, Vol. 79, 458–465 (2001)

trix would moderate effectively the release rate of the biocide.

EXPERIMENTAL

Instrumentation

Particle sizing was carried out on a Shimadzu CP-4 particle sizer (centrifugation). Thermal analyses were done with a Shimadzu DSC-50 and TGA-50 (DSC: differential scanning calorimetry; TGA: thermal gravimetric analysis). Scanning electron microscopy (SEM) was performed with a JOEL 100 SEM. Transmission electron microscopy (TEM) was done with a JOEL 100CX TEM.

Materials

Tebuconazole and chlorothalonil were supplied by Bayer, Inc., and ISK Biosciences, respectively. Tween and Span were from Calgon, and all other materials were purchased from Aldrich. Fungal tests employed *Gloeophyllum trabeum* (ATCC 11539, a common basidomycete brown rot wood decay fungus), and wood blocks were cut from southern pine (*Pinus* spp.) sapwood.

Procedures

Preparation of Polyvinylpyridine Nanoparticles Containing Tebuconazole

In a modification of the procedure described by Fessi et al.,[2] tebuconazole (10 mg) was dissolved in methanol (2 mL) and the solution was mixed with polyvinylpyridine (PVPy) (50 mg, 20% w/w methanol). The solution was dripped into preheated water (60°C, 50 mL) containing a mixture of Tween 80 (100 mg) and Span 80 (100 mg), and stirred at 450 rpm. Following completion of the addition the mixture was stirred for an additional 0.5 h. Nanoparticle yield: 95 ± 5%.

Preparation of PVPy-co-Sty Nanoparticles Containing Tebuconazole

Tebuconazole (10 mg) was dissolved in methanol (2 mL) and the solution was mixed with PVP-co-Sty (10% styrene, 10 mg), and N-methylpyrrolidone (3 mL). The solution was dripped into preheated water (60°C, 50 mL) containing a mixture of Tween 80 (100 mg) and Span 80 (100 mg), and stirred at 500 rpm for 0.5 h. The PVPy-co-Sty (30% styrene) nanoparticles were prepared in the same way except the surfactant system was Tween 80 (60 mg) and Span 80 (120 mg). Nanoparticle yield: 95 ± 5%.

Preparation of PVPy Nanoparticles Containing Chlorothalonil

Chlorothalonil (10 mg) and PVPy (10 mg, 20% w/w methanol) were dissolved in NMP (4 mL). The solution was dripped into water (50 mL) containing a mixture of Tween 80 (100 mg) and Span 80 (100 mg), that was preheated to 60°C and stirred at 450 rpm for 0.5 h. Nanoparticle yield: 93 ± 5%.

Preparation of PVPy-co-Sty (10%) Nanoparticles Containing Chlorothalonil

The procedure for PVPy nanoparticles was followed. Nanoparticle yield: 87 ± 5%.

Preparation of PVPy-co-Sty (30%) Nanoparticles Containing Chlorothalonil

The procedure for PVPy nanoparticles was followed except the surfactant system consisted of Tween 80 (80 mg) and Span 80 (160 mg). Nanoparticle yield: 85 ± 5%.

Determination of Nanoparticle Yield and Nanoparticle Size

The yield of nanoparticles was measured by gravimetric analysis. The yield of nanoparticles with a diameter below 220 nm was determined by filtering a known mass of nanoparticles, suspended in water, through 220 nm filter paper. The mass of dry filter paper was determined before and after filtration. The filtrate was also dried to confirm the yield of nanoparticles that passed through the filter paper. The size and dispersity was confirmed by both TEM and particle sizing.

Determination of the Incorporation Efficiency of the Active Ingredient in Nanoparticles

A known mass of freeze-dried nanoparticles was heated in a DSC (10°C/min) to determine the enthalpy of melting for the active ingredient (a.i.). Comparison of the enthalpy of melting of a known mass of pure a.i. with the enthalpy of melting observed for the a.i. in a known mass of nanoparticles yielded an estimate of the average mass of a.i. incorporated in the mass of nanoparticles. A melting endotherm was found for chlorothalonil-containing nanoparticles but not for tebuconazole, showing complete solubilization of tebuconazole. ^{1}H-NMR (doped with a known amount of

methyl ethyl ketone to yield "control peaks") was then used to confirm the amount of tebuconazole incorporated in the polymeric nanoparticles. UV and gravimetric analysis were used to confirm the amount of chlorothalonil incorporated into the polymeric nanoparticles. The results indicate quantitative incorporation of the tebuconazole in the nanoparticles and 90–95% incorporation of chlorothalonil with ~75% of the chlorothalonil in the nanoparticles present as a soluble fraction and the remaining ~25% present in a crystalline state.

