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Properties of wood-plastic composites (WPCs) reinforced with extracted and delignified wood flour

Abstract: The water sorption and mechanical properties of wood-plastic composites (WPCs) made of extracted and delignified wood flour (WF) has been investigated. WF was prepared by extraction with the solvent systems toluene/ethanol (TE), acetone/water (AW), and hot water (HW), and its delignification was conducted by means of sodium chlorite/acetic acid (AA) solution. A 2⁴ full-factorial experimental design was employed to determine the effects of treatments and treatment combinations. WPCs were prepared with high-density polyethylene (HDPE) and treated WF was prepared by means of extrusion followed by injection molding, and the water absorption characteristics and mechanical properties of the products were evaluated. WPCs produced with extracted WF had lower water absorption rates and better mechanical properties than those made of untreated WF. WPCs containing delignified WF had higher water absorption rates and improved mechanical performance compared with those made of untreated WF.

Keywords: delignification, diffusion, extractives, MOE, moisture performance, MOR, wood flour, wood-plastic composites (WPCs)

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Introduction

Wood-plastic composites (WPCs) have remarkable environmental and economic advantages (Tabari et al. 2011). In recent years, WPC utilization has developed rapidly, especially in Europe, the United States, and Canada. Wood flour (WF) is a common filler in WPCs, which has the advantages of low density, low abrasion, and low material cost compared to conventional glass fibers and other inorganic materials. One of the challenges in WF-based WPCs is the improvement of physical and mechanical performance. Here, the WF characteristics and their interfacial compatibility with the plastic matrix play a pivotal role (Stark and Rowlands 2003; Stokke and Gardner 2003; Bouafif et al. 2009). Maldas et al. (1989) focusing on the effects of wood species in WPCs observed the differences in the mechanical properties as a function of morphology, density, and aspect ratios of wood fibers. Rowell et al. (2000) found a high aspect ratio (length/width) to be essential for satisfactory strength properties. Lu et al. (2005) demonstrated that the tensile and flexural strengths of WPCs reach a maximum between 15% and 35% WF content.

So far, few studies have investigated the effect of chemical composition of wood on WPC performance. Saputra and Simonsen (2004), Kim et al. (2009), and Shebani et al. (2009) focused on the influence of extractives on the strength of WPCs. In the preparation of WPCs, WF is mixed with thermoplastics at about 200°C. At these temperatures, wood extractives may migrate to the WF surface and accumulate at the wood-plastic interphase and modify the hygroscopicity and color of WPCs (Colom et al. 2003; Stark 2006). Various components from WF were removed before WF incorporation into WPCs as a method to improve weathering performance (Stark and Mueller 2008; Fabiyi et al. 2009). In this context, Stark and Mueller (2008) washed WF of salt cedar (*Tamarix chiensis*) and mixed pine (*Pinus* spp.) in water before the incorporation into a polyethylene matrix, and as a result, the extractive contents were decreased from 12% to 3% and from 6% to 3%, respectively. The color stability of the WPCs was not improved after washing. Fabiyi et al. (2009) extracted

WF with acetone and removed lignin from WF by means of acetic acid (AA). The removal of extractives caused little color change on WPCs after accelerated weathering, while removing lignin improved the color stability. Thus, the authors concluded that lignin is the main contributor to color change in WPCs. This raises expectations that cellulose or holocellulose fibers in WPCs may minimize color change problems in outdoor utilization. Pure cellulose fibers offer the additional benefit of higher thermal stability (up to 270°C) (Sears et al. 2001). The removal of hemicelluloses by hot water (HW) extraction from WF for WPC production was also tested (Sears et al. 2001; Andrusyk et al. 2008; Hosseinaei et al. 2012; Pelaez-Samaniego et al. 2013). The mechanical properties of WPCs in flexure and tension mode after HW extraction may be related to the removal of hemicelluloses and other extractives or the modification of the microroughness of fiber. Expectedly, the removal of hydrophilic materials contributes to the compatibility with thermoplastic resins.

Little is known about WPCs based on high-density polyethylene (HDPE) and extracted WF. The current work systematically investigates this area focusing on exhaustively extracted WF and or delignified WF in the context of water sorption behavior and mechanical properties of the WPCs. The expectation is that the results will contribute to a better understanding of the optimization of WPC production with improved properties.

Materials and methods

WF from postindustrial mixed pine species, supplied by American Wood Fibers (AWF 4020; Schofield, WI, USA), 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.

