Holzforschung, Vol. 58, pp. 205–208, 2004 • Copyright © by Walter de Gruyter • Berlin • New York

Wood/plastic ratio: Effect on performance of borate biocides against a brown rot fungus

John Simonsen*, Camille M. Freitag, Antonio Silva and Jeffrey J. Morrell

Department of Wood Science and Engineering, Oregon State University, Corvallis, Oregon, USA

*Corresponding author: Department of Wood Science and Engineering, Oregon State University, Corvallis, Oregon 97331, USA; Fax: +1-541-737-3385
E-mail: john.simonsen@oregonstate.edu

Abstract

The effect of wood/plastic ratio and the presence of a boron compound on resistance to biodegradation of wood plastic composites (WPC's) by the brown rot fungus *Gloeophyllum trabeum* was investigated in a soil block exposure. Weight losses of all WPC's were generally lower than those of solid wood, even when only the wood component of the WPC was used in calculating weight loss. Higher wood content was associated with greater weight losses, suggesting that the plastic encapsulated wood at lower wood levels. Borates markedly reduced weight losses at all wood/plastic ratios. Weight losses tended to be slightly lower with a Na/Ca borate than with similar levels of zinc borate. Mechanical properties did not correlate well with weight losses under the conditions evaluated, but these effects may have been masked by moisture sorption. The causes and implications of these differences are discussed.

Keywords: borate; brown rot; Gloeophyllum trabeum; wood/plastic composites.

Introduction

The use of wood plastic composites (WPC's) continues to grow as producers seek to blend the unique material properties of these two polymers (Sellers et al. 2000). Recently, the use of WPC's as a substitute for wood decking has been increasing (Wolcott and Englund 1999). The decking market has long been dominated by western red cedar, coastal redwood and pressure-treated wood. While these materials provide excellent performance, they require some level of maintenance by the homeowner. WPC's have been marketed for these applications as decay-resistant materials that require little or no maintenance.

The plastic component in the original WPC's was presumed to protect the wood against biological attack, but several reports have suggested that the wood remains susceptible to fungal degradation despite its close association with the plastic (Schmidt 1993; Naghipour 1996; Morris and Cooper 1998; Verhey et al. 2001). These studies have shown that the wood component sorbs water and eventually decays, albeit more slowly initially than does solid wood of the same species. The industry has responded by incorporating zinc borate (Zn B) into the WPC. Borates are excellent fungicides and insecticides, but the primary borate used for wood preservation, sodium octaborate tetrahydrate, is highly water soluble and tends to leach from wet wood (Murphy et al. 1995). Zinc borate (Zn B) is far less soluble, and field tests suggest that composites incorporating this material perform reasonably well under harsh sub-tropical conditions. While these results are promising, there are relatively few data on the ability of Zn B and other borate compounds to protect the wood component in a WPC against fungal attack, nor is there a substantial literature on the effects of other variables, such as wood/plastic ratio, on the performance of these systems.

In this report, we describe the ability of zinc borate and a sodium/calcium borate salt (Na/Ca B) to protect WPC's containing various ratios of wood and plastic against fungal attack in a soil block test.

Materials and methods

Materials

Wood Wood flour (pine wood flour ground to pass a 60-mesh screen) was supplied by Professor M. Wolcott, Washington State University, Pullman.

Plastics Injection grade polypropylene (PP) (Fortilene HB 1602) was donated by Solvay Polymers, Houston, TX, USA. High-density polyethylene (HDPE) was contributed by Phillips Petrochemical Company (Houston, TX, USA) as Marlex EHM 6007. The molecular weight was 120,000 (by gel permeation chromatography); the density, 0.964; and the melt index, 0.65 g 10 min^{-1} (190°C 2 kg^{-1}).

Preservatives Zinc borate (Zn B) was donated by U.S. Borax Inc., Valencia, CA, USA, as their product Borogard B. A blend of calcium and sodium borates (Na/Ca B) was donated by the Quality Borate Co., Cleveland, OH, USA, as their product QB-13.

Composite preparation

The test materials were prepared in a Brabender Plasticorder with mixing bowl and cam blades attached. The temperature was controlled at 190°C. The components of each sample were added to the mixing bowl in the order plastic, filler (wood flour) and preservative. The wood/plastic ratios were 0:100, 20:80, 40:60, and 60:40 (wt wt^{-1}). The preservatives were added to the mixture as powders at 0.0, 0.5 or 1.0% (wt chemical wt $wood^{-1}$). The mixture was blended for at least 10 min after addition of all the components to ensure thorough mixing. The samples were then removed from the mixing bowl, cooled, and ground to a coarse powder in a Wiley mill before compression

Table 1 Weight loss after exposure to *G. trabeum* of wood/polypropylene (PP) composites with differing wood/plastic ratios and with or without zinc borate (Zn B) or sodium/calcium borate (Na/Ca B). (A negative value indicates a gain).

