HIGH-DENSITY POLYETHYLENE-BASED COMPOSITES WITH PRESSURE-TREATED WOOD FIBERS

Lu Shang,[a] Guangping Han,[a,]* Fangzheng Zhu,[b] Jiansheng Ding,[b]
Todd Shupe,[c] Qingwen Wang,[a] and Qinglin Wu[c,]*

High-Density Polyethylene (HDPE)-based composites with alkaline copper quaternary (ACQ)- and micronized copper quaternary (MCQ)-treated wood fibers were manufactured through injection molding. The mechanical properties, water absorption, and biological resistance properties of the fabricated composites with different coupling treatments were investigated. Composites with ACQ- and MCQ-treated wood had mechanical properties comparable with those made of untreated wood. The different coupling agents worked well for the treated wood materials. Similar water absorption behaviors were observed for the HDPE composites containing treated wood and those containing untreated wood. The results of the termite test showed that the composites containing untreated wood had slightly more weight loss. The decay test revealed that the composites containing treated wood had less decay fungal growth on the surfaces, compared with samples from untreated wood, indicating enhanced decay resistance for the composites from the treated material. The stable mechanical properties and improved biological performances of the composites containing treated wood demonstrated the feasibility of making wood-plastic composites with pressure-treated wood materials, and thus offered a practical way to recycle treated wood into value-added composites.

Keywords: Pressure-treated wood; HDPE; Mechanical property; Termite; Decay

Contact information: a: Key Laboratory of Bio-based Material Science and Technology (Ministry of Education), Northeast Forestry University, Harbin 150040, China; b: Nanjing Jufeng Advanced Materials Co., Ltd, Nanjing 210061, China; c: School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, USA;
** Corresponding authors: a, guangpingh@hotmail.com; c, wuqing@lsu.edu*

INTRODUCTION

Over the past two decades, extensive effort has been devoted to wood-plastic composites (WPCs) due to their many emerging applications as building materials, automobile components, and materials for infrastructure and decking/fencing (Clemons and Caulfield 2005). As new generation composite products, WPCs presents many advantages for both structural and non-structural uses, including availability in a variety of colors, shapes, and surface textures, ease of maintenance, lack of need for painting or other finishes, and little tendency to warp compared with wood materials. The outdoor application of structural WPCs has led to increased exposure of the materials to wetting. WPCs are susceptible to bio-deterioration under prolonged exposure to high humidity or liquid water, which can severely affect the economic value and usefulness of the product. This is due to the fact that the wood component in WPCs can be attacked by decay fungi, termites, and mold fungi (Laks *et al.* 2000 and Verhey *et al.* 2001). Like other wood materials, WPCs need to be treated with the appropriate chemicals to prevent biological attack. Various preservatives and treatments have been used in WPC manufacturing to enhance its biological performances (Simonsen *et al.* 2004).

Durability concerns of wood products have historically been addressed through the use of chemical treatments employing a variety of application methods, including surface coating, spraying, pressure impregnation, immersion or dipping, diffusion, and vacuum-assisted treatments. Of these, pressure impregnation is the most popular treatment method. Pressure-treated wood is widely used for durable outdoor applications. However, there are some environmental concerns when wood is pressure-treated. The proper disposal of the treated wood after its service life poses a significant industrial problem. Recycling treated wood fiber into WPC manufacture offers advantages in recovering valuable wood resources and in helping to create WPC products that are less bio- and photodegradable. Previous work in the field has been limited to chromated copper arsenate (CCA)-treated wood under compression molding (Kamdem *et al.* 2004). A large quantity of alkaline copper quaternary (ACQ)- and micronized copper quaternary (MCQ)-treated wood is available. Successful development of WPCs from pressure-treated wood materials requires detailed information about the manufacturing variables and understanding of the coupling system and coupling efficiency between treated wood fiber and plastics in the composite.

