Controlled Release of Biocides in Solid Wood. II. Efficacy Against *Trametes versicolor* and *Gloeophyllum trabeum* Wood Decay Fungi

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ABSTRACT: Biocide-containing nanoparticles were suspended in water to prepare wood treating suspensions able to deliver up to 0.8 kg biocide/m^3 of wood. The nanoparticle preparation method was versatile, and three fungicides (tebuconazole, chlorothalonil, and KATHON 930) and one insecticide (chlorpyrifos) were incorporated into the nanoparticles with little customization of the preparative method. Greater customization was required when the polymer matrix was changed, but the method was generally robust; nanoparticles could be prepared from several different polymers, copolymers, and polymer blends. The median nanoparticle size increased as the matrix hydrophobicity increased. Nanoparticles were quantitatively delivered into birch and southern yellow pine (SYP) at low suspension loadings, but the delivery efficiency decreased with increased suspension loading and with increased matrix hydrophobicity. The delivery efficiency was also less for birch than for SYP. Undelivered nanoparticles were found to have undergone aggregation. Greater aggregation occurred in the more hydrophobic formulations than in the hydrophilic formulations. High biological efficacy was found for all the biocides tested. Nanoparticle-treated birch was exposed to *Trametes versicolor* for 55 days and some protection was afforded, even at biocide loading levels of only 0.1 kg/m^3. At the highest loadings (~0.6 kg/m^3) the weight loss after exposure to *T. versicolor* was generally ~10% for most formulations. The SYP was treated with KATHON 930 in polyvinylpyridine. At levels of 0.1 kg of biocide/m^3 of wood less than 5% of the SYP mass was lost after 50 days of exposure to *Gloeophyllum trabeum*. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 608–614, 2002

Key words: controlled release; nanoparticles; wood preservatives; tebuconazole; chlorothalonil

INTRODUCTION

Tebuconazole and chlorothalonil were previously shown to be effectively incorporated into polymeric nanoparticles with median diameters of ~100–250 nm using different polymers and polymer blends and introduced into southern yellow pine (SYP).[1,2] These nanoparticles can be suspended in water, and the suspension can be used to treat wood using conventional water-based pressure treatment methods. Wood treated with these nanoparticles was effectively protected from attack by the brown rot fungus *Gloeophyllum trabeum*. Incorporating wood biocides in polymeric nanoparticles is advantageous because with this method even biocides (such as chlorothalonil) that have very low solubility can be introduced into wood using water-based methods; previously low solubility biocides could only be introduced into wood using toxic oils or solvents as carriers. Wood treated in this way can only be used in applications where it does not come into contact with humans. Also, once within the wood the nanoparticle serves as a reservoir for the biocide, possibly protecting it from being removed from the wood through "blooming" to the surface or random degradative processes within the wood itself. The nanoparticle itself serves as a controlled release device, releasing the biocide by a slow diffusion process. These features might improve the lifetime of the treated wood.

It was also found in that work[1,2] that the wood treated with biocide-containing nanoparticles appeared to be effectively protected at unexpectedly low levels of biocide loading within the wood. There is no single number that can be universally applied for a biocide level in wood for efficacy or for a mass loss of wood for a test method before the system would be considered efficacious; however, the wood industry would likely seek an active ingredient (AI) loading level for tebuconazole in wood of 2 kg/m^3. Generally, a mass loss of 5% or less after exposure to fungicides using a soil jar test method is considered to be background.[3] No loading level number for chlorothalonil efficacy is reported in the wood industry because, prior to this nanoparticle method, chlorothalonil was only introduced into wood in solution in organic oils

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that are also biologically active. However, chlorothalonil is generally considered to be a less active fungicide than tebuconazole.[3] In the wafer test method used,[1,4] mass losses of less than 5% were found after 50 days of exposure to *G. trabeum* with a tebuconazole content as low as 0.2 kg/m^3 of SYP. In one matrix less than 5% mass loss was also found with a chlorothalonil content of only 0.2 kg/m^3 of SYP and several nanoparticle matrices afforded ~5% mass loss or less once the chlorothalonil content reached 0.6 kg/m^3 of SYP.

