Proceedings IRG Annual Meeting (ISSN 2000-8953)

IRG/WP 14-40655

THE INTERNATIONAL RESEARCH GROUP ON WOOD PROTECTION

Section 4 **Processes and properties**

Decay resistance of wood-plastic composites reinforced with extracted or delignified wood flour

Rebecca E. Ibach, Yao Chen*, Nicole M. Stark, Mandla A. Tshabalala, Yongming Fan*, Jianmin Gao*

U.S. Department of Agriculture Forest Service
Forest Products Laboratory
One Gifford Pinchot Drive
Madison, WI 53726-2398 USA

*College of Material Science and Technology
Beijing Forestry University, Beijing 100083, China

Paper prepared for the 45th IRG Annual Meeting
St George, Utah, USA
11-15 May 2014

IRG SECRETARIAT
Box 5609
SE-114 86 Stockholm
Sweden
www.irg-wp.com

Decay resistance of wood-plastic composites reinforced with extracted or delignified wood flour

Rebecca E. Ibach[1], Yao Chen[2], Nicole M. Stark[1], Mandla A. Tshabalala[1], Yongming Fan[2], Jianmin Gao[2]

[1] U.S. Department of Agriculture Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726-2398, ribach@fs.fed.us

[2] College of Material Science and Technology, Beijing Forestry University, Beijing 100083, China

ABSTRACT

The moisture and decay resistance of wood-plastic composites (WPCs) reinforced with extracted or delignified wood flour (WF) was investigated. Three different extractions were preformed: toluene/ethanol (TE), acetone/water (AW), and hot water (HW). Delignification (DL) was performed using a sodium chlorite/acetic acid solution. All WPCs specimens were made with 50% by weight HDPE and WF, first compounded using extrusion followed by injection molding. After preconditioning in water at 70 °C for 5 days, the specimens were exposed for 12 weeks to the brown-rot fungus, *Gloeophyllum trabeum* in the AWPA D1413 standard soil block test. The WPC made with untreated wood flour had the highest overall weight loss (24.9 ±3.6%), followed by the HW (22.3 ±4.6%) and DL (16.4 ±3%). The TE (7.8 ±0.8%) and AW (7.7 ±2.3%) had the lowest weight losses. WPC moisture content was monitored before and after decay. Cracking was observed in some blends after the preconditioning, which may explain the differences in weight loss.

Keywords: wood-plastic composites, brown-rot, decay, extractives, delignification, water sorption, soil block test

1. INTRODUCTION

Wood plastic composites (WPCs) are a combination of wood in the form of flour, fibers or particles, and a thermoplastic matrix. Wood is a natural and renewable resource that is light and cheap so therefore incorporating it as a filler in WPCs has environmental and economic advantages (Tabari et al., 2011). At present, wood fiber is the most commonly used filler in the production of WPCs. The advantages of using wood fibers compared with using inorganic fibers are their low density, low abrasion, and low materials cost. Although untreated wood is susceptible to decay, some wood species have a natural resistance to microbial deterioration (Scheffer & Cowling, 1966).

Utilization of WPCs has grown rapidly in Europe, the United States, and Canada and with this comes an increase in the expected performance. The mechanical properties of WPCs depend on the properties of the filler, matrix, and the interfacial compatibility. The interface between the hydrophobic plastic and hydrophilic wood is typically weak and fails to transfer stress.

Little attention has been given to the effect of chemical composition of wood on WPC performance. Wood is a complex polymeric composite, which contains cellulose, hemicellulose, lignin and extractives. Extractives can be divided into three major classes: (1) aliphatic compounds (fatty acids, fatty alcohols, waxes and fats, gums, glycosides), (2) terpenes and terpenoids, (pinene, cadinene, abietic acid), and (3) phenolic structures (phenolic acids, tannins, flavonoids, lignans, stilbenes). Although extractives contribute only a few percent to the entire

wood composition, they have significant influence on properties such as mechanical strength, color, and the quality of wood (Shebani et al., 2008).

The effect of wood extractives on the strength, thermal and weathering properties of WPCs has been studied (Kim et al., 2009, Shebani et al., 2009, Saputra & Simonsen, 2004, Stark & Mueller, 2008, Fabiyi et al., 2009). At high molding or extrusion temperatures, wood extractives may migrate to the wood flour surface and accumulate in the wood-plastic interphase. Wood extractives can influence the weathering performance of WPCs by influencing hygroscopicity and color. Removal of extractives using acetone had little effect on composite lightness after accelerated weathering while removing the lignin had a significant effect (Fabiyi et al., 2009).