The overall goal of the study was to investigate the feasibility of using ACQ- and MCQ-treated wood in the manufacture of WPCs. The specific objective of this work was to investigate the effect of coupling treatments on the properties of manufactured WPCs through injection-molding.

EXPERIMENTAL

Raw Materials

Shavings from ACQ- and MCQ-treated and untreated southern yellow pine (SYP) wood were collected from Elder Wood Preserving Co. Inc (Mansura, LA). Virgin high-density polyethylene (HDPE 6761 ExxonMobile Chemical Co., Houston, TX, USA), maleated polyethylene (MAPE Epolene^{TM} G2608 from Eastman Chemical Co., Kingsport, TN, USA), ethylene-propylene rubber (EPR, ExxonMobile Chemical Co., Houston, TX, USA), ethylene-co-glycidyl methacrylate (EGMA, Arkema Inc. Philadelphia, PA, USA), and polyolefin elastomer (POE, ExxonMobile Chemical Co., Houston, TX, USA) were used.

Preparation of Wood Fibers

The wood shavings were granulated with a laboratory granulator to the size required to pass through a 12-mesh screen, and the ground material was dried to a moisture content of about 3% prior to use. Samples from both ACQ- and MCQ-treated wood were used to perform copper loading analysis in accordance with the American Wood Preservers' Associations test standard A9.

Blend Design and Sample Fabrication

The composite blends were prepared in the Engineering Composite Laboratory, LSU AgCenter using a CW Brabender Intelli-torque twin-screw extruder with a pair of 32 mm conical twin screws and a 13:1 L/D ratio (CW Brabender Instruments, South Hackensack, NJ, USA). The blending temperature profile was 155 °C, 175 °C, 180 °C, 180 °C, and 170 °C from the feeding zone to die, and the extruder rotation speed was 90 rpm. Table 1 shows the design for various blends. Plastics (HDPE 6761 – 58.8% by weight), wood fiber (*i.e.*, ACQ, MCQ, and the untreated control – 39.2% by weight), and the coupling agent (*e.g.*, MAPE – 2% by weight) were added to the extruder, thoroughly mixed, and then pelletized by a BT 25 Strand Pelletizer (Bay Plastics machinery, Bay City, MI, USA). The test samples (4 mm thickness) were made through injection-molding using a Battenfeld PLUS 35 injection system (Wittmann Battenfeld GmbH, Kottingbrunn, Austria) at 190 ºC with a mold temperature of 85 ºC.

Table 1. Wood Fiber and HDPE Blend Design Through Injection-Molding

Blend Number	Wood Type	HDPE (%)	Wood Fibers (%)	Coupling Agent Type and Loading (% of total HDPE/Wood fiber weight)			
				MAPE	EPR	EGMA	POE
1	ACQ-Treated Wood	60	40	2			
2		60	40		2		
3		60	40			2	
4		60	40				2
5	MCQ-Treated Wood	60	40	2			
6		60	40		2		
7		60	40			2	
8		60	40				2
9	Untreated Wood Control	60	40	2			
10		60	40		2		
11		60	40			2	
12		60	40				2

Mechanical Properties

Flexural and tensile properties were measured according to the ASTM D638 using a Model 5582 Advanced Mechanical Testing System (Instron, Norwood, MA). For each treatment level, five replicate samples were tested. A TINIUS 92T impact tester (Tinius Olsen, Horsham, PA) was used for the Izod impact strength test. All the samples were notched at the center of one longitudinal side in accordance with the ASTM D256.

Water Absorption

The specimens with a size of 25 mm × 25 mm × 3 mm were prepared for water absorption measurements in the Engineering Composite Laboratory, LSU AgCenter. They were first dried to a constant weight and then immersed in water maintained at 20 °C. The weight gain of the specimens was carefully monitored through periodic weight measurements.

Precautions were taken to remove the surface moisture from all specimens by carefully wiping them off each time before weighing. The percentage of weight gained (M) by the specimen was calculated as follows,

$$M\,(\%) = [(W_2-W_1)/W_1] \times 100 \qquad (1)$$

where W_2 is the weight of the wet specimen and W_1 is the weight of the dry specimen. The percentages of weight gained were then plotted against the square roots of the time in order to generate the moisture absorption curves.