Determination of Nanoparticle Size and Polydispersity

The size and size dispersity were measured by particle sizing and confirmed by TEM. Samples for particle sizing were prepared by preparing a 0.04% suspension of nanoparticles in water and analyzing by sedimentation particle sizing to get the average diameter, the median diameter, and the dispersity of the nanoparticles. Samples observed and sized by TEM were prepared by placing 10 μL of the suspension on carbon film that was covered with 200 mesh grids. The excess suspension was removed by placing a Whatman No. 1 filter paper to the edge of the grid. Uranyl acetate stain (2% solution, 5 μL) was filtered through a 220 nm filter and applied to the grid. Excess stain was removed by Whatman No. 1 filter paper and the staining procedure was repeated. The samples were dried under reduced pressure (40°C, 12 h).

Determination of Aqueous Biocide Release Rates

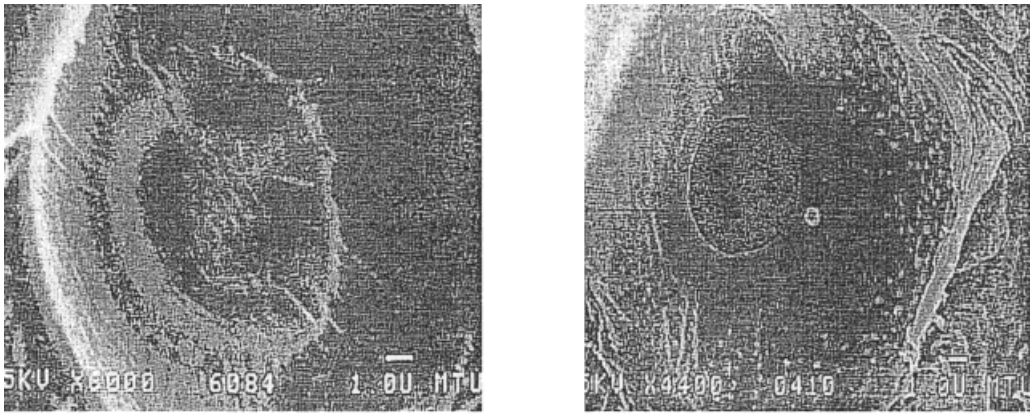
Nanoparticles were collected from the "as-made" suspensions by centrifugation (20,000 rpm, 20 min) followed by decanting the liquid and freeze drying to collect the dry nanoparticles. A fresh, stable suspension (800 mg in 200 mL of double-distilled water) was prepared and divided into multiple samples (10 mL) which were placed into 50 mL Erlenmeyer flasks. Each flask was sealed with a filter paper, which retained all particles with a diameter greater than 50 nm. This in turn was covered with a Whatman No. 1 filter paper. The flask was placed upside down into a beaker containing water (1 L) and placed in an incubator (25°C). Samples were harvested after specified time periods. The sample mass that was retained was subtracted from the original mass to determine the mass of biocide released. "Blank" samples were also prepared (nanoparticles without biocide) and harvested at identical times to allow the mass loss to be adjusted for extracted surfactant. The extraction medium was checked by NMR for the presence of polymer, which would indicate failure of the filter paper, so any failed samples could be discarded. Samples were used only once, and then discarded to prevent accumulation of error.