Lignin is a highly unordered, three-dimensional polymer of coniferyl, syringyl, and coumaryl alcohol units. It influences WPC performance, especially color change during weathering (Fabiyi et al., 2005). The use of cellulose or holocellulose fiber for WPC production minimizes the problem of color change during weathering. Pure cellulose fibers instead of wood fiber in WPCs produce higher thermal stability (up to 270°C) for potential structural applications (Sears et al., 2001).

The first generations of WPCs were considered to be very resistant to biological decay, and one reason for this was the slow moisture transport into the material achieved by the polymer matrix. However, the outermost layer of the composite has been shown capable of reaching moisture levels high enough to initiate biological decay (Wang & Morrell, 2004, Gnatowski, 2009) (Ibach et al., 2013). WPCs have a thermoplastic-rich surface layer that is created during their processing (through extrusion, compression molding, or injection molding) that produces high levels of water repellency (Clemons & Ibach, 2004). To simulate long-term field conditions in laboratory decay tests, it is necessary to expose WPCs to moisture conditions for long periods of time or at elevated temperatures, which ensures a moisture content high enough (around 25%) to support fungal growth (Ibach et al., 2004, Ibach et al., 2013, Lopez et al., 2005, Shirp et al., 2008, Shirp & Wolcott, 2005, Manning & Ascherl, 2007, Kim et al., 2008, Kim et al., 2009, Lomelí-Ramírez et al., 2009, Defoirdt et al., 2010, Fabiyi et al., 2011, Segerholm et al., 2012).

Little has been published about the effects of wood extractives and lignin on the biological performance of high-density polyethylene (HDPE)-based WPCs. This research is part of a larger study on the effect of extracted and delignified wood flour on the properties of WPCs (Chen et al., 2014). The objective of this study was to investigate the effect that the removal of solvent and water soluble extractives and lignin have on the durability of WPCs with regard to moisture and fungal decay.

2. EXPERIMENTAL METHODS

2.1 Materials

The high density polyethylene (HDPE) had a melt index of 33.0g/10min and density of 0.951 g/cm^3 (Exxon Mobil, Houston, Texas). The wood flour (WF) was derived from post-industrial mixed pine species (American Wood Fibers, AWF 4020. Schofield, Wisconsin). The large particles were removed through a 40-mesh screen (0.425 mm) and the fine particles with a 60 mesh screen (0.250 mm).

2.2 Wood flour extractions and delignification

Samples of WF were extracted separately with three solvent systems, or delignified with one solution. The solvent systems were toluene/ethanol (TE, 2:1 volume ratio), acetone/water (AW, 9:1 volume ratio), hot water (HW) and each were performed in a Soxhlet extractor for 24 h. Sodium chlorite/acetic acid solution was used for delignification (Wise *et al*. 1946).

2.3 Manufacture of WPC specimens

The WPC material was first compounded with 50% WF and 50% HDPE, by weight, and then injection molded using DSM Xplore micro-processing equipment (DSM Research, Geleen, Netherlands). The DSM Xplore has a 15-mL conical, twin-screw compounder and a 12-mL injection molder. The compounding temperature was run at 180 °C, and the injection molding at 190 °C. The mold cavity dimensions of the injection die was 3 x 12 x 120 mm (ASTM 2010). The composition and WF treatments of the WPC blends are shown in Table 1.

Table 1: Composition and wood flour treatments of 5 WPC blends.

WF treatments	Abbreviation	Volume Ratio	Extraction time [h]	Wood:Polymer [%]
Untreated Control	C		0	50:50
Toluene:Ethanol	TE	2:1	24	50:50
Acetone:Water	AW-	9:1	24	50:50
Hot Water	HW		24	50:50
Delignified ($NaClO_2$ (80%): CH_3CO_2H)	DL	3x(30g:10ml)/1L H_2O	5	50:50

2.4 Soil block test

The injection molded specimens were cut (3 x 12 x 87 mm) to allow insertion into the horizontal soil bottles for eventual testing of flexural properties and for greater surface area. Initial oven-dried weight was determined by drying for 48 h at 105 °C in a forced-draft oven, cooling in a desiccator for 1 h, and then weighing each specimen. Specimens were preconditioned by water soaking for 5 days at 70 °C, weighed, and moisture content was calculated. At the end of preconditioning, five specimens of each blend were air dried for 24 h, oven dried for 48 h in a forced-draft oven, cooled for 1 h in a desiccator, and then weighed. Percentage mass loss, due to water/temperature conditioning was calculated.

