Effects of Fungicides on Mold Resistance and Mechanical Properties of Wood and Bamboo Flour/High-Density Polyethylene Composites

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The main objective of this study was to determine the mold resistance and mechanical properties of fungicide-treated wood and bamboo flour/high density polyethylene (HDPE) composites. Zinc borate (ZB), 4,5-dichloro-2-octyl-isothiazolone (DCOIT), zinc pyrithione (ZPT), and carbendazim (MBC) were used as fungicides. Then, treated and untreated samples were exposed to mold fungi (*Aspergillus niger*, *Trichoderma viride*, *Penicillium funiculosum*, and *Aureobasidium pullulans*) for 28 days. Mechanical properties, including the tensile strength, modulus of elasticity (MOE), modulus of rupture (MOR), and impact strength of treated and untreated composites, were evaluated. The experimental results indicated that incorporation of all four fungicides greatly improved the mold resistance of wood flour/HDPE composites. ZB-, DCOIT-, and ZPT-treated bamboo flour/HDPE composites were also more resistant to mold fungi, while no inhibitory effect on mold growth was observed for MBC-treated bamboo flour/HDPE composites. In most cases, fungicides lowered the tensile strengths and MOR of wood flour/HDPE samples but increased the impact strengths of wood flour/HDPE composites and tensile strengths and MOE of bamboo flour/HDPE composites, while other mechanical properties behaved differently. Accordingly, some fungicides can be effectively used as preservatives for both wood flour/HDPE and bamboo flour/HDPE composites.

Keywords: Fungicides; Mold resistance; Mechanical properties; Wood flour/HDPE composites; Bamboo flour/HDPE composites; Wood-plastic composites

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INTRODUCTION

Wood-plastic composites (WPCs), or natural fiber reinforced thermoplastic composites, consist of natural fibers (such as wood, bamboo, bagasse, or rice bran), thermoplastics (such as polyethylene (PE), high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC)), and other additives. WPCs have been extensively used for buildings, automotive, packaging, siding, car interior parts, furniture, and other applications. Initially, WPCs were generally considered to be more resistant to fungi because the wood particle is completely encapsulated by plastic and decay rates are much slower than those in solid wood (Verhey and Laks 2002a; Kartal *et al*. 2013). However, recent studies have shown that WPCs still remain susceptible to fungi (Gardner *et al*. 2003).

Ever since Morris and Cooper (1998) observed the presence of fungal decay and discoloration on WPC deck boards in Florida, the fungal resistance of WPCs has been studied by many researchers (Morris and Cooper 1998). The decay fungi *Coniophora puteana*, *Coriolus versicolor*, *Gloeophyllum trabeum*, *Trametes versicolor*, *Postia placenta*, *Schizophyium commune*, *Pycnoporus sanguineus*, *Tyromyces palustris*, *Pycnoporus coccineus*, *Alternaria alternate* (Clemons and Ibach 2002; Pendleton *et al*. 2002; Wu *et al*. 2003; Schirp and Wolcott 2005; Schirp and Wolcott 2006; H'ng *et al*. 2011; Hamzeh *et al*. 2012; Naumann *et al*. 2012; Ashori *et al*. 2013; Kartal *et al*. 2013; Wei *et al*. 2013), and the mold fungi *Aspergillus niger*, *Trichoderma viride*, *Penicillium funiculosum*, *Penicillium chrysogenum*, and *Aureobasidium pullulans* have been separately used as test fungi (Kartal *et al*. 2013; Feng *et al*. 2014).

Various factors, such as plastic monomer type, wood species, wood content, particle size, moisture content, additives, and biocides, have been shown to influence the fungal resistance of WPCs (Chow *et al*. 2002; Verhey and Laks 2002b; Morrell *et al*. 2002; Wei *et al*. 2013). In most cases, composites containing higher wood content and larger particle sizes are more susceptible to mold and/or decay fungi (Ibach and Clemons 2002; Kartal *et al*. 2013; Feng *et al*. 2014). Wood species also affect the biodegradation of WPCs. Fabiyi *et al*. (2011) reported that there were no significant gravimetric differences in composites produced using Douglas-fir, poplar, or pine after being exposed to *G. trabeum*. Treatment with *Trametes versicolor*, however, produced significantly higher weight losses of HDPE/poplar composites, while Douglas-fir-based WPCs were less susceptible to this fungus. Xu *et al*. (2015) stated that the sequence of mold resistance of WPCs made with six different wood species were ranked as follows: *Cunninghamia lanceolata* and *Melaleuca leucadendra* (level 0) > *Eucalyptus grandis* × *Eucalyptus urophylla* (level 1) > *Pinus massoniana* (level 2) > *Liquidambar formosana* and *Ricinus communis* (level 4).

Fungicides can significantly improve the decay and mold fungi resistance of WPCs. To protect WPCs, commercial fungicides such as zinc borate (ZB), chitosan-copper complex (CCC), chlorothalonil (CTL), 3-iodo-2-propynyl butylcarbamate (IPBC), and 2-thiazol-4-yl-1H-benzoimidazol (TBZ) have been employed to improve the fungal resistance of WPCs. Verhey *et al*. (2001) stated that the incorporation of ZB into PP/pine composites provided protection against brown rot fungi attack at 1%, 3%, and 5% loadings. The addition of ZB also significantly improved the fungal resistance of WPC, and it completely or partly prevented weight loss or mold growth on WPC specimens caused by decay or mold fungi (Pendleton *et al*. 2002; Laks *et al*. 2005; Klyosov 2007; Kartal *et al*. 2013; Feng *et al*. 2014). Decay resistance was significantly improved by 3% CCC-treated wood/HDPE composites against *T. versicolor* and *G. trabeum*, and CCC-treated wood/HDOE composites performed, as well as ZB-treated wood/HDPE composites regarding fungal decay resistance (Lu *et al*. 2008). Loading of CTL into WPCs resulted in significantly less mold growth on WPCs than untreated controls (Laks *et al*. 2005). IPBC and TBZ have been effectively used as preservatives for wood/HDPE composites, and treated samples are more resistant to *C. versicolor* (Ashori *et al*. 2013).

When exposed to an outdoor environment, especially in ground contact or above-ground, the durability of WPC composites is greatly affected by degradation from biological agents. As a result, deterioration, discoloration, and disintegration of these materials can be observed over time; this not only results in economic loss, but could also be a source of pathogens (Kositchaiyong *et al*. 2014b). To prevent fungal colonization and deterioration and then improve the fungi resistance of WPCs, chemical fungicides often have to be incorporated into the material formulations. The fungicides added into WPCs

should have broad-spectrum activity, good compatibility, long-term stability, and tolerance under processing conditions (Kositchaiyong *et al*. 2014b). ZB, DCOIT (4,5-dichloro-2-octyl-isothiazolone), ZPT (Zinc pyrithione), and MBC (Methyl-N-(2-benzimidazolyl) carbamate)) are a class of commercial fungicides that are consistent with the properties mentioned above and then can be recommended as potential fungicides for WPCs. However, few published reports are available regarding the effects of such fungicides on antifungal performance and material properties of WPCs.