Wood:PP	Preservative concentration (%, wt wt^{-1})	Wafer weight loss (%)[a]					
		Total wafer			Wood basis		
		No additive	Zn B added	Na/Ca B added	No additive	Zn B added	Na/Ca B added
0:100		−0.10 (0.15)					
20:80	0	−0.35 (0.24)			−1.75 (1.21)		
	0.5		−0.30 (0.30)	−0.36 (0.32)		−1.50 (1.50)	−1.81 (1.61)
	1.0		−0.49 (0.22)	−0.15 (0.41)		−2.47 (1.11)	−0.76 (2.03)
40:60	0	0.86 (0.67)			2.16 (1.67))		
	0.5		0.26 (0.15)	0.63 (0.18)		0.65 (0.38)	1.58 (0.45)
	1.0		0.19 (0.18)	0.77 (0.08)		0.46 (0.45)	1.93 (0.19)
60:40	0	3.60 (1.87)			6.00 (3.12)		
	0.5		0.16 (0.24)	0.92 (0.11)		0.27 (0.40)	1.53 (0.19)
	1.0		0.25 (0.12)	1.02 (0.09)		0.42 (0.19)	1.70 (0.16)

[a] Mean (SD) of 20 wafers per treatment.

molding into wafers (3 mm×12 mm×56 mm) at 175°C and 10 MPa (1500 psi).

In commercial manufacture, WPC's typically contain additives such as lubricants or compatibilizers. However, in the interest of reducing the number of variables in this test and obtaining more direct comparisons between preservatives, we added only the preservative.

Testing

Durability The wafers were oven-dried at 54°C and weighed before sterilization at 121°C for 20 min. The sterile wafers were exposed to the test fungi according to the American Wood Preservers' Association Standard E10 (AWPA 1999). Briefly, 454-ml French square bottles were half-filled with moist forest loam, and a feeder strip (3×12×50 mm) of western hemlock [*Tsuga heterophylla* (Raf) Sarg.] was placed on the soil surface. The jars were loosely capped and autoclaved for 40 min at 121°C. The jars were cooled overnight and then heated to 121°C for 15 min to help eliminate spore-forming bacteria. After cooling, the feeder strip was inoculated with the test fungus by cutting a small disc (3 mm in diameter) from the actively growing edge of a culture and placing the disc, mycelium down, on the feeder strip surface. The fungus tested, *Gloeophyllum trabeum* (Pers. ex Fr) Murr (Isolate Mad 617), causes brown rot decay and has been isolated from a number of decaying building components.

The bottles were incubated at room temperature until the fungus had thoroughly covered the feeder strip. Four test samples were then placed on each feeder strip. The bottles (5/treatment) were loosely capped and incubated at 28°C for 12 weeks. Ponderosa pine (*Pinus ponderosa* Laws.) sapwood blocks (19 mm cubes) were also tested to demonstrate the decay activity of the test. At the end of the test period, the samples were removed, scraped clean of adhering mycelium, weighed, oven-dried and reweighed to the nearest mg. Oven-drying often required 2–3 days to reach a steady weight. The difference between initial and final oven-dry weight was used as a measure of decay resistance.

Mechanical properties The strength (Modulus of Rupture, MOR) and stiffness (Modulus of Elasticity, MOE) of the wafers, both decayed and undecayed, were measured in 3-point bending on an Instron universal testing machine in accordance with ASTM D790-02 (ASTM 2002). The stiffness is defined as the steepest slope in the initial, presumably elastic, region on the stress-strain curve. The strength is the highest stress value achieved by the sample, whether the sample actually fractured or just yielded (slope=0 on the stress-strain curve). Five wafers were tested for each sample composition and the means and standard deviations (SDs) reported.

Results and discussion

Weight losses were uniformly low for all of the wood/plastic composite treatments tested. Weight losses of the untreated solid ponderosa pine sapwood comparators averaged 33.6% (SD 4.3%), indicating that the conditions were suitable for growth of the test fungus.