Determination of Fungal Resistance using a Wafer Test

Wood blocks ($19 \times 19 \times 19$ mm^3, dried to equilibrium moisture content) were weighed and measured, placed in beakers, covered with a mesh screen, and a nanoparticle suspension of known nanoparticle concentration, prepared by suspending freeze-dried nanoparticles in water at the desired suspension concentration, was poured over the wood. The beaker was placed in a pressurized cylinder and subjected to a pressure treatment consisting of a partial vacuum of 17.3 kPa for 25 min, followed by pressurization at 790 kPa for 45 min. Specimens were removed, excess liquid wiped off, and weighed to determine the mass of suspension retained. The samples were then dried overnight in an oven (40°C). The wood blocks were cut longitudinally into four wafers, two interior and two exterior, and reweighed. The blocks were sterilized in an autoclave for 15 min at 120°C. Using forceps, sterile toothpicks were placed on agar plates inoculated with *G. trabeum,* and the coded wafer sections were then placed directly on the toothpicks. Untreated control wafers were also placed in each agar dish to allow fungal activity to be verified. The petri dishes were sealed with parafilm and placed in a walk-in incubator maintained at 80°F and 80% relative humidity. Following 55 days of exposure, the wafers were harvested, cleaned, dried, and reweighed to determine the mass loss. Mass loss was measured for control wafers, and for interior and exterior sections. Reported weight losses are the average of at least three separate samples.

Visualization of Nanoparticles in Wood by Ultraviolet Light

Good nanoparticle distribution in the wood was confirmed by two methods. Treated wood blocks were sectioned and sprayed with dichlorofluorescein (0.02% in ethanol) and observed under UV light. Untreated blocks appeared greenish-yellow while the treated wood fluoresced intensely blue with no apparent difference in intensity for inte-



a) b)

Figure 1 SEM micrograph of (a) untreated sample of southern pine, and (b) southern pine treated with tebuconazole in a PVPy matrix.

rior and exterior sections. An indicator (7-hydroxy-4-methylcoumarin, 10% w/w a.i.) was then incorporated into the nanoparticles along with the a.i. and the "doped" nanoparticles used to treat wood. Freshly exposed wood surfaces were sprayed with dilute sodium hydroxide and then visualized under UV light. Control samples containing no indicator showed no fluorescence, while samples containing the indicator fluoresced intensely blue with no obvious intensity difference between interior and exterior wood sections.

Preparation of Wood Samples for SEM

PVPy nanoparticles were prepared as described and isolated by freeze drying. Nanoparticles (50 mg) were then resuspended in water (10 mL) containing $CuCl_2$ (3 g) and stirred for 10 min at 40°C. The nanoparticles were isolated by centrifuge (2 min, 1000 rpm) and washed extensively until the rinse water was colorless. The nanoparticles were further washed and then resuspended and isolated again by freeze drying to get nanoparticles with copper complexed to the nitrogen of the PVPy. Wood specimens were prepared (with and without complexed PVPy). Wood blocks were cut in a microtome. The samples were glued to an SEM sample holder, painted with gold paint, and the radial wood surfaces were observed. Nanoparticle-treated samples as well as untreated controls were observed at a magnification of 3000–6000×.

RESULTS AND DISCUSSION

Simple, one-step, nanoparticle preparation methods were developed and employed in this work. Two a.i.s, chlorothalonil and tebuconazole, were evaluated. DSC, UV, and ^{1}H-NMR were used to assess the a.i. incorporation efficiency in the nanoparticles. The analysis methods indicated 95–100% incorporation of tebuconazole and 90–95% incorporation of chlorothalonil in the nanoparticles with small variations (±5%), depending on the matrix, that were typically less than the error associated with the measurement (~5–10%).

The particle size varied with the a.i. incorporated, the matrix employed, and the hydrophile lipophile balance (HLB) number of the surfactant system. Tebuconazole-containing nanoparticles typically possessed a median diameter of ~120 nm (±10 nm) and ranged in size from ~50–400 nm. Chlorothalonil-containing nanoparticles typically had a median diameter of ~175 nm and ranged primarily from ~50–500 nm but some nanoparticles as large as 600 nm were detected. TEM and SEM were employed to observe tebuconazole-containing PVPy nanoparticles, and both confirmed the median nanoparticle diameter found by particle sizing and showed the nanoparticles were spherical and well formed. SEM was employed to visualize the nanoparticles in treated wood by microtoming and observing the wood tangentially. Figures 1a and 1b show untreated and tebuconazole-containing nanoparticle treated wood sections respectively. Tebuconazole-containing nanoparticles are seen distributed nearly uniformly in the wall around the wood pit pore in Figure 1b. The identity of the tebuconazole-containing nanoparticles was initially inferred from the size and appearance of these "nanoparticles," but was subsequently confirmed by repeating this