The previously reported work investigated nanoparticles prepared with two different fungicides (tebuconazole and chlorothalonil) and several different matrices [polyvinylpyridine (PVP) and copolymers of PVP and styrene (PVP-*co*-St with 10 or 30% St)]. The particle size and size distribution, the AI release rates in water, the ability to be introduced into SYP, and the efficacy against *G. trabeum* were studied. That work also described nanoparticles prepared with polymer matrices that were blends of PVP and second through fifth generations of hyperbranched polyesters (HBPs) (PVP/HBP G2–G5) and a blended nanoparticle control with PVP and a linear polyester (PVP/LPE), and the same studies were performed.

This is a continuation of that work, but we also address issues dealing with the fact that wood products must in practice be treated with several different biocides to protect it from attack by different fungi, as well as insects. Although SYP is one of the most important wood species used in North America, other wood species are also important and have smaller pit pores, making them harder to treat. Therefore, this publication addresses the overall robustness of the nanoparticle method through preparation of nanoparticles with some additional biocides and polymer matrices. We also give the results of a study of the ability to treat birch wood, a wood species with smaller pit pores, and the ability of treated birch wood to resist attack from a common white rot fungi, *Trametes versicolor*.

To demonstrate the robustness of the method for using different matrices, nanoparticles were prepared using polyvinylchloride (PVC) as a matrix. Although PVC would be an unlikely choice for a polymer matrix in the wood industry, the ability to prepare nanoparticles from this matrix would indicate that a relatively unlimited range of polymers could be used as a polymer matrix. Nanoparticles were also prepared with an additional fungicide, KATHON 930 (supplied as a 30% solution in xylene, with the active fungicide RH287), and an insecticide, chlorpyrifos.

EXPERIMENTAL

Materials

Tebuconazole was supplied by Miles, Inc. (Pittsburgh, PA). Chlorothalonil was supplied by ISK Biosciences (Memphis, TN). KATHON 930 (AI is RH287) and chlorpyrifos were provided by Rohm & Haas Company (Philadelphia, PA). The surfactants were Span 80 and Tween 80 obtained from Calgon Company (Pittsburgh, PA). All chemicals, including HBP G2–G5, were purchased from Aldrich Chemical Company (Milwaukee WI). Wood specimens were cut from birch trees (*Betula papyrifera*). The fungal tests were performed with *T. versicolor* (ATCC 42462, a common white rot basidomycete) and *G. trabeum* (ATCC 11539).

Instrumentation

Particle sizing was carried out on a Shimadzu CP-4 particle sizer (centrifugation).

Nanoparticle preparation

The details of the preparation and characterization of the nanoparticles are given elsewhere,[1] but the nanoparticles are generally prepared from a 1:1 (w/w) mixture of matrix (polymer, copolymer, or polymer blend) to fungicide dissolved in a minimal amount of acetone or *N*-methylpyrrolidone (NMP). This solution is dripped slowly in a water–surfactant mixture (typically a mixture of Span 80 and Tween 80, most commonly used in a 1:1 ratio) that is most commonly stirred between 200 and 400 rpm and typically heated in the range of 40–60°C. The fungicide is incorporated nearly quantitatively when using this method. The nanoparticles can be prepared at a level sufficient to deliver up to 0.8 kg AI/m^3 wood. In practice, the nanoparticles are collected by freeze-drying and suspended in water at the desired levels. Typically, the nanoparticles are suspended at loading levels sufficient to deliver 0.2–0.8 kg AI/m^3 of wood, assuming the nanoparticles are quantitatively delivered into the wood blocks used (19 × 19 × 19 cm), because these suspensions are typically stable for several weeks. More concentrated suspensions could be prepared but needed to be used immediately.

