

**THERMAL AND TENSILE PROPERTIES OF TREATED
AND UNTREATED RED BALAU(*SHOREA*
DIPTEROCARPACEAE)/LDPE COMPOSITES**

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ABSTRACT

Using wood as fillers in Wood Plastic Composites (WPC) often leads to enhanced properties. However, incompatibility between the

polar wood and the non polar matrix posses a problem which can result in poor interfacial adhesion, leading to poor mechanical properties. This paper is aimed at alleviating this problem by modifying wood with heat treatment. Red balau saw dust was heat-treated at 180°C and 200°C for one hour and compounded with Low Density Polyethylene (LDPE) at 20%, 40% and 60% volume fraction loadings (equivalent to 8.78%, 20.4% and 36.6% weight fractions respectively). Thermal and tensile properties of the resultant composites were investigated as a function of filler loadings and treatment temperature. Tensile moduli increased up to 398.27% compared to the neat LDPE matrix when heat treated wood at 200°C was used as filler, relative to 308.23% for the untreated wood. Wood treated at 180°C gave the highest tensile strength for all filler loadings. Differential scanning calorimetric investigations revealed a decreasing trend in the degree of crystallinity (X_c) of the matrix when heat treated wood was used as filler. On the other hand, untreated wood showed an increase in X_c with increasing wood content. Wood treated at 200°C showed a rapid decrease in the

degree of crystallinity with values of 33.26%, 29.40%, 19.25%, and 13.97% degree crystallinity for 0%, 20%, 40% and 60% volume fractions respectively. Melting temperatures were not significantly altered. Thermogravimetric analysis revealed an increase in degradation peak temperature (T_p) of the composites of up to 40% volume fraction for wood treated at 180°C and 200°C. However, an increase was observed for untreated wood for all compositions. Reduction in the degree of crystallinity and increase in thermal stability offer advantages in WPC processing.

Keywords: Wood plastic composites; Injection moulding; Thermal properties; Tensile properties; Degree of crystallinity.

Introduction

Wood Plastic Composites (WPCs) are an emerging class of materials which combines the favorable performance and cost 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]. Also wood is considered as a readily available, relatively inexpensive filler that can lower resin costs, improve stiffness, increase profile extrusion rates, and act as an environmentally friendly way to decrease the use of petroleum-based plastics [2]. It has a good strength to weight ratio and aesthetic appearance [3]. However, wood also suffers a number of disadvantages because of its hygroscopic nature. This leads to poor resistance against fungal and insect attack, swelling and shrinkage resulting from water absorption and desorption [4], [5].

Many studies have been carried out to improve the unfavourable properties of wood. These include chemical and thermal modification. 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 hemicelluloses are the first structural compounds to be thermally affected even at low temperatures. The degradation starts by deacetylation, so that the released acetic acid acts as a depolymerization 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].

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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 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 has 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. Also degree of crystallinity, size and number of spherulites are factors affecting the mechanical properties of polymeric matrices. Addition of fillers to LDPE matrix can affect its crystallization and consequently, the mechanical properties which is 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

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behavior is also investigated to determine the processibility of 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 μm) sizes using a locally fabricated mill. The moisture content before heat treatment was less than 7%. Commercially available LDPE (Titanlene LDI300YY), with a density of 0.920 g/cm^3 , molecular weight of 350,000 – 380,000 g/mol and MFI 20 g/10 min, supplied by Titan Petchem (M) Sdn Bhd, Malaysia, was used as the polymeric matrix.

2.2. Chemical constituents of wood flour

Acid insoluble lignin was determined using ASTM D 1106-96 [14] standard. Hemicelluloses and cellulose was analysed according to the method described by Rowel et al [15]. Extractives of moisture free samples were assessed using ASTM D 1105-96 standard method with slight modifications [16]. After extracting a known mass with 95% ethyl alcohol and ethanol-toluene solution for six hours respectively, the percentage mass difference was calculated. A known mass of the already extracted, oven dried moisture free wood was also

taken through three rounds of hot water extractions. The combined percentage mass of the extractives was then taken. The ash content was determined according to the

ASTM D 1755-01 [17]

2.3 Processing

2.3.1 Wood pretreatment

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. The wood sawdust for thermal treatment was spread on an aluminium tray to a maximum height of 8-10 mm to provide maximum heat transfer for efficient thermal modification. It was subjected to 180°C and 200°C temperatures in an oven for one hour effective treatment time.

