Thermal and Tensile Properties of Treated and Untreated Red Balau (*Shorea Dipterocarpaceae*) Filled LDPE Composites

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Abstract

Red balau saw dust was heat-treated at 180° C and 200° C for one hour, extrusion compounded with Low Density Polyethylene (LDPE) at 20%, 40% and 60% volume fraction loadings and injection moulded. Thermal and tensile properties of the resultant composites were investigated as a function of filler loadings and treatment temperature. Increase in tensile moduli and decrease in tensile stress and strain were observed as filler loading and treatment temperature increased. Thermogravimetric analysis revealed an increase in degradation peak temperature of the composites from heat treated compared to the untreated wood composites. Differential scanning calorimetry revealed a decreasing trend in the degree of crystallinity (X_c) of the matrix when heat treated wood was used as filler. However, untreated wood showed an increase in X_c with increasing wood content.

Keywords: Wood thermoplastic composites; Extrusion and injection moulding; Thermal properties; Degree of crystallinity; Tensile properties

1. INTRODUCTION

The emergence of Wood Plastic Composites (WPCs) presents a class of materials which combines the favourable performance and cost effective properties of both wood and plastics. Because of these attributes, WPCs are seen as a way to increase the value-added utilization of waste wood and wood of low commercial value. Wood, a natural cellulose composite material of botanical origin is useful for many applications because of its many excellent structural and chemical properties [1]. Incorporating wood into WPC lowers production cost, improves stiffness and increases the profile extrusion rate of products and acts as an environmentally friendly way of reducing the use of petroleum based plastics. This is because wood is cheap, readily available and renewable. Also, it has good strength to weight ratio and aesthetic appearance [2, 3]. However, because of the moisture absorbing tendency in wood, it suffers a number of disadvantages. Poor resistance against fungal and insect attack, swelling and shrinkage resulting from water absorption and desorption are some of these shortcomings [4, 5]. Many studies have been carried out to improve the unfavourable properties of wood. These include chemical and thermal modifications. Others are densification, surface treatments, corona or plasma discharge and enzymatic modifications [6-8].

Thermal treatment is one of the ways of improving wood quality. It has been reported to be an effective method to improve wood dimensional stability and/or its durability. High temperature treatment of wood results in several changes occurring in the wood chemistry. The hemicellulose is the first structural compound to be thermally affected even at low temperatures. The degradation starts by deacetylation, so that the released acetic acid acts as a depolymerisation catalyst which further increases polysaccharide decomposition. This acid catalyzed degradation leads to the formation of formaldehyde, furfural and other aldehydes. 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 [5, 9].

The use of thermally modified wood as reinforcement in WPC is gradually gaining attention. The essence of thermal treatment of wood in WPC is to enhance the compatibility of the wood and the matrix by reducing hydrophilicity of wood. However, wood is thermally unstable, degrading at temperatures above 200°C. Therefore, lower processing temperatures are generally permissible because of the possibility of lignocellulosic degradation and/or the possibility of volatile emissions that could affect composite properties. Processing temperatures are thus limited to about 200°C, although it is possible to use higher temperatures for short periods [10].

It has been reported that exposing wood to higher temperatures than normal drying should, in principle, result in wood with higher thermal stability because the vulnerable components (hemicelluloses) are expected to have been decomposed or at least gone through some structural changes. Also, heat treatment modifies the polar nature of wood possibly resulting in better compatibility between wood and the polymer matrix, thus leading to high quality and thermally stable composites [11, 12]. Furthermore, wood flour encounters intense heat during composite processing. Therefore, thermal analysis study is important to determine the extent of degradation during treatment and composites fabrication. In addition, semi crystalline thermoplastics composites have properties that are a complex function of a number of variables such as mechanical properties, shape, size, orientation and distribution of fillers and the mechanical properties of the matrix. Furthermore, degree of crystallinity, size and number of spherulites are factors affecting the mechanical properties of polymer matrices. Incorporation of fillers to LDPE matrix can affect its crystallization and consequently, the mechanical properties which are dependent on the crystalline structure [13].

Therefore, this paper is aimed at modifying red balau saw dust with heat treatment and studying the effects on the tensile and thermal properties of the resultant composites. Melting and

crystallization behaviours are also investigated to determine the processability of the heat treated wood and LDPE composites.