The main goal of this research was to evaluate the effects of those four fungicides at different concentrations on anti-mold performance of HDPE-based composites. Furthermore, the mechanical properties of composites were also investigated and analyzed in association with fungicides addition. Two fiber types, wood flour and bamboo flour, which have different chemical constituents, were used and mixed with HDPE in this study.

EXPERIMENTAL

Materials

Wood flour (WF) and bamboo flour (BF) were obtained from a commercial factory, were milled down to particle sizes of 60 to 80 mesh, and were then dried to less than 3% moisture content prior to the compounding process. HDPE (DGDA6098) was obtained from China Petrochemical Co. (Qi Lu Branch), with a density and melt index of 0.95 g/cm^3 and 13 g/10 min, respectively. The coupling agent, maleic anhydride grafted polyethylene (MAPE), with a melt flow index of 2 g/10 min, was obtained from NanJing Juxing Polymer Materials Co., China. Chemical fungicides (ZB, DCOIT, ZPT, and MBC) were all obtained from Sigma-Aldrich Co., China. The solutions of fungicides were prepared by dissolving them in ethanol (95%) or dimethyl sulfoxide (DMSO) at room temperature, respectively. Four mold fungi, *Aspergillus niger* (ATCC 16404), *Trichoderma viride* (AS 3.2941), *Penicillium funiculosum* (GIM 3.103), and *Aureobasidium pullulans* (AS 3.387), were supplied by the Microbial Culture Collection Center of Guangdong Institute of Microbiology, China.

Methods

Compression molding of WPC composites

The WPC materials were produced from multi-component formulations (Table 1). In the first stage, WF and BF were pretreated with various fungicide solutions (ZB, DCOIT, ZPT, and MBC) at four different concentration levels. The concentration of each of the fungicides used in this study were based on the results of our pre-experiments. The treated and untreated WF or BF, HDPE, and MAPE were then premixed based on each formulation before composites were compressed. The mixture was poured into an aluminum mold, and the mold was placed on the lower platen of an automatic benchtop press (Carver, USA). A heated press with a pressure level of 12.5 MPa was used for the compression molding. The press platens were maintained at 190° C, and the press cycle consisted of two phases. The first phase involved the heating of the Carver mold assembly to 190° C for 10 min. After the mold assembly reached the desired temperature, the press was closed slowly. The second phase was the closure of the press for 5 min. After the 15-min main press cycle, the molten wood-plastic was removed from the hot press and cooled under pressure at ambient conditions. After molding, the WPC samples were cut into small test specimens. The test specimens were kept at 20° C ± 2° C and 65 ± 5% RH before further testing.

Table 1. Formulations of WPCs

No. of WPC composites	WF or BF (wt.%)	HDPE (wt.%)	MAPE (wt.%)	Fungicides (wt.%)			
				ZB	DCOIT	ZPT	MBC
WF composites							
W1	50	50	2	0	0	0	0
W2	50	50	2	1	0	0	0
W3	50	50	2	1.5	0	0	0
W4	50	50	2	2	0	0	0
W5	50	50	2	5	0	0	0
W6	50	50	2	0	0.05	0	0
W7	50	50	2	0	0.1	0	0
W8	50	50	2	0	0.2	0	0
W9	50	50	2	0	0.5	0	0
W10	50	50	2	0	0	0.5	0
W11	50	50	2	0	0	1	0
W12	50	50	2	0	0	2	0
W13	50	50	2	0	0	5	0
W14	50	50	2	0	0	0	0.3
W15	50	50	2	0	0	0	0.5
W16	50	50	2	0	0	0	1.0
W17	50	50	2	0	0	0	2.0
BF composites							
B1	50	50	2	0	0	0	0
B2	50	50	2	1	0	0	0
B3	50	50	2	1.5	0	0	0
B4	50	50	2	2	0	0	0
B5	50	50	2	5	0	0	0
B6	50	50	2	0	0.05	0	0
B7	50	50	2	0	0.1	0	0
B8	50	50	2	0	0.2	0	0
B9	50	50	2	0	0.5	0	0
B10	50	50	2	0	0	0.5	0
B11	50	50	2	0	0	1	0
B12	50	50	2	0	0	2	0
B13	50	50	2	0	0	5	0
B14	50	50	2	0	0	0	0.3
B15	50	50	2	0	0	0	0.5
B16	50	50	2	0	0	0	1.0
B17	50	50	2	0	0	0	2.0

Chemical analysis of WF and BF

Ethanol/benzene (1:2) solvent extractions and the acid-insoluble (Klason) lignin content were performed according to GB/T 2677.6 (1994) and GB/T 2677.8 (1994), respectively. The holocellulose content was determined according to GB/T 2677.10 (1995) with sodium-chlorite method. The cellulose content was determined by Nitric-acetic acid method (Wright and Wallis 1998). The hemicellulose content was then calculated by subtracting the cellulose content from the holocellulose content.

Mold resistance

Mold resistance tests were carried out according to the American Society for Testing and Materials (ASTM) G21 (2013) Standard, as well as referring to the previous literature (Kartal *et al*. 2013; Xu *et al*. 2015). First, four mold fungi (*A. niger, T. viride, P. funiculosum*, and *A. pullulans*) were separately grown and maintained on potato dextrose ager plates at 28 ± 2 °C and 85% relative humidity for 10 to 15 days, until the whole surface of the petri plate was covered with fungal hyphae. Then, a spore suspension of each of the four test fungi was prepared by washing the surface culture of each fungus with 10 to 15 mL of sterile water. The suspension was then put into a sterile Erlenmeyer flask with sterile water and solid glass beads. The flask was vibrated vigorously to separate the spores and break the spore clumps. A precipitate was obtained when the spore suspension was filtered and centrifuged. The precipitate was then re-suspended in 100 mL of sterile water which yielded approximately 1×10^7 spores/mL. This operation was repeated for each mold fungi used in the test. Equal volumes of the resultant spore suspensions were blended to obtain the final mixed spore suspension. This suspension was then transferred to a 25-mL spray bottle and used as the source of fungal inocula for testing. WPC specimens were sprayed with equal amounts of mixed mold spore suspension and incubated at 28 °C ± 2 °C and 85% RH for 28 days. Following incubation, the mold ratings of specimens were visually rated according to ASTM G21 (ratings of 0 to 4, with 0 indicating no mold growth and 4 indicating heavy mold growth (60% to complete coverage)).

Mechanical properties

Tensile tests were determined by a SUNS CMT5504 universal test machine (Shenzhen, Chain), according to ASTM D638 (2014). Tests were conducted at room temperature with a speed of 2 mm/min. Three-point flexural tests to determine modulus of elasticity (MOE) and modulus of rupture (MOR) were carried out on a SUNS CMT5504 universal test machine according to ASTM D790 (2010). Tests were conducted at room temperature with a speed of 2 mm/min. The unnotched izod impact strength was evaluated following ASTM D256 (2010), using a Zwick/Roell 5113 pendulum impact tester (Zwick/Roell, Germany). All samples were tested with at least five specimens per composite.

