Combined Effect of Zinc Borate and Coupling Agent against Brown and White Rot Fungi in Wood-Plastic Composites

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Fungal resistance was investigated for wood-plastic composites (WPCs) containing zinc borate, maleic anhydride grafted polyethylene (MAPE) as a coupling agent, wood fiber (*Pinus sylvestris*), and high-density polyethylene (HDPE). Decay resistance, water absorption, and surface hardness (Shore D) of the WPCs were tested. The reinforced wood-plastic composites were exposed to brown-rot fungus (*Coniophora puteana*, *Postia placenta*) and white-rot fungus (*Trametes versicolor)* in agar tests. The results showed that zinc borate improved the decay resistance of the WPCs against brown and white rot fungus according to their weight losses. Moreover, the water absorption and surface hardness tests indicated that the physical properties of the composites were weakened after fungal decay tests. The usage of MAPE and zinc borate alone or together was effective against both rot fungus species in WPCs. The synergy of 1% zinc borate and 3% MAPE in WPCs could considerably increase the fungal attack resistance. Scanning electron microscopy (SEM) revealed that both brown and white rot fungus attacked the surface of WPCs samples without both MAPE and zinc borate.

Keywords: Composite; Decay resistance; Rot fungus; Zinc borate; Coupling agent; Combined effect

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INTRODUCTION

Applications for wood-plastic composites are gaining attention due to their low resin costs, dimensional stability, and improved stiffness. Lignocellulosic material as a filler for wood-plastic composites (WPCs) is easily available and less expensive than other fillers. Composites reinforced with lignocellulosic waste can reduce the use of plastics (Najafi *et al.* 2006; Hosseinihashemi *et al.* 2011; Ozdemir *et al.* 2014). WPCs have many advantages; however, there are some disadvantages to consider when using lignocellulosic fibers as filler. Because these materials have a low bulk density, low thermal stability, and high tendency to absorb moisture; accordingly they are susceptible to fungal attack (Clemons 2002). Although plastics are normally resistant to fungal decay, a major concern with WPCs material is that the use of lignocellulosic filler makes the composite vulnerable to biological degradation (Mankowski and Morrell 2000). It is important to provide resistance against to fungus and fire in outdoor applications of WPCs (Turku *et al.* 2014). Earlier investigations assumed that the lignocellulosic filler in WPCs was encapsulated by plastic matrix (Naghipour 1997; Morris and Cooper 1998; Mankowski and Morrell 2000). However, several studies showed that lignocellulosics could not be completely encapsulated by the plastics (Kord *et al.* 2014). Consequently, it was determined that

lignocellulosic filler used in WPCs is susceptible to moisture and rot fungal attack (Naghipour 1997; Morris and Cooper 1998; Mankowski and Morrell 2000). The useful lifetime of WPCs exposed to moisture is directly related to environmental conditions. Therefore, it is necessary to take several precautions in the production of WPCs (Islam *et al.* 2003). Zinc borate is a low-cost material that has multifunctional properties such as fire retardancy and antifungal activity in WPCs manufacturing. Moreover, it is thermally stable, with a decomposition temperature of about 300 °C (Klyosov 2007). The amount of lignocellulosic material in WPCs cannot exceed a certain amount to maintain compatibility with polymers (Turku *et al.* 2014). Maleic anhydride grafted thermoplastics are very effective compatibilizers for lignocellulosic filler and polymer matrix interfaces in WPCs. They also improve the interfacial adhesion between the filler and matrix. Furthermore, the chemical modification occurs between the grafting matrix polymer and hydrophilic functional groups (Rowell *et al.* 1997; Li and Matuana 2003; Plackett 2004; Yang *et al.* 2007).

Maleic anhydride grafted polyethylene (MAPE) and zinc borate are widely used in WPCs applications to improve mechanical properties and fire retardancy, respectively (Li and Matuana 2003; Plackett 2004; Turku *et al.* 2014). However, the combined effect of MAPE and zinc borate against brown and white rot fungi in WPCs with high lignocellulosic filler content has not sufficiently been investigated. This study investigated the combined effect of zinc borate and MAPE against brown and white rot fungi in WPCs. This study also shows that the zinc borate used in composite samples has an effect against rot fungi. Properties of the produced composite samples, such as weight loss, water absorption, surface hardness (Shore D), and texture (SEM), were studied after exposure to fungal decay.

EXPERIMENTAL

Materials

Wood fibers were prepared from timber wastes (*Pinus sylvestris*), which were milled and separated into 60-mesh fibers by using a sieve. The obtained fibers were dried at 103 °C prior to the manufacturing process. High-density polyethylene (HDPE, density: 0.965 g/cm^3) and polyethylene wax as a lubricating agent were provided by the Petkim Petrochemical Co. (Izmir, Turkey). Maleic anhydride grafted polypropylene (MAPE) as a coupling agent was supplied by Clariant International Co. (Shanghai, China). Zinc borate ($ZnO•2B_2O_3$) as an antifungal agent was obtained from the Eti Mine Works Factory (Balikesir, Turkey).

Methods

The oven-dried fibers, HDPE, zinc borate, and MAPE were prepared according to Table 1 prior to production of the composite materials. The prepared materials were homogeneously mixed with a high-speed mixer (speed range of 5 to 1000 rpm) at 800 rpm for 5 min before the extrusion process. A twin-screw extruder was used to produce the composite samples. The temperature of the extruder barrel was set to 160, 165, 170, and 170 °C at each of the extruder's heating zones. The extruded composite fibers were pelletized and dried at 103 °C until a moisture content of 1 to 2% before the hot pressing process. The obtained pellets were pressed for 10 min at a pressure of 100 bars and a temperature of 180 °C. The test specimens obtained from the composite boards were

conditioned according to the ASTM D-618 (2013) standard.