Termite Test

A laboratory termite test according to AWPA E1 was done in the Wood Durability Laboratory, LSU AgCenter using injection-molded samples. Five samples (31.0 mm × 18.0 mm × 3.5 mm) from each of the groups of WPCs containing the treated wood and five samples of untreated southern pine, the controls, were used. Prior to each termite test, the blocks were oven-dried at 105 °C for 24 hours and the sample weights (W_1) and dimensions were measured. Each test bottle was autoclaved for 30 minutes at 105 kPa and dried. Autoclaved sand (150 g) and distilled water (30 mL) were added to each bottle. Finally, four hundred termites (360 workers and 40 soldiers) were added to opposite sides of the test block in the container. All containers were maintained at room conditions for 4 weeks. The bottle cap was placed on loosely. After testing, each bottle was dismantled. Live termites were counted, and the test blocks were removed and cleaned. Each block was oven-dried again at 105 °C for 24 hours to determine the dry sample weight (W_2). The sample mass losses $[(W_1-W_2)/W_1]$ and termite mortalities were determined. The tested samples were ranked visually by five people on a scale of 1 to 10 with 10 as no damage and 1 as the most damage.

Decay Test

A decay test, using part of the injection-molded samples (31.0 mm × 18.0 mm × 3.5 mm), was performed in the Wood Durability Laboratory, LSU AgCenter in accordance with the AWPA Standard Method of Testing Wood Preservatives by Laboratory Soil-Block Cultures (E10-06). Brown rot fungus *Gloeophyllum trabeum* (ATCC 11539) was used in this study. The samples were exposed to the fungus for 16 weeks. For each type of the sample, three replications were conducted, and the mass loss data was collected after the close of the test.

RESULTS AND DISCUSSION

Preservative Loading

Table 2 shows the results of the preservative loading analysis. As shown, the MCQ-sawdust had a CuO loading level of 2.8 kg/m^3 with a quaternary loading level below the detection limit. The ACQ-treated wood had a CuO loading level of 4.08 kg/m^3 with a quaternary loading level of 2.51 kg/m^3. The WPC blend contained 50% MCQ-treated wood fiber loading and the CuO loading level was roughly 50% of that for MCQ-treated wood fibers.

Table 2. Results of CuO/Quat Analysis for Ground Treated Wood Fibers

Sample ID	CuO [1] (kg/m^3)	Quat [2] as DDAC [3] (kg/m^3)	Total (kg/m^3)
MCQ wood	2.8 (0.02)	Below detection limit	2.80
ACQ wood	4.08 (0.03)	2.51 (0.10)	6.59
WPC blend (MCQ-Wood)	1.49 (0.15)	Below detection limit	1.49

[1] CuO: Copper Oxide
[2] Quat: Quaternary
[3] DDAC: didecyl dimethyl ammonium chloride
The values in parentheses are standard deviations from the mean values of 3 samples.

Composite Mechanical Properties

Table 3 lists the flexural, tensile, and impact properties of the injection-molded samples from treated and untreated wood, together with the statistical ranking information for each property. Figure 1 shows the typical plot of the mechanical properties (*i.e.*, modulus of rupture) for different types of coupling agents. The samples with ACQ- and MCQ-treated wood had property values comparable with those of untreated wood. Thus, the blends with treated wood materials could be injection-molded very well. The distinct situation was observed when the four coupling agents were individually added. Among them, EGMA contributed to the highest flexural and tensile strength values for all types of panels (*i.e*., the ACQ treated, MCQ-treated, and the untreated); POE contributed to the highest impact strength for the composites with MCQ-treated wood; MAPE contributed to the highest flexural and tensile modulus properties for the composites with ACQ-treated wood. In general, the MAPE system led to relatively balanced values in all properties. The EGMA system led to the best bending, tensile, and impact strength except for the impact strength of the composites containing MCQ-treated wood. However, it may not be very cost-competitive at a similar loading level when compared with the most commonly used MAPE coupling system. The EPR and POE showed less effect on bending and tensile properties than did MAPE and EGMA systems.