RESULTS AND DISCUSSION

Chemical Analysis of WF and BF

Cellulose, hemicellulose, lignin, and ethanol/benzene extractive contents were determined for WF and BF. The two samples were measured in triplicate, and the results are presented in Table 2. As can be seen, WF and BF showed a clear difference in their chemical compositions. The contents of cellulose, hemicellulose, and lignin of WF were

higher than that of the BF, whereas the opposite was found for ethanol/benzene extractives. Chemical compositions of wood species were associated with the interaction and interfacial adhesion between wood and plastic, and then can be expected to affect the performance of the WPC materials (Kim *et al.* 2009; Shebani *et al*. 2009; Bouafif *et al*. 2009; Fabiyi *et al*. 2010).

Table 2. Chemical Composition of the WF and BF

Components (wt. %)	WF	BF
Cellulose	48.82 (1.26)	42.53 (0.56)
Hemicellulose	22.79 (0.29)	21.24 (1.71)
Lignin	24.90 (0.87)	22.75 (1.04)
Ethanol/benzene extractives	2.44 (0.58)	5.22 (0.26)
Others	1.05 (0.24)	8.26 (0.86)

Effects of Fungicides on Mold Resistance

Mold resistance of WF/HDPE composites

Table 3 and Fig. 1 illustrate the mold colonization of untreated and treated WF/HDPE composites after incubation for 28 days. There were obvious differences in the mold resistance ratings for untreated and treated WF/HDPE samples. WF/HDPE composites treated with ZB, DCOIT, ZPT, and MBC were more resistant to the mold fungi attack than untreated samples. After 28 days of incubation, the untreated WF/HDPE samples were covered seriously by the four common mold fungi tested, and they were rated 4. However, treated WF/HDPE composites presented an excellent resistance to the mold fungi, mold coverage decreased greatly, and the visual ratings were 1 or 0. In addition, greater protection of WPC could be achieved with an increase in concentration of fungicides, which is consistent with previous studies (Klyosov 2007; Lu *et al*. 2008; Ashori *et al*. 2013).

With concentrations of ZB at 1.5%, 2%, and 5% and of MBC at 1% and 2%, mold colonization could be completely prevented; the mold ratings of these treated samples were all 0 after 28 days of exposure. The mold resistance results of ZB-treated samples agreed with those reported by Klyosov (2007) and Feng *et al*. (2014), but differed from the results of Kartal *et al*. (2013), who stated that 0.6% ZB has no inhibitory effect on mold growth for any of the wood/PP or bamboo/PP specimens. The fungicides DCOIT and ZPT provided an efficient protection against mold fungi. No mold growth or coverage (rating of 0) was observed for all DCOIT- and ZPT-treated samples, regardless of the fungicide concentration. This clearly indicated that the addition of all four fungicides can remarkably improve the mold resistance and prevent mold growth effectively for WF/HDPE composites.

It was reported that the biological durability of WPC was closely correlated with types and content of used fungicide materials. Weight loss caused by *C. versicolor* on WPC samples treated by IPBC was slightly lower than the samples treated by TBZ. With increasing of the fungicide content, there was a significant reduction of weight losses (Ashori *et al*. 2013). The effectiveness of fungicides was dependent on their mechanisms of action, active ingredient, and anti-fungal performance (Klyosov 2007).

Table 3. Average Visual Ratings of WF/HDPE Composites after Exposure to Mold Fungi

WPC composites	Fungicides		Mold ratings			
	Type	Concentration (wt. %)	0 d	7 d	14 d	28 d
WF/HDPE	-	0	0	1(0.00)	1.5(0.58)	4(0.00)
WF/HDPE	ZB	1	0	0	0.75(0.50)	1(0.00)
		1.5	0	0	0	0
		2	0	0	0	0
		5	0	0	0	0
WF/HDPE	DCOIT	0.05	0	0	0	0
		0.1	0	0	0	0
		0.2	0	0	0	0
		0.5	0	0	0	0
WF/HDPE	ZPT	0.5	0	0	0	0
		1	0	0	0	0
		2	0	0	0	0
		5	0	0	0	0
WF/HDPE	MBC	0.3	0	0	0.75(0.50)	1(0.00)
		0.5	0	0	0	1(0.00)
		1	0	0	0	0
		2	0	0	0	0

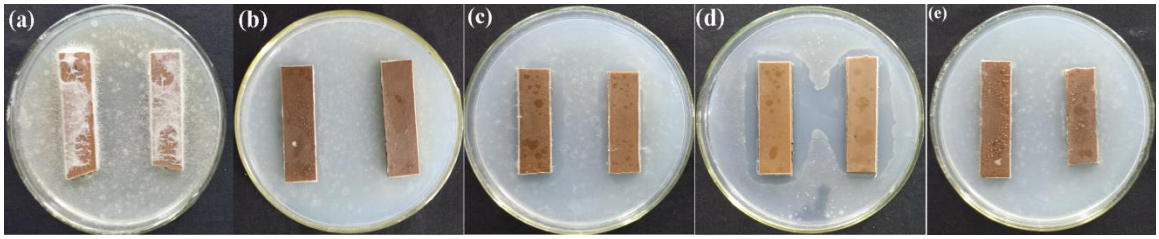

Fig. 1. Photos of petri dishes of WF/HDPE composites after 28 days of incubation with mold fungi: (a) untreated WF/HDPE composite; (b) 1% ZB-treated WF/HDPE composite; (c) 0.05% DCOIT-treated WF/HDPE composite; (d) 0.5% ZPT-treated WF/HDPE composite; and (e) 0.3% MBC-treated WF/HDPE composite

Mold resistance of BF/HDPE composites

Mold growth and ratings of the untreated and treated BF/HDPE specimens after 28 days of incubation with mold fungi are summarized in Table 4 and Fig. 2. As shown, untreated BF/HDPE samples were most susceptible to mold, and specimens were seriously or completely covered by mold fungi and rated 2, 4, and 4 after 7, 14, and 28 days of incubation, respectively. Conversely, BF/HDPE composites treated with ZB, DCOIT, and ZPT fungicides at high concentration showed higher mold resistances, and mold growth and coverage on their surfaces were decreased greatly. However, no inhibitory effect on

mold growth was found for MBC-treated BF/HDPE samples, and the surfaces were almost completely covered by mold spores and mycelium after 28 days of exposure.