2.3.2. Compounding.

LDPE, untreated and the heat treated wood flour were pre-mixed in varying weight fractions calculated from their respective volume fractions in 200 g portions and compounded in a twin screw co-rotating extruder (Brabender KETSE 20/40 Lab Compounder, Germany). The barrel temperatures were set between 150 - 155°C along the barrel zones and screw speed was 250 rpm. The melt pressure varied between 34 and 39 bars depending on the wood content, while the die temperature was between 164°C - 178°C. Vacuum venting was

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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 using a pelletiser. Extruded pellets were oven dried at 80°C for 24 hours and stored in sealed plastic bags for further use. Wood flour was applied at 20%, 40% and 60% volume fractions, equivalent to 8.78%, 20.40% and 36.60% weight fractions based on the total weight of the composites.

2.3.3 Injection moulding

The pellets were injection molded into tensile (ASTM638) [18] test strips 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.

2.4. Thermal analysis

2.4.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) measurements were carried out using the Perkin Elmer TG 6 on 8-10 mg samples of each of the composites in a ceramic crucible, over a temperature range from 30°C to 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. TGA data were collected and analyzed with the Pyris software.

2.4.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) was done using the Perkin Elmer Diamond DSC (Hyper DSC) on 5-7 mg samples crimped in aluminium pans. Each sample was scanned from -50°C to 200°C at a heating rate of 10°C/min, it was held at this temperature for 2 minutes to erase the thermal history, then cooled at the same rate under nitrogen atmosphere at a flow rate of 20 mL/min and heat again from -50°C to 200°C at the same heating rate. Results were analyzed with the Pyris software. 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 of the composites was calculated according to the following equation [19]

$$X_c = \frac{\Delta H_m}{\Delta H_m^0 w} \times 100(\%) \quad (1)$$

where X_c is the percentage crystallinity, ΔH_f is the heat of fusion of the neat LDPE and composites, w is the mass fraction of LDPE in the composite and $\Delta H_m^0 = 293 \text{ J/g}$ was taken as the heat of fusion for the 100% crystalline LDPE [20].

2.6 Mechanical testing

2.6.1 Tensile Testing

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Tensile tests were carried out using an Instron universal testing machine (Instron 5569, USA) equipped with a load cell of 50 kN and a mechanical extensometer according to ASTM 638-99 [18] under ambient conditions at a cross head speed of 5 mm/min. A zero span of 50 mm was chosen for the extensometer. Average Specimen thickness and width of 3.26 mm and 12.98 mm respectively were used. Ten samples of each composition were tested and the average results taken. Results were analyzed using the Blue Hill software. Reported properties were measured at yield point.

3. Results and Discussion

3.1. DSC analysis.

3.11. Melting Behaviour

Incorporating wood into LDPE has marginal effects on the melting behavior of WPC as no particular trend was observed. This is in contrast with earlier findings [15], [17]. However, wood treated at 200°C presented the highest set of T_m values of 100.93°C, 101.66°C and 100.96°C respectively for 20%, 40% and 60% volume fractions. This is an increase over the T_m for neat LDPE which gave 100.39°C.

This may be due to the fact that wood modified at 200°C has more ability to restrict the flow of LDPE during the melting process.

3.12. Crystallization Behaviour

Heat treated wood seems to have little effects on the crystallization temperature as T_c values of between 86.16 and 87.83 were obtained for the various compositions as seen in Table 1. Loading untreated wood onto LDPE at 60% V_f increased the X_c more than the neat LDPE. This trend was 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 transcrystalline regions around the wood fibres[15], [18]. The higher the wood content, the higher the transcrystalline layer formed leading to higher X_c . On the other hand, a decreasing pattern in X_c was observed for the heat treated wood at the various levels of loading. 180°C treated wood has X_c between 34.49 and 31.38%. However, it

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was observed that 40% V_f of untreated and heat treated wood at 180°C seems to influence crystallinity to the same degree with values of 31.66 % and 31.38% respectively. These values are higher than 200°C treated wood, presenting X_c from 29.40% for 20% V_f through 19.25 for 40% V_f to 13.97% for the 60% V_f formulations. Heat treatment seems to deactivate the nucleating sites on wood resulting in lower X_c .

Table 1. DSC and TGA parameters for wood, LDPE and composites.