2. EXPERIMENTAL

2.1. Materials

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 (450-150 μ m) sizes using a locally fabricated mill. Commercially available LDPE (Titanlene LDI300YY), with a density of 0.92 g/cm³, molecular weight of 350,000 – 380,000 g/mol and MFI 20 g/10 min, supplied by Titan Petchem (M) Sdn. Bhd. was used as the matrix.

2.2. Chemical constituents of wood flour

Acid insoluble lignin was determined according to the ASTM D1106 standard [14]. Hemicellulose and cellulose were analysed according to the method described by Rowel *et al.* [15]. Extractives of moisture free samples were assessed according to the ASTM D1105 standard method with slight modifications [16]. After extracting a known weight with 95% ethyl alcohol and ethanol-toluene solutions for six hours each, the percentage mass difference was calculated. A known weight of the extracted, oven dried moisture free wood was also taken through three rounds of hot water extractions. The combined percentage weight of the extractives was then taken. The ash content was determined according to the ASTM D1755 [17].

2.3. Processing

2.3.1. Wood pre-treatment

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 prior to compounding. Treated wood was subjected to 180°C and 200°C temperatures in a vacuum oven for one hour effective treatment time.

2.3.2. Compounding

LDPE, untreated and the heat treated wood flours were pre-mixed in different compositions in 200 g portions and compounded in a twin screw co-rotating extruder (Brabender KETSE 20/40 Lab Compounder). The barrel temperatures were set between 150° C - 155° C along the barrel zones and screw speed was 250 rpm. The melt pressure was varied between 34 - 39 bars (($3.4x10^{6} - 3.9 \ 10^{6}$ Pa) depending on the wood content, while the die temperature between 164° C - 178° C. Vacuum venting was used to ventilate out the volatile compounds. The samples were extruded out through a circular die of 3 mm in diameter. The extruded strand was cooled in a water bath and pelletised to a length of about 3 mm for injection moulding. Extruded pellets were oven dried at 80° C for 24 hours and stored in sealed plastic bags for injection moulding. Composites were prepared at three different fibre loadings of 20%, 40% and 60% volume fractions (equivalent to 9%, 20% and 37% weight fractions).

2.3.3. Injection moulding

The pellets were injection moulded into tensile test pieces with dimensions according to the ASTM D638, type 1 standard [18] using the BOY 55M injection moulding machine at a barrel temperature of between 150°C and 155°C, an injection pressure of 100-120 bars (10 - 12 MPa) and mould temperature of 25°C.

2.4. Thermal analysis

2.4.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) measurements were carried out using the Perkin Elmer TGA 6 on 8-10 mg samples of each of the composites in a ceramic crucible, over a

temperature range from 30°C - 700°C at a heating rate of 10°C/min. The tests were conducted in a nitrogen atmosphere at a flow rate of 20 mL/min.

2.4.2. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was carried out using the Perkin Elmer Diamond DSC (Hyper DSC) on 5-7 mg samples crimped in aluminium pans. Each sample was characterised between -50°C to 200°C at a scan rate of 10°C/min. Prior to this measurement, the specimen was heated to 200°C and held at this temperature for 2 minutes to erase the thermal history, then cooled under nitrogen atmosphere at a flow rate of 20 mL/min and heat again for the actual measurement. The melting temperature, T_m , was taken as the peak of the endothermic curve while the crystallization temperature, T_c , was the peak of the exothermic curve. The relative percentage crystallinity, X_c of the composites was calculated according to the following equation [19],

$$X_{c} = \frac{\Delta H_{m}}{\Delta H_{m}^{*} W_{m}} \times 100(\%) \tag{1}$$

where ΔH_m is the melting enthalpy of specimen, W_m is the weight fraction of LDPE in the composite and ΔH_m is the heat of fusion for the fully crystalline LDPE, taken as 293 J/g [20].

2.5. Tensile Testing

Tensile tests were carried out using a universal testing machine (Instron 5569) equipped with a load cell of 50 kN and a mechanical extensometer according to ASTM D638 [18] under ambient condition at a cross-head speed of 5 mm/min. A zero span of 50 mm was chosen for the extensometer.