HDPE with a melt index of 33.0 g/10 min and density of 0.951 g cm⁻³ (59.3 lb ft⁻³), was supplied by ExxonMobil (ExxonMobil Excorene HD-6733 HDPE; Houston, TX, USA).

The extractions and delignification treatments and their combinations were carried out according to a 2⁴ full-factorial experimental design presented in Table 1. Extraction was performed for 24 h in a Soxhlet apparatus with toluene/ethanol (TE; 2:1 by volume), acetone/water (AW; 9:1), HW, and various combinations of these solvents. Lignin removal (LR) was done according to Wise et al. (1946). A 100 g sample of air-dried WF was dispersed under constant stirring in 1 l deionized water containing 30 g sodium chlorite (NaClO₂; 80%), 10 ml AA, and 100 µl octan-2-ol (as antifoaming agent; Acros Organics, Morris Plains, NJ, USA) and heated to 70°C for 1 h. A further aliquot of 30 g NaClO₂ (80%) and 10 ml AA was added, and the reaction was continued for another 1 h. The addition of NaClO₂ and AA 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

Table 1 2⁴ full factorial design showing WF treatments

WF treatments	Extraction time ^a (h)	Treatments ^b			
		TE	AW	HW	LR
C	0	0	0	0	0
TE	24	1	0	0	0
AW	24	0	1	0	0
TE-AW	48 (24+24)	1	1	0	0
HW	24	0	0	1	0
TE-HW	48 (24+24)	1	0	1	0
HW	48 (24+24)	0	1	1	0
TE-AW-HW	72 (24+24+24)	1	1	1	0
LR	5	0	0	0	1
TE-LR	29 (24+5)	1	0	0	1
AW-LR	29 (24+5)	0	1	0	1
TE-AW-LR	53 (24+24+5)	1	1	0	1
HW-LR	29 (24+5)	0	0	1	1
TE-HW-LR	53 (24+24+5)	1	0	1	1
AW-HW-LR	53 (24+24+5)	0	1	1	1
TE-AW-HW-LR	77 (24+24+24+5)	1	1	1	1

^aTotal extraction time. Numbers in parentheses are the extraction time of individual treatments.

^bTE, AW, HW, and LR with NaClO₂/AA solution. “1” means solvent applied and “0” means solvent not applied.

WF slurry was filtered on a Büchner funnel lined with filter paper. The filter cake was rinsed with 1 l RO water followed by 500 ml of 95% ethanol, 500 ml absolute ethanol, and 1 l acetone. The filter cake was air-dried under suction for 30 min. This sample is designated as LR. All WF samples, including the control, untreated WF, were oven-dried at 120°C for 24 h prior to composite processing.

Injection-molded WPC composite samples were manufactured in a microprocessing equipment (DSM Xplore; DSM Research, Geleen, The Netherlands). This 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 the process conditions can be monitored and controlled. The production temperature was 180°C. After compounding via extrusion, the extrudate was collected and injection molded. An ASTM flexural property die was used with mold cavity dimensions of 3×12×120 mm³ (ASTM 2010). The injector temperature was 190°C. All WPC samples were made of WF and HDPE (1:1 by weight).

For testing the moisture resistance, the injection-molded flexural samples were cut in half to a nominal sample size of 3×12×60 mm³. 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 the 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 the weight increment is linearly related to moisture content (MC). MC%, thickness swelling (TS), and width swelling (WS) were calculated.

The apparent diffusion coefficient (D_A) of the HDPE composite was calculated according to Fick's diffusion equation and based on the water sorption data.

$$D_A = \frac{\pi}{16} \left(\frac{h}{MC_{\max}} \right)^2 \left(\frac{\partial MC}{\partial \sqrt{t}} \right)^2 \quad (1)$$

where MC_{\max} is 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 (Steckel et al. 2007).

For testing the mechanical properties, samples were conditioned at 22°C and 63% relative humidity (RH) for 30 days. Flexural tests were carried out according to ASTM D790 (ASTM 2010) on an Instron universal testing machine (three-point loading system, cross-head speed of 1.3 mm min⁻¹). Five replicate specimens were tested for each formulation. The stress at maximum load (strength) and tangent modulus of elasticity (MOE) was calculated according to ASTM D790 (ASTM 2010).