After 28 days of incubation, the mold resistance of ZB-treated BF/HDPE composites did not change noticeably when ZB concentration was 1% or 1.5% (visual ratings of 3 and 2, respectively). However, with increasing ZB content from 2% to 5%, the mold resistance greatly improved, with both rated 0. DCOIT-treated specimens performed similar to ZB-treated BF/HDPE composites regarding mold resistance. DCOIT, at a high concentration, provided an effective protection from mold attack. The 0.5% DCOIT-treated BF/HDPE composites had a better resistance to mold (ratings of 1) after exposure to mold for 28 days, while 0.05% DCOIT-treated samples were not obviously different from the untreated control regarding mold resistance. The incorporation of ZPT in BF/HDPE composites also provided a high level of protection against mold fungi. No difference in mold resistance was observed between the ZPT-treated BF/HDPE composites when the concentration of ZPT increased from 0.5% to 5%, and all the visual ratings of mold growth were 1 after 28 days of incubation. The addition of MBC, however, different from the three other fungicides, did not enhance the mold resistance of BF/HDPE composites. No inhibitory effect on mold growth was seen for any of the MBC-treated BF/HDPE composites. All specimens were rated 4 after 28 days of exposure, either at a high (2%) or low (0.3%) concentration of MBC. The results showed that MBC, a traditional biocide, could not be effectively used as a preservative for BF/HDPE composites.

Compared to the WF/HDPE composites, both samples untreated or treated by the same type and level of fungicides used, BF/HDPE samples were shown to be more susceptible to mold fungi. This result indicated that there was an important correlation between the fungi resistance and wood filler species. Different carbohydrates and nitrogen contents, as well as other chemical components exist in various wood species, which will result in a passive or negative effect on the susceptibility and resistance to fungi (Theander *et al*. 1993; Xu *et al*. 2015). Fabiyi *et al*. (2011) investigated the durability of white rot for different PE-based WPC made by poplar, Douglas-fir, black locust, white oak, and ponderosa pine, which demonstrated that poplar and Douglas-fir were more suitable for fungal attack, while black locust showed the highest resistance to *G. trabeum*. Lomeli-Ramirez *et al*. (2009) indicated that PP-based WPC containing either maple or oak were more susceptible to fungal attack than those containing pine. Xu *et al*. (2015) stated that the PVC-based WPC containing *C. lanceolata* and *M. leucadendra* had the best resistance to mold attack.

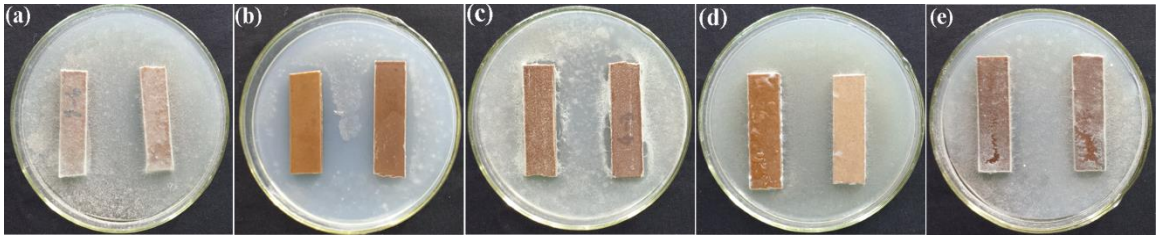

Fig. 2. Photos of Petri dishes of BF/HDPE composites after 28 days of incubation with mold fungi: (a) untreated BF/HDPE composites; (b) 5% ZB-treated BF/HDPE composites; (c) 0.5% DCOIT-treated BF/HDPE composites; (d) 5% ZPT-treated BF/HDPE composites; and (e) 2% MBC-treated BF/HDPE composites

Table 4. Average Visual Ratings of BF/HDPE Composites after Exposure to Mold Fungi

WPC composites	Fungicides		Mold ratings			
	Type	Concentration (wt. %)	0 d	7 d	14 d	28 d
BF/HDPE	-	0	0	2(0.00)	3.5(0.58)	4(0.00)
BF/HDPE	ZB	1	0	0	1(0.00)	3(0.00)
		1.5	0	0	1(0.00)	2(0.00)
		2	0	0	0	0
		5	0	0	0	0
BF/HDPE	DCOIT	0.05	0	0	2(0.00)	4(0.00)
		0.1	0	0	2(0.00)	2(0.00)
		0.2	0	0	2(0.00)	2(0.00)
		0.5	0	0	1(0.00)	1(0.00)
BF/HDPE	ZPT	0.5	0	0	1(0.00)	1(0.00)
		1	0	0	1(0.00)	1(0.00)
		2	0	0	1(0.00)	1(0.00)
		5	0	0	0	1(0.00)
BF/HDPE	MBC	0.3	0	1(0.00)	3(0.00)	4(0.00)
		0.5	0	1(0.00)	3(0.00)	4(0.00)
		1	0	1(0.00)	2(0.00)	4(0.00)
		2	0	1(0.00)	2(0.00)	4(0.00)

Effect of Fungicides on Mechanical Properties

Tensile strength

Figure 3 shows the effect of fungicides ZB, DCOIT, ZPT, and MBC on tensile strengths of untreated and treated WF/HDPE and BF/HDPE composites. As can be seen, the tensile strengths of all the four fungicides treated WF/HDPE composites were lower than that of the control (untreated WF/HDPE composites) (Fig. 3(a)); this indicated weak interaction between the wood and HDPE matrix. It was reported that the strength of wood plastic composites depend on the properties of constituents and the interface interactions (Ashori and Nourbakhsh 2011). When comparing the tensile properties of all fungicides used, ZB-treated samples showed the lowest tensile strength, while DCOIT- and ZPT-treated samples tended to have higher tensile strength value than the other samples. A possible reason proposed for this kind of behavior may involve the difference between the thermal, physical properties as well as the deformation mechanisms of the fungicides used (Kositchaiyong *et al.* 2014b). Moreover, for each of the four fungicides-treated WF/HDPE samples, the highest tensile strength were observed at 2% ZB, 0.1% DCOIT, 1% or 2% ZPT, and 0.3% or 0.5% MBC, respectively.

On the contrary, the BF/HDPE composites treated with fungicides showed higher tensile strength than that of the control sample (untreated BF/HDPE composites) (Fig. 3(b)). The explanation for these phenomena was related to the findings of Kositchaiyong *et al*. (2013, 2014a), which demonstrated that the addition of fungicide to WPC composites enhanced the hydrophobicity and molecular interaction between polar components such as

wood and non-polar polymer matrix in the composites. The tensile strength of BF/HDPE samples changed with the content of fungicides used, when the concentration of ZB was 2%, DCOIT was 0.5%, ZPT was 0.5%, and MBC was 0.3%, the BF/HDPE samples exhibited the highest tensile strength, respectively.