Table 1. Weight Percentages of Composite Sample Compositions

Sample Codes	Wood Fiber (%)	HDPE (%)	Zinc Borate (%)	MAPE (%)	Polyethylene Wax (%)
B1	50	49	0	0	1
B2	50	48	1	0	1
B3	50	45	1	3	1
B4	60	39	0	0	1
B5	60	38	1	0	1
B6	60	35	1	3	1

Fungal decay and water absorption tests of composites

The assessment of the durability of the composite samples against fungal attack by basidiomycetes was conducted according to modified European standard EN 113 (1996). The laboratory decay test was carried out based on the loss of mass after the samples were exposed to the brown-rot fungi, *Coniophora puteana* (Schumach:, P. Karst) and *Postia placenta* (Lars:, & Lombard), and the white-rot fungus, *Trametes versicolor* (Lloyd), which were provided by the United States Department of Agriculture, Forest Products Laboratory of Madison Field Office. The fungal decay tests were conducted for 16 weeks, and the weight loss values of the composite samples were recorded every 4 weeks. The test used dimensions 25 x 20 x 2 mm, a modification from those recommended in the EN 113 standard. Eight identical samples were prepared from each sample group for each fungal decay experiment. At the end of the fungal decay period, the fungal mycelia were removed from the surface of the samples, and the specimens were dried at 103 °C for 24 h and weighed. The mass loss values were calculated as a percentage of the total mass. The obtained mass loss was divided by the mass loss of the reference samples (B1 and B4), resulting in a ratio referred to as "*x* value", as suggested by the European standard EN 350-1. The relative frequency (%) obtained within the specified classes for 8 identical samples for each composite samples after inoculation with rot fungi.

For the water absorption (WA) tests, the composite samples were immersed in distilled water for 24 h after being exposed to the fungal tests for 0, 4, 8, 12, and 16 weeks. A digital balance with a precision of 0.01 g was used to weigh in the specimens before and after immersing in water. WA was measured and expressed as a percentage for each specimen using the following equation,

$$WA\ (\%) = [(M\text{-}M_0)/M_0] \times 100 \quad (1)$$

where M_0 and M are the weights of the composite samples before and after being immersed in distilled water for 24 h, respectively.

Hardness performance

Hardness tests were performed using a digital durometer (ENPQIX EHS5D, IKKI Co, Bangkok, Thailand). The hardness property of the composite specimens was analyzed according to ASTM D 2240 (Shore-D) method. For each composite group, ten specimens were prepared with dimensions 50 mm x 20 mm x 5 mm.

Scanning electron microscopy (SEM) analysis of decayed composites

The appearance of the composite surface after fungal decay tests was investigated using a JEOL Neo Scope JSM-500 (JEOL Co, Freising, Germany) scanning electron

microscope under an acceleration voltage of 10 kV. The specimens were coated with gold (Cressington Scientific Instruments Co, Watford, England) under vacuum prior to scanning.

Statistical analysis

SPSS 20.0 statistical analysis program was used for the fungal decay and water absorption tests results. The results were subjected to an analysis of variance (ANOVA) at the 95% confidence level, and significant differences between mean values of the samples were determined using Duncan's multiple range test. The significant differences between the samples were shown with letters, such as A, B, C, and D.

RESULTS AND DISCUSSION

Fungal Decay and Water Absorption Test Results

Weight loss and natural durability results of composite samples

Figures 1 through 3 showed that the using 1% zinc borate and 3% MAPE in the composite samples had a combined effect on fungal decay. The coexistence of zinc borate and MAPE in composites containing 60% wood fiber reduced the weight losses by 7, 1, and 1.5% after the composite samples were exposed to *P. placenta, C. puteana*, and *T. versicolor*, respectively, for 16 weeks.

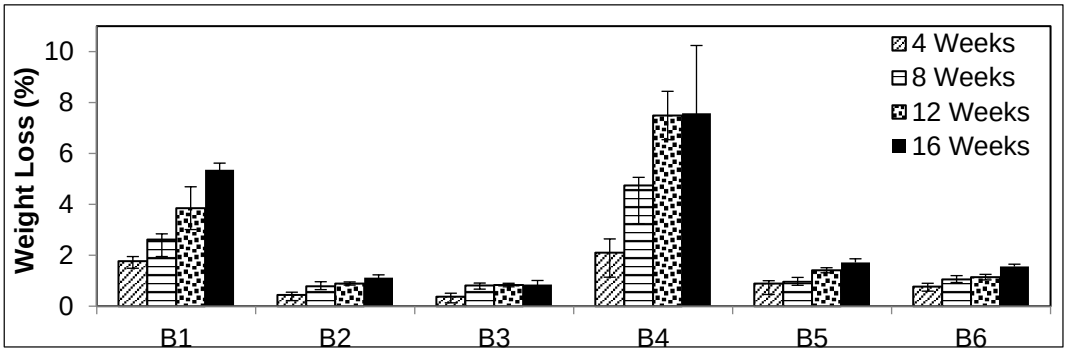

Fig. 1. Weight loss of composite samples exposed to *P. placenta*

There was a significant difference in the weight losses between the composite samples exposed to the brown and white rot fungi. The largest weight loss (8%) occurred in the composite containing 60% wood fiber, which was exposed to *P. placenta* for 16 weeks. The weight losses of the composite samples clearly decreased with the addition of 1% zinc borate. This decrease was more evident in the composite samples containing 60% wood fiber. The results indicate that the weight loss was lower in composites containing both zinc borate and MAPE. The effect of zinc borate was more obvious against brown-rot fungus than white rot fungus. Brown-rot fungus is more aggressive than white-rot fungus in wood composites (Fabiyi *et al.* 2011; Zabel and Morrell 2012). Thus, as the amount of lignocellulosic material increased in the composites exposed to the brown-rot fungus (*C. puteana, P. placenta*) and the white-rot fungus (*T. versicolor),* the weight loss also increased. Table 2 shows the statistical analysis results obtained from weight loss data of the composite samples along with relative frequencies of natural durability classes according to the European standard EN350-1.