A modified soil block test procedure based on AWPA E10 (AWPA, 2012) and outlined in Clemons and Ibach (Clemons & Ibach, 2004) was used to evaluate the specimens. Five replicates of each blend were autoclaved wet and then placed in horizontal soil bottles under one of two fungal exposure conditions:

1. No fungus (nf)
2. *G.trabeum*, a brown-rot fungus (br)

After 12 weeks exposure, specimens were taken out, wiped to remove fungal mycelium if present, weighed, air dried at room temperature for 24 h, oven dried for 48 h at 105 °C in a forced-draft oven, cooled in a desiccator for 1 h, and weighed again. Mass loss and moisture content were calculated.

3. RESULTS AND DISCUSSION

The overall mass loss and moisture content of the WPC blends are shown in Table 2. The untreated controls had the highest overall weight loss (24.9 ±3.6%) and moisture content (28.9 ±3.1) after decay. This was expected because it contained all the wood components that were available for moisture sorption and fungal decay, especially the hemicelluloses. The HW extracted WPC had an overall weight loss of 22.3 ±4.6%, followed by the DL (16.4 ±3%). The TE (7.8 ±0.8%) and AW (7.7 ±2.3%) had the lowest weight losses of all the WPC blends.

Table 2. WPC overall percentage mass loss and moisture content of injection molded specimens made with 50% extracted or delignified wood flour and 50% HDPE, before and after decay. All were preconditioned by water soaking at 70 °C for 5 days.

Wood Treatment	Exposure	Mass loss [%] (stdev)	MC [%] (stdev)
C	Brown-rot	24.9 (3.6)	28.9 (3.1)
C	No fungus	1.7 (0.1)	16.5 (1.0)
C	Just water soak	1.10 (0.1)	18.8 (0.6)
HW	Brown-rot	22.3 (4.6)	25.4 (2.3)
HW	No fungus	1.0 (0.1)	15.3 (0.7)
HW	Just water soak	0.3 (0.1)	12.9 (0.9)
DL	Brown-rot	16.4 (3.0)	24.3 (0.8)
DL	No fungus	4.0 (0.1)	21.7 (1.2)
DL	Just water soak	2.6 (0.1)	19.5 (1.0)
TE	Brown-rot	7.8 (0.8)	17.1 (0.7)
TE	No fungus	0.7 (0.0)	14.19 (0.3)
TE	Just water soak	0.2 (0.2)	10.2 (0.2)
AW	Brown-rot	7.7 (2.3)	18.3 (2.5)
AW	No fungus	0.7 (0.1)	14.3 (0.3)
AW	Just water soak	0.0 (0.0)	10.3 (0.2)

The preconditioning at 70 °C for 5 days was performed to get the moisture content of the WPC specimens up to the fiber saturations point so that fungal decay could occur (around 25% wood moisture content). A result of this conditioning was the cracking of some of the specimens. All of the untreated controls had cracks on both sides. The HW and DL specimens had cracks mainly on one side. The AW specimens had only a few small cracks on both sides, while the TE had almost no visible cracks. Cracking from the preconditioning opened up the composites therefore providing better accessibility to more surface area and also more wood particles to moisture and then decay. This WPC cracking could have resulted because of the chemistry and/or incompatibility between the wood and HDPE. There was a correlation between the amount of cracking and the moisture content after preconditioning. The blends that had less cracking also had less moisture sorption i.e. TE and AW.

The LR WPCs had less weight loss than the controls and HW, but more than TE and AW. This could be because there was less cracking than the controls and HW, but more than TE and AW. Another reason could be the chemical composition after the delignification is mainly holocellulose, which is most susceptible to attack by the brown-rot fungus.

