

MOISTURE PERFORMANCE OF WOOD-PLASTIC COMPOSITES REINFORCED WITH EXTRACTED AND DELIGNIFIED WOOD FLOUR

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Abstract

This study investigated the effect of using extracted and delignified wood flour on water sorption properties of wood-plastic composites. Wood flour (WF) extraction was performed with three solvent systems: toluene/ethanol (TE), acetone/water (AW), and hot water (HW); delignification was conducted using sodium chlorite/acetic acid solution. A 2⁴ full-factorial experimental design was employed to determine the effects of treatments and combinations of treatments. WF/HDPE composites for testing were manufactured using extrusion and injection molding. Compared with composites containing untreated WF, composites produced with extracted WF had lower water absorption rates and composites containing delignified WF had higher water absorption rates.

Introduction

The effective use of wood-based particles and fibers as fillers or reinforcements in thermoplastic composites requires a fundamental understanding of the morphology and chemical characteristics of wood [1]. The morphological and chemical properties of the raw materials used to produce wood-plastic composites are important variables in defining the final properties [2]. While the influence of the physical characteristic of the wood reinforcement on composite properties has been studied, not much attention has been paid to the effect of chemical composition of wood on WPC performance.

Wood flour is routinely mixed with thermoplastics at temperatures approaching 200 °C during manufacturing. At these processing temperatures, wood extractives may migrate to the wood flour surface and accumulate at the wood-plastic interphase. Wood extractives can influence the weathering performance of WPCs by influencing hygroscopicity and color [3]. Removal of various wood components from WF before incorporation into WPCs as a method to improve weathering performance has been [4,5]. In an effort to improve color stability through removal of water soluble extractives, Stark and Mueller [4] washed salt cedar (*Tamarix chiensis*) and pine wood flour in water before incorporation into a polyethylene matrix. This decreased the water soluble extractive

content from 12% to 3% for the salt cedar wood flour and from 6% to 3% for the pine wood flour, but did not improve color stability of the WPCs. Fabiyi *et al.* [5] treated WF to improve weathering performance using two techniques. The first was to remove extractives using acetone, and the second was to remove lignin using acetic acid. Acetone extraction resulted in removal of 3% extractives based on initial weight. Acetic acid extraction resulted in wood fibers with only 1–1.5% lignin. Composites manufactured from polyethylene and the modified wood were then weathered and analyzed. The removal of extractives using acetone had little effect on composite lightness after accelerated weathering while removing lignin improved the color stability and wood retention of WPC after weathering. Lignin has been suggested to be a great contributor to WPC color change during weathering [5].

At present, little has been published about the effects of wood extractives and lignin on the performance of high-density polyethylene (HDPE)-based WPCs. The current work investigates the effect of using delignified and exhaustively extracted wood flour on water sorption of wood-plastic composites. The results from this study will help to identify a method of wood fiber modification to enhance the performance of HDPE-based WPCs.

Materials and Methods

Wood flour, supplied by American Wood Fibers (AWF 4020; Schofield, Wisconsin), was sieved through a 40-mesh screen (0.425 mm) to remove the larger particles and through a 60-mesh screen (0.250 mm) to remove the fine particles. The wood flour was derived from post-industrial mixed pine species and was selected because it is the most common WF used for WPC decking.

HDPE with a melt index of 33.0 g/10 min and density of 0.951 g/cm³ (59.3 lb/ft³), was supplied by ExxonMobil (ExxonMobil Excorene HD-6733 HDPE, Houston, Texas).

Samples of WF were treated with three solvent systems and one delignification solution. Solvent extractions and delignification treatments and their combinations were carried out according to a 2⁴ full-