Sample/ Compositi on (% V_f)	Treat ment	Parameter					
		DSC					TGA
		$T_m(^{\circ}C)$	$T_c(^{\circ}C)$)	$\Delta H_f(J/g)$	$\Delta H_c(J/g)$	$X_c(\%)$	$T_p(^{\circ}C)$
WOOD	Untre ated	ND*	ND*	ND*	ND*	ND*	351.3 8
	180°	ND*	ND*	ND*	ND*	ND*	355.9

	C						2
	200°	ND*	ND*	ND*	ND*	ND*	361.8
	C						2
Neat LDPE	None	100.39	86.38	97.73 2	- 77.418 7	33.26	446.0 3
	Untreated	100.69	86.66	58.92	- 63.542 2	22.04	466.0 9
20	180° C	99.87	86.87	92.18 2	- 61.638 7	34.49	448.7 3
	200° C	100.93	86.61	78.57	- 57.618 4	29.4	457.3 0
40	Untreated	100.38	87.21	73.85	-57.10	31.66	465.3

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	ated						3
	180° C	99.39	87.19	73.18	59.056 3	31.38	465.4 5
	200° C	101.66	87.29	44.89	57.427 4	19.25	470.9 6
60	Untre ated	99.30	87.83	64.99	48.867 7	34.99	462.0 1
	180° C	99.55	87.55	61.81	48.831 9	33.27	457.9 7
	200° C	100.96	87.24	25.95	50.377	13.97	462.5 9

* Not determined

This deactivation is more pronounced with wood treated at 200°C since it is expected to be modified the most through heat treatment. Although heat treated wood may contain some nucleating sites, these sites are not sufficient to influence the crystallinity index [13]. In addition, 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 the resistance to formation of crystal structures [19], 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.

3.2. Thermogravimetric analysis

Figure 1 presents the TGA and DTG curves for wood treated at different temperatures. The slight weight loss below 100°C is attributed to the evaporation of moisture from the wood.

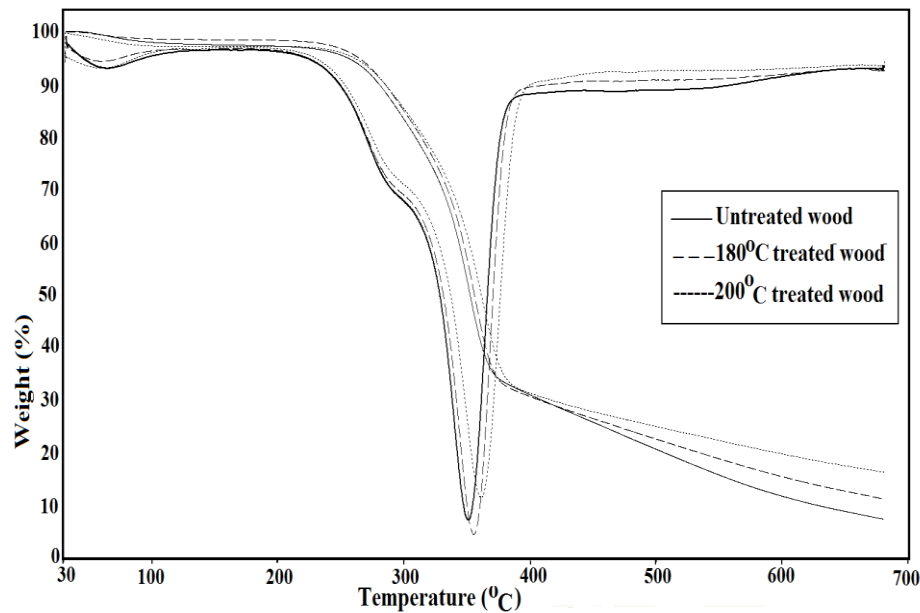


Fig 1. TG and DTG curves for untreated and heat treated wood

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 revealed a higher resistance to heat with the highest ash content. Treating wood at 180°C indicated an intermediate thermal property between the untreated and the 200°C treated wood. However, percentage mass loss of 48.544%, 49.799% and 50.283 % were obtained for untreated, 180°C treated

and 200°C treated respectively with corresponding degradation peak temperatures of 351.38°C, 355.92°C and 361.82°C. The increase in T_p is an evidence of improvement in thermal resistance in heat treated wood. This may be due to the removal of hemicelluloses by heat treatment thereby rendering the wood more thermally stable. It has also been reported that heat treatment of wood improves its thermal properties by reducing its heat transfer coefficient [20].