3. **RESULTS AND DISCUSSION**

3.1. Chemical composition

Table 1 illustrates the percentage composition of lignin, carbohydrates, extractives and ash in the wood flour samples. The results suggest that carbohydrates were more susceptible to thermal degradation than lignin at the treatment temperature.

Treatment Temperature (°C)	Lignin (%)	Hemicellulose (%)	Cellulose (%)	Extractiv es (%)	Ash Content (%)
Untreated	29	29	41	2	2
180	27	28	42	2	2
200	31	25	42	3	2

Table 1. Chemical composition of Red balau saw dust before and after heat treatment.

Hemicellulose degraded faster than cellulose as the values decreased from 29% in untreated wood to 28% and 25% when wood is subjected to heat treatment at 180°C and 200°C respectively. This may possibly be because cellulose is more crystalline than hemicellulose which confers better resistance to thermal degradation. Zaman *et al.* [21] have suggested that cellulose (a linear homo-polysaccharide 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. This finding is in agreement with literature [22]. Total extractives were also determined for the

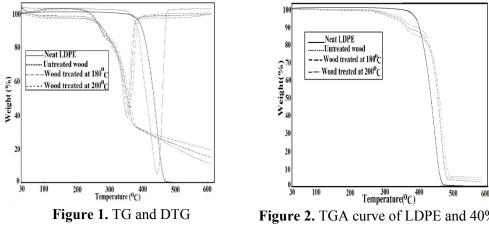
untreated and heat treated wood samples. However, a slight increase in the amount of extractives was observed. This may be due to the fact that during heat treatment, most of the lower molecular weight components of wood could probably have evaporated. Also, lignin and carbohydrates may have been gradually converted into extractive-like compounds [23]. It should be mentioned here that detailed compositions of this fraction was not studied in this investigation. The ash content of the wood samples indicated no particular trend.

3.2. Thermal properties

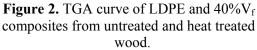
3.2.1. Thermogravimetric analysis

Figure 1 presents the TGA and DTG thermograms of LDPE, untreated wood and heat treated wood. The curves exhibits two mass loss peaks. The first slight mass loss at about 100°C is attributed to the evaporation of moisture from the wood. The second peak occurs between approximately 200°C to 400°C. This is due to the degradation of the three main components of wood fibre, which are, hemicellulose, cellulose and lignin. Lignocellulosic materials being chemically active, decompose thermo-chemically in the range of 150°C to 500°C. Hemicellulose degrades between 150°C and 350°C, cellulose decomposes between 240°C and 350°C and lignin between 250°C and 500°C [27, 28].

The effect of heat treatment on thermal stability of wood is also shown in Figure 1. Untreated wood has the lowest thermal stability, degrading at a lower temperature and at a faster rate than the treated ones. Wood treated at 200°C reveals a higher resistance to heat. Treating wood at 180°C indicates an intermediate thermal property between the untreated and the wood treated at 200°C. However, percentage mass loss of 49%, 50% and 50% are obtained for untreated, 180°C treated and wood treated at 200°C respectively with corresponding degradation peak temperatures of 351.4°C, 355.9°C and 362.4°C. The increase in T_p of heat treated wood over untreated ones is an evidence of improvement in thermal resistance of heat treated wood. This observation may be due to the removal of hemicellulose by heat treatment thereby rendering the wood more thermally stable [23]. In addition, the heat treatment of wood may improve the thermal properties by reducing its heat transfer coefficient [29]. It should also be noted here that neat LDPE is more thermally stable than the wood. However, when LDPE is compounded with the wood, a different thermal property is displayed. Figure 2 shows the TGA curves for neat LDPE and the composites from untreated and heat treated wood at 40% V_f filler loading. The thermal degradation patterns of the LDPE and the resultant composites reveal that the neat matrix is less thermally stable than the composites. The neat LDPE degrades faster at a temperature range between 350°C and 480°C, with a lower initial mass loss. From Figure 1, it can be seen that the degradation of wood, though starts at a lower temperature than the neat matrix and composites, it is more gradual with a broad onset. Furthermore, the degradation profiles of the composites indicate an improvement over the wood and the neat matrix, which degrade between 250°C and 500°C, with a wider onset. T_p values of the composites are also found to have increased appreciably over the values obtained for the neat matrix and the wood (Table 2). Composites at 40% V_f from wood treated at 200°C has the highest T_p value of 471.0°C. This value is higher than wood and the neat LDPE, with maximum T_p values of 362.4°C and 446.0°C respectively. This is indicative of an improvement in the thermal stability of the composites [30]. In addition, the temperature at which 50% mass of the composites degraded, $T_{50\%}$ decreases with filler content for untreated wood composites (Table 2). However, for the heat treated wood composites, $T_{50\%}$ increases up to 40% V_f , then decreases sharply at 60% V_f . This implies that 40% V_f may be the optimum composition at which the thermal stability of heat treated wood composites is highest. It should also be noted that this composition also gives the highest T_p for the composites from heat treated wood. Reinforcing polymers with heat treated wood has proved to increase the thermal properties of the neat matrix [12].