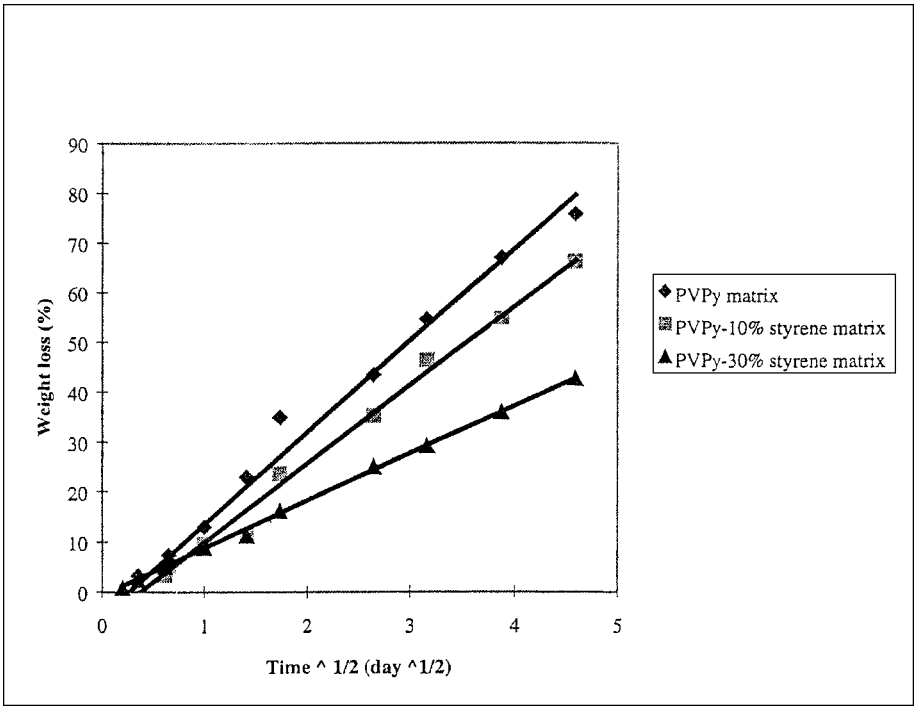


Figure 2 Tebuconazole weight loss from PVPy and PVPy-co-Sty (10% Sty and 30% Sty) nanoparticles as a function of time $(\text{days})^{1/2}$.

experiment with copper-complexed nanoparticles and using EDS to analyze the wood surface, which confirmed the presence of copper apparently uniformly distributed.

Particle sizing found less than 12%, by mass, of PVPy/tebuconazole nanoparticles had a diameter in excess of 220 nm. Gravimetric analysis of the fraction of nanoparticles unable to pass through 220 nm filter paper confirmed this data with ~15% of the mass of the tebuconazole-containing PVPy nanoparticles failing to pass through a 220 nm filter when the surfactant system (a blend of Tween 80 and Span 80) possessed an HLB number of approximately 10. When the HLB number was less than 8 or above 11, gravimetric analysis of the fraction of nanoparticles with diameters greater than 220 nm generally increased and the suspension stability generally decreased. Suspensions prepared with an HLB number of 8–11 were typically stable for several weeks. If the nanoparticles were freeze dried and resuspended the suspension stability increased to about 4–6 weeks.

The median diameter of nanoparticles containing chlorothalonil and tebuconazole increased as the matrix hydrophobicity increased. PVPy/tebuconazole nanoparticles had a median diameter of ~112 nm but increased to 132 nm when the polymer matrix was PVPy-co-Sty (30% styrene). PVPy/chlorothalonil nanoparticles had a median diameter of 169 nm but increased to 194 nm for PVPy-co-Sty (30% styrene). This data will be presented in greater detail in a paper to follow.

The a.i. release rate was studied with tebuconazole- and chlorothalonil-containing nanoparticles and varied as the hydrophobicity of the nanoparticles was varied form hydrophilic PVPy, to more hydrophobic PVPy-co-Sty (10% styrene), and PVPy-co-Sty (30% styrene). As the matrix hydrophobicity increased the release rate of both a.i.s was found to decrease, demonstrating that the a.i. release rate can be controlled by optimizing the matrix polarity. The release rate of tebuconazole as a function of the matrix is shown in Figure 2, and shows a simple release pattern with a decrease in a.i. release as the styrene content in the polymer matrix increases. The chlorothalonil release appears more complex (Figure 3) with an initial "fast" release, corresponding to approximately ~25% of the a.i. followed by a slower release corresponding to the remaining ~75% of the a.i. mass. The curve appears to be the result of two different release rates. This may be due to the fact that the chlorothalonil contained within the polymer nanoparticle is present in two physical states. DSC analysis of the chlorothalonil-containing nanoparticles showed that approximately

