

WATER ABSORPTION BEHAVIOR AND ITS EFFECTS ON THE MECHANICAL PROPERTIES OF TREATED AND UNTREATED RED BALAU SAW DUST /LDPE COMPOSITES

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Abstract

Due to the hygroscopic nature of wood, its use in wood thermoplastic composites (WTC) in outdoor industrial and domestic applications is limited. Wood is usually modified to reduce this tendency. Red balau saw dust was modified by heat treatment at 180°C and 200°C for 1 hour, compounded with LDPE into 20% and 40% weight fractions and molded into test specimens by injection molding. Samples were immersed in distilled water at room temperature for four months. Pure LDPE did not absorb water as no weight gain was recorded throughout the experimental period. Heat treated wood composites shows remarkable water resistance than untreated ones. Reduced water absorption of treated wood relative to untreated ones indicates a degree of modification by heat treatment. Tensile and flexural tests results revealed that untreated wood composites have poorer mechanical properties with water immersion as a result of degradation due to moisture. The mechanical properties of the heat treated wood composites were not adversely affected with water absorption. Therefore, heat treatment is capable of reducing the proneness to water absorption in WTC, alleviate the detrimental effects on mechanical properties and provides a good way of improving the WTC properties in applications that poses moisture related challenges.

Key words: heat treatment, thermoplastic composites, water absorption, injection molding

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Introduction

One of the shortcomings of using wood in thermoplastic composites production is the hygroscopic nature of wood. This leads to swelling and shrinkage due to moisture absorption

and desorption, resulting in poor mechanical properties of the resultant product. As a result, the use of wood thermoplastic composites (WTC) in industrial and domestic applications is limited. In certain use, the environmental conditions can be so unfavorable that the performance of these composites is adversely affected. Several treatment methods have been employed to checkmate these limitations and enhance better moisture resistance (Joseph *et al.*, 2002). Heat treatment is one of the wood modification methods. In heat treatment, wood is subjected to higher temperatures than drying (160–250°C). This results in the degradation of hemicellulose which has the lowest molecular weight among the wood constituents, leading to reduction of the OH groups and the formation of O-acetyl groups. Thermal softening of cell wall matrix, mainly lignin also sets in with cross-linking occurring between carbohydrate polymers and/or between lignin and carbohydrate polymers, resulting in an increase in the crystallinity of amorphous cellulose with consequent improvement in dimensional stability and decreased hygroscopicity of wood. Also the softened lignin flows and blocks the cell pores, thereby contributing to the reduction in moisture absorption (Tjeerdsma *et al.*, 1998). Therefore, heat treated wood is expected to become more hydrophobic with increase in treatment temperature.

The ability of wood particles treatment to reduce the water absorption tendencies in wood plastic composites has been reported (Demir *et al.*, 2006). However, moisture absorption in WTC is still a major concern especially for their outdoor applications. It has been observed that the sorption of water by non polar polymers containing fillers depends mainly on the nature of the filler (Marcovich, Reboedo and Aranguren, 1999). Therefore, for hydrophilic fillers such as wood particles, increase in water absorption should be expected.

Another very important concern is the negative effects moisture has on physical and mechanical properties. Research has shown that mechanical properties of WTC decreased with water absorption (Joseph *et al.*, 2002). Hence it is necessary that this problem is tackled so that natural fillers can be seen as a viable reinforcement material in WTC.

Therefore, this paper is aimed at modifying red balau saw dust with heat treatment, compounding with LDPE and studying the effects of water absorption on the tensile and flexural properties of the resultant composites.

Materials and methods

Red Balau (*Shorea dipterocarpaceae*) saw dust was obtained from a local saw mill in the Klang Valley, Selangor, Malaysia. It was milled to between 40-100 mesh (400-150 µm) sizes

using a locally fabricated mill. Commercially available LDPE (Titanlene LDI300YY), with a density of 920 kg/m³, molecular weight of 3.5–3.8x10⁵ g/mol and MFI of 20 g/10 min, supplied by Titan Petchem (M) Sdn Bhd, Malaysia, were used as the matrix.

Acid insoluble lignin was determined using ASTM D 1106 (1996) standard. Hemicellulose and cellulose were analyzed according to the method described by Rowel *et al.* (2005).