Table 2. Homogeneity Groups, Durability Classes, and Relative Frequency of Composite Samples for Different Fungal Incubation Periods

P. placenta		**B1**	**B2**	**B3**	**B4**	**B5**	**B6**
4 Weeks	HG[a]	*EF*[c]	*AB*	*A*	*FG*	*ABCDE*	*ABC*
	x value	Ref.	0.29	0.25	Ref.	0.42	0.37
	Durability class[b]	-	d (63%)[d]	d (75%)	-	md (75%)	md (75%)
8 Weeks	HG	*G*	*ABCD*	*ABCD*	*I*	*BCDEF*	*ABCDE*
	x value	Ref.	0.30	0.31	Ref.	0.20	0.22
	Durability class	-	d (75%)	md (63%)	-	d (100%)	d (88%)
12 Weeks	HG	*H*	*ABCDE*	*ABCDE*	J	*ABCDEF*	*J*
	x value	Ref.	0.23	0.22	Ref.	0.19	0.15
	Durability class	-	d (100%)	d (100%)	-	d (100%)	vd (63%)
16 Weeks	HG	*I*	*ABCDE*	*ABCD*	J	*DEF*	*ABCDE*
	x value	Ref.	0.21	0.16	Ref.	0.23	0.21
	Durability class	-	d (100%)	d (63%)	-	d (100%)	d (100%)
C. puteana		**B1**	**B2**	**B3**	**B4**	**B5**	**B6**
4 Weeks	HG	*ABC*	*B*	*A*	*FGH*	*CDEF*	*BCD*
	x value	Ref.	0.79	0.60	Ref.	0.73	0.62
	Durability class	-	sd (88%)	md (38%)	-	sd (88%)	sd (50%)
8 Weeks	HG	*BCD*	*BCDE*	*CDEF*	*K*	*IJ*	*GHI*
	x value	Ref.	0.88	0.79	Ref.	0.69	0.60
	Durability class	-	sd (88%)	sd (75%)	-	sd (75%)	md (63%)
12 Weeks	HG	*DEF*	*CDEF*	*CDEF*	*K*	*IJ*	*HIJ*
	x value	Ref.	0.92	0,86	Ref.	0.64	0.62
	Durability class	-	nd (75%)	sd (50%)	-	sd (75%)	sd (63%)
16 Weeks	HG	IJ	*EFG*	*DEFG*	*L*	*J*	*J*
	x value	Ref.	0.70	0.68	Ref.	0.60	0.56
	Durability class	-	sd (88%)	sd (100%)	-	md (38%)	md (75%)
T. versicolor		**B1**	**B2**	**B3**	**B4**	**B5**	**B6**
4 Weeks	HG	*A*	*AB*	*A*	*CD*	*BCD*	*EFG*
	x value	Ref.	0.71	0.64	Ref.	0.86	0.65
	Durability class	-	sd (63%)	sd (50%)	-	sd (63%)	sd (63%)
8 Weeks	HG	*CD*	*CD*	*ABC*	*GH*	*GH*	*GH*
	x value	Ref.	0.94	0.80	Ref.	0.97	0.92
	Durability class	-	nd (50%)	sd (63%)	-	nd (75%)	nd (75%)
12 Weeks	HG	*DEF*	*DEF*	*CD*	*HIJ*	*GHI*	*GH*
	x value	Ref.	0.98	0.81	Ref.	0.96	0.83
	Durability class	-	nd (75%)	sd (50%)	-	nd (75%)	sd (75%)
16 Weeks	HG	*GH*	*DEF*	*CDE*	*J*	*IJ*	*FG*
	x value	Ref.	0.93	0.77	Ref.	0.66	0.54
	Durability class	-	nd (75%)	sd (88%)	-	sd (75%)	md (100%)

[a] Homogeneity groups; [b] Durability class: Very durable (vd): $x \leq 0.15$; Durable (d): $0.15 < x \leq 0.3$; Moderately durable (md): $0.3 < x \leq 0.6$; Slightly durable (sd): $0.6 < x \leq 0.9$; Not durable (nd): $0.9 < x$. [c] Homogeneity groups with capital letters are given from lowest to highest in the order letter (A-O) and those around it ($\alpha<0.05$). The capital letters indicate the statistical differences between properties of composite samples by Duncan' mean separation test. [d] Relative frequency.

According to the relative frequencies of natural durability classes, most of the samples were classified as durable for *P. placenta.* However, the results showed variations for a few weeks due to the changes in the structure of composite samples after exposed to the fungus. Especially, for the sample B3 at end of the 16 weeks, an *x* value of 0.16 was obtained, which was quite close to those of durability class "very durable". This finding

indicated that the combined usage of MAPE and zinc borate was significantly effective in obtaining high resistance for this fungus species. The obtained x values after exposure to *C. puteana* resulted in a more scattered scenario. Most of the samples were slightly and moderately durable, while on the other hand there was any sample were classified as durable or very durable. At the end of the 16 weeks, although it had more lignocellulosic filler comparing the sample B3, the best performance was demonstrated by the sample B6 with an *x* value of 0.54 for this fungus. Finally, the samples exposed to the *T. versicolor* tended to be in lower durability classes as not or slightly durable. By investigating the weight losses and durability classifications relations, it was noticed that when the weight loss or the activity of fungus increased for the reference sample, the natural durability of the reinforced composite samples considerably increased.