Nanoparticles prepared with tebuconazole, chlorothalonil, and chlorpyrifos were prepared using a single method. Nanoparticles prepared with KATHON 930 in PVP used the same method, except the surfactant-containing water was maintained at room temperature because the RH287, the fungicide in KATHON 930, has a melting point of 40°C, and higher temperatures resulted in particle coagulation.

When the polymer matrix was varied, the general preparative method needed more customization. Typically, the customization involved identifying a solvent or solvent mixture for the AI and polymer matrix that were completely or at least mostly water soluble. Acetone, methanol, and NMP were typically employed, but small amounts of hydrocarbon solvent could be tolerated if necessary. A suitable surfactant

mixture could be prepared using Tween 80 and Span 80, usually in ~1:1 ratio, but with the relative amounts customized for each formulation.[4]

General procedure for wood preservation studies

The wood block specimens were prepared (cut into cubes of 19 mm on each side), and the exact dimensions and mass of each block were measured. The wood blocks were placed in beakers and covered with a coarse steel mesh, and the treating suspension was carefully poured into the beaker. The steel mesh was used to keep the wood block immersed in the treating suspension. The beaker was then 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, and the liquid on the surface was wiped away. The blocks were weighed to determine the mass of suspension (nanoparticles plus water) retained in the wood. The samples were dried overnight (40°C), and then cut into four nearly equal wafer sections (two interior and two exterior), and each section was reweighed. The wafers were sterilized in an autoclave for 15 min at 120°C. Forceps were used to place sterile toothpicks on agar plates inoculated with *T. versicolor* or *G. trabeum*, and the labeled wafer sections were then placed directly on the toothpicks. Untreated control wafers were placed in each agar dish so fungal activity within the dish could 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. The reported weight losses are the average of at least three samples. Suspensions of "blank" nanoparticles (nanoparticles without AI) were prepared and used with each system to determine if the polymer matrix and/or surfactant (mixtures of Tween 80 and Span 80) possessed any biological activity.

Procedure for calculating nanoparticle and biocide delivery into wood

Wood blocks (six at a time, 19 cm on each side) were treated as described with a nanoparticle suspension prepared to deliver a known amount of biocide into the wood. Following the treatment, the undelivered nanoparticles were recovered from the suspension by freeze-drying. The mass of recovered nanoparticles was measured and subtracted from the mass of nanoparticles in the original suspension to determine the average mass of nanoparticles delivered into the treated wood. The AI delivered into the wood was determined by calculating the total mass of AI contained within the nanoparticles (most nanoparticles were 47–50% of the total AI mass) and assuming the delivered nanoparticles were uniformly distributed within the wood to determine the amount of AI per cubic meter of wood. The recovered nanoparticles were resuspended in water, and the particle size of the recovered nanoparticles was measured to determine the effect of pressure treatment on the particle size.

RESULTS AND DISCUSSION

The majority of this research with biocide-containing nanoparticles employed PVP, copolymers of PVP and St (PVP-*co*-St) and 1:1 blends of PVP with HBP or LPE as polymer matrices. The primary limitation of this method is that the matrix polymer(s) and biocide(s) must be soluble in a water-soluble organic solvent. The prior work showed that as hydrophobicity of the polymer and AIs increased, the median size of the nanoparticles tended to become larger. To determine how robust the nanoparticle method could be the nanoparticles were prepared with PVC as the matrix, and two additional biocides (fungicide RH287 and insecticide chlorpyrifos) were incorporated into the PVP nanoparticles. The same formulations used previously to treat SYP were also used to treat birch wood, and the efficiency of nanoparticle delivery was determined so that the effect of the wood species on the nanoparticle treatment could be determined. The undelivered nanoparticles were also recovered, and the particle size was measured again to determine if the nanoparticles could be recycled. Finally, the biological efficacy of the biocides against *T. versicolor* was evaluated with the treated birch wood.