Untreated wood sawdust was dried in an oven at 60°C for 48 hours to a moisture content of less than 2% and stored in sealed plastic bags over dried silica gel in desiccators prior to compounding. Undried wood flour was subjected to 180°C and 200°C temperatures in an oven for one hour effective treatment time.

LDPE, untreated and the heat treated wood flours were pre-mixed in different compositions in 200 g portions at 20% and 40% weight fractions (Table 1) and compounded in a twin screw co-rotating extruder (Brabender KETSE 20/40 Lab Compounder, Germany) at a barrel temperature of between 150–155°C along the barrel zones and screw speed of 250 rpm. The melt pressure varied between 34–39 bars depending on the wood content, while the die temperature was between 164–178°C. The samples were extruded out through a circular die of 3 mm in diameter, cooled in a water bath and pelletized. Extruded pellets were oven dried at 80°C for 24 hours and stored in sealed plastic bags over silica gel in desiccators for injection molding.

The pellets were injection molded into tensile (ASTM 638, 1999) test pieces using the BOY 55M (Germany) injection molding machine at a barrel temperature of between 150°C and 155°C, an injection pressure of 100–120 bars and mold temperature of 25°C.

Table 1. Formulations of the composites

Sample code	Weight fraction of LDPE (%)	Weight fraction of wood flour (%)	Treatment temperature (°C)
LDPE/W _{UN-20}	80	20	-
LDPE/W _{UN-40}	60	40	-
LDPE/W ₁₈₀₋₂₀	80	20	180
LDPE/W ₁₈₀₋₄₀	60	40	180
LDPE/W ₂₀₀₋₂₀	80	20	200
LDPE/W ₂₀₀₋₄₀	60	40	200

Water absorption tests were performed on samples cut from tensile test stripes according to ASTM D-570 (1998).

Tensile tests were carried out at room temperature on dry and water soaked specimens using a universal testing machine (Instron 5569, USA.) equipped with a load cell of 50 kN and a mechanical extensometer according to ASTM D-638 (1999) at a cross-head speed of 5 mm/min. A zero span of 50 mm was chosen for the extensometer. Ten samples were tested and the average value of at least six best results was recorded.

The same instrument used for tensile testing was used for the flexural testing but in three point bending mode according to ASTM D-790 (2003). Dry as molded and moisture saturated tensile test specimens were tested at room temperature with a span of 50 mm. Samples were tested to a maximum deflection of 30 mm at a crosshead speed of 1.28 mm/min. Ten samples were tested and the average value of at least six best results was recorded.

Results and Discussion

Chemical composition

Table 2 illustrates the percentage composition of lignin, carbohydrates, extractives and ash in the wood flour samples.

Table 2. Chemical composition of Red balau saw dust

Treatment Temperature (°C)	Lignin (%)	Hemicellulose (%)	Cellulose (%)	Extractives and inorganics (%)
Untreated	29	29	41	1
180	29	28	42	1
200	31	25	42	2

* Determined by difference

The results suggest that carbohydrates were more susceptible to thermal degradation than lignin at the treatment temperature. Hemicellulose degraded faster than cellulose as the values decreased when wood is subjected to heat treatment. This may possibly be because cellulose is more crystalline than hemicellulose which confers better resistance to thermal degradation. Zaman, Allen and Kotilainen, (2000) have suggested that cellulose (a linear homopolysaccharide of β -D-glucopyranose) is more thermally stable than hemicellulose. On the other hand, a steady increase in lignin content was observed as the treatment temperature increased. This clearly indicates that lignin is more thermally stable than carbohydrates.

Water absorption behavior

Percentage water uptake, W_t , was calculated with the formula,

$$W_t (\%) = \frac{W_2 - W_1}{W_1} \times 100 \tag{1}$$

where W_1 and W_2 are the dry weight and weight after time t of immersion in water. A plot of percentage water absorption (moisture content) against time for the different treatment temperatures and fiber loading presented in Fig. 1. The neat LDPE shows no water absorption as no weight increase was observed over the period of study. This is because neat LDPE is hydrophobic and has no tendency of absorbing water. However, both the untreated and the treated wood composites absorbed water to various extents. Because the neat LDPE did not absorb water, it can be assumed that the wood flour is responsible for all the moisture absorbed by the composites. This is as a result of the hydrophilic nature of wood flour. It is sometimes believed that moisture is not an issue with WTC because wood is totally encapsulated by the matrix. If that is the case, the matrix would shield the wood from moisture because they are hydrophobic. Nevertheless, composites still exhibits a degree of moisture absorption tendency (Balatincez and Park, 1997). This seems to indicate that wood must have been exposed on the surface of the samples.