These biological and moisture results correlate with the previous study (Chen et al., 2014). The removal of extractives from the wood flour resulted in a decrease in water sorption rate, a

decrease in diffusion coefficient and maximum thickness swelling and thickness swelling rates, and an increase in MOE. The WF hydrophobicity increased after removal of extractives because these compounds tend to be hydrophilic (e.g. phenol and carbonyl groups). The WPCs filled with TE extracted WF showed better mechanical properties and water resistant compared with AW or HW extracted WF, which may be attributed to a higher metal content remaining in the TE or the increased hydrophobic nature of the extracted wood. The compatibility between the WF and HDPE plastic matrix, and the various extractives remaining in the WF after extractions could affect moisture sorption (Chen et al., 2014). Extractive-free wood generally absorbs less water and swells less than non-extracted wood from decreased availability of moisture sites previously occupied by extractives and decreased diffusion coefficient (Spalt, October 29, 1979, Nearn, 1955).

The DL WF absorbed water faster and had a higher swelling rate than the untreated WF (Chen et al., 2014). The removal of lignin from WF increased the hydrophilic nature of the WF and that contributed to a faster water sorption. Removal of lignin could increase the availability of hygroscopic sites previously blocked by lignin.

Water sorption characteristics of extracted pine WPCs are more influenced by the interaction between the wood flour and the polymer matrix than by the properties of the wood flour itself. The swelling of the wood component in WPCs affects the composite's microstructure by expanding cracks, debonding wood-plastic interface, and thereby providing more pathways for water penetration (Steckel et al., 2007).

4. CONCLUSIONS

Wood-plastic composites have moisture resistance properties, but given moisture and time, they do sorb moisture and wood decay can follow. The extractives and lignin do have an effect on the durability of WPCs. The effect of extractives and lignin in pine wood flour on the moisture and biological resistance of WPCs was studied. WPCs made with TE or AW extracted WF showed the highest fungal and moisture resistance. Preconditioning of samples at elevated temperature (70 °C/5 days) resulted in significant cracking of untreated Control, HW and DL WPC specimens that allowed greater pathways for moisture and decay to enter. This resulted in higher percentage moisture contents and weight losses.

These results are important when considering product exposure conditions and use i.e. indoors or outdoors. Preconditioning should always be considered for laboratory testing of the moisture and fungal decay and overall durability of WPCs. Bending tests and microscopic evaluations are underway to understand the impact of moisture and decay on the structure and mechanical properties of these composite blends.

5. ACKNOWLEDGEMENTS

Thanks to Angeline Juan and Kolby Hirth from the Forest Products Laboratory for their assistance with the soil block testing.

6. REFERENCES

AWPA. 2012. E10-12 Standard Method of Testing Wood Preservatives by Laboratory Soil-Block Cultures. In. *American Wood Protection Association Book of Standards.* Birmingham, Alabama: AWPA.

Chen Y, Stark NM, Tshabalala MA, Gao J, Fan Y. 2014. Properties of wood-plastic composites reinforced with extracted and delignified wood flour. *Holzforschung. Accepted for publication*.

Clemons CM, Ibach RE. 2004. Effects of processing method and moisture history on laboratory fungal resistance of wood-HDPE composites. *Forest Products Journal* **54**, 50-7.

Defoirdt N, Gardin S, Van Den Bulcke J, Van Acker J. 2010. Moisture dynamics of WPC and the impact on fungal testing. *International Biodeterioration and Biodegradation* **64**, 65-72.

Fabiyi J, Mcdonald A, Mcilroy D. 2009. Wood Modification Effects on Weathering of HDPE-Based Wood Plastic Composites. *Journal of Polymers and the Environment* **17**, 34-48.

Fabiyi JS, Mcdonald AG, Morrell JJ, 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**, 501-10.

Fabiyi JS, Mcdonald AG, Wolcott Michael P. 2005. Chemical changes that occur during the weathering of wood plastic composites. *Proceedings of the 8th International Conference on Woodfiber-Plastic Composites (and other natural fibers)*. Madison, WI: Forest Products Society, 191-6.

Gnatowski M. 2009.Water Absorption and Durability of Wood Plastic Composties. In: Stark N, ed. *Proceedings of the 10th International Conference on Wood & Biofiber Plastic Composites*, Madison, WI: Forest Products Society, 90-109.

Ibach R, Gnatowski M, Sun G, 2013. Field and laboratory decay evaluations of wood-plastic composites. *Forest Products Journal*. **63**(3/4) pp. 76-87.