The mechanical performance was modeled by a full-factorial statistical analysis (2⁴ factorial design) with the four treatments (TE, AW, HW, and LR) and their combinations are presented in Table 1. For experimental design and data analysis, Design Expert 7.0.0 software by Stat-Ease (Minneapolis, MN, USA) was available. The derived equations are reported in terms of actual factors. In this design, 0 represents “no treatment” and 1 represents “treatment performed.”

Results and discussion

Water sorption and TS

The MC of the WPCs with the various WF are presented in Figure 1a as a function of soaking time up to 3000 h. The MC during the first 300 h is shown in Figure 1b. Each data point is an average of five replicates. As visible, the MC initially increases linearly then plateaus with increasing soaking time. WPCs containing extracted WF (WF_{EX}) absorbed water more slowly than those with the control, untreated WF (WF_C), while WPCs with delignified WF (WF_{LR}) absorbed water faster than those with WF_C . WPCs containing WF_{EX} led to lower water absorption compared to WPCs containing WF_C because extractives are mainly hydrophilic (e.g., phenol and carbonyl groups). Chen et al. (2013) extracted WF with TE, AW, and HW and demonstrated that toluene removes nonpolar extractives such as resins, wax, and fat, while ethanol dissolves tannins, pigments, some carbohydrates, and traces of lignin, accounting for 4.7% by weight of dry WF. HW is effective for dissolving inorganic substances and tannins, gums, sugars, and starches, accounting for 5.3% by dry weight of WF. AW extraction is effective in removing tannins due to the partial cleavage between tannins and molecular protein, accounting for 4.1% by weight of dry WF. Although AW extractions remove less polar extractives than TE or HW extractions, all extractions

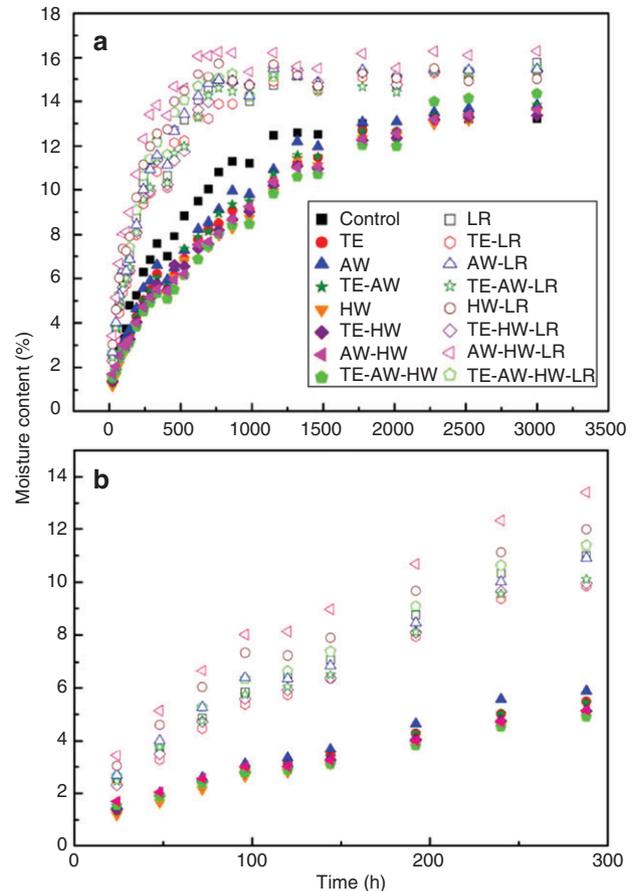


Figure 1 MC% versus soaking time of WPCs containing untreated, extracted, and delignified WF.

For abbreviations, see text.

lead to an increase in hydrophobicity. In contrast, LR leads to elevated hydrophobicity due to the exposure of the polysaccharides with their abundant OH groups.

The D_A can be calculated based on Equation (1) with the data presented in Figure 2. The D_A is related to both the initial rate of water sorption with respect to the square root of time and the final MC. Compared with WPCs containing WF_C , the initial rate of water sorption with respect to the square root of time is lower in WPCs containing WF_{EX} and higher in WPCs containing WF_{LR} (Figure 2a). On average, the initial rate of water sorption was almost two times higher for WPCs containing WF_{LR} than those containing WF_C (0.70 ± 0.05 vs. 0.31 ± 0.02 , respectively). The final MC is presented in Figure 2b. Although the trend was similar, the differences on average in final MC between WPCs with WF_{LR} compared with WF_C were much smaller (15.4 ± 0.3 vs. 13.5 ± 0.5 , respectively). Accordingly, the variability in D_A for these composites is primarily impacted by the differences in initial water absorption rates as opposed to the final MC.