Versatility of nanoparticle preparation method

Our prior work [1–3] investigated the AIs tebuconazole and chlorothalonil in polymer matrices of PVP, PVP-*co*-St, and blends of PVP/HBP. Two additional AIs, the insecticide chlorpyrifos and the fungicide RH287 (as KATHON 930) are used here. The AIs were easily incorporated into the polymer matrix to afford nanoparticles with a median diameter (140 and 118 nm, respectively) that would allow them to be efficiently incorporated into wood. Nanoparticles were also prepared with tebuconazole using PVC as the polymer matrix. PVC was selected as the matrix because of the difficulty in working with it, its low solubility, and its extreme hydrophobicity; thus, it was considered to represent an "extreme" for difficult matrices. In the second modification of the procedure PVC/tebuconazole nanoparticles were prepared with a median diameter of ~300 nm. These were too large to be used to treat SYP efficiently, and no additional characterization was done with these nanoparticles; but PVC was selected only because it represented an extreme in matrix difficulty. The fact that only two attempts were required to get to 300 nm was considered proof that

TABLE I
Effect of Formulation on Median Particle Size

Polymer matrix	AI	Median particle size (nm)
PVC	Tebuconazole	~300
PVP	Tebuconazole	112
PVP	Chlorpyrifos	140
PVP	RH287	118

the general method could be adapted with relatively little difficulty for any desired formulation. The data are summarized in Table I.

Nanoparticle incorporation into birch

Birch wood samples were treated with aqueous nanoparticle suspensions containing a sufficient mass of nanoparticles to deliver selected amounts of the AI. The suspensions were prepared to deliver 0.1, 0.2, 0.4, or 0.8 kg of AI/m^3 of birch wood, assuming quantitative delivery of the nanoparticles. The AI actually introduced into the birch was calculated from the known AI content in the nanoparticles (measured) and the mass of nanoparticles introduced into the wood, which was known from measuring the mass of undelivered nanoparticles recovered from the treating suspension. The results are summarized in Table II. The numbers shown are the AI actually delivered into the birch. For comparison, the amount of AI delivered into SYP is shown in parentheses when the amount delivered differs from the AI delivered into the birch. As with SYP, the delivery is essentially quantitative for those suspensions that are able to deliver 0.1 and 0.2 kg AI/m^3 wood. The nanoparticles were also able to be delivered into SYP in most cases quantitatively, even at 0.4 kg AI/m^3 wood, but in the birch the more hydrophobic matrices delivered only 50–75% of the theoretical nanoparticle mass. The hydrophobic matrices typically afforded nanoparticles with larger median particle diameters than the more hydrophilic systems, and they also had a greater percentage of the nanoparticle mass present as particles with diameters of 300 nm or more. The delivery efficiency dropped off further when the treating suspension was 0.8 kg AI/m^3 wood. Most systems delivered enough nanoparticles to introduce 0.5–0.6 kg AI/m^3 wood, and the best result was only 0.7 kg AI/m^3 wood. Delivery was not quantitative with the SYP system either; but the delivery efficiency was generally less for birch than for SYP, which was expected because birch has smaller pit pores than SYP. The decreased delivery is attributed to the larger pit pores becoming blocked with larger nanoparticles and then preventing the introduction of further nanoparticles into the wood. Because wood has different size pit pores, it is thought that only a given percentage of the pit pores are able to be penetrated at all by the nanoparticles; thus, as these pit pores become blocked by larger nanoparticles, they are removed from the available sites through which even the smaller nanoparticles can access the wood interior. Therefore, even though the median particle diameter is suitable, the small percentage of larger nanoparticles represents a serious obstacle for this approach to be as efficient as it should be.