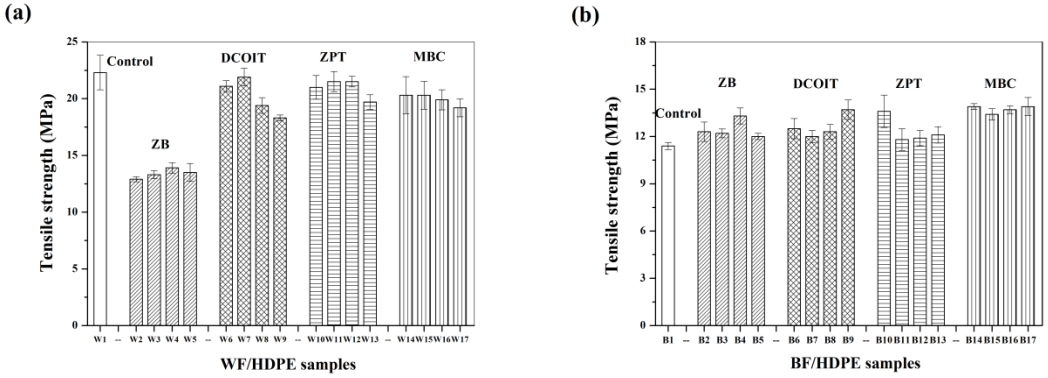

Fig. 3. Effect of fungicides ZB, DCOIT, ZPT, and MBC on tensile strengths of (a) WF/HDPE and (b) BF/HDPE composites

MOR

The MOR of untreated and treated WF/HDPE and BF/HDPE composites are shown in Fig. 4. As can be seen from Fig. 4(a), except for the 1% ZPT-treated samples, WF/HDPE samples treated with fungicides showed a decrease in MOR in comparison with the control sample. The decreased flexural properties of WF/HDPE composites may be the result of the deterioration of the interfacial adhesion and compatibility between the wood flour and polymer matrix. As expected, this caused a reduction in MOR of composites (Pilarski and Matuana, 2005; Behzad *et al.* 2012; Hamzeh *et al.* 2012; Ashori *et al*. 2013). As for the effect of fungicide addition, the ZB-treated WF/HDPE samples showed the lowest MOR than those of DCOIT-, ZPT-, and MBC-treated samples. In addition, the highest MOR of treated WF/HDPE composites was found at the content of 2% for ZB, 0.1% for DCOIT, 1% for ZPT, and 0.5% for MBC, respectively.

Types of fungicides added into the BF/HDPE composites, however, showed a different effect on the MOR. For ZB-treated BF/HDPE composites, the MOR was lower than that of the control, while DCOIT-, ZPT-, and MBC-treated BF/HDPE samples showed a slightly higher MOR in comparison with the control. Thermal and physical properties of the fungicides used, as well as the deformation mechanisms of the flexural test, may explain this (Kositchaiyong *et al.* 2014b). Moreover, wood species can also affect the mechanical properties of WPC composites due to their different chemical constituents (Kim *et al*. 2009; Shebani *et al*. 2009). BF/HDPE composites, because of lower cellulose, hemicellulose, and lignin content of BF than WF, showed a poor interfacial adhesion than WF/HDPE composites. The added fungicides (DCOIT, ZPT, and MBC) increased the MOR of BF/HDPE composites, which may relate to the fact that the fungicides would enhance the compatibility between wood and polymer matrix by reducing the gaps between wood and HDPE (Lu *et al.* 2008; Kositchaiyong *et al*. 2013, 2014a). However, no great difference was found in MOR between the control and the four fungicides-treated BF/HDPE samples. For BF/HDPE samples, the highest MOR were observed at 2% content of ZB, 0.2% of DCOIT, 2% of ZPT, and 0.3% of MBC, respectively.

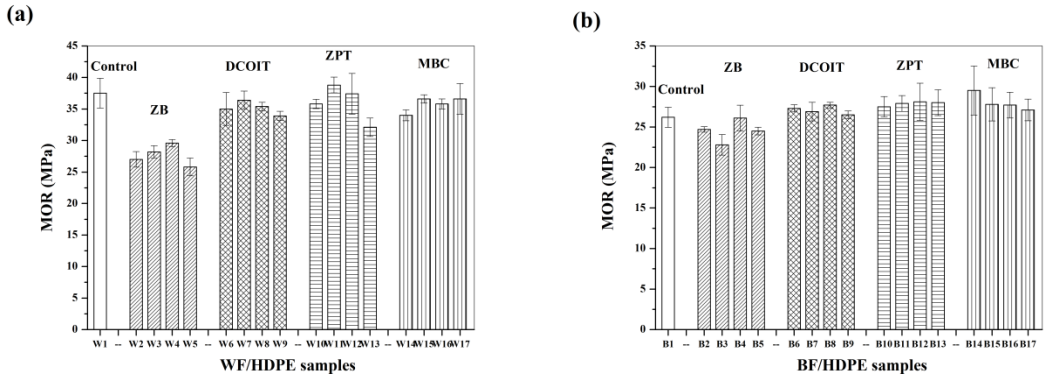

Fig. 4. Effect of fungicides ZB, DCOIT, ZPT, and MBC on MOR of (a) WF/HDPE and (b) BF/HDPE composites

MOE

The results for the MOE evaluation of treated and untreated WF/HDPE and BF/HDPE composites are presented in Fig. 5(a) and 5(b), respectively. As shown, the MOE of ZB-treated WF/HDPE specimens was slightly lower than that of the control at 1% and 1.5% concentration of ZB, but it increased and was higher than the control when content of ZB was increased to 2% and 5%. For DCOIT-treated WF/HDPE samples, however, all samples showed a lower MOE in comparison with the control sample. The MOE of ZPT-treated WF/HDPE samples were higher than that of the control when the content of ZPT ranged between 0.5% and 2%. However, 5% ZPT-treated WF/HDPE samples showed lower MOE in comparison with the control. The MOE of MBC-treated WF/HDPE samples increased with increasing content of MBC. Samples treated with MBC at 0.3% and 0.5% content showed a reduction in MOE, while 2% MBC obviously increased the MOE of treated samples. The highest MOE of treated WF/HDPE composites was found at the content of 2% for ZB, 0.1% for DCOIT, 1% or 2% for ZPT, and 2% for MBC, respectively. Irregular change of MOE may be explained by the different chemical structure and chemical interfering mechanism of fungicides used, which could interfere with the interaction and compatibility between the wood and plastic matrix, and subsequently affect the mechanical properties of WPC materials (Kositchaiyong *et al.* 2014b).

It can be observed from Fig. 5(b) that the treated-BF/HDPE samples showed an increase in MOE in comparison with the control, except for the samples treated with 1 % ZB. This result also suggested that the added fungicides would increase the compatibility and molecular interaction between polar wood and non-polar polymer matrix in the composites (Kositchaiyong *et al*. 2013, 2014a). The variations of MOE for ZB- and ZPT-treated BF/HDPE samples exhibited similar tendency; both of them were increased with increasing content of the fungicides used, and therefore the 5% ZB- and 5% ZPT-treated samples exhibited the highest MOE, respectively. The MOE for DCOIT- and MBC-treated samples, however, were randomly changed; the highest MOE were discovered at the concentration of 0.2 % for DCOIT and 0.3% for MBC, respectively.