Ibach RE, Clemons CM, Stark N, M. 2004. Combined Ultraviolet and Water Exposure as a Preconditioning Method in Laboratory Fungal Durability Testing. In: Stark N, ed. *Proceedings of the The Seventh International Conference on Woodfiber-Plastic Composites*. Madison, Wisconsin: Forest Products Society, 61-7.

Kim J-W, Harper DP, Taylor AM,.2008. Effect of wood species on water sorption and durability of wood-plstic composites. *Wood and Fiber Science* **40**, 519-31.

Kim J-W, Harper DP, Taylor AM. 2009. Effect of extractive on water sorption and durability of wood-plastic composites. *Wood and Fiber Science* **41**, 279-90.

Lomelí-Ramírez MG, Ochoa-Ruiz HG, Fuentes-Talavera FJ, García-Enriquez S, Cerpa-Gallegos MA, Silva-Guzmán JA. 2009. Evaluation of accelerated decay of wood plastic composites by Xylophagus fungi. *International Biodeterioration & Biodegradation* **63**, 1030-5.

Lopez JL, Cooper PA, Sain M, 2005. Evaluation of proposed test methods to determine decay resistance of natural fiber plastic composites. *Forest Products Journal* **55**, 95-9.

Manning MJ, Ascherl F. Wood-plastic composite durability and the compelling case for field testing. *Proceedings of the 9th International Conference on Wood & Biofiber -Plastic Composites, 2007*. Madison, WI: Forest Products Society, 217-24.

Nearn WJ, 1955. Effect of water-soluble extractives on the volumetric shrinkage and equilibrium moisture content of eleven tropical and domestic woods. Bull.598 Penn State Univ Agric.Exp Sta. University Park, PA. pp. 38.

Saputra H, Simonsen J. 2004. Effect of extractives on the flexural properties of wood/plastic composites. *Composite Interfaces* **11**, 515-24.

Scheffer TC, Cowling EB. 1966. Natural Resistance of Wood to Microbial Deterioration. *Annual Review of Phytopathology* **4**, 147-68.

Sears KD, Jacobson RD, Caulfield DF, Underwood J. 2001. Reinforcement of engineering thermoplastics with high purity wood cellulose fibers. In. *Proc. of the 6th International Conf. on Wood-Plastic Composites*. Madison, WI: Forest Products Society, 27-34.

Segerholm BK, Ibach RE, Walinder MEP. 2012. Moisture sorption in artificially aged wood-plastic composites. *Bioresources* **7**, 1283-93.

Shebani AN, Van Reenen AJ, Meincken M. 2008. The effect of wood extractives on the thermal stability of different wood species. *Thermochimica Acta* **471**, 43-50.

Shebani AN, Van Reenen AJ, Meincken M. 2009. The effect of wood extractives on the thermal stability of different wood-LLDPE composites. *Thermochimica Acta* **481**, 52-6.

Shirp A, Ibach RE, Pendleton DE, Wolcott MP. 2008. *Chapter 29. Biological degradation of wood-plastic composites (WPC) and strategies for improving the resistance of WPC against biological decay*. USA: American Chemical Society (ACS). 480-507

Shirp A, Wolcott MP. 2005. Influence of fungal decay and moisture absorption on mechnaical properties of extruded wood-plastic composites. *Wood and Fiber Science* **37**, 643-52.

Spalt HA. 1979. Water-vapor sorption by woods of high extractive content. *Proceedings of the Wood moisture content -- tempertaure and humidity relationships, October 29, 1979.* Virginia Polytech. Inst. and State Univeristy, Blacksburg, VA, 55-61.

Stark N, Mueller S. 2008. Improving the Color Stability of Wood-Plastic Composites Through Fiber Pre-Treatment. *Wood and Fiber Science* **40**, 271-8.

Steckel V, Clemons CM, Thoemen H. 2007. Effects of material parameters on the diffusion and sorption properties of wood-flour/polypropylene composites. *Journal of Applied Polymer Science* **103**, 752-63.

Tabari HZ, Nourbakhsh A, Ashori A, 2011. Effects of nanoclay and coupling agent on the physico-mechanical, morphological, and thermal properties of wood flour/polypropylene composites. *Polymer Engineering & Science* **51**, 272-7.

Wang W, Morrell JJ, 2004. Water sorption characteristics of two wood-plastic composites. *Forest Products Journal* **54**, 209-12.