Table 3. Mechanical Properties of Treated and Untreated Wood/HDPE Composites

Wood Type	Coupling Agent	Strength			Modulus	
		Flexural (MPa)	Tensile (MPa)	Impact (KJ/m^2)	Flexural (GPa)	Tensile (GPa)
ACQ-Treated Wood	MAPE	36.85 (0.36) C	20.79 (0.34) C	2.96 (0.09) E	2.05 (0.03) A	2.80 (0.27) AB
	EPR	28.41 (0.20) H	14.13 (0.43) G	3.27 (0.18) DE	1.91 (0.06) CD	2.64 (0.90) AB
	EGMA	40.63 (0.41) B	23.52 (0.21) B	3.32 (0.26) CD	1.97 (0.05) B	2.67 (0.15) AB
	POE	28.13 (0.26) H	14.18 (0.37) G	3.25 (0.16) DE	1.82 (0.03) E	2.50 (0.23) AB
MCQ-Treated Wood	MAPE	30.54 (0.18) G	16.39 (0.41) F	3.59 (0.31) BC	1.75 (0.02) F	2.73 (0.25) AB
	EPR	28.12 (0.19) H	14.36 (0.42) G	3.93 (0.11) A	1.72 (0.02) F	2.44 (0.33) AB
	EGMA	36.23 (0.27) D	20.05 (0.20) D	3.75 (0.27) AB	1.83 (0.02) E	3.07 (1.01) A
	POE	27.99 (0.35) H	14.07 (0.40) G	3.99 (0.39) A	1.73 (0.04) F	2.33 (0.30) B
Untreated Wood Control	MAPE	36.22 (0.23) D	20.80 (0.21) C	3.22 (0.16) DE	1.92 (0.03) C	2.33 (0.27) B
	EPR	34.07 (0.36) E	19.95 (0.19) D	3.19 (0.49) DE	1.83 (0.03) E	2.43 (0.56) AB
	EGMA	41.45 (0.54) A	25.20 (0.30) A	3.58 (0.69) BC	1.90 (0.03) CD	2.35 (0.19) B
	POE	32.54 (0.57) F	17.99 (0.46) E	3.19 (0.38) DE	1.86 (0.05) DE	3.01 (0.60) AB

* The values in parentheses are standard deviations from the mean values of 5 samples.

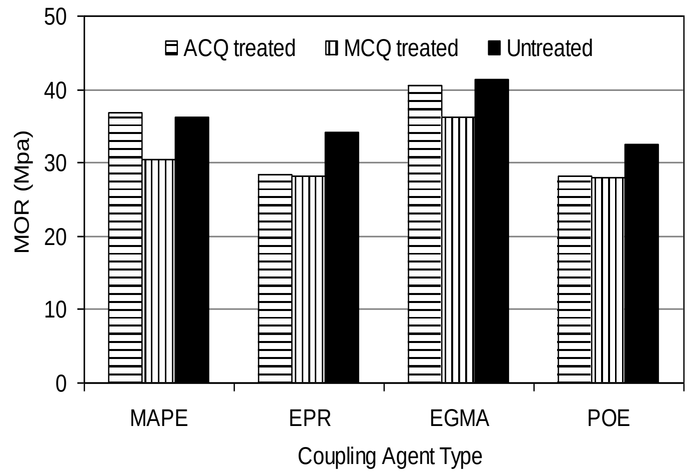

Fig. 1. Modulus of rupture (MOR) for treated and untreated wood-filled HDPE composites

Composite Water Absorption Properties

Figure 2 shows the moisture absorption curves for ACQ- and MCQ-treated wood/HDPE composites with the application of different coupling agents.