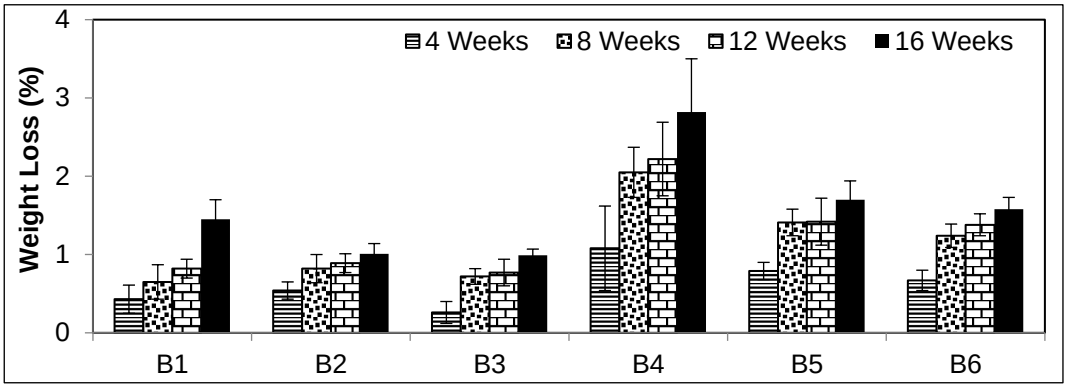

Fig. 2. Weight loss of composite samples exposed to *C. puteana*

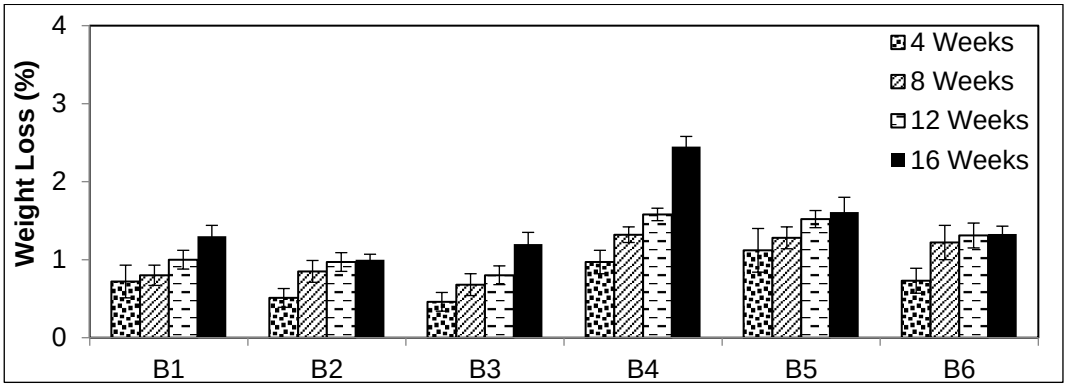

Fig. 3. Weight loss of composite samples exposed to *T. versicolor*

The fact that zinc borate, even in minimal quantities, functioned as an effective antifungal agent in WPCs materials can be attributed to its disruption of the biochemical processes that occurred during the development of the fungi. Boron compounds prevented the development of fungi by causing abnormal growths of hives and spores in fungi and by causing the failure of gametes to separate during reproduction. Moreover, the metabolic systems of fungal organisms were deteriorated by co-enzymes in the form of oxides as a target of boron ions. In addition, boron ions can penetrate cell walls easily, causing toxic effects and starvation effects in living organisms *via* the complexes they form (Yamaguchi 2003). Compatibilizers such as maleic anhydride grafted plastics used in wood plastic composites provide better encapsulation of the fiber surface. Moreover, the interaction between polymer-coated (grafted) fiber and the composite matrix may involve co-

crystallization and the formation of supramolecular chemical structures (Karger-Kocsis *et al.* 2015; Lu *et al.* 2000).

Karimi *et al.* (2007) reported a weight loss of almost 3% for WPCs with 2% MAPE composed of wood flour/HDPE (50/50%) after exposure to *Coriolus versicolor* fungus. They also showed that using 2% MAPE in the formulation reduced the weight loss by about 2%. Besides they reported that the usage of MAPE in WPCs production has an effect against fungal degradation. Kord *et al.* (2014) reported a weight loss of about 4% for WPCs composed of wood flour/polyethylene (50/40%) treated with nanoclay when exposed to *T. versicolor* fungus. They demonstrated that using 1% nanoclay in WPCs reduced the weight loss. Schmidt (2006) showed that white-rot fungus prefers hardwoods, while brown-rot fungus likes softwoods. Farahani and Banikarim (2013) reported a weight loss of almost 10% for WPCs treated with nano-zinc oxide after exposure to *C. puteana* fungus. They also showed that nano-zinc oxide at loadings as high as 1% made an impact in the wood-polypropylene composite.