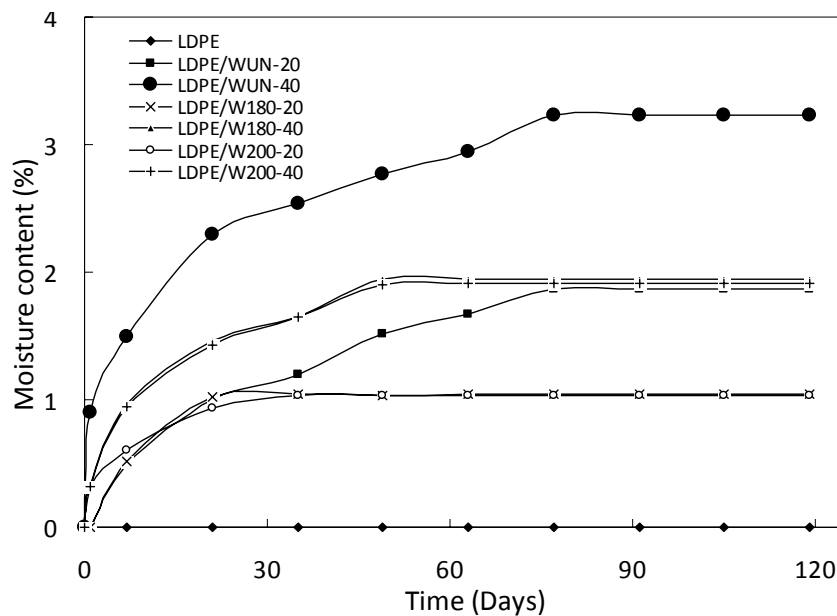


Fig. 1. Water absorption curves of neat LDPE, treated and untreated LDPE/red balau composites.

This may account for the various degree of water absorption exhibited by the composites. Also, it can be seen that water absorption increases with time of immersion, reaching a certain value (the equilibrium point), when the composite's water content remained constant. LDPE/W₁₈₀₋₂₀ and LDPE/W₂₀₀₋₂₀ reached equilibrium (1.03% and 1.04%) at 35 days while LDPE/W₁₈₀₋₄₀ and LDPE/W₂₀₀₋₄₀, attained equilibrium point (1.94% and 1.91%) on the 49th day of immersion. This may be due to the presence of more OH groups on the surface of the composites with higher filler content, leading to more ability to absorb water. However LDPE/W_{UN-20} and LDPE/W_{UN-40} exhibits a saturation point of 1.87% and 3.23% on the 77th day of immersion. This may be a result of the higher number of free OH groups on the surfaces of untreated wood composites which interact with water via hydrogen bonding. It is also possible that at 40 wt%, the polymer matrix was not continuously distributed and most of the wood fibers contacted one another directly, in which case, complete encapsulation was not achieved. This could result in the higher water absorption values recorded for 40 wt%. It has been observed that water absorption in WTC is not only dependent on the fiber and matrix structure, but also on the fiber-matrix interface. Hydrophilic fibers leads to lower fiber-matrix interaction resulting in poor interface which facilitates the sorption process. Furthermore, moisture can be sorbed into the composite by the dissolution of water into the polymer network, moisture sorption into the free volume, if present, in the glassy structure and by hydrogen bonding between the hydrophilic group of water and the components of the composite. Micro-cracks can also allow for moisture transportation involving flow and storage of water within the cracks (Sreekala, Kumaran and Thomas, 2002). Untreated wood composites generally show higher water absorption than treated ones. LDPE/W_{UN-20} absorbed 55% more water compared to LDPE/W₁₈₀₋₄₀ and LDPE/W₂₀₀₋₂₀ while LDPE/W_{UN-40} absorbed about 60% water higher than LDPE/W₁₈₀₋₄₀ and LDPE/W₂₀₀₋₄₀. This may be attributed to the removal of the water sensitive components, hemicelluloses, in wood flour by heat treatment, thereby rendering the composites more water resistant. Furthermore, free hydroxyl groups of the cellulose are reduced with heat treatment. This may lead to decrease in the water absorption of the wood flour and consequently, the composites. This is in agreement with the findings of Follrich, Muller and Gindl, (2006), who discovered that at 200°C, hydrophilicity of spruce wood decreased appreciably. While 20 wt% absorbed water quickly and reached saturation faster, 40 wt% absorbed water more slowly, attaining saturation more gradually (Fig. 1). This is observed for both treated and untreated composites. Increase in water