factorial experimental design. Each extraction process was performed for 24 h in a Soxhlet apparatus to ensure exhaustive removal of either polar or non-polar extractives. Three different solvents, toluene/ethanol (TE), acetone/water (AW), hot-water (HW) and various combinations of these solvents were used to remove extractives from wood flour. TE solvent was prepared based on volume ratio (2:1) of toluene and ethanol. AW solvent was prepared based on volume ratio (9:1) of acetone and distilled water. Lignin was removed following the method developed by Wise *et al.* [6]. A 100-g sample of air-dried WF was dispersed (under constant stirring) in 1 L of deionized water containing 30 g of NaClO₂ (80%), 10 ml of acetic acid, and 100 µl of octan-2-ol (antifoaming agent, Acros Organics), and heated to 70 °C for 1 h. A further aliquot of 30 g of NaClO₂ (80%) and 10 ml of acetic acid was added, and the reaction was continued for another 1 h. Addition of NaClO₂ and acetic acid was repeated three more times for a total reaction time of 5 h before the mixture was allowed to cool to room temperature. The liquid layer was siphoned off, and the delignified WF was rinsed with 1-L aliquots of reverse osmosis (RO) water until a neutral pH was attained. The wood flour slurry was filtered on a Buchner funnel lined with filter paper. The filter cake was rinsed with 1 L of RO water, followed by 500 ml of 95% ethanol, 500 ml of absolute ethanol and 1 L of acetone. The filter cake was air-dried under suction for 30 min. All samples of WF, including the untreated WF, were vacuum-dried before further experimentation. All WF was oven-dried at 120 °C for 24 h prior to composite processing.

Injection-molded WPC composite samples were manufactured using micro-processing equipment (DSM Xplore, DSM Research, Geleen, The Netherlands). The DSM Xplore system consists of a 15 mL conical, twin-screw compounder and a 12-mL injection molder, which allows for processing in small batch sizes during which time process conditions can be monitored and controlled. Temperature in the compounder was set to 180 °C. After compounding, the extrudate was collected and injection molded. An ASTM flexural property die was used with mold cavity dimensions of 3 × 12 × 120 mm [7]. The temperature of the injector was set to 190 °C. All WPC samples were 50% by weight WF and 50% by weight HDPE.

The samples tested for moisture resistance were injection molded flexural samples cut in half with a nominal sample size of 3 × 12 × 60 mm. The samples were oven-dried for 24 h at 105 °C, and the weight, thickness, and width of these samples were determined before soaking in distilled water under an average temperature of 18.5 °C. The samples were periodically removed to measure weight, thickness, and width. For each treatment, five replicates were weighed, and five

different spots on each specimen were measured for thickness and width. It was assumed that an increase in weight corresponded with an increase in moisture content (MC). Percent MC, thickness swelling (TS), and width swelling (WS), were calculated based on Equations (1), (2), and (3), respectively.

$$MC(\%) = \frac{(M_t - M_0)}{M_0} \times 100 \quad (1)$$

$$TS(\%) = \frac{(T_t - T_0)}{T_0} \times 100 \quad (2)$$

$$WS(\%) = \frac{(W_t - W_0)}{W_0} \times 100 \quad (3)$$

Where M_0 is the oven-dry weight and M_t is the weight at time t , T_0 is initial thickness, and T_t is thickness at time t , W_0 is the initial width, and W_t is the width and time t .

The apparent diffusion coefficient (D_A) of HDPE Composite was calculated using Fick's diffusion equation based on the water sorption data.

$$D_A = \frac{\pi}{16} \left(\frac{h}{MC_{max}} \right)^2 \left(\frac{\partial MC}{\partial \sqrt{t}} \right)^2 \quad (4)$$

Where MC_{max} is the maximum MC measured at the end of the test, $\partial MC / \partial \sqrt{t}$ is the slope taken from the plot of MC versus square root of time, and h is the thickness of the sample [8].

Results and Discussion

The moisture content of composites containing untreated WF or a combination of extracted WF and/or delignified WF relative to soaking time is shown in Figure 1. Each data point represents an average of five replicates. For all composites, the moisture content initially increased linearly and reached a plateau as soaking time increased. In general, composites containing extracted WF absorbed water more slowly than composites containing untreated WF, while composites containing delignified WF absorbed water faster than composites containing untreated WF. The removal of extractives from WF with TE, AW, HW-extraction or combination extractions with those solvents systems led to lower water absorption compared to unextracted control because extractives tend to be hydrophilic (e.g., phenol and carbonyl groups). It has been reported in a previous work that HW removed inorganic substance and the polar extractives including tannins, gums, sugars, and starches, which take to 5.26% [9]. Acetone dissolved less polar extractives account to 4.15%, while toluene removed non-polar extractives. TE extracts takes 4.69%, involving benzaldehyde and