thermograms of LDPE, untreated and heat treated wood.



However, as the wood content increases, T_p is found to decrease reasonably for untreated wood and wood treated at 180°C. This is in line with literature, whereby increase in filler content in lignocellulosic-filler thermoplastic composites was found to result in decreased thermal stability. This is as a result of the lower thermal stability of wood compared to LDPE [28]. On the other hand, composites from wood treated at 200°C seems to impact more positively on the thermal stability of the matrix than that from180°C treated wood, which in turn shows better thermal stability than composites from untreated wood (Figure 2). This is because lignin is the most thermally stable components in wood. Therefore, treatment at 200°C which could significantly degrade other components of wood will have little or no decomposition effects on lignin [23]. As a result, wood treated at 200°C has higher lignin content (Table 1) and leads to more thermally stable composites.

Volume Fraction, V _f (%)	Treatment Temperature (°C)	T _p (°C)	Onset (°C)	T _{50%} (°C)	Degradation Temperature (°C)
100	-	351.2	255.7	352.5	213.5-397.8
100	180	356.6	275.6	355.7	207.1 - 391.7
100	200	362.4	297.0	361.6	226.5 -400.7
0	-	446.0	398.3	436.5	350.0 -479.0
	-	466.1	424.1	458.6	305.8 - 492.3
20	180	448.7	361.3	434.9	250.9-478.6
	200	457.3	359.8	443.0	255.0-487.0
	-	465.3	420.2	457.8	279.4-494.8
40	180	465.5	395.6	456.5	257.2-493.6
	200	471.0	417.7	461.7	258.7-500.1
	-	462.0	397.9	447.2	245.7 -488.5
60	180	458.0	366.7	440.1	232.1 -488.5
	200	462.6	384.6	439.8	231.4-492.4

Table 2. TGA parameters of LDPE composites.

3.2.2. Differential scanning calorimetry

3.2.2.1. Melting behaviour

Figures 3 and 4 show the typical DSC curves corresponding to the cooling and the second heating scans of the neat matrix and composites from untreated wood and wood treated at 200°C respectively.

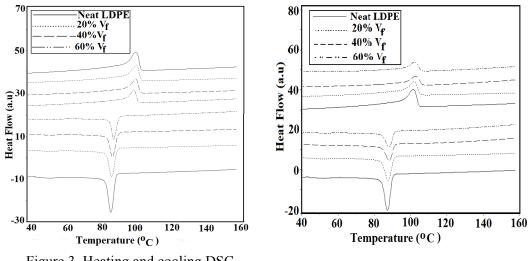


Figure 3. Heating and cooling DSC thermograms of untreated wood/LDPE composites.

Figure 4. Heating and cooling thermograms of 200°C treated wood/LDPE composites

Incorporating wood into LDPE seems to have marginal effect on the melting behaviour of WPC as no particular trend was observed and no correlation with the filler loading can be established (Table 3).

Wood content, V _f (%)	Treatment temperature (°C)	T _m (°C)	T _c (°C)	$\begin{array}{c} \Delta H_m \\ (J/g) \end{array}$	-ΔH _c (J/g)	Xc (%)
0	-	100.4	86.4	97.7	77.4	33
20	-	100.7	86.7	58.9	63.5	22
	180	99.9	86.9	92.2	61.6	35
	200	100.9	86.6	78.6	57.6	30
40	-	100.4	87.2	73.9	57.1	32
	180	99.4	87.2	73.2	59.1	31
	200	101.7	87.3	44.9	57.4	19
60	-	99.3	87.8	65.0	48.9	35
	180	99.6	87.6	61.8	48.8	34
	200	101.0	87.2	26.0	50.4	14

Table 3. DSC Parameters of LDPE composites.