Figure 4 reveals the appearances of the composite samples with and without zinc borate and MAPE after the fungal decay tests. The fungal attack caused black spots on the surface of the composite samples in the absence of zinc borate (Figs. 4a and 4b). In contrast, the composite samples B5 and B6 had no fungal decay patterns due to the presence of zinc borate and its combined effect with MAPE (Figs. 4c and 4d). Fungal devastation can result in composite discoloration, or release of extracellular metabolites or pigments, which stain the surface of the composite material with spots varying from green to red to black in color (Klyosov 2007).

Fig. 4. Appearance of the composite samples exposed to *P. placenta* after 16 weeks of fungal decay: a,b) sample B4; c) sample B5; d) sample B6

Water absorption test results of composites

Table 3 provides the average WA values for the composite samples after exposure to fungal decay for 0, 4, 8, 12, and 16 weeks. The maximum WA (20%) occurred in the composite with 60% wood fiber after exposure to *P. placenta* for 16 weeks. The WA values of the composites were considerably higher after exposure to fungal decay for 16 weeks. The WA was higher for the composite samples containing 1% zinc borate compared with those without zinc borate. The combination of zinc borate and MAPE in composites containing 60% wood fiber also had clearly lower WA values. Karimi *et al.* (2007) reported a WA of almost 4% for WPCs with 2% MAPE after exposure to *C. versicolor*.

There were significant differences in the WA values of the composite samples after exposure to *P. placenta*, *C. puteana*, and *T. versicolor* for 16 weeks. Although the

composite samples exposed to the white-rot fungus had a low weight loss, the WA values of the same samples were quite high. The addition of the MAPE in the formulation decreased WA values of the composite samples after exposure to the brown-rot fungus as well as the white-rot fungus. Consequently, it can be revealed that the usage of MAPE in the composites not only improved the physical properties, but it also improved the resistance against the brown and white rot fungus.

Table 3. Water Absorption Results of Composites after Exposure to Fungal Decay

	P. placenta				***C. puteana***				***T. versicolor***			
	Weeks				Weeks				Weeks			
	4	**8**	**12**	**16**	**4**	**8**	**12**	**16**	**4**	**8**	**12**	**16**
B1	6.31 1.34[a] *CD*[b]	7.37 0.82 *DEF*	8.40 0.82 *F*	9.73 0.85 *G*	6.66 0.65 *CDE*	7.75 0.27 *E*	7.63 0.76 *DE*	7.8 0.62 *E*	5.22 0.37 *CDEFG*	5.87 0.18 *EFGH*	6.24 0.31 *FGHI*	6.57 1.97 *GHI*
B2	5.61 0.96 *BC*	6.67 0.29 *CDE*	7.90 1.42 *F*	8.39 0.97 *F*	5.55 0.27 *ABC*	5.93 0.76 *BC*	6.44 0.48 *C*	6.56 0.44 *CD*	4.59 0.50 *ABCDE*	4.91 0.17 *ABCDEF*	5.05 0.31 *BCDEFG*	5.54 0.32 *DEFG*
B3	4.27 0.48 *A*	5.03 0.31 *AB*	6.38 0.44 *CD*	7.71 1.24 *EF*	4.59 0.11 *A*	4.75 0.06 *AB*	4.88 0.33 *AB*	5.29 0.59 *AB*	3.82 0.28 *ABC*	3.45 0.40 *A*	3.71 0.24 *AB*	4.18 0.10 *ABCD*
B4	13.4 1.50 *K*	15.29 1.10 *L*	19.6 1.85 *M*	20.0 0.16 *M*	16.1 0.53 *I*	17.1 1.29 *J*	17.44 0.68 *J*	17.8 1.25 *J*	12.8 1.82 *LM*	13.6 1.33 *MN*	14.9 2.36 *NO*	15.7 0.96 *O*
B5	11.2 1.67 *HI*	12.6 0.72 *JK*	13.6 1.24 *K*	14.6 2.01 *L*	12.2 0.62 *H*	12.7 1.27 *H*	12.82 0.46 *H*	13.0 1.57 *H*	8.20 1.30 J	8.98 0.94 J	11.0 2.41 K	11.5 0.71 KL
B6	9.60 1.99 *GHI*	10.41 0.32 *GH*	11.1 0.50 *HI*	11.6 1.61 *IJ*	9.02 0.90 *F*	10.7 0.75 *G*	10.92 0.87 *G*	11.0 0.34 *G*	7.05 0.52 *HI*	7.17 0.68 *HI*	7.36 0.60 *IJ*	8.06 0.66 *HI*

[a] Standard deviation, [b] Homogeneity groups with capital letters are given from lowest to highest in the order letter (A-O) and those around it ($\alpha<0.05$). The capital letters indicate the statistical differences between properties of composite samples by Duncan' mean separation test. .

Studies have shown that WPCs absorb higher moisture content in agar tests than those in soil-block tests (Mankowski and Morrell 2000). Moreover, in WPCs, when the lignocellulosic content of the material increases, the amount of water absorbed increases considerably. This suggests that manufacturers should take precautions for WPCs against brown and white rot fungi. Fungal decay is directly related to the water absorption capacity of the composite sample (Schirp and Wolcott 2005; Schmidt 2006; Karimi *et al.* 2007; Mankowski and Morrell 2000; Kord *et al.* 2014). Anti-fungal agents can be used to reduce the weight loss caused by fungal decay in WPCs. However, the wood content of the composite must also be considered. By arranging the wood filler content in optimum values, water uptake and fungal decay properties of the composite sample can be controlled. The weight losses of wood-plastic composites with a mixture ratio of 50:50 (wood/plastic) are around 1% (Muller *et al.* 2013; Schirp and Wolcott 2005). Fabiyi *et al.* (2011) reported a weight loss of almost 3% for WPCs with wood flour/HDPE (60/40%) after exposure to *T. versicolor* fungus. They also showed that the WA of WPCs increased by about 16%.