numerous terpenic compounds such as cedrol, agathadiol, epimanol, bornyl acetate, α -cedrene and β -cedrene. Therefore, WF hydrophobicity and likely composite hydrophobicity increased with the removal of these extractives. In contrast, the hydrophilicity of WF increased with lignin removal because of the exposure of holocellulose, which would have more hydroxyl groups available for bonding water and contribute to faster water sorption by the composite. Additionally, the removal of lignin may have increased the availability of hygroscopic sites previously blocked by lignin.

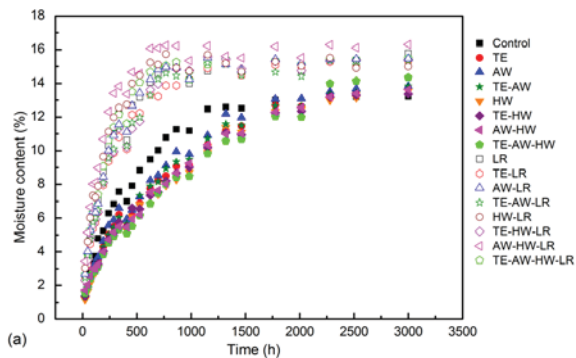
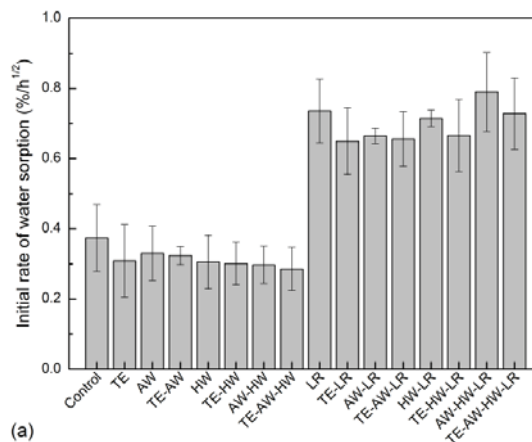


Figure 1. Water sorption characteristics of WPCs containing untreated and treated wood flour.

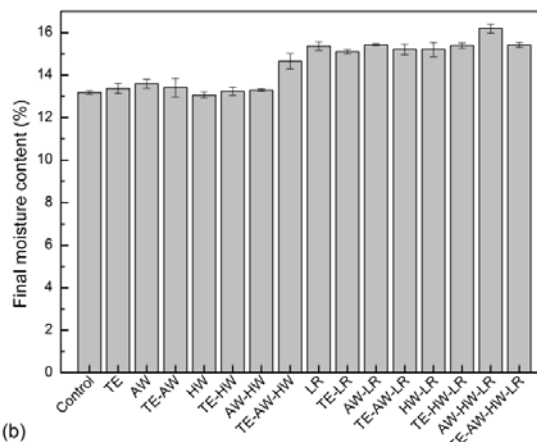
The data from Figure 1 can be used to determine the apparent diffusion coefficient (D_A) as shown in Equation (4). The D_A is related to both the initial rate of water sorption with respect to the square root of time and the final moisture content. The plot of water sorption versus square root of time showed a linear increase over the first 1,000 hours. The initial slope of this plot is shown in Figure 2a. Generally, compared with the composites containing untreated WF, the initial rate of water sorption was lower after extraction and higher after delignification. The initial rate of water sorption was almost two times higher for composites containing delignified WF than that composites containing extracted WF (0.70 ± 0.05 versus 0.31 ± 0.02 , respectively). The final moisture content is shown in Figure 2b. Although the trend was similar, the differences in final moisture content between composites containing delignified WF compared with extracted WF were much smaller (15.4 ± 0.3 versus 13.5 ± 0.5 , respectively). This suggests that the variability in D_A for these composites is primarily impacted by the differences in initial water absorption rate as opposed to the final MC.