In WPC, wood particles penetrate the chains of the bulk polymer, thereby interfering with the formation of continuous chains. This results in the WPC polymer chains being shorter than the neat polymer, leading to lower melting temperatures, T_m [24]. Therefore, higher wood content means shorter polymer chains and consequently, lower T_m. This is observed for wood treated at 180°C, whereby a slight decrease in T_m values is noted in the composites as the wood content increases compared to the neat matrix. Untreated wood composites also display this type of results, but the difference is quite small until at 60% Vf. This is in contrast with earlier findings, whereby incorporation of natural fibres into a thermoplastic matrix was reported to result in an increase in T_m of the composites [19, 25]. On the other hand, wood treated at 200°C presents the highest T_m of 100.9°C, 101.7°C and 101.0°C respectively for 20%, 40% and 60% V_f specimens. This is an increase over the T_m of neat LDPE recorded at 100.4°C. This may be due to the fact that wood treated at 200°C has more ability to restrict the mobility of LDPE chains during the melting process. The possible reasoning is that modification by heat renders the wood particles a bit less polar, enhancing better interaction with the non polar matrix which leads to better encapsulation of the filler by the melted matrix. This could result in inhibition of the mobility of the polymer chain, resulting in higher T_m

3.2.2.2. Crystallization Behaviour

Heat treated wood seems to have little effect on T_c The neat matrix has the lowest T_c value of 86.4°C, while composites from untreated wood at 60% V_f loading has the highest T_c value of 87.8°C (Table 2). There is a slight increase in T_c values for composites from untreated and wood treated at 180°C for all filler levels. Tc values for wood treated at 200°C increase up to 40% V_f , but dropped slightly at 60% V_f . Loading untreated wood onto LDPE at 60% V_f increases the X_c more than the neat LDPE. This trend is also observed for 20%V_f of wood treated at 180°C. However, there is a consistent increase in X_c for all compositions of the untreated wood. This may be attributed to the surface of untreated wood acting as a nucleating agent, which promotes crystalline growth and formation of trans-crystalline regions around the wood fibres [19, 26]. The higher the wood content, the higher is the formation of the trans-crystalline layer, thus leading to higher X_c. This is displayed in the X_c trend for untreated wood composites. At lower V_f, the amount of wood present is not sufficient to influence X_c. This result in lower values of X_c of the composites compared to the neat matrix. However, at 60% V_f, the nucleating ability of the untreated wood becomes predominant and an increase in X_c over the neat matrix is observed. On the other hand, a decreasing pattern in X_c is observed for the heat treated wood at the various levels of loading. Wood treated at 180°C has X_c of 34% for 20% V_f , 31% for 40% V_f and 33% for 60%Vf respectively. These values are higher than 200°C treated wood composites, which exhibit X_c values from 29% for 20% V_f through 19% for 40% V_f to 14% for the 60% V_f. Heat treatment seems to deactivate the nucleating sites on wood resulting in lower X_c. This deactivation is more pronounced with wood treated at 200°C since it is expected to be modified the most through heat treatment [24]. Although heat treated wood may contain some nucleating sites, these sites are not sufficient to influence the X_c [13]. This is evident in the X_c values for composites from wood treated at 180°C. While there is an increase in X_c value of the composites at 20% V_f relative to the neat matrix, a decrease is observed for the 40%Vf. Subsequently, the value rises to 33% for the 60% V_f, which is the X_c value for the neat matrix. It has been reported that at higher filler loading, the particles acts as diluents to the matrix and restrict crystal growth, thereby slowing down crystallization. Therefore, for the heat treated wood, the higher the wood fraction, the more is the resistance to formation of crystal structures [25], leading to lower X_c. This may also be the reason for the increasing value of ΔH_c as the wood content increases, indicating that higher energy is needed for crystallization.