Discussion of Hardness (Shore D) Results

Changes in the surface hardness of composite samples are compared to their initial state in Figs. 5 through 7. The hardness of all samples generally decreased after fungal exposure. Moreover, the three investigated fungus species showed very similar trends for all samples and weeks during decay tests. The changes in surface hardness of the composite samples with wood filler ratio of 50% are less clear when compared with the composite samples with 60% wood filler. A significant decrease was observed in the sample B4 due to having high lignocellulosic filler content, which is an important factor for the fungal attack in the absence of zinc borate and MAPE in the formulation. The composite samples including the increased proportion of wood filler are more susceptible to degradation of brown- and white-rot fungus. Thus, the integrity and rigidity of the composites were impaired, and the surface hardness values was decreased. The opposite relationship was found between weight loss percentage and surface hardness values of the samples. Hosseinihashemi *et al.* (2011) reported that wood-plastic composites were exposed to the brown-rot fungus (*C. puteana*) and the white-rot fungus (*T. versicolor)* in agar tests. They also showed that the hardness values of composites reduced by about 14.7% and 15.6% after, respectively.

Surface hardness loss is less for composite samples including 1% zinc borate and 3% MAPE, according to Figs. 5 through 7. The highest loss in hardness values (13%) was found in the sample B4 for the brown rot fungus, *P. placenta* while the lowest loss (2%) was in the sample B3 for the white rot fungus, *T. versicolor*. The combined usage of MAPE and zinc borate in the composite samples prevented the deterioration of surface hardness after fungal attacks throughout the 16 weeks of exposure.

In the wood exposed to white rot fungus, the decay process caused holes and channels to form. The degradation of lignin and cellulose continued, and the wood density dropped significantly. Later, the wood became porous and lighter, and eventually it lost its rigidity. In contrast, for the wood exposed to brown-rot fungus, the hardness reduction was low in the initial stage. After significant cellulose destruction, a rapid drop in hardness is observed (Bozkurt *et al.* 1995).

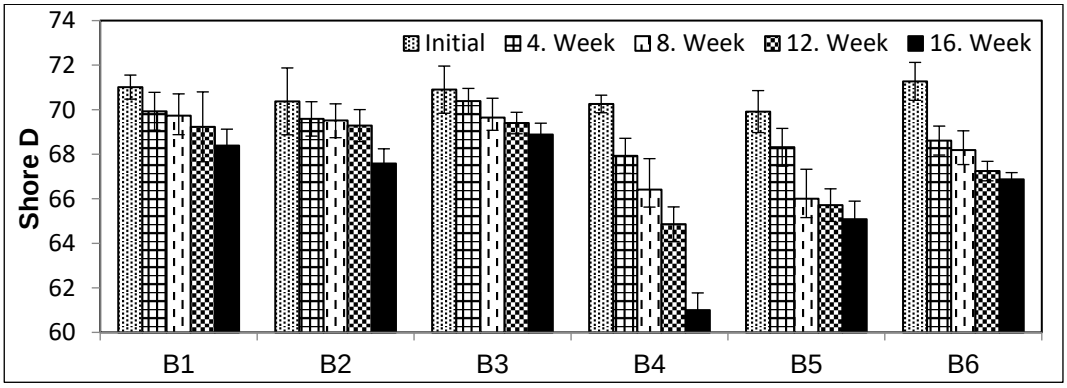

Fig. 5. Hardness of composite samples exposed to *P. placenta*

Kord *et al.* (2014) investigated decay resistance of WPCs with nanoclay, showing that if nanoclay is used, the composite hardness is not compromised. Karimi *et al.* (2007) investigated the changes in water absorption properties of WPCs with 2% MAPE after samples were exposed to *Coriolus versicolor* fungus, and they reported that the usage of MAPE in WPCs significantly reduced the water absorption values of the samples.