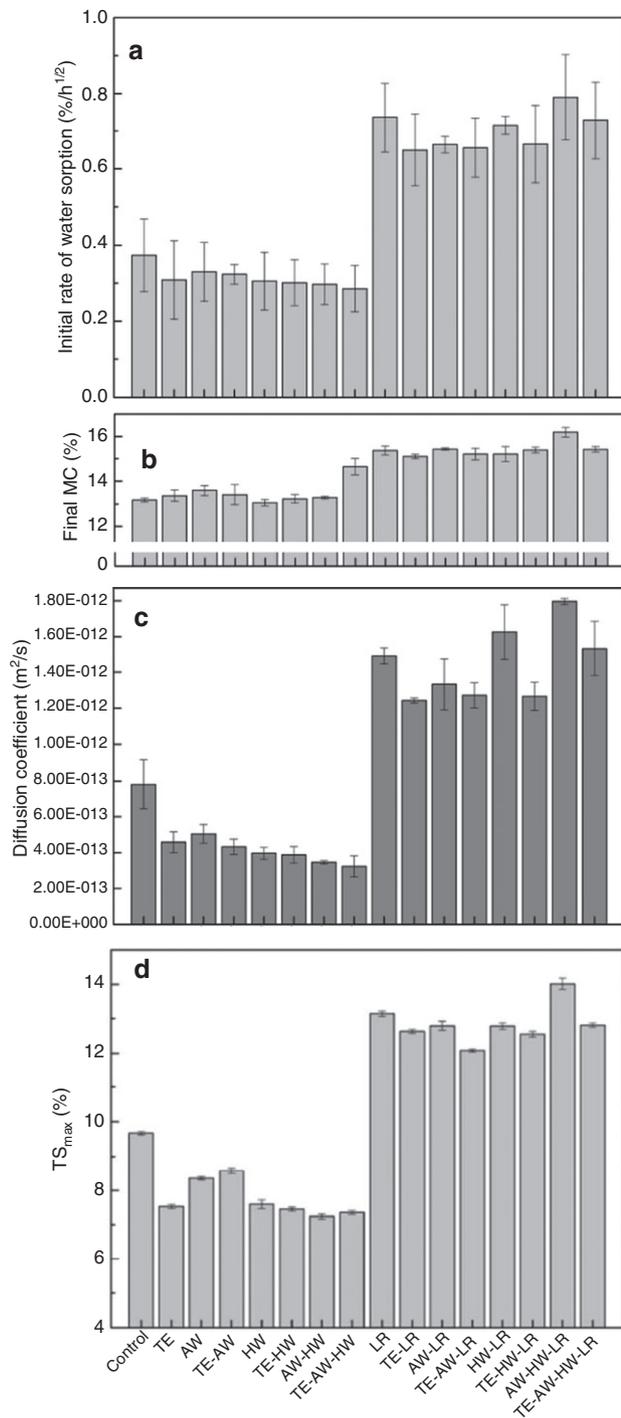


Figure 2 Water sorption characteristics of WPCs containing untreated, extracted, and delignified WF: (a) initial rate of water sorption, (b) final MC, (c) diffusion coefficient, and (d) TS_{max} .

The D_A according to Fick's law is presented in Figure 2c. The water sorption characteristics are significantly affected by the incorporation of either WF_{EX} or WF_{LR} . Overall, extractions were significantly lowered and delignification elevated the D_A . The reduction in water uptake of the composites with WF_{EX} can be attributed to

the removal of hydrophilic extractives. Comparing the WPCs with WF after a single extraction, WPCs containing HW extracted WF had the lowest D_A , while WPCs containing AW extracted WF had the highest D_A . Thus, solvents with higher polarity are more effective to suppress water uptake. Because the three extraction systems remove different hydrophilic extractives, combining all three extractions, TE-AW-HW resulted in the lowest overall D_A . The D_A increased significantly when WPCs contained WF_{LR} compared with WPCs containing either WF_C or WF_{EX} . The largest D_A was found in the case of WPCs containing WF both delignified and extracted with HW, AW-HW, or TE-AW-HW. However, WPCs containing WF both delignified and extracted with TE, AW, TE-AW, or TE-HW led to lower D_A compared with WPCs containing only delignified WF.