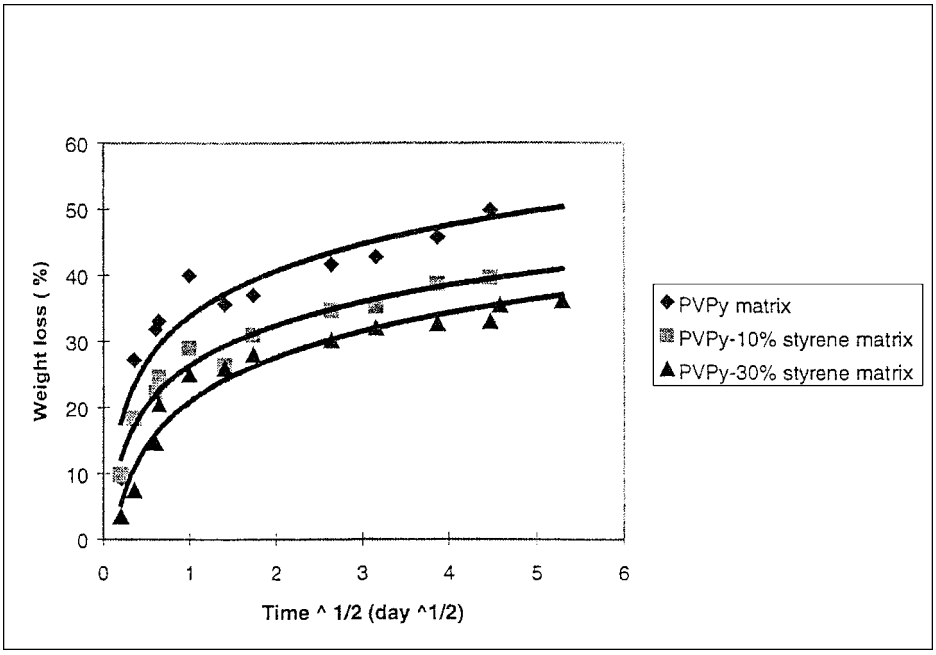


Figure 3 Chlorothalonil weight loss from PVPy and PVPy-co-Sty (10% Sty and 30% Sty) nanoparticles as a function of time $(\text{days})^{1/2}$.

25% of the theoretically incorporated chlorothalonil was present in a crystalline state, while approximately 75% of the chlorothalonil was solubilized in the matrix. If this complex release rate is related to the phase state of the a.i., then it is possible that the insoluble fraction observed may have been a.i. that was physically adsorbed onto the surface of the nanoparticle and was more rapidly extracted by the water providing a "burst" affect. The solvated a.i. was then released by a slower diffusion-controlled process. While the polymer matrix affected the overall release rates for the a.i.s the release profile was the same for all three polymer matrices investigated. That is, tebuconazole showed a simple release profile in all three polymer matrices investigated, while chlorothalonil showed the same, "two-step" release profile in all three polymer matrices.

Wood blocks (southern pine) were treated with nanoparticle suspensions with different theoretical loadings of a.i. The theoretical a.i. delivered into the wood via the nanoparticles ranged from 0.1 kg a.i./m^3 wood up to a maximum of 0.8 kg a.i./m^3 wood. The theoretical a.i. content in wood was calculated by assuming the nanoparticles in the suspension, prepared by resuspending a known mass of freeze-dried nanoparticles in water, were quantitatively delivered into the wood. The mass of nanoparticles in the suspension was multiplied by the mass fraction due to a.i., which was determined experimentally. For example, if a nanoparticle suspension was prepared that contained 500 mg of nanoparticles, and 47% of the nanoparticle mass is a.i., then assuming all the nanoparticles were delivered into the wood, the a.i. content in the wood is 235 mg. Since the wood dimensions are also known the a.i. content in wood is reported as kg of a.i./m^3 of wood. Tebuconazole-containing nanoparticle suspensions could be prepared directly at levels sufficient to deliver up to 0.8 kg a.i./m^3 wood, which is the generally accepted minimum level required for efficacy. Chlorothalonil-containing nanoparticle suspensions were less stable than those with tebuconazole, and could only be prepared directly at levels sufficient to deliver up to 0.5 kg a.i./m^3 wood, which is well below the generally accepted minimum level of efficacy for this a.i. Higher levels of biocide delivery were achieved, but to do this the nanoparticles had to be collected by freeze drying and then resuspended in water at higher concentrations. However, these suspensions were extremely unstable, and needed to be used immediately. Also, it must be noted that the a.i. content in wood reported in this work is a maximum possible value since the nanoparticles were not always delivered quantitatively.