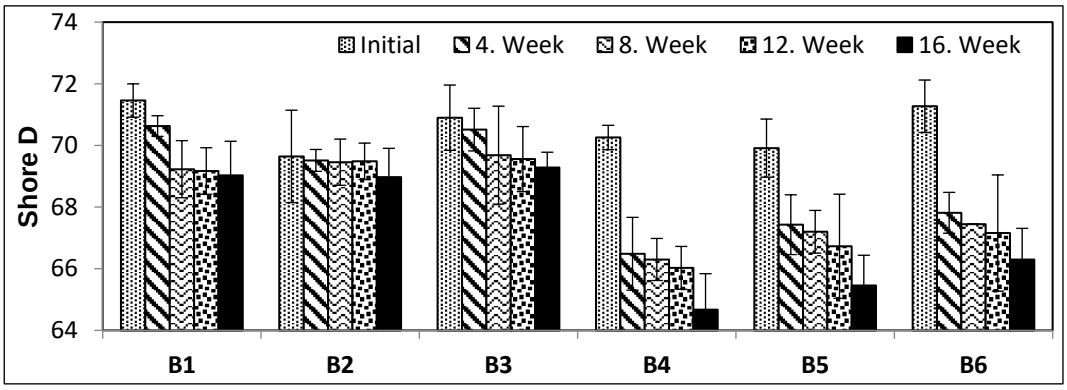

Fig. 6. Weight loss of composite samples exposed to *C. puteana*

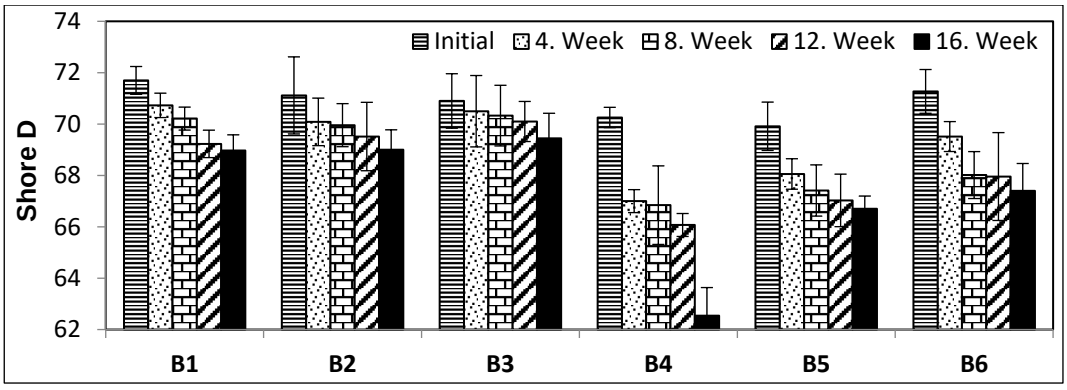

Fig. 7. Hardness of composite samples exposed to *T. versicolor*

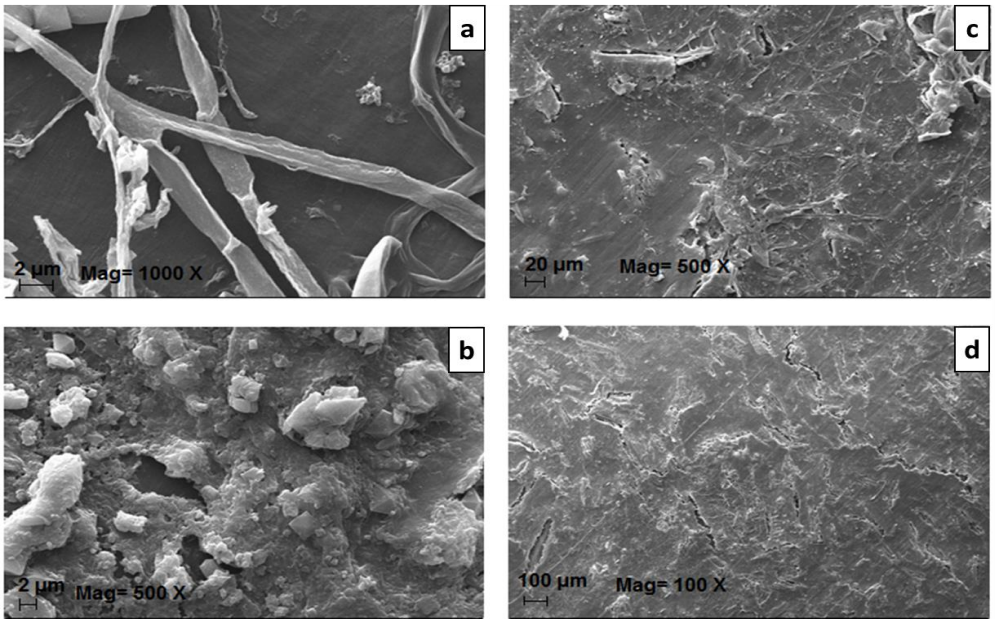

Fig. 8. SEM images of the composite samples after exposed to *P. placenta*: a) fungus mycelium; b) distribution of zinc borate; c, d) surface cracks.

Scanning Electron Microscopy

The fungus mycelium (Fig. 8a), the distribution of zinc borate (Fig. 8c), and the surface cracks (Figs. 8b, 8d) in the composite samples were analyzed using SEM. The brown-rot fungus attacked the composite samples and caused cracks and gaps on the surface. Moreover, the zinc borate in the composite was uniformly distributed. Pendleton *et al.* (2002) found the fungus tracks in the interfacial spaces between the wood and the thermoplastic material in the areas near the surface.

CONCLUSIONS

1. Zinc borate increased the resistance of wood-plastic composites against brown- and white-rot fungi. Coexistence of MAPE and zinc borate in composite samples also effectively prevented the composite samples from fungal decay. The use of 1% zinc borate in the WPCs significantly reduced the decay caused by *P. placenta*.
2. Zinc borate influenced the WA of WPCs with high lignocellulosic filler content. The WA of the composite samples with 1% zinc borate was less compared with those without zinc borate. Furthermore, the coexistence of MAPE and zinc borate in composite samples dramatically reduced WA after fungus exposure for 16 weeks.
3. The surface hardness of the composite samples exposed to the rot fungi was reduced with the combined usage of MAPE and zinc borate. SEM analysis showed that rot fungi attacked the composite samples, causing damage to their surfaces.
4. Consequently, the combined use of MAPE and zinc borate in the composite formulations could be adequate to protect the WPCs samples with 60% wood filler.

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REFERENCES CITED

ASTM D2240 (2010). "Standard test method for rubber property—Durometer hardness," ASTM International, West Conshohocken, PA.

ASTM D618 (2013). "Standard practice for conditioning plastics for testing," ASTM International, West Conshohocken, PA.

Bozkurt, A., Erdin, N., and Unligil, H. (1995). *Wood Pathology*, The Istanbul University Forestry Faculty Publications, Istanbul, Turkey.

Clemons, C. (2002). "Wood-plastic composites in the United States: The interfacing of two industries," *Forest Products Journal* 52(6), 10.