Weight losses of the wafers without the borate amendment were low at the higher plastic ratios (near 0% weight loss), but steadily increased with increasing wood content (Tables 1 and 2). While wafer weight losses were still relatively low at the 60:40 wood/plastic ratio, they averaged 6% on PP when only the wood component was used to calculate weight loss (Table 1). Weight losses tended to be higher for WPC's containing PP, suggesting that this material may not provide as much of a barrier against fungal attack as HDPE. The PP mass losses in our tests did not approach those found with untreated solid wood, but previous laboratory trials of solid wood suggest that significant strength losses can occur even at these low mass losses (Wilcox 1978). Given the importance of the wood in overall WPC performance (Simonsen 1997), the loss of even small amounts of fiber might translate into much larger effects on composite performance, particularly if the primary fungal effect is near the wood/plastic interface. Previous studies of a WPC fabricated with coarser wood particles suggested that the fungus readily grew through the material, taking advantage of the open microstructure (Mankowski and Morrell 2000). The smaller size of the wood particles in the current study may limit such growth, but it is clear that the test fungus could move into and degrade the wood in the system.

The addition of a biocide to the mixture before molding dramatically reduced weight losses for all treatments. At either treatment level, weight losses were negligible with Zn B and tended to remain below 1% with Na/Ca B. The differences in weight loss for the two chemicals may reflect some leaching of the Na/Ca borate, rather than fungal growth. Both chemicals tended to affect the growth of the test fungus on the feeder strip, suggesting that boron had migrated from the wafers into the feeder strip below. There were no large differences in performance between the two borate compounds.

The decay fungus had little effect on mechanical properties except at the 60% wood filler level, where strength (MOR) and MOE of specimens exposed to the decay fungus were consistently lower than those of undecayed specimens. Most of this effect, however, appeared to be related to the physical effect associated with wetting, rather than a real biological activity. An example of the mechanical properties of HDPE containing wood flour and 1.0% Zn B is shown in Figure 1. The mechanical properties for the other samples were similar to those in the figure and are not shown. These results suggest that borate preservatives did not protect the wood component of the composite from decay. Recent data, however, indicate that water absorption by the composites may significantly impact the mechanical properties apart from any fungal impacts (Laks 2002). Thus, specimens exposed to similar conditions, but not the decay fungus, might have shown a similar drop in properties at the higher filler contents. This effect was not investigated in this study, but may be a factor in these types of studies. Such effects point out the need for the development of appropriate, reliable, and accurate tests for evaluating biodegradability of wood-filled plastic composites.

The relative permanence of the borate in the WPC can have important implications for long-term performance, particularly under severe leaching exposures such as those in a deck. Initially, diffusion from the interior of the WPC would replenish surface levels of borate, but continued leaching would eventually deplete the reservoir within the material, leaving the decking vulnerable to fungal attack. Changes in borate solubility that reduce the risk of leaching while retaining sufficient solubility to maintain biological activity may be especially important for improving long-term performance in such applications. Conversely, cheaper boron formulations could be added at initial higher loadings under the assumption that the rate of release can be tailored to provide comparable performance.

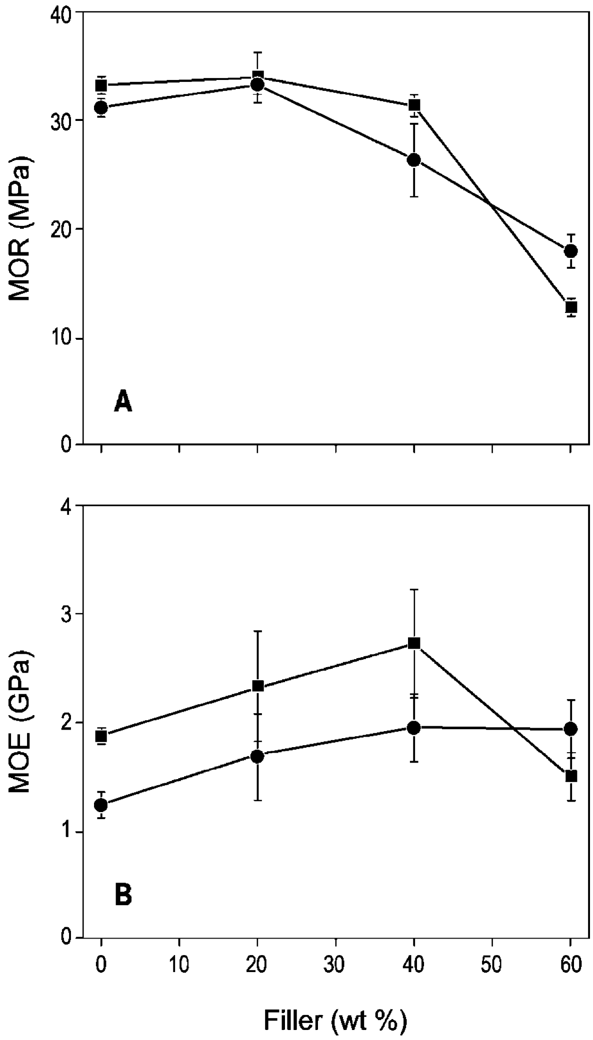

Figure 1 Mechanical properties of wood-filled HDPE with 1% Zn B preservative: A) MOR; B) MOE. ■ decayed; ● undecayed.