Despite the fact that the biocide delivered was of a level generally considered to be at or below the minimum effective level for wood preserva-

Table I Affect of Tebuconazole Containing PVPy Nanoparticle Loading on Fungi Decay Resistance of Wood

Loading[a] (kg a.i./m^3 wood)	Weight Loss (%) Exterior Section	Weight Loss (%) Interior Section	Weight Loss (%) Average
0	16.6	17.5	17.0
0.05	11.7	17.2	14.5
0.1	5.8	8.2	7.0
0.2	2.9	6.5	4.7
0.4	1.6	5.7	3.7
0.8	1.1	3.2	2.1

[a] Represents the amount of a.i. in wood if the nanoparticles are delivered quantiatively.

Table III Affect of Nanoparticle Matrix on Fungi Decay Resistance of Wood Treated with Chlorothalonil (0.5 kg a.i./m^3)[a]

Matrix	Weight Loss (%) Exterior Section	Weight Loss (%) Interior Section	Weight Loss (%) Average
0			18.5
PVPy[b]	16.6	17.5	17.0
PVPy	16.7	15.3	16.1
PVPy/Sty (10%)	6.3	6.0	6.1
PVPy/Sty (30%)	9.0	8.4	8.7

[a] Represents the amount of a.i. in wood if the nanoparticles are delivered quantitatively.
[b] PVPy nanoparticle "blanks" that contained no a.i.

tion, it was found that wood blocks treated with nanoparticles containing tebuconazole and chlorothalonil did provide protection against *G. trabeum* (Tables I and II, respectively). Table I shows the mass loss of wood treated with tebuconazole in PVPy nanoparticles at different levels of a.i. loading. Generally, mass loss of under 5% is considered negligible. At a theoretical loading level of only 0.2 kg a.i./m^3 wood, the mass loss is only 4.7%, and at 0.8 kg/m^3, the treatment level usually considered to be the minimal required a.i. loading level, the mass loss is 2.1%. Therefore, the biological efficacy of the a.i. is not compromised by using a polymer carrier to introduce the a.i. into wood. The data also show that the inner wafer sections exhibited close to the same resistance to fungal decay as the exterior sections, confirming good nanoparticle penetration into the interior of the wood. The a.i. loading level is barely within the minimal level for effective protection, so higher a.i. treatment levels should result in identical fungal resistance between interior and exterior wood sections.

Table II Affect of Chlorothalonil Containing PVPy Nanoparticle Loading on Fungi Decay Resistance of Wood

Loading[a] (kg a.i./m^3 wood)	Weight Loss (%) Exterior Section	Weight Loss (%) Interior Section	Weight Loss (%) Average
0			18.5
0.1	15.4	15.7	15.6
0.2	15.5	13.5	14.5
0.4	13.0	12.5	12.7
0.8	10.7	10.3	11.1

[a] Represents the amount of a.i. if the nanoparticles are delivered quantitatively.