EN 113 (1996). "Wood preservatives—Test method for determining the protective effectiveness against wood destroying basidiomycetes—Determination of the toxic values," European Committee for Standardization, Brussels, Belgium.

EN 350-1 (1994). "Durability of wood and wood-based products — natural durability of solid wood — Part 1: Guide to the principles of testing and classification of the

natural durability of wood" European Committee for Standardization, Brussels.
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
Farahani, M. R. M., and Banikarim, F. (2013). "Effect of nano-zinc oxide on decay resistance of wood-plastic composites," *BioResources* 8(4), 5715-5720. DOI: 10.4172/2324-8777.1000146
Hosseinihashemi, S. K., Modirzare, M., Safdari, V., and Kord, B. (2011). "Decay resistance, hardness, water absorption, and thickness swelling of a bagasse fiber/plastic composite," *BioResources* 6(3), 3289-3299.
Islam, M. N., Khan, M. A., Alam, M. K., Zaman, M. A., and Matsubayashi, M. (2003). "Study of water absorption behavior in wood plastic composites by using neutron radiography techniques," *Polymer-Plastics Technology and Engineering* 42(5), 925-934. DOI: 10.1081/Ppt-120025004
Karimi, A. N., Tajvidi, M., and Pourabbasi, S. (2007). "Effect of compatibilizer on the natural durability of wood flour/high density polyethylene composites against rainbow fungus (*Coriolus versicolor*)," *Polymer Composites* 28(3), 273-277. DOI: 10.1002/pc.20305.
Karger-Kocsis, J., Mahmood, H., and Pegoretti, A. (2015). "Recent advances in fiber/matrix interphase engineering for polymer composites," *Progress in Materials Science*, 73, 1-43. DOI:10.1016/j.pmatsci.2015.02.003.
Klyosov, A. A. (2007). *Wood-plastic Composites*, Wiley, Hoboken, NJ, USA.
Kord, B., Jari, E., Najafi, A., and Tazakorrezaie, V. (2014). "Effect of nanoclay on the decay resistance and physicomechanical properties of natural fiber-reinforced plastic composites against white-rot fungi (*Trametes versicolor*)," *Journal of Thermoplastic Composite Materials* 27(8), 1085-1096, DOI: 10.1177/0892705712465302
Li, Q. X., and Matuana, L. M. (2003). "Foam extrusion of high density polyethylene/wood-flour composites using chemical foaming agents," *Journal of Applied Polymer Science* 88(14), 3139-3150. DOI: 10.1002/app.12003
Lu, J. Z., Wu, Q. L., and McNabb, H. S. (2000). "Chemical coupling in wood fiber and polymer composites: A review of coupling agents and treatments," *Wood and Fiber Science*, 32(1), 88-104
Mankowski, M., and Morrell, J. J. (2000). "Patterns of fungal attack in wood-plastic composites following exposure in a soil block test," *Wood and Fiber Science* 32(3), 340-345.
Morris, P., and Cooper, P. (1998). "Recycled plastic/wood composite lumber attacked by fungi," *Forest Products Journal*, 48(1), 86.
Muller, M., Gellerich, A., Militz, H., and Krause, A. (2013). "Resistance of modified polyvinyl chloride/wood flour composites to basidiomycetes," *European Journal of Wood and Wood Products* 71(2), 199-204. DOI: 10.1007/s00107-013-0665-8
Naghipour, B. (1997). *Effects of Extreme Environmental Conditions and Fungal Exposure on the Properties of Wood-plastic Composites*, Master's Thesis, University of Toronto, Canada.
Najafi, S. K., Tajvidi, M., and Chaharmahli, M. (2006). "Long-term water uptake behavior of lignocellulosic-high density polyethylene composites," *Journal of Applied Polymer Science* 102(4), 3907-3911. DOI: 10.1002/app.24172
Ozdemir, F., Ayrilmis, N., Kaymakci, A., and Kwon, J. H. (2014). "Improving

dimensional stability of injection molded wood plastic composites using cold and hot water extraction methods," *Maderas-Ciencia y Tecnologia* 16(3), 365-372. DOI: 10.4067/S0718-221x2014005000029

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.

Plackett, D. (2004). "Maleated polylactide as an interfacial compatibilizer in biocomposites," *Journal of Polymers and the Environment* 12(3), 131-138.

Rowell, R. M., Sanadi, A. R., Caulfield, D. F., and Jacobson, R. E. (1997). "Utilization of natural fibers in plastic composites: Problems and opportunities," *Lignocellulosic-Plastic Composites*, 23-51.

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.

Schmidt, O. (2006). *Wood and Tree Fungi*, Springer-Verlag, Heidelberg, Berlin, Germany.

Turku, I., Nikolaeva, M., and Karki, T. (2014). "The effect of fire retardants on the flammability, mechanical properties, and wettability of co-extruded PP-based wood-plastic composites," *BioResources* 9(1), 1539-1551. DOI: 10.15376/biores.9.1.1539-1551.

Yamaguchi, H. (2003). "Silicic acid: Boric acid complexes as wood preservatives," *Wood Science and Technology* 37(3-4), 287-297. DOI: 10.1007/s00226-003-0190-8

Yang, H. S., Kim, H. J., Park, H. J., Lee, B. J., and Hwang, T. S. (2007). "Effect of compatibilizing agents on rice-husk flour reinforced polypropylene composites," *Composite Structures* 77(1), 45-55. DOI: 1 0.1016/j.compstruct.2005.06.005

Zabel, R. A., and Morrell, J. J. (2012). *Wood Microbiology: Decay and its Prevention*, Academic Press, San Diego, CA, USA.

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