Characterization of undelivered nanoparticles

Lower suspension loadings were able to deliver the theoretical amount of AI into the wood, but deviations were found at suspension loading levels sufficient to deliver 0.8 kg of AI/m^3 of wood. The failure to deliver

TABLE II
Efficacy of AI Delivery into Birch Using Nanoparticle Treating Suspensions Sufficient to Deliver 0.1–0.8 kg of AI/m^3 of Wood

		Suspension loading (kg AI/m^3)			
AI	Matrix	0.1	0.2	0.4	0.8
Tebuconazole	PVP	0.1	0.2	0.4	0.6 (0.7)
	PVP-*co*-10% St	0.1	0.2	0.3	0.5
	PVP-*co*-30% St	0.1	0.2	0.3	0.4
	PVP/HBP G2	0.1	0.2	0.2 (0.4)	0.4 (0.6)
	PVP/HBP G3	0.1	0.2	0.3 (0.4)	0.5 (0.7)
	PVP/HBP G4	0.1	0.2	0.4	0.7 (0.8)
	PVP/HBP G5	0.1	0.2	0.4 (0.3)	0.5 (0.7)
Chlorothalonil	PVP	0.1	0.2	0.3	0.6
	PVP-*co*-10% St	0.1	0.2	0.3	0.5
	PVP-*co*-30% St	0.1	0.1 (0.2)	0.2	0.4
	PVP/HBP G2	0.1	0.2	0.2 (0.3)	0.4 (0.6)
	PVP/HBP G3	0.1	0.2	0.3 (0.4)	0.5 (0.6)
	PVP/HBP G4	0.1	0.2	0.4	0.7
	PVP/HBP G5	0.1	0.2	0.3 (0.4)	0.6

The numbers in parentheses are the measured AI content in SYP and are shown only when the amount differs from the AI content delivered into birch.

TABLE III
Effect of Pressure Treatment on Median Particle Size

Matrix–AI	Initial particle size (nm)	Particle size after treating (nm)	
		SYP	Birch
PVP–none	118	169	275
PVP–tebuconazole	111	179	295
PVP-*co*-10% St–tebuconazole	118	226	298
PVP-*co*-30% St–tebuconazole	132	598	802
PVP–chlorothalonil	169	354	878
PVP-*co*-10% St–chlorothalonil	176	518	ppt
PVP-*co*-30% St–chlorothalonil	194	845	ppt
PVP/HBP G2–tebuconazole	256	381	785
PVP/HBP G3–tebuconazole	208	364	ppt[a]
PVP/HBP G4–tebuconazole	193	299	ppt[a]
PVP/HBP G5–tebuconazole	252	457	ppt[a]
PVP/HBP G2–chlorothalonil	244	470	—
PVP/HBP G3–chlorothalonil	231	464	—
PVP/HBP G4–chlorothalonil	172	323	—
PVP/HBP G5–chlorothalonil	213	645	—

[a] Complete aggregation and precipitation of the nanoparticles.

the nanoparticles quantitatively is problematic not only because the wood is inadequately protected if the AI is not delivered in sufficiently high loadings but also because the nanoparticles would be expensive to prepare and clearly the process is uneconomical if 25–50% of the nanoparticles cannot be delivered. Undelivered nanoparticles from suspensions that could theoretically deliver up to 0.8 kg AI/m^3 wood were recovered by freeze-drying and reanalyzed in a particle sizer. The median particle size of the recovered nanoparticles after treating the SYP and birch is shown in Table III.

The recovered nanoparticles are in all cases larger than prior to treating the wood, but two trends are evident. First, the nanoparticles recovered from treating the birch are consistently significantly larger than the nanoparticles recovered from treating the SYP. This is probably indicative of two factors: it suggests that the nanoparticles are insufficiently stabilized and hence aggregate during the pressure treatment process and that the birch pit pores are blocked at an earlier point in the pressure treatment than the SYP and thus undergo more aggregation, resulting in the larger nanoparticles. Second, the more hydrophobic nanoparticles undergo more aggregation than the more hydrophilic one. An example of this is the PVP-*co*-St (30% St) nanoparticles containing tebuconazole that had a median diameter of nearly 600 nm after treatment, although initially the median diameter was 132 nm, compared with PVP/tebuconazole that was only 179 nm versus an initial median diameter of 118 nm after treatment. There are two possible explanations for this. It is possible the more hydrophobic systems are simply less effectively stabilized than the hydrophilic nanoparticles and therefore underwent aggregation more easily than better stabilized nanoparticles. This seems a likely possibility because on standing many of the hydrophobic nanoparticle suspensions began to precipitate after 1–2 weeks while the more hydrophilic systems showed no sign of precipitation for 4 weeks or more. The second possibility is that, because the more hydrophobic nanoparticles typically had a larger percentage of nanoparticles above 300 nm,[2] it is possible that the available pit pores in the wood being treated were blocked at an earlier point in the pressure treatment and began aggregating earlier in the process. It is also possible that both these possibilities contributed to some extent. The data clearly show however that after one treatment, unless the nanoparticles can be more effectively stabilized, the undelivered nanoparticles could not be recovered to be used in further treatment of solid wood.