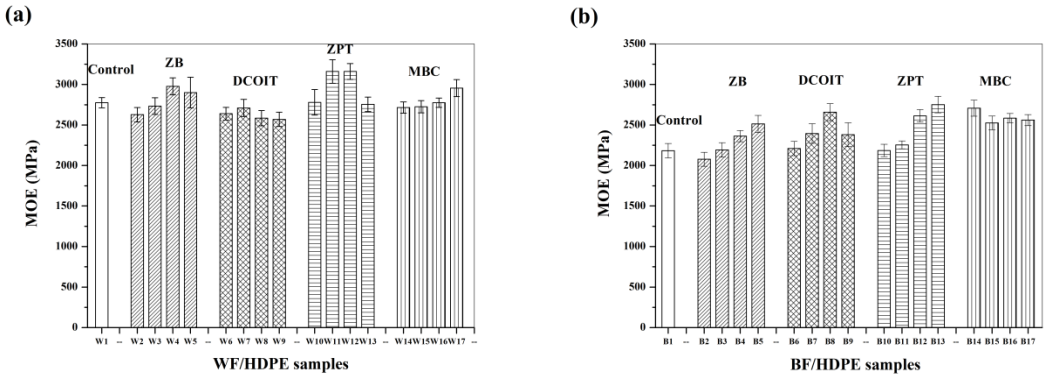

Fig. 5. Effect of fungicides ZB, DCOIT, ZPT, and MBC on MOE of (a) WF/HDPE and (b) BF/HDPE composites

Impact strength

Figure 6 illustrates the results of the impact strengths of WF/HDPE and BF/HDPE composite specimens treated and untreated with fungicides. Figure 6(a) indicated that there were significant differences for impact strengths among the treated and untreated WF/HDPE specimens. The impact strengths of all the four fungicides-treated WF/HDPE composites were higher than that of the control. The possible reason for this phenomenon might involve the better interfacial adhesion between the matrix and/or wood flour with the used fungicide agents. Hamzeh *et al*. (2012) reported that fungicide agents play an important role in determining the crack initiation process by affecting the interaction between the lignocellulosic materials and the coupling agent. As a result, the mechanical properties of panels were, in general, significantly influenced by the addition of fungicide (Behzad *et al*. 2012). When comparing the impact strengths of all fungicides used, MBC-treated samples showed the highest impact strength value than the other fungicides-treated samples. It is also noted that the impact strength of ZB-treated samples was lowered slightly with the increasing content of ZB. The impact strength of ZPT-treated specimens, however, increased with increasing concentration of ZPT. The impact strength of MBC-treated WF/HDPE composites were also increased with increasing MBC content when MBC concentration ranged from 0.3% to 1%, while DCOIT-treated samples changed irregularly. For WF/HDPE samples, the highest impact strengths for each fungicide treated samples were observed at 1% ZB, 0.2% DCOIT, 5% ZPT, and 1% MBC, respectively.

As can be derived from Fig. 6(b), the impact strength of ZB-treated BF/HDPE composites decreased with increasing ZB content. The ZB-treated BF/HDPE composites at 1% and 1.5% levels showed higher impact strength than that of the control, while impact strength greatly decreased and was lower than that of the control when the ZB concentration was increased to 2% and 5%. For DCOIT-treated BF/HDPE composites, the impact strength was lower than that of the control, except the 0.5% DCOIT-treated samples. The impact strength of ZPT-treated BF/HDPE composites, similar with that of ZB-treated samples, also decreased with increasing ZPT content, and all treated samples showed lower impact strength than that of the control. MBC-treated BF/HDPE samples, however, showed a greater increase in impact strength than that of the control at low MBC concentration (0.3% and 0.5%), while no great difference was observed at high MBC concentration (1% and 2%). The highest MOE strength of treated BF/HDPE composites was found at the content of 1% for ZB, 0.5% for DCOIT, 0.5% for ZPT, and 0.5 % for MBC, respectively.

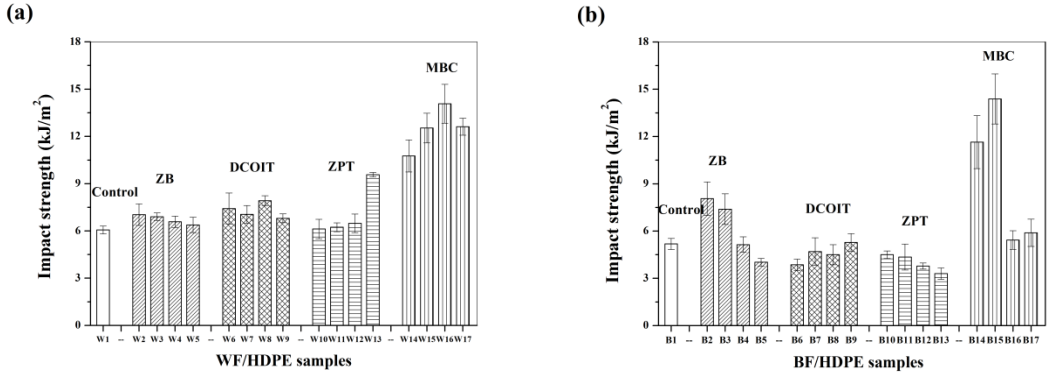

Fig. 6. Effect of fungicides ZB, DCOIT, ZPT, and MBC on impact strengths of (a) WF/HDPE and (b) BF/HDPE composites

Significant differences were found in the mechanical properties between the WF/HDPE and BF/HDPE samples. The tensile strength, MOE, and MOR of WF/HDPE samples were higher than that of the BF/HDPE composites, both for untreated and treated samples. The differences in mechanical properties between WF/HDPE and BF/HDPE composites could be explained by the different chemical composition of WF and BF, which associated with the interaction and interfacial adhesion between wood and plastic (Bouafif *et al*. 2009; Kim *et al.* 2009; Fabiyi *et al*. 2010). WF composites, because of the higher cellulose, hemicellulose, and lignin contents of WF than that of the BF, showed better mechanical properties than the BF composites. Bledzki and Gassan (1998, 1999) reported that an increase in the composite's strength can be ascribed to higher cellulose and lignin contents, as well as better dispersion and adhesion to the matrix. Shebani *et al*. (2009) investigated the properties of WPCs made with different wood species. Acacia composite showed the higher tensile strength than that in the eucalyptus, pine, and oak composites, due to their higher cellulose content which could be lead to a strong interfacial adhesion between LLDPE and acacia particles. The MOE of acacia and oak composites was higher than for the other two WPCs, this difference can again be related to the difference in cellulose content.

Impact strength, however, varied significantly with fiber type and fungicides used. WF/HDPE composites exhibited higher impact strength than that of the BF/HDPE for untreated and most of the treated samples, except the samples treated by ZB and MBC with low concentration (1% and 1.5% for ZB and 0.3% and 0.5% for MBC). This probably can be attributed to the addition of fungicides with low concentration, which could be reduce the gaps between wood and HDPE, thus improving the interfacial adhesion and then enhancing the mechanical properties of WPC (Lu *et al*. 2008; Hamzeh *et al*. 2012; Kositchaiyong *et al*. 2013, 2014a).