absorption of untreated wood composites relative to the treated ones is as a result of the hydrophilicity of wood imparted by the free OH groups in the wood structure which has a high tendency for hydrogen bonding with water. It can also be seen from the Table 2 that the untreated wood has higher hemicellulose content which is responsible for moisture attraction.

Effect of water absorption on mechanical properties

Tensile properties

Figs. 2a-c shows the tensile properties at equilibrium moisture content for WTC immersed in water. Tensile properties of the untreated wood composites were generally found to decrease appreciably with water immersion relative to the treated ones. This may be due to the deteriorating effects of water molecules interacting with the wood at the composites interface because of the inherent incompatibility between the polar wood and the non polar matrix. As a result of the hydrophilic nature of wood, when WTC is exposed to water, the wood particles takes up water resulting in the swelling of the cell wall, leading to changes in the dimensional stability of the composites and consequently, reduced mechanical properties. Also, water molecules present at the interface degrades the interaction between the wood particles and the matrix which can lead to poor mechanical properties (Mat Taib *et al.*, 2006). Tensile modulus of LDPE/W₁₈₀₋₂₀ shows the highest reduction with water absorption among the treated wood composites. LDPE/W₁₈₀₋₄₀, LDPE/W₂₀₀₋₂₀ and LDPE/W₂₀₀₋₄₀ (Fig. 2a) show a marginal reduction in tensile modulus. This may be due to the reduced hydrophilicity in heat treated wood which enhanced better compatibility between the wood particle and the matrix and indicates that the amount of water absorbed at equilibrium moisture content has minimal effects on the stress transfer capability. Also, the tensile modulus of a composite is determined by the stiffness of the filler and the matrix.

a	b
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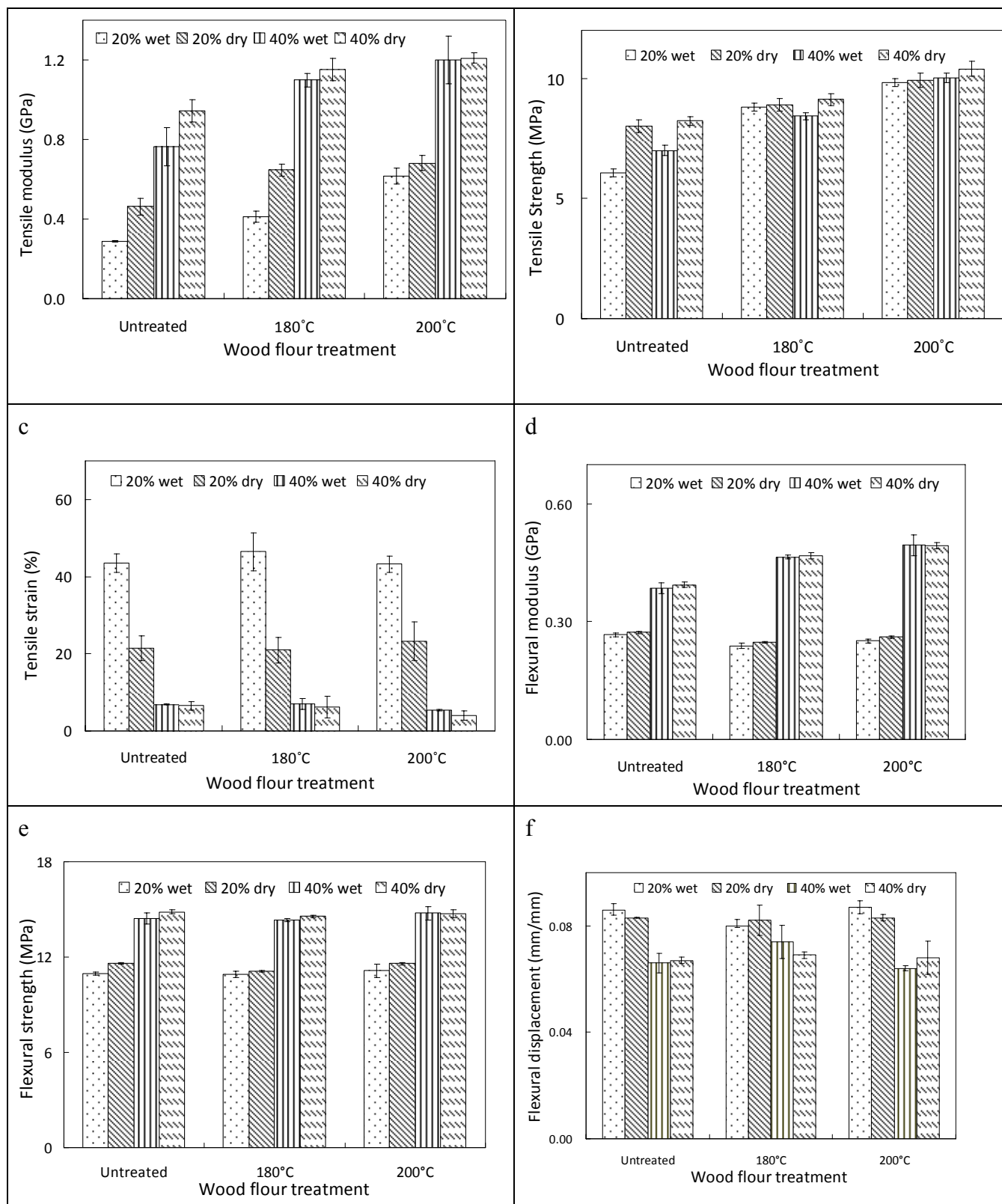