3.4. Mechanical Properties

3.4.1. Tensile Properties.

The tensile modulus, strength and strain are shown in Figures 5-7. Tensile modulus increases with both heat treatment and filler loading (Figure 5). At 20% V_f , a composite from

wood treated at 180°C has a slightly lower modulus value compared to the neat matrix. Untreated wood composites show an increasing trend in tensile modulus at all filler loadings. Percentage increase of 69%, 100% and 309% are obtained for 20%, 40% and 60% Vf respectively compared to the pure matrix. However, the effect of the heat treated wood is more pronounced at higher filler levels. An increase in tensile moduli from 57% for 20%V_f, through 183% for 40% V_f to 400% for 60% V_f is observed for wood treated at 180°C relative to the neat LDPE. Increase in tensile modulus of composites from heat treated wood relative to untreated ones indicates better adhesion/wetting of the filler by the matrix. The tensile strength of the composites decreases with increasing filler loading (Figure 6). This may be due to weak interfacial adhesion and low compatibility between the wood and the matrix. Also wood fibres may act as notches on the matrix leading to premature failure, resulting in low strength. Despite the general decreasing trend with increasing filler loading, wood treated at 180°C maintained a consistently higher tensile strength for all volume fractions, indicating that heat treatment at 180°C has improved the compatibility between the hydrophilic wood flour and the hydrophobic polymer matrix to a certain degree and a fibre/matrix interfacial adhesion. In addition, wood treated at 200°C seems to have the least influence on tensile strength. It is worth noting that composites from wood treated at 200°C also exhibited a significantly decreasing trend in degree of crystallinity for the various compositions. It has been reported that in semi-crystalline thermoplastic composites, degree of crystallinity is an important parameter influencing the mechanical properties [31]. Therefore, it is not surprising that it presented the least tensile strength. Tensile strain decreases with increasing filler loading (Figure 7). A composite from wood treated at 200°C also has the lowest tensile strain. This is because incorporating fillers into a matrix renders it more brittle. Furthermore, low X_{c} means that the composite is more amorphous, making it more glassy and consequently, more brittle, leading to low strain.

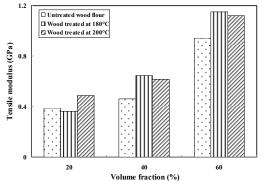


Figure 5. Tensile modulus of composites as a function of heat treatment and composition.

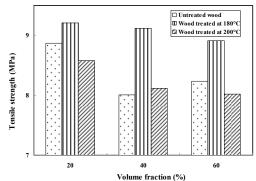


Figure 6. Tensile strength of composites as a function of heat treatment and composition.

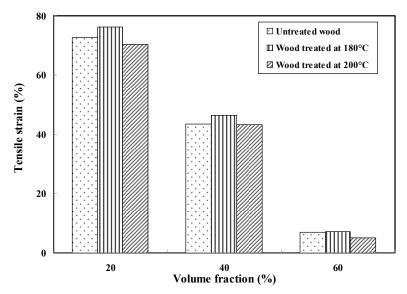


Figure 7. Tensile strain of composites as a function of heat treatment and composition

4. CONCLUSION

Heat treatment was found to improve the thermal stability of the wood saw dust because of the removal of hemicellulose. Thermal stability of the composites from treated and untreated wood was higher than the neat matrix, with the heat treated wood giving higher stability compared to the untreated ones. Composite with 40% V_f from wood treated at 200°C resulted in composites with the highest T_p. It was also observed that incorporating wood into LDPE has minimal effects on the melting behaviour of the composites. X_c increased with increasing filler loading of untreated wood due to the nucleating ability of the wood surface. Heat treated wood influenced X_c to a lesser extent as a result of deactivation of the surface by heat treatment. Tensile tests revealed an increase in tensile modulus when heat treated wood was used in comparison with untreated ones, as a result of improved wetting of the wood by the matrix, leading to better interfacial adhesion. Tensile strength and strain at maximum load decreased with filler loading and treatment due to embrittlement of the matrix by the filler. The influence of wood treated at 200° C on the tensile strength and strain at maximum load was related to its effects on X_c. It was found that 200°C treated wood resulted in lower crystallinity and lowest tensile strength and stress at maximum load. Low crystallinity and improved thermal properties are advantageous in WPC processing.

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