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 revealed that the neat matrix is less thermally stable than the composites. The neat LDPE degraded very fast at a temperature range of 130°C, between 350°C and 480°C. From Fig 1, it can be seen that the degradation of wood, though started at a lower temperature, was more gradual with a broad onset. Furthermore, the degradation profiles of the composites indicated

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an improvement over the wood and the neat matrix, which degraded between 250°C and 500°C, with a wider onset. T_p values of the composites were also found to have increased appreciably over the values obtained for the neat matrix and the wood. 40% V_f composites from 200°C treated wood has the highest T_p value of 470°C

(Table 1). This is indicative of an improvement in the thermal stability of the composites [21]. Reinforcing polymers with heat treated wood has proved to increase the thermal properties of the neat matrix [12]. From Figure 2, composites from wood treated at 200°C seems to impact more positively on the thermal stability of the matrix than that from 180°C treated wood, which in turn shows better thermal stability than composites form untreated wood.

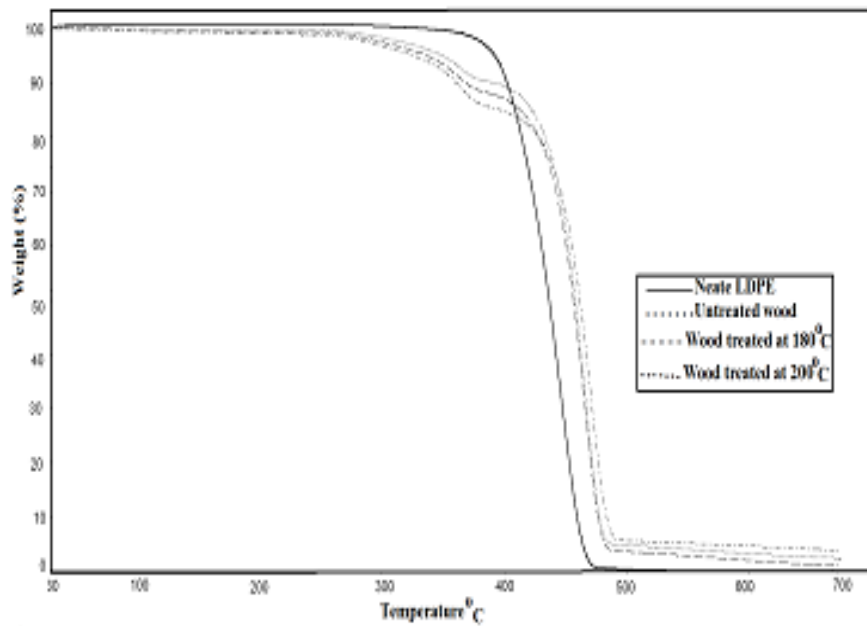


Fig.2. TGA curve for 40% Vf composites from untreated and heat treated wood

3.3. Tensile Properties.

The tensile strength, modulus and strain at maximum load are shown in Figures 3-5.

Tensile modulus increased with both heat treatment and filler loading. Increase in tensile modulus of heat treated wood relative to untreated ones indicates better wetting of the filler by the matrix.

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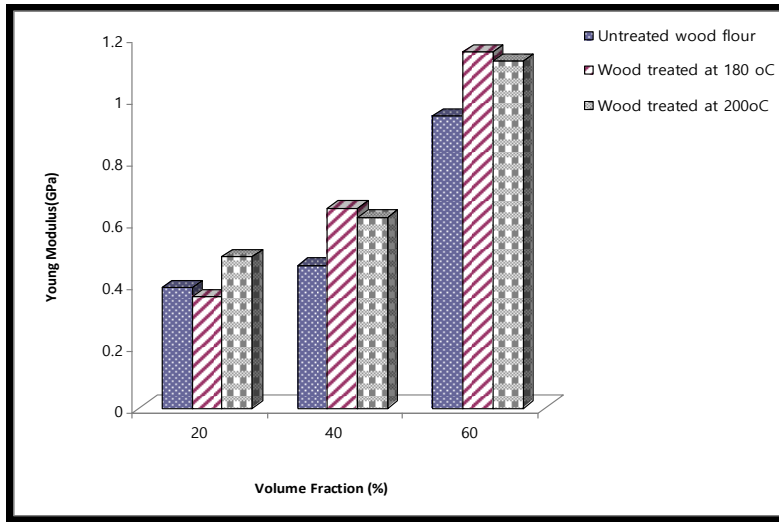


Fig. 3. Young modulus of composites as a function of heat treatment and composition