Fig. 2. Tensile and flexural properties of treated and untreated wood/LDPE composites.

In addition, it is a filler sensitive property in composites that is affected by moisture absorption (Dhakal, Zhang and Richardson, 2007).

Tensile strength decreases noticeably after immersion in water in the untreated wood

composites (Fig. 2b). This may be a result of the plasticization effects of water on WTC. This is in agreement with literature (Cui *et al.*, 2010). It is expected that the absorption of moisture should plasticize the system, leading to a reduction in tensile strength. More so, in the presence of moisture, the cellulose particles at the filler-matrix interface tend to swell. This results in a shear stress at the interface which favors ultimate debonding of the fibers, leading to a reduction in the tensile strength (Joseph *et al.*, 2002). However, tensile strength for heat treated wood composites shows a slight decrease. This could mean higher interfacial adhesion in these composites due to heat treatment. Tensile strain of the wet composites decreased generally for all the composites studied relative to the dry ones. This is anticipated because of the plasticization effect of water (Fig. 2c).

Flexural properties

Figs. 2d-f presents the flexural properties of water soaked and dry as molded composites. Water absorption seems to have no pronounced effects on the flexural modulus of wet composites compared to dry ones (Fig. 2d). Generally, there is a slight decrease in flexural modulus values at equilibrium moisture content and increases with filler loading. Furthermore, a slight decrease was observed for water soaked composites from heat treated wood. Also, a marginal decrease in flexural strength was recorded for water soaked specimens relative to the dry ones (Fig. 2e). Untreated wood composites show more observable decrease on exposure to moisture than heat treated ones. It is possible that the better compatibility of heat treated wood composites may be responsible for this trend. This may have alleviated the interfacial degradation of the filler- matrix interface, resulting in better stress transfer. This result agrees with the work of Dhakal, Zhang and Richardson, (2007). However, no particular trend is observed for the flexural displacement with moisture absorption.

Conclusion

All the composites were found to absorb moisture to various extents due to the hydrophilic nature of wood. However, composites from heat treated wood showed lower water absorption tendency because of the reduced hydrophilicity imparted to the wood by heat treatment. Tensile properties decreases generally with water absorption for all composites studied but the extent of decrease is more observable in untreated wood composites compared to the heat treated ones. In addition, flexural modulus and strength presents a marginal decrease for all the composites. Again, the heat treated composites shows a lower decrease compared to the

untreated ones. However, flexural displacement presents no particular trend. From these results, it is evident that heat treatment can reduce the moisture absorbing tendency in wood leading to a more water resistant composites with the ability to retain its mechanical properties after long time exposure to moisture. It is therefore a good way of improving the WTC properties in applications that poses moisture related challenges.

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