The chlorothalonil-containing PVPy nanoparticles gave less effective protection to wood (Table II), but at higher loadings biological efficacy was seen (11% mass loss for treated wood at 0.8 kg/m^3 compared with 18.5% for the untreated control). Chlorothalonil is considered to be a less potent a.i. than tebuconazole, so it is not surprising that a higher a.i. loading is required. However, the affect of the identity of the polymer matrix on the protection provided by chlorothalonil (at a theoretical loading of 0.5 kg a.i./m^3 wood) against *G. trabeum* (Table III) showed that chlorothalonil delivered in the hydrophobic PVPy-co-Sty (10% styrene) matrix was more effective than in a pure PVPy matrix. The wood treated with chlorothalonil-containing nanoparticles prepared from PVPy-co-Sty (10% sty) and PVPy-co-Sty (30% styrene) lost 6 and 8.7%, respectively, compared with wood treated with nanoparticles from PVPy, which lost 15% of its mass. This is despite the fact that the aqueous release rate data that showed that the hydrophilic PVPy matrix released a.i. most rapidly, while the most hydrophobic matrix employed, PVPy-co-Sty (30%) had the slowest a.i. release rate, and the fact that the a.i. loading is only ~0.5 kg/m^3 wood, which is generally thought to be below the minimum level of chlorothalonil efficacy. The difference in mass loss of the wood treated with chlorothalonil in PVPy-co-Sty (10% sty) and PVPy-co-Sty (30% sty) is too small to be considered to be significant, but there is a clear difference in protection afforded to the wood when the chlorothalonil is introduced into the wood in a pure PVPy matrix compared with the PVPy-co-

Sty matrices. This result can not be explained by differences in solubilized and nonsolubilized chlorothalonil giving a different effective level of a.i. in the wood since the DSC results showed little difference in the ratio of solvated to crystalline chlorothalonil phases in the matrices. The solvated chlorothalonil fraction in the polymer matrices was 78, 78, and 75% for PVPy, PVPy-co-Sty (10% styrene), and PVPy-co-Sty (30% styrene), respectively. Therefore, the enhanced efficacy for the chlorothalonil in the PVPy-co-Sty matrices may be due to some optimal interaction of the nanoparticles with the wood structure, but at this point these results are not understood.

CONCLUSIONS

A new and effective method for the introduction of organic biocides into solid wood has been developed. A simple "one-pot" procedure gave a nearly quantitative incorporation of the biocide into the nanoparticles, and a near quantitative yield of nanoparticles. The median diameter varied with the biocide and the matrix used but was below 200 nm. The nanoparticles prepared in this manner could be suspended in water and introduced into southern yellow pine using conventional pressure treatment methods. Incorporation of the biocide into polymeric nanoparticles allows biocides to be introduced into solid southern pine sapwood by conventional pressure treatment methods using water as the carrier regardless of the solubility of the biocide. Chlorothalonil, a very poorly soluble biocide, was introduced into wood in the same manner and with nearly equal ease as the highly soluble tebuconazole. However, the suspension from the chlorothalonil-containing nanoparticles was less stable than the suspension from the tebuconazole-containing nanoparticles, indicating that the surfactant system for the chlorothalonil-containing nanoparticles must be improved. The polarity of the polymeric matrix effectively moderated the release rate of the biocides, but also affected the nanoparticle size and the suspension stability. As the hydrophobicity of the polymer matrix increased, the release rate of the biocide decreased, the nanoparticle size increased, and the nanoparticle suspension stability decreased. Chlorothalonil was not completely soluble in the polymer matrices used, which resulted in its release occurring in two stages, a fast release, attributed to desorption of a crystalline fraction, and a slow release attributed to diffusion of the solvated chlorothalonil fraction.

Both chlorothalonil and tebuconazole showed biological efficacy against *G. trabeum* when introduced into southern yellow pine contained within polymeric nanoparticles, even thought the maximum loading level studied was 0.8 kg a.i./m^3 wood, which is considered to be a low a.i. loading level. Tebuconazole showed efficacy at loading levels in wood of 0.1 kg a.i./m^3, while chlorothalonil showed efficacy at loading levels in wood of 0.5 kg a.i./m^3 wood when the matrix was PVPy-co-Sty. The level of protection afforded to the wood at low a.i. loading levels suggests that a.i. introduced into wood via a polymer matrix might be delivered more effectively than when it is introduced into wood in a solution or liquid-in-liquid emulsion, possibly because it is delivered preferentially to sites within the wood that are susceptible to degradation, and/or because the nanoparticle results in less environmental degradation or leaching of the a.i. Chlorothalonil is a low cost a.i. that is difficult to use in many applications because of its low solubility in most solvents, so this wood preservation method may provide a new application for chlorothalonil.

The authors gratefully acknowledge the support of the United States Department of Agriculture and the Research Excellence Fund at Michigan Technological University. The authors also extend their sincere appreciation to Mr. Owen Mills, Dr. Bruce Pletka, and Dr. Michael Gretz, for their assistance with SEM and TEM.

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