Efficacy against *T. versicolor* of birch treated with biocide-containing nanoparticles

Birch wood was treated with blank nanoparticles (nanoparticles with no AI) and with nanoparticles containing tebuconazole and chlorothalonil. The treated wood was exposed to *T. versicolor* for 55 days and the mass loss was measured. The control study with the nanoparticle blanks was to determine if any of the polymers or surfactants used had any effect on wood preservation. Those results are shown in Table IV, and they confirm that neither the polymer matrix nor the surfactants had any significant effect on wood preservation.

Nanoparticle-treated birch samples were placed in agar dishes with an untreated birch wood wafer to verify the fungal activity in each dish. The wood specimens were exposed to *T. versicolor* for 55 days, and the mass loss was measured to determine if tebuconazole protected the birch from fungal attack when introduced into the wood in polymer nanoparticles. The results are shown in Table V. In each case, the untreated birch controls lost ~35–43% of their mass

TABLE IV
White Rot Resistance of Birch Treated with Nanoparticle Blanks

Polymer matrix	Ave. wt loss (%)
None	37 (6)
PVP	43 (8)
PVP-*co*-10% St	36 (4)
PVP-*co*-30% St	35 (6)
PVP/HBP G2	30 (10)
PVP/HBP G3	32 (7)
PVP/HBP G4	39 (9)
PVP/HBP G5	40 (10)

The standard deviations are in parentheses.

TABLE V
White Rot Resistance of Birch Treated with Tebuconazole-Containing Nanoparticles

	Weight loss (%) at different AI suspension loadings (kg AI/m^3)			
Matrix	0	0.1	0.4	0.8
PVP	43	18.6 (0.1)	13.0 (0.4)	7.0 (0.6)
PVP-*co*-10% St	36	23.0 (0.1)	12.8 (0.4)	10.4 (0.5)
PVP-*co*-30% St	35	7.0 (0.1)	6.1 (0.3)	5.7 (0.4)
PVP/HBP G2	37	28 (8)	7 (3)	7 (4)
PVP/HBP G3	37	22 (9)	8 (2)	7 (1)
PVP/HBP G4	37	10 (5)	9 (3)	7 (2)
PVP/HBP G5	37	20 (10)	14.9 (0.7)	9.9 (0.9)

The standard deviations are in parentheses.

after 55 days of exposure, which confirmed the white rot fungi cultures were active. The birch treated with tebuconazole in this way showed the tebuconazole protected the birch from attack by *T. versicolor* at very low loading levels. Some protection was afforded to the birch by tebuconazole in all the matrices used, even at theoretical AI loading levels of only 0.1 and 0.4 kg AI/m^3 birch. Once the theoretical AI loading was 0.8 kg AI/m^3 wood (actual AI loading of 0.4–0.7 kg AI/m^3 wood), only ~6–10% mass loss occurred.