For good mold resistance and mechanical properties of WPC, an optimum bonding level for fungicides is necessary. According to the aforementioned, for WF/HDPE composites, a better balance between mechanical properties and mold fungi resistance can be achieved at the concentration of 1.5% or 2% for ZB, 0.1% or 0.2% for DCOIT, 1% or 2% for ZPT, and 0.5% or 1% for MBC, respectively. For BF/HDPE samples, the incorporation of ZB at the content level of 1.5% or 2%, DCOIT at 0.2% or 0.5%, and ZPT at 1% or 2% was more appropriate. However, as mentioned above, because no inhibitory effect on mold growth was achieved for MBC-treated BF/HDPE composites, it may be meaningless to discuss the incorporation of MBC in BF/HDPE samples.

CONCLUSIONS

1. Incorporation of all four fungicides into WF/HDPE composites greatly improved the mold resistance, and greater protection could be achieved with increasing concentration of fungicides. Bamboo/HDPE composites treated with ZB, DCOIT, and ZPT fungicides showed a better mold resistance than the untreated samples, while no inhibitory effect on mold growth was observed for MBC-treated BF/HDPE composites.
2. In most cases, regardless of the type of fungicide, incorporation of fungicides into WF/HDPE composites lowered the tensile strength and MOR but increased the impact strength of WF/HDPE samples. For BF/HDPE composites, fungicide incorporation had a positive effect on tensile strength and MOE. However, changes in the MOE strength of WF/HDPE samples and MOR and impact strength of BF/HDPE composites were related to the type of fungicide agent.
3. For WF/HDPE composites, the mold fungi resistance and mechanical properties were well balanced at concentrations of 1.5% to 2% of ZB, 0.1% to 0.2% of DCOIT, 1% to 2% of ZPT, and 0.5% to 1% of MBC, separately. However, the incorporation of 1.5% to 2% of ZB, 0.2% to 0.5% of DCOIT, and 1% to 2% of ZPT, separately, was more appropriate for BF/HDPE composites.

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REFERENCES CITED

Ashori, A., Behzad, H. M., and Tarmian, A. (2013). "Effects of chemical preservative treatments on durability of wood flour/HDPE composites," *Composites Part B: Engineering* 47, 308-313. DOI: 10.1016/j.compositesb.2012.11.022

Ashori, A., and Nourbakhsh, A. (2011). "Preparation and characterization of polypropylene/wood flour/nanoclay composites," *European Journal of Wood and Wood Products* 69(4), 663-666. DOI: 10.1007/s00107-010-0488-9

ASTM D790. (2010). "Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials," ASTM International, West Conshohocken, PA.

ASTM D256. (2010). "Standard test methods for determining the izod pendulum impact resistance of plastics," ASTM International, West Conshohocken, PA.

ASTM D638. (2014). "Standard test method for tensile properties of plastics," ASTM International, West Conshohocken, PA.

ASTM G21. (2013). "Standard practice for determining resistance of synthetic polymeric materials to fungi," ASTM International, West Conshohocken, PA.

Behzad, H. M., Ashori, A., Tarmian, A., and Tajvidi, M. (2012). "Impacts of wood preservative treatments on some physico-mechanical properties of wood flour/high

density polyethylene composites," *Construction and Building Materials* 35, 246-250. DOI: 10.1016/j.conbuildmat.2012.04.007

Bledzki, A. K., and Gassan, J. (1999). "Composites reinforced with cellulose based fibers," *Progress in Polymer Science* 24(2), 221-274.

Bledzki, A. K., Gassan, J., and Theis, S. (1998). "Wood-filled thermoplastic composites," *Mechanics of Composite Materials* 34(6), 563-568.

Bouafif, H., Koubaa A., Perré, P., and Cloutier, A. (2009). "Effects of fiber characteristics on the physical and mechanical properties of wood plastic composites," *Composites Part A: Applied Science and Manufacturing* 40(12), 1975-1981. DOI:10.1016/j.compositesa.2009.06.003

Chinese Standard. GB/T 2677.6. (1994). "Fibrous raw material-Determination of solvent extractives," China Standards Press, Beijing.

Chinese Standard. GB/T 2677.8. (1994). "Fibrous raw material-Determination of acid-insoluble lignin," China Standards Press, Beijing.

Chinese Standard. GB/T 2677.10. (1995). "Fibrous raw material-Determination of holocellulose," China Standards Press, Beijing.

Chow, P., Nakayama, F. S., Youngquist, J. A., Muehl, J. H., and Krzysik, A. M. (2002). "Durability of wood/plastic composites made from Parthenium species," in: *33rd Annual Meeting of the International Research Group on Wood Preservation,* May 14-17, Cardiff, Wales, pp. 2-11.

Clemons, C. M., and Ibach, R. E. (2002). "Laboratory tests on fungal resistance of wood filled polyethylene composites," in: *ANTEC 2002 Annual Technical Conference*, May 5-9, San Francisco, CA, pp. 2219-2222.

Fabiyi, J. S., and McDonald, A. G. (2010). "Effect of wood species on property and weathering performance of wood plastic composites," *Composites Part A: Applied Science and Manufacturing* 41(10), 1434-1440. DOI: 10.1016/j.compositesa.2010.06.004

Fabiyi, J. S., McDonald, A. G., Morrell, J. J., and Freitag, C. (2011). "Effects of wood species on durability and chemical changes of fungal decayed wood plastic composites," *Composites Part A: Applied Science and Manufacturing* 42(5), 501-510. DOI: 10.1016/j.compositesa.2011.01.009

Feng, J., Shi, Q. S., Chen, Y. B., and Huang, X. M. (2014). "Mold resistance and water absorption of wood/HDPE and bamboo/HDPE composites," *Journal of Applied Sciences* 14(8), 776-783. DOI: 10.3923/jas.2014.776.783

Gardner, D. J., Tascioglu, C., and Wålinder, M. E. P. (2003). "Wood composite protection," in: *Wood Deterioration and Preservation*, B. Goodell, D. D. Nicholas, and T. P. Schultz (eds.), American Chemical Society, Washington, DC, pp. 399-419. DOI: 10.1021/bk-2003-0845.ch025

Hamzeh, Y., Ashori, A., Marvast, E. H., Rashedi, K., and Olfat, A. M. (2012). "A comparative study on the effects of *Coriolus versicolor* on properties of HDPE/wood flour/paper sludge composites," *Composites Part B: Engineering* 43(5), 2409-2414. DOI: 10.1016/j.compositesb.2011.11.043

H'ng, P. S., Lee, A. N., Hang, C. M., and Lee, S. H. (2011). "Biological durability of injection moulded wood plastic composite boards," *Journal of Applied Sciences* 11(2), 384-388. DOI: 10.3923/jas.2011.384.388

Ibach, R. E., and Clemons, C. M. (2002). "Biological resistance of polyethylene composites made with chemically modified fiber or flour," in: *Proceedings of Sixth*

Pacific-rim Bio-based Composites Symposium, November 10-13, Portland, OR, pp. 574-583.