At the end of the test, the maximum TS (TS_{max}) of WF_{LR} filled WPC samples was greater than that of samples made with WF_C followed by the WF_{EX} (Figure 2d). The TS_{max} data follow a similar pattern as D_A . There is little difference in TS_{max} among the WPC samples prepared with WF_{EX} . However, WPCs with AW or TE-AW extracted WF display relatively higher TS_{max} values. For samples with WF_{LR} , the higher TS_{max} value was obtained when WPCs contained delignified WF in combination with AW-HW extraction. The change in TS_{max} value is a clear manifestation of the lowered hygroscopicity after extraction (Nearn 1955; Wangaard and Granados 1967; Spalt 1979; Mantanis et al. 1994; Maldas and Kamdem 1999; Nzokou and Kamdem 2004).

Figure 3a and b show the TS and WS curves of the WPCs, respectively. Both parameters have a similar pattern as a function of soaking time. The data for WPCs with WF_{LR} were higher compared with WPCs containing WF_C , while the TS and WS of WF_{EX} were lower compared with the WPCs containing WF_C . In general, TS% is higher than WS%.

Flexural properties of modified wood-based WPC

The MOE (Figure 4a) generally increased after WF extraction and delignification, which is indicative of improved interfacial bonding between the fiber and polymer matrix after removing the extractives (Saputra and Simonsen 2004; Bledzki et al. 2005). In general, WPCs containing WF that had been extracted in combination with delignification exhibited a higher MOE compared with WPCs containing WF_{EX} . It may be that delignification results in stiffer WF particles compared with WF_C due to increased availability for hydrogen bonding in the remaining cellulose.

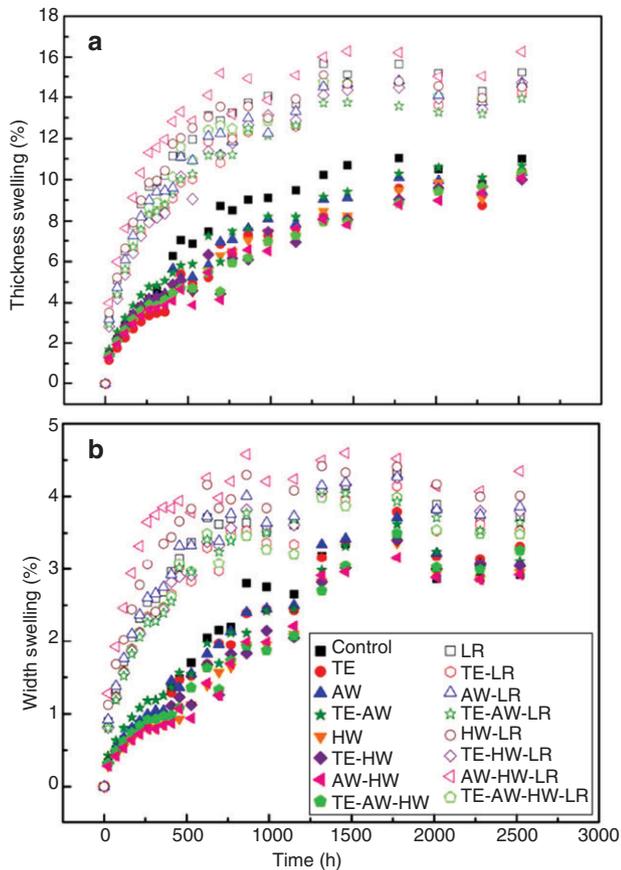


Figure 3 Swelling characteristics of WPCs containing untreated, extracted, and delignified WF: (a) TS and (b) WS. For abbreviations, see text.