The D_A according to Fick's law is presented in Figure 3. The water sorption characteristics of composites were significantly affected by the incorporation of either extracted or delignified WF. Overall extractions significantly decreased the D_A while delignification increased the D_A . The reduction in water uptake of the composites with extracted WF could be attributed to the removal of large parts of hygroscopic extractives with OH

groups. Comparing the composites containing WF after a single extraction, composites containing HW and TE extracted WF had the lowest D_A followed by AW extracted WF. This may suggest that water uptake becomes slower with an increase in the polarity of the solvent used. Combining all three extractions, TE-AW-HW resulted in the lowest overall D_A . It indicated that thorough removal of TE, AW, and HW extractives resulted in the lowest D_A . The D_A increased significantly when composites contained delignified WF compared with composites containing either untreated WF or extracted WF. The largest D_A was found when composites contain delignified WF combined with HW extraction, AW-HW extraction, and TE-AW-HW extraction. However, composites containing delignified WF combined with TE, AW, TE-AW, and TE-HW-extracted WF showed a lower D_A compared with only delignified WF.



(a)



(b)

Figure 2. Initial rate of water sorption and final moisture content of WPCs containing untreated and treated wood flour.

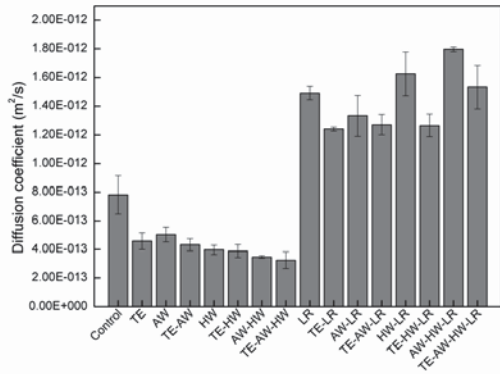


Figure 3. Diffusion coefficient of WPCs containing untreated and treated wood flour.

Figures 4 and 5 show the thickness swelling and width swelling, respectively, of the composites. Both thickness and width swelling of the composites showed a similar pattern to the water uptake data. Thickness and width swelling of composites containing delignified WF was higher compared with composites containing untreated WF, while thickness and width swelling of composites containing solvent extracted WF was lower compared with composites containing untreated WF. For all composites, the percent thickness swelling was higher than the percent width swelling.

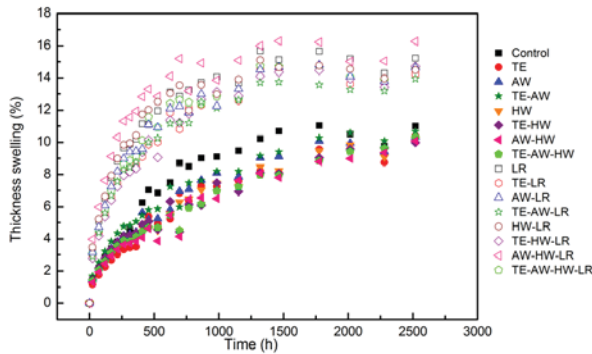


Figure 4. Thickness swelling of WPCs containing untreated and treated wood flour.