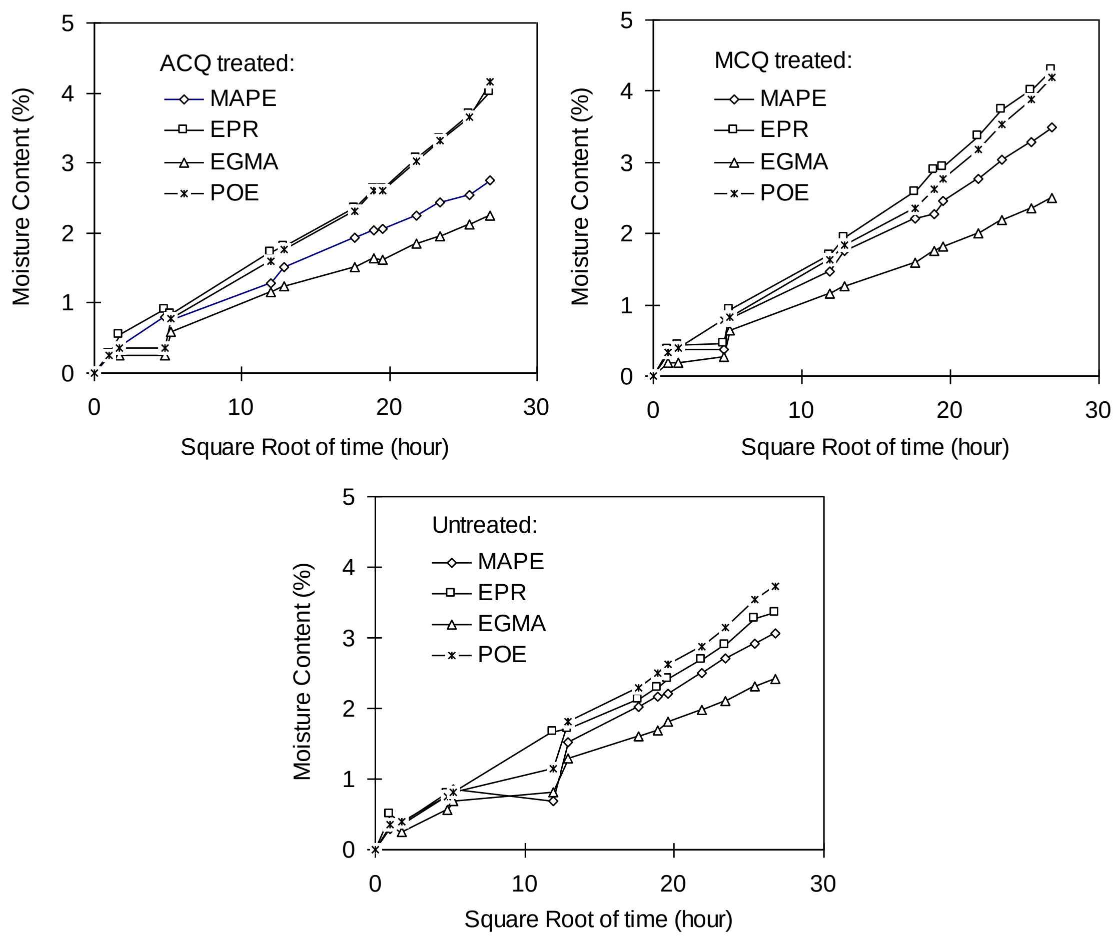

Fig. 2. Moisture absorption *vs.* time for treated and untreated wood-filled HDPE composites with different coupling agents

Generally, the composites with ACQ- and MCQ-treated wood particles had moisture absorption behaviors similar to the untreated wood-filled HDPE composites. It was observed that the composites with EPR and POE coupling agents absorbed the most moisture, while the composites with EGMA showed the lowest moisture absorption values. This result is also reflected in the bonding between the fiber and plastic matrix, where EGMA had the best effect on strength. In addition, EPR and POE coupling agents had similar effect on moisture absorption for the composites containing ACQ-treated wood.