The MOE ranged from 3.02 GPa (WF_c) to 3.68 GPa (HW-LR treatment). A model was developed relating MOE to WF treatments to illustrate the effects of individual treatments and their combinations [Equation (2)]:

$$\begin{aligned} \text{MOE} = & 2.98 + 0.45(\text{TE}) + 0.23(\text{AW}) + 0.29(\text{HW}) \\ & + 0.55(\text{LR}) - 0.20(\text{TE})(\text{AW}) - 0.20(\text{TE})(\text{HW}) \\ & - 0.32(\text{TE})(\text{LR}) - 0.15(\text{AW})(\text{HW}) \\ & - 0.15(\text{AW})(\text{LR}) - 0.11(\text{HW})(\text{LR}) \end{aligned} \quad (2)$$

All terms in the model are significant, except for AW, which was included to maintain the hierarchy of the model. Three single treatments (TE, HW, and LR), represented in the model as positive coefficients, significantly increase the MOE. The data confirm that the largest MOE increment is due to LR in WPC followed by TE and HW extractions. The high correlation coefficient ($r^2=0.98$) between the predicted MOE and the measured average MOE (Figure 5a) demonstrates the good agreement between the data.

All possible two-factor interactions appear in the model. The coefficients of the two-factor interactions are

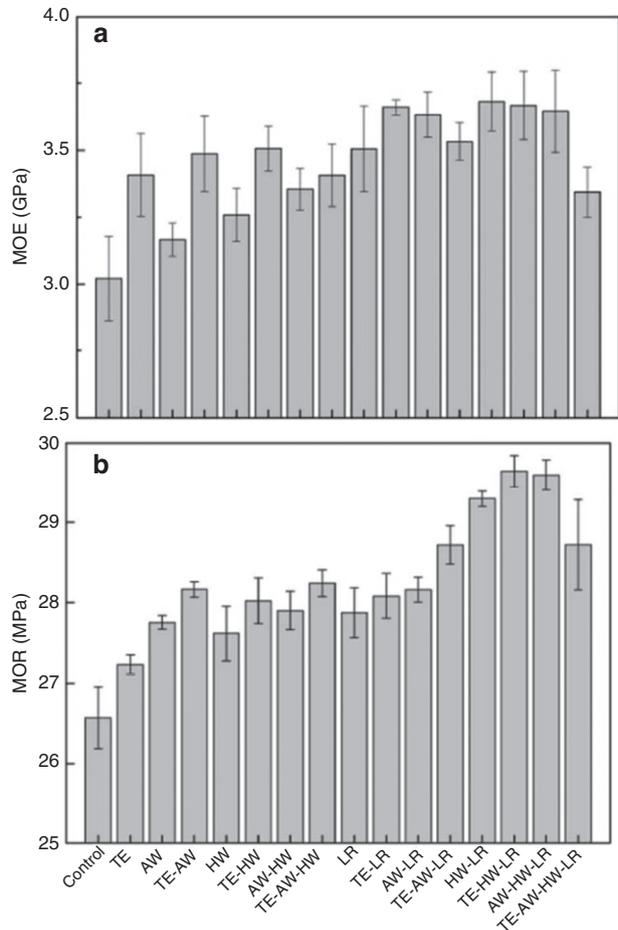


Figure 4 Flexural properties of WPCs containing untreated, extracted, and delignified WF: (a) MOE and (b) MOR. For abbreviations, see text.

all negative. The interaction graphs presented in Figure 6A allows a further analysis of the negative interactions. Each data point represents the predicted value and the error bars represent the least significant difference. Figure 6Aa and Ab show the interactions between TE-AW and TE-HW, respectively. Accordingly, TE extraction followed by extraction with either AW or HW does not increase MOE beyond the value of TE extraction alone. The positive effect by TE extraction and LR alone was not further improved by the successive application of these treatment, that is, the effects are not additive (Figure 6Ac). A similar trend was seen for the HW-AW, AW-LR, and HW-LR interactions (Figure 6Ad-f, respectively). The combination of the two treatments is not additive either, although each treatment alone was successful.

Expectedly, the modulus of rupture (MOR) of composites (Figure 4b) also increased after extraction and delignification. As with MOE, extractions likely improved interfacial strength increasing MOR. Delignification