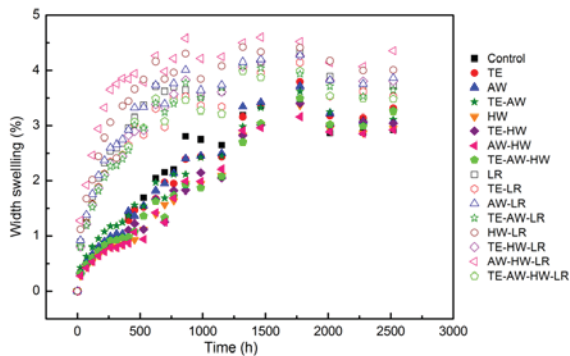


Figure 5. Width swelling of WPCs containing untreated and treated wood flour

At the end of the test, the maximum thickness swelling (TS_{max}) of delignified WF filled WPC samples were greater than that of samples made with non-extracted control, followed by the solvents extracted WF (Figure 6). The thickness swelling rate results followed a similar pattern as the diffusion coefficient results. There is little difference in TS_{max} among the WPC samples prepared with solvent-extracted WF. However, the samples filled with AW or TE-AW extracted WF show relatively higher TS_{max} values. For samples filled with delignified WF, the higher TS_{max} value was obtained when AW-HW-LR extracted WF was used as filler. The change in TS_{max} value after extraction indicates that hygroscopic properties of wood decreased with the removal of extractives [10-13]. The WPC samples made with extracted WF absorbed less water and swell less than those made from non-extracted control WF. Extractive-free wood generally absorbs less water and swells less than non-extracted wood from decreased availability of hydrogen bonding sites previously occupied by extractives and decreased diffusion coefficient [14]. Lignin could be another contributor to the decrease in hygroscopic properties. It can be seen that composites made from the delignified wood flour absorbed more water and swelled more than non-extracted WF filled composites.

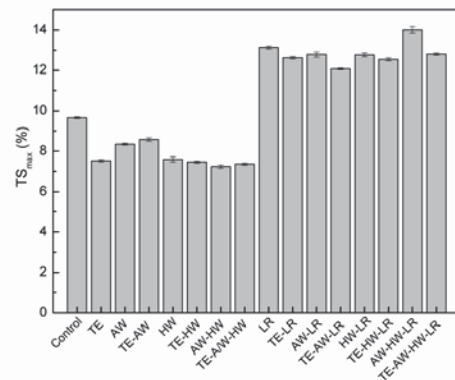


Figure 6. TS_{max} of WPCs containing untreated and treated wood flour.

Conclusions

Solvent extracted WF, delignified WF or extraction in combination with subsequent delignified WF and polyethylene were used to make WPC samples. In general, 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. These trends could be due to the removal of hydrophilic extractives. Composites prepared with delignified WF showed higher water sorption rates, diffusion coefficients and increased swelling compared with composites containing extracted or untreated WF.

Acknowledgments

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References

- 1) Bouafif, H., Koubaa, A., Pierre, P., Cloutier, A. (2009) *Compos Appl Sci Manuf.* 40(12):1975-1981.
- 2) Stokke, D.D., Gardner, D.J. (2003) *J Vinyl Addit Technol.* 9(2): 96-104.
- 3) Stark, N.M. (2006) *J Appl Polymer Sci.* 100 (4):3131-3140.
- 4) Stark, N.M., Mueller, S.A. (2008) *Wood Fiber Sci.* 40(2):271-278.
- 5) Fabiyi, J.S., McDonald, A.G., McIlroy, D. (2009) *J Polym Environ.* 17(1):34-48.
6. Wise, L.E., Murphy, M., D'Addireco, A.A. (1946) *Paper Trade J.* 122:35-43.
- 7) ASTM Standard (2010) ASTM 790. *Annual Book of ASTM Standards*, vol. 8.01, American Society for Testing and Materials, Conshohocken, PA.
- 8) Steckel, V., Clemons, C.M., Thoemen, H. (2007) *J Appl Polym Sci.* 103(2):752-763.
- 9) Chen, Y., Tshabalala, M.A., Stark, N.M., Gao, J., Fan, Y., Ibach, R.E. In: *Proceedings of the Advancements in Fiber-Polymer Composites: Wood Fiber, Natural Fibers and Nanocellulose.* Milwaukee, WI, US. May 6-7, 2013. pp 32.
- 10) Wangaard, F.F., Granados, L.A. (1967) The effect of extractives on water-vapor sorption by wood. *Wood Sci Technol.* 1(4):253-77.
- 11) Mantanis, G.I., Young, R.A., Rowell, R.M. (1994) Swelling of wood- Part 1. Swelling in water. *Wood Sci Technol.* 28 (2):119-134.
- 12) Nzokou, P., Kamdem, D.P. (2004) Influence of wood extractives on moisture sorption and wettability of red oak (*Quercus rubra*), black cherry (*Prunus serotina*), and red pine (*Pinus resinosa*). *Wood Fiber Sci.* 36(4):483-492.
- 13) Maldas, D.C., Kamdem, D.P. (1999) *Forest Prod J.* 49(11-12):91-93.
- 14) Spalt, H.A. (1979) In: *Proceeding Wood moisture content —temperature and humidity relationships.* Virginia Polytech. Inst. and State Univ., Blacksburg, VA, pp. 55-61.



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