The EGMA and MAPE as compatibilizers can interact with the hydrophobic polymer and hydrophilic wood fibers through their long olefinic chain and through their glycidyl or anhydride group (Lu *et al.* 2000). The reaction leads to an improvement in the interfacial adhesion between the polymers and wood fibers, resulting in an enhancement of the properties of composites (*i.e.*, strength and water absorption).

Composite Biological Properties

Table 4 summarizes the termite test data (mortality, mass loss, and damage rating with statistical ranking) of injection-molded samples in comparison with those from untreated solid wood controls and pure HDPE. All wood plastic composite and pure HDPE samples performed well, while solid wood controls had large mass losses (37%) and low sample damage ratings. Of the samples of the two groups of WPC containing treated wood fibers, the samples with ACQ-treated wood had lower mass losses than those with MCQ-treated wood. This may be due to the higher copper and quat loading in the wood, as shown in Table 2. The composite group containing the untreated wood had a slightly larger mass loss.

Table 4. Termite Test Data for the Composites with Treated and Untreated Wood Fibers

Sample Group	Type of Wood	Mortality (%)	Mass Loss (%)	Ratings (0-10)
WPC-MAPE WPC-EPR WPC-EGMA WPC-POE	ACQ-treated SYP wood	2.65(1.51) AB 3.35(1.91) ABC 4.05(1.11) ABCD 8.25(4.29) CDE	0.37(0.53) A 0.36(0.37) A 0.25(0.44) A 0.93(0.62) A	8.9(0.43) D 9.3(0) D 9.3(0.15) D 8.8(0.18) D
WPC-MAPE WPC-EPR WPC-EGMA WPC-POE	MCQ-treated SYP wood	9.95(4.2) E 8.80(4.1) DE 9.75(4.52) E 7.40(4.79) BCDE	3.25(0.67)B 3.38(0.56) B 3.65(0.85) BC 4.61(0.03) BCD	7.9(0.28)B 7.9(0.18) BC 8.9(0.29)D 8.3(0.15)BC
WPC-MAPE WPC-EPR WPC-EGMA WPC-POE	Untreated-SYP wood control	6.80(1.96) ABCDE 6.80(3.81) ABCDE 6.20(2.70)ABCDE 7.15(3.35) ABCDE)	4.61(0.46)CD 4.92(0.18) D 3.43(0.81) B 4.94(0.31) D	8.7(0.44) D 8.7(0)D 8.1(0.29) C 8.1(0.64) BC
Pure HDPE	No wood	7.25(2.8) ABCDE	0 (0) A	10.0(0) E
Solid wood	Untreated wood	2.15(0.96) A	37.09(2.08) E	0.0 (0) A
* The values in parentheses are standard deviations from the mean values of 5 samples.				

The average mass losses for ACQ-treated wood-HDPE (ACQ-HDPE), MCQ-treated wood-HDPE (MCQ-HDPE), untreated wood-HDPE (CTL-HDPE), pure HDPE, and the solid wood control (Solid WD) are presented in Fig. 3. The ACQ- and MCQ-treated wood-HDPE composites had lower mass losses than the untreated wood-HDPE, indicating the enhanced decay resistant performances of polymer composites from pressure-treated wood materials. There were significant differences in mass loss between various HDPE composites and the solid wood control sample, as expected. Pure HDPE showed the lowest mass loss values, which further demonstrated that the wood in WPCs can be attacked by decay fungi and termites.