Conclusions

WPC's decay under suitable environmental conditions, but the rates are far slower than those found for comparable solid wood. Both borate compounds protected

Table 2 Weight loss after exposure to *G. trabeum* of wood/high density polyethylene (HDPE) composites with differing wood/plastic ratios, with or without zinc borate (Zn B) or sodium/calcium borate (Na/Ca B). (A negative value indicates a gain).

Wood:HDPE	Preservative concentration (%, wt wt^{-1})	Wafer weight loss (%)[a]					
		Total wafer			Wood basis		
		No additive	Zn B added	Na/Ca B added	No additive	Zn B added	Na/Ca B added
0:100		−0.24 (0.18)					
20:80	0	−1.21 (0.13)			−6.07 (0.64)		
	0.5		−1.39 (0.12)	−1.63 (0.21)		−6.96 (0.58)	−8.13 (1.05)
	1.0		−1.42 (0.13)	−2.11 (0.19)		−7.09 (0.63)	−10.54 (0.97)
40:60	0	−1.13 (0.25)			−2.83 (0.64)		
	0.5		−1.5 (0.27)	−1.11 (0.15)		−3.75 (0.68)	−2.79 (0.37)
	1.0		−1.3 (0.18)	−1.0 (0.16)		−3.25 (0.45)	−2.49 (0.39)
60:40	0	0.93 (0.42)			1.56 (0.69)		
	0.5		0.17 (0.08)	0.48 (0.23)		0.29 (0.13)	0.79 (0.39)
	1.0		0.15 (0.13)	1.01 (0.14)		0.25 (0.22)	1.69 (0.24)

[a] Mean (SD) of 20 wafers per treatment.

the wood component in the WPC from fungal attack, although our results suggest that the HDPE material is more resistant. Borate leaching from WPC under harsh exposure conditions may be problematic and merits further study. Mechanical properties were inconclusive in terms of detection of decay in the samples.

Acknowledgements

This work was supported in part by the Center for Wood Utilization Research. This is paper 3570 of the Forest Research Laboratory, Oregon State University, Corvallis, Oregon, USA.

References

AWPA (American Wood Preservers' Association). 1999. Standard E10-91. Standard method of testing wood preservatives by laboratory soil block cultures.

ASTM. 2002. D790-02. Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials.

Laks, P. 2002. Fungal and termite attack on thermoplastic/wood fiber composites. *In*: Proceedings, 98th AWPA, April 21-24, 2002, Memphis, Tennessee. (Abstr.).

Mankowski, M. and J.J. Morrell. 2000. Patterns of fungal attack in wood-plastic composites following exposure in a soil block test. Wood and Fiber Sci. *32*(3), 340–345.

Morris, P.I. and P. Cooper. 1998. Recycled plastic/wood composite lumber attacked by fungi. For. Prod. J. *48*(1), 86–88.

Murphy, R.J., H. M. Barnes and S.M. Gray. 1995. Decay and soil depletion studies with polymer/boron preservative systems. For. Prod. J. *45*(9), 77–81.

Naghipour, B. 1996. Effects of extreme environmental conditions and fungus exposure on the properties of wood-plastic composites. M.S. thesis. University of Toronto, Toronto, Canada.

Schmidt, E.L. 1993. Decay testing and moisture changes for a plastic-wood composite. *In*: Proceedings AWPA *89*, 108–109 (Abstr.)

Sellers, T., G. D. Miller, Jr. and M. Katabian. 2000. Recycled thermoplastics reinforced with renewable lignocellulosic materials. For. Prod. J. *50*(5), 24–28.

Simonsen, W.J. 1997. Efficiency of reinforcing materials in filled polymer composites. For. Prod. J. *47*(1), 74–81.

Verhey, S., P. Laks, and D. Richter. 2001. Laboratory decay resistance of woodfiber/thermoplastic composites. For. Prod. J. *51*(9), 44–49.

Wilcox, W.W. 1978. Review of literature on the effects of early stages of decay on wood strength. Wood and Fiber *9*(4), 252–257.

Wolcott, M.P. and K. Englund. 1999. A technology review of wood-plastic composites. *In*: Proceedings 33rd International Particleboard/Composite Materials Symposium, Washington State University, Pullman. pp. 103–111.

Received February 12, 2003