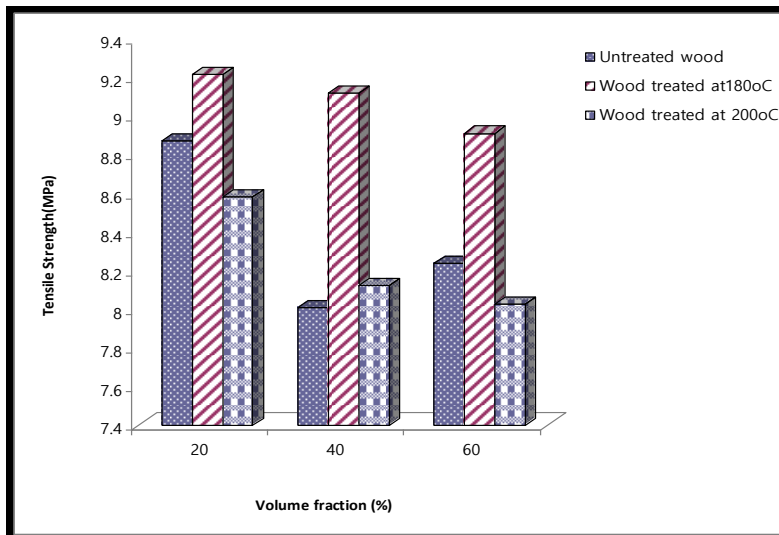


Fig. 4. Tensile strength of composites as a function of heat treatment and composition

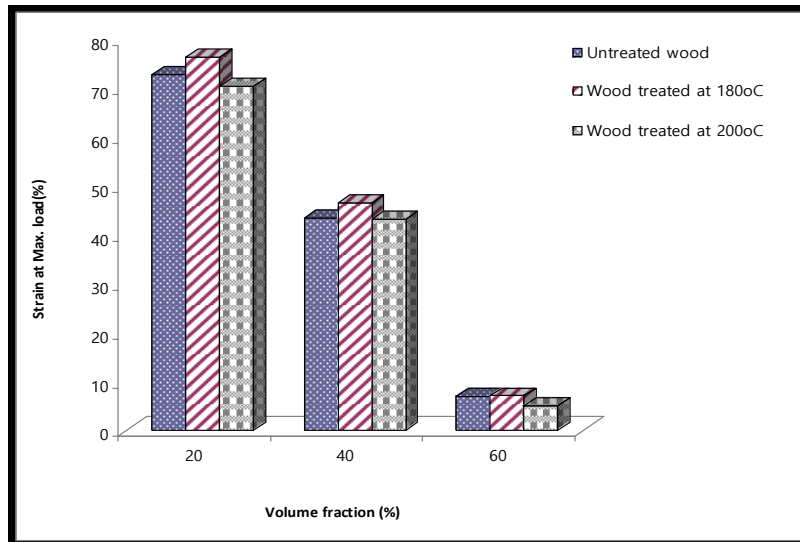


Fig.6. Strain at maximum load of composites as a function of heat treatment and composition

This is achieved by the plasticization of lignin leading to a reorganization of the lignocellulosic polymeric components of the

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wood [22] and the decrease in the hydrophilicity by heat treatment [23]. Untreated wood showed an increasing trend in tensile modulus at all filler loadings. However, the effect of the heat treated wood is more pronounced at higher filler levels though, wood treated at 180°C revealed higher results. The tensile strength of the composites decreased with increasing filler loading. This may be due to weak interfacial adhesion and low compatibility between the wood and the matrix. 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 matrix to a certain degree. In addition, wood treated at 200°C seems to have the least influence on tensile strength. It is worth noting that 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 semicrystalline thermoplastic composites, crystalline features such as degree of crystallinity is an important parameter influencing

the mechanical properties [24]. Therefore, it is not surprising that it presented the least tensile strength. Strain at maximum load decreases with increasing filler loading. This is because incorporating fillers into a matrix renders it more brittle.

4. Conclusion

Composites from heat treated and untreated red balau wood saw dust and LDPE were prepared and analyzed for tensile and thermal properties. It was observed that incorporating wood into LDPE has minimal effects on the melting behavior of the composites. X_c increases 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 due to the deactivation of the surface by heat treatment. TGA investigations showed that heat treatment improves the thermal properties of wood because of the degradation of hemicelluloses and modification of the lignin component in wood. Also, thermal stability of the composites was increased relative to

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the neat matrix, with the heat treated wood giving higher stability compared to the untreated ones. Tensile tests revealed an increase in tensile modulus when heat treated wood are 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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