Chlorothalonil-containing nanoparticles were also used to treat birch wood exposed to *T. versicolor*. The results are shown in Table VI. Again, some efficacy against *T. versicolor* was observed at loading levels of only 0.1 kg/m^3, particularly for the PVP-*co*-St (30% St). Chlorothalonil is a less potent AI than tebuconazole, so seeing any efficacy at that low loading level was unexpected. At nominal chlorothalonil loadings of 0.4 and 0.8 kg/m^3 there was no significant difference in efficacy based on the nanoparticle matrix with the exception of PVP/HBP G4 and G5. The reasons why birch treated with these nanoparticles underwent more weight loss is not known; but, in general, the results show that chlorothalonil, which is considered to be a less potent biocide than tebuconazole, afforded protection to birch wood at AI loading levels of ~0.4–0.7 kg/m^3 because the mass loss was ~10% after 55 days of exposure to *T. versicolor*.

Efficacy against *G. trabeum* of SYP treated with nanoparticles containing RH287

SYP was treated with PVP nanoparticles containing RH287 and exposed for 50 days to *G. trabeum* using the same wafer test method. The results are shown in Table VII. The mass loss of the SYP is below the 5% mass loss that is considered the background level at AI loading levels of only 0.1 kg/m^3. The minimum level for biological activity reported for this biocide is not known; substantial protection against fungal attack is evident at extremely low levels of biocide incorporation.

CONCLUSIONS

Wood biocides were incorporated into polymeric nanoparticles and the nanoparticles were introduced into birch and SYP using water-pressure treatments. A general method for the preparation of nanoparticles required little customization with different formulations and worked well with three different fungicides and an insecticide and different polymer matrices. Variation of the polymer matrix required greater method customization, but even PVC afforded nanoparticles. Hydrophobic nanoparticles possessed larger median particle diameters than more hydrophilic ones. Nanoparticles were incorporated quantitatively

TABLE VI
White Rot Resistance of Birch Treated with Chlorothalonil-Containing Nanoparticles

	Weight loss (%) at different AI suspension loadings (kg AI/m^3)			
Matrix	0	0.1	0.4	0.8
PVP	43	20.1 (0.1)	14.6 (0.3)	12.4 (0.6)
PVP-*co*-10% St	35	21.68 (0.09)	14.0 (0.3)	10.5 (0.5)
PVP-*co*-30% St	35	15.41 (0.08)	11.5 (0.3)	10.6 (0.4)
PVP/HBP G2	37	21 (4)	14 (7)	10 (9)
PVP/HBP G3	37	31 (4)	19 (4)	14 (5)
PVP/HBP G4	37	34 (7)	31 (9)	27 (1)
PVP/HBP G5	37	38 (4)	35 (4)	24 (4)

The standard deviations are in parentheses.

TABLE VII
Resistance of SYP Treated with RH287/PVP Nanoparticles Against *Gloeophyllum Trabeum*

Nanoparticle	Loading (kg AI/m^3)	Weight loss (%)
Control	0	19 (4)
PVP/RH287	0.05	6 (3)
	0.1	3 (3)
	0.2	1 (1)
	0.4	1 (1)

The standard deviations are in parentheses.

into birch and SYP at lower suspension loadings but not at higher suspension loadings. Hydrophobic nanoparticles were incorporated into the wood less efficiently than hydrophilic systems, and birch was more difficult to treat than SYP. These differences were attributed to the fact that the hydrophilic nanoparticles typically possessed smaller median particle diameters and birch wood has smaller pit pores than SYP. Consequently the pit pores were more rapidly blocked in birch, especially with hydrophobic nanoparticles, thereby hindering additional treatment. Undelivered nanoparticles were recovered and found to have aggregated, preventing them from being reused to treat additional solid wood samples. Biological studies of birch wood treated with nanoparticle blanks showed that the polymer matrices had no biological activity but tebuconazole and chlorothalonil had biological activity against *T. versicolor* at biocide levels as low as 0.1 kg/m^3 when introduced in nanoparticles. Mass loss was reduced in most cases to ~10% once the AI loading level reached ~0.4–0.6 kg AI/m^3. When SYP was treated with RH287 in PVP nanoparticles and exposed to *G. trabeum* mass loss was reduced to below 5% at loading levels as low as 0.1 kg AI/m^3 of SYP. These results show a high level of biocide activity using nanoparticles as the carriers for wood preservatives.

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