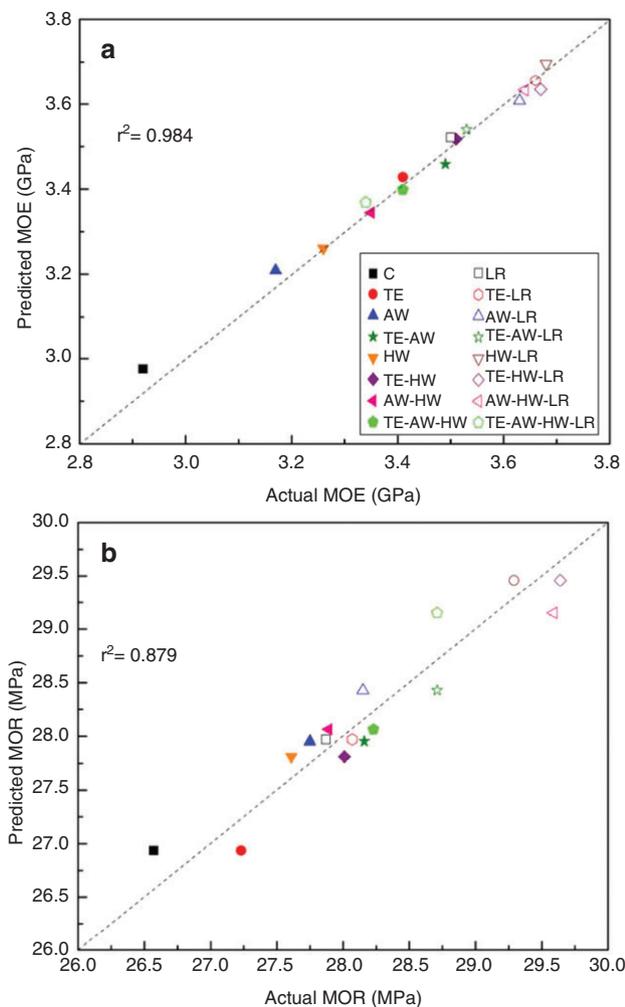


Figure 5 Predicted MOE and MOR data versus their corresponding actual values derived of WPCs containing untreated, extracted, and delignified WF.

For abbreviations, see text.

decreased the specific gravity of the WF particles, resulting in more WF particles added to the WPC on a weight basis.

The MOR ranged from 26.6 MPa (WF_c) to 29.6 MPa (TE-HW-LR treatment and AW-HW-LR treatment). Also here, a model was developed relating the MOR to WF treatments [Equation (3)]:

$$\text{MOR} = 26.94 + 1.02(\text{AW}) + 0.88(\text{HW}) + 1.04(\text{LR}) - 0.77(\text{AW})(\text{HW}) - 0.56(\text{AW})(\text{LR}) + 0.61(\text{HW})(\text{LR}) \quad (3)$$

All terms in the model are significant. Three single treatments (AW, HW, and LR) significantly increase the MOR. According to the model, the largest MOR increase occurs when WPCs contain WF_{LR} followed by WPCs containing WF extracted with AW and HW, respectively. The plot

predicted MOR versus the actual average MOR (Figure 5b) illustrates a good correlation ($r^2 = 0.88$).

The interaction graphs (Figure 6B) illustrate the negative interactions. Each data point represents the predicted value, and the error bars represent the least significant difference. Figure 6Ba and Bb show the negative interactions between AW-HW and AW-LR, respectively. The AW-HW interaction demonstrates that either AW or HW extraction alone increases the MOR significantly. However, the improvement after AW-HW extraction is not significantly different to that obtained after either AW or HW extraction (Figure 6Ba). Thus, the MOR increment by AW or HW extraction follows the same mechanisms. The AW-LR interactions are similar to the AW-HW interaction in that the two are not additive; however, there is a small increase in the MOR after the combined AW extraction and LR compared to a single treatment (Figure 6Bb). The HW-LR interaction plot illustrates the synergism between the two treatments.

Equation (2) shows that for single treatments TE extraction increased the MOE the most. Concerning the combination of two treatments, TE-LR and HW-LR were most effective, but the results are not significantly different between these treatments. Equation (3) shows that for single treatments AW, HW, and LR increased the MOR with no significant difference observed between them (Figure 4b). The evaluation of the combination of treatments reveals that HW-LR interacts synergistically. The largest improvements in the MOR were observed for HW-LR, AW-HW-LR, and TE-HW-LR, and these were not significantly different from each other (Figure 6B).

Conclusions

WPC samples were prepared with untreated WF (WF_c), solvent extracted WF (WF_{EX}), delignified (WF_{LR}), or extracted WF with subsequent delignification and HDPE. In general, WPCs containing WF_{EX} were more hydrophobic compared with WPCs containing WF_c as evidenced by decreased water sorption rates, diffusion coefficients, and swelling. This was due to the removal of hydrophilic extractives. WPCs containing WF_{LR} were more hydrophilic compared with WPCs containing WF_c as evidenced by increased water sorption rates, diffusion coefficients, and swelling. This was due to the exposure of OH groups in the WF after delignification. In choosing a single solvent for extraction, either TE or HW extraction provides the most improvement in moisture performance.