Kartal, S. N., Aysal, S., Terzi, E., Yılgör, N., Yoshimura, T., and Tsunoda, K. (2013). "Wood and bamboo-PP composites: Fungal and termite resistance, water absorption, and FT-IR analyses," *BioResources* 8(1), 1222-1244. DOI: 10.15376/biores.8.1.1222-1244

Kim, J. W., Harper, D. P., and Taylor, A. M. (2009). "Effect of wood species on the mechanical and thermal properties of wood–plastic composites," *Journal of Applied Polymer Science* 112(3), 1378-1385. DOI: 10.1002/app.29522

Klyosov, A. A. (2007). *Wood-Plastic Composites,* John Wiley and Sons, Hoboken, NJ. DOI: 10.1002/9780470165935

Kositchaiyong, A., Rosarpitak, V., Prapagdee, B., and Sombatsompop, N. (2013). "Molecular characterizations, mechanical properties and anti-algal activities for PVC and wood/PVC composites containing urea- and triazine-based algaecides," *Composites Part B-Engineering* 53, 25-35. DOI: 10.1016/j.compositesb.2013.04.036

Kositchaiyong, A., Rosarpitak, V., Hamada, H., and Sombatsompop, N. (2014a). "Anti-fungal performance and mechanical-morphological properties of PVC and wood/PVC composites under UV-weathering aging and soil-burial exposure," *International Biodeterioration and Biodegradation* 91, 128-137. DOI: 10.1016/j.ibiod.2014.01.022

Kositchaiyong, A., Rosarpitak, V., and Sombatsompop, N. (2014b). "Antifungal properties and material characteristics of PVC and wood/PVC composites doped with carbamate-based fungicides," *Polymer Engineering and Science* 54(6), 1248-1259. DOI: 10.1002/pen.23672

Laks, V. K., Verhey, S., and Richter, D. (2005). "Effect of manufacturing variables on mold susceptibility of wood-plastic composites," in: *Proceedings of the Eighth International Conference on Woodfiber-plastic Composites*, May 23-25, Madison, WI, pp. 265-270.

Lomeli-Ramirez, M. G., Ochoa-Ruiza, H. G., Fuentes-Talavera, F. J., Garcia-Enriquez, S., Cerpa-Gallegos, M. A., and Silva-Guzman, J. A. (2009). "Evaluation of accelerated decay of wood plastic composites by Xylophagus fungi," *International Biodeterioration and Biodegradation* 63(8), 1030-1035. DOC:10.1016/j.ibiod.2009.08.002

Lu, J. Z., Duan, X. F., Wu, Q. L., and Lian, K. (2008). "Chelating efficiency and thermal, mechanical and decay resistance performances of chitosan copper complex in wood–polymer composites," *Bioresource Technology* 99(13), 5906-5914. DOI:10.1016/j.biortech.2007.09.086

Morris, P. I., and Cooper, P. (1998). "Recycled plastic/wood composite lumber attacked by fungi," *Forest Products Journal* 48(1), 86-88.

Morrell, J. J., Stark, N. M., Pendleton, D. E., and McDonald, A. G. (2002). "Durability of wood-plastic composites," in: *10th International Conference on Wood and Biofiber Plastic Composites and Cellulose Nanocomposites Symposium*, May 11-13, Madison, WI, pp. 71-75.

Naumann, A., Stephan, I., and Noll, M. (2012). "Material resistance of weathered wood-plastic composites against fungal decay," *International Biodeterioration and Biodegradation* 75, 28-35. DOI: 10.1016/j.ibiod.2012.08.004

Pendleton, D. E., Hoffard, T. A., Adcock, T., Woodward, B., and Wolcott M. P. (2002). "Durability of an extruded HDPE/wood composite," *Forest Products Journal* 52(6), 21-27.

Pilarski, J. M., and Matuana, L. M. (2005). "Durability of wood flour-plastic composites exposed to accelerated freeze-thaw cycling. Part I. Rigid PVC matrix," *Journal of Vinyl and Additive Technology* 11(1), 1-8. DOI: 10.1002/vnl.20029

Schirp, A., and Wolcott, M. P. (2005). "Influence of fungal decay and moisture absorption on mechanical properties of extruded wood-plastic composites," *Wood and Fiber Science* 37(4), 643-652.

Schirp, A., and Wolcott, M. P. (2006). "Fungal degradation of wood-plastic composites and evaluation using dynamic mechanical analysis," *Journal of Applied Polymer Science* 99(6), 3138-3146. DOI: 10.1002/app.22945

Shebani, A. N., Van Reenen, A. J., and Meincken, M. (2009). "The effect of wood species on the mechanical and thermal properties of wood-LLDPE composites," *Journal of Composite Materials* 43(11), 1305-1318. DOI: 10.1177/0021998308104548

Theander, O., Bjurman, J., and Boutelje, J. B. (1993). "Increase in the content of low-molecular weight carbohydrates at lumber surface during drying and correlation with nitrogen content, yellowing, and mould growth," *Wood Science and Technology* 27(5), 381-389.

Verhey, S. A., Laks, P. E., and Richter, D. (2001). "Laboratory decay resistance of woodfiber/thermoplastic composites," *Forest Products Journal* 51(9), 44-49.

Verhey, S. A., and Laks, P. E. (2002a). "Fungal resistance of wood fiber/thermoplastic composites," in: *Enhancing the Durability of Engineered Wood Products*, Forest Products Society, Madison, WI, pp. 179-189.

Verhey, S. A., and Laks, P. E. (2002b). "Wood particle size affects the decay resistance of wood fiber/thermoplastic composites," *Forest Products Journal* 52(11/12), 78-81.

Wei, L., McDonald, A. G., Freitag, C., and Morrell, J. J. (2013). "Effects of wood fiber esterification on properties, weatherability and biodurability of wood plastic composites," *Polymer Degradation and Stability* 98(7), 1348-1361. DOI: 10.1016/j.polymdegradstab.2013.03.027

Wright, P. J., and Wallis, A. F. A. (1998). "Rapid determination of cellulose in plantation eucalypt woods to predict kraft pulp yields," *Tappi Journal* 81(2), 126-130.

Wu, Q., Lee, S., and Jones, J. P. (2003). "Decay and mold resistance of borate modified oriented strandboard," in: *Proceedings of the 34th Annual Conference for the International Research Group on Wood Preservation*, May 18-23, Brisbane, Australia, pp. 1-13.

Xu, K. M., Feng, J., Zhong, T. H., Zheng, Z. F., Chen, T. A. (2015). "Effects of volatile chemical components of wood species on mould growth susceptibility and termite attack resistance of wood plastic composites," *International Biodeterioration and Biodegradation* 100, 106-115. DOI: 10.1016/j.ibiod.2015.02.002

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