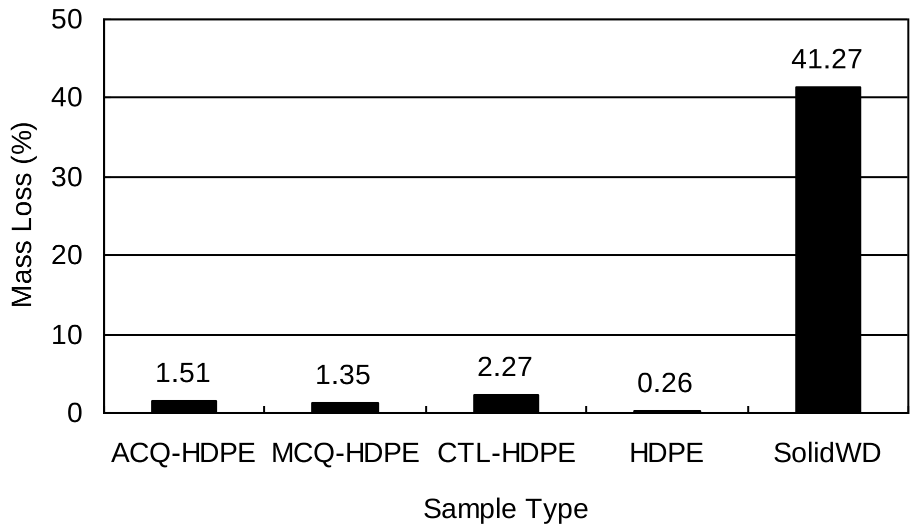

Fig. 3. The mass loss of different composite samples after decay test

CONCLUSIONS

1. Both ACQ- and MCQ-treated wood materials can be successfully used to make wood plastic composites with stable mechanical properties and improved biological performances. The different coupling agents that were used worked well for the treated wood materials.
2. The composites containing the treated wood materials had water absorption behaviors similar to the untreated wood-filled HDPE composites. The samples with EPR and POE coupling agents absorbed moisture most significantly, while those with EGMA showed the lowest moisture absorption values.
3. The results of this study demonstrated the feasibility of wood-plastic composites containing pressure-treated wood materials and therefore offer a practical approach to recycling treated wood into value-added composites.

ACKNOWLEDGMENTS

This work was financially supported by the United States Department of Agriculture, Grant No. 68-3A75-6-508 and by the National Natural Science Foundation of China (NSFC), Grant Number 31010103905. The authors would like to thank Dr. Fei

Yao, Dr. Kevin Ragon, and Mr. Jay Curole for their assistance in carrying out part of experimental work. Part of the material was presented at the 40th Annual IRG Meeting (Beijing, China, 24-28 May 2009).

REFERENCES CITED

American Wood-Preserver's Association (2006). "Standard method of testing wood preservatives by laboratory soil-block cultures," AWPA Standard AWPA E10-06, Granbury, TX, USA.

American Wood-Preserver's Association (2001). "Standard method of laboratory evaluation to determine resistance to subterranean termites," AWPA Standard AWPA E1-01, Granbury, TX, USA

Clemons, C. M., and Caulfield, D. (2005). "Natural fibers," In: *Functional Fillers for Thermoplastics*, M. Xanthos (ed.), Wiley-VCH Verlag, Chapter 11, 195-206.

Kamdem, D. P., Jiang, H., Cui, W., Freed, J., and Matuana, M. L. (2004). "Properties of wood plastic composites made of recycled HDPE and wood flour from CCA-treated wood removed from service," *Composite Part A* 35, 347-355.

Laks, P. E., Richter, D. L., and Larkin, G. L. (2000). "Biological deterioration of wood-based composite panels," *Wood Design Focus* 11(4), 7-14.

Lu, J. Z., Wu, Q., and McNabb, Jr., 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.

Simonsen, J., Freitag, C. M., Silva, A., and Morrell, J. J. (2004). "Wood/plastic ratio: Effect on performance of borate biocide against a brown rot fungus," *Holzforchung* 58, 205-208.

Verhey, S. P., Laks, E., and Richter, D. L. (2001). "Laboratory decay resistance of wood fiber/thermoplastic composites," *Forest Prod. J.* 51(9), 44-49.

Article submitted: June 3, 2012; Peer review completed: July 11, 2012; Revised version received: August 28, 2012; Accepted: September 1, 2012; Published: September 6, 2012.