The MOE and MOR of the WPCs increased with both the removal of extractives and lignin. The removal

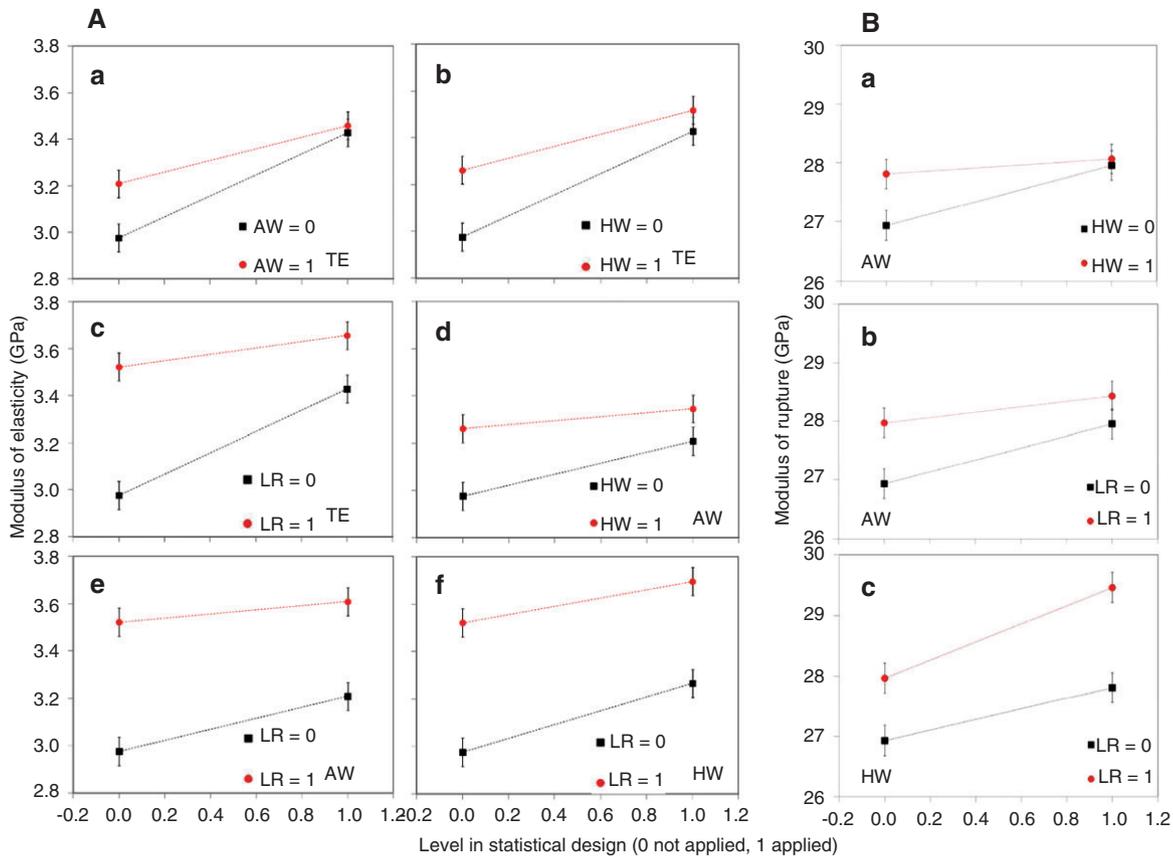


Figure 6 Variation in MOE (A) and MOR (B) as a function of the two-factor interactions between treatments. (A) MOE: (a) TE-AW, (b) TE-HW, (c) TE-LR, (d) AW-HW, (e) AW-LR, and (f) HW-LR. (B) MOR: (a) AW-HW, (b) AW-LR, and (c) HW-LR. For abbreviations, see text.

of extractives increased the interfacial bond between the hydrophobic HDPE matrix and the hydrophilic WF. Delignification resulted in the addition of more WF particles to the matrix, increasing mechanical properties as well as increasing the stiffness of the WF particles. Because extractive removal and delignification improve the strength performance in different modes, the combination of the two allows for the largest increases in strength performance. Delignification with the single-solvent HW extraction provides for the most improvement in strength performance without resorting to a combination of extractions.

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