Effect of Heat Treatment of Wood Flour on the Mechanical Properties of Outdoor Weathered Red Balau/LDPE Composites

R. A. Lafia-Araga[1,2], H. Aziz [1], Y. Rosiyah[1] and A.R. Normasmira [1]

[1] *Chemistry department, Faculty of Science, University of Malaya, 50603, Kuala Lumpur. Malaysia.*
[2] *Chemistry department, School of Science and Science Education, Federal University of Technology, P.M.B, 65. Minna. 920001, Niger State. Nigeria.*

Corresponding author's e-mail: rutharaga@yahoo.ca

Abstract

The interest in replacing synthetic fillers with biodegradable natural fillers from renewable resource in thermoplastic composites is gradually gaining attention. This has led to an upsurge in the use of wood flour as fillers in wood thermoplastic composites (WTC). Wood offers the advantages of being renewable, biodegradable, good strength to weight ratio and tribological properties. However, the hydrophilic properties of wood, intrinsically connected with its cell wall polymers confer some limitations in its use in WTC. Therefore, some modification is required. Usually, chemicals are used to modify wood to enhance the properties of WTC. This possesses environmental challenges as effluents are generated and disposal becomes a problem. Thermal treatment is another wood modification method employed to checkmate the limitations of wood. In thermal treatment, wood is subjected to higher temperatures than drying in a controlled environment. This results in the reduction of the OH groups on the surface of the wood polymers, resulting in reduced polarity. This offers a better alternative as an environmentally benign way to modify wood. In this study, Red Balau saw dust was modified by subjecting it to 180˚C and 200˚C in an oven and compounded with LDPE, then moulded in an injection moulding machine. Samples were exposed to outdoor weathering and tested for mechanical properties to assess the effects of heat treatment on the tensile and flexural properties of weathered and unweathered samples. Results revealed that the mechanical properties of untreated weathered samples deteriorated more than the heat treated composites. Reduced hydrophilicity, resulting from wood flour heat treatment which led to better compatibility between the matrix and the fillers, conferred better interfacial adhesion and resulted in the observed trend. Therefore, heat treatment is an environmental friendly way of modifying the chemistry of wood polymers for property enhanced composites.

Keywords: Wood thermoplastic composites, injection moulding, heat treatment, outdoor exposure, mechanical properties.

Introduction

Ecological concerns have resulted in a renewed interest in natural/renewable materials. This has led to an upsurge in the use of wood flour as fillers in wood thermoplastic composites (WTC). Petroleum-based synthetic thermoplastic polymers are used in different applications because of their excellent chemical resistance, good mechanical properties and low cost. However, most synthetic polymers are extremely resistant to microbial attack and are therefore detrimental to the ecosystem because of their consequent non-degradability which leads to environmental problems associated with their disposal. A result of the current phenomenal use is their increasing presence in municipal solid waste [1].

Wood fillers when combined with thermoplastic matrices in WTC, offers, at least, a partial solution to the problem of non-degradable plastic waste pollution. This is because wood is renewable, biodegradable, possessing good strength to weight ratio and tribological properties. However, the hydrophilic properties of wood, intrinsically connected with its cell wall polymers confer some limitations on its use in WTC. Therefore, some modification is required. Usually, chemicals are used to modify wood to enhance the properties of WTC [2]. This posseses environmental challenges as

effluents are generated and disposal becomes a problem. 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 [3].

In general, studies have shown that composites made from natural fillers are more environmentally superior to those from synthetic fillers in their specific applications. In addition, the cultivation and harvest of natural fillers results in less severe environmental impact than the production of synthetic fillers. Also, due to their light weight, they can be used in high volume fractions relative to the synthetic ones. This reduces the volume of the base polymer used and the weight of the final product. Furthermore, at the end of the service life, incineration of WTC theoretically results in no net addition of CO_2 emissions because plants from which natural fillers are obtained utilises atmospheric CO_2 during their growth which is released during combustion of natural fillers. Thus, incineration of WTC, inherently containing lower base polymer should, in principle, lead to positive carbon credits and lower global warming effects [4].

Also, outdoor applications of WTC require that the materials to withstand a wide variety of environmental factors including moisture, UV radiation, high temperatures, freeze-thaw cycles, mechanical action, and biological invasion. In almost all cases, more than one of these factors act at the same time and in cycles. Swelling, warping, twisting, mould growth, decay, colour changes, and connector failure are some of the problems often encountered from normal outdoor use [5]. These contribute to mechanical property losses by eroding the surface and increasing surface wettability.

This study was therefore intended to investigate the mechanical properties of composites from heat treated Red Balau saw dust after exposure to outdoor environment for a period of time. It is expected that deterioration of properties is a function of the extent of environmental degradability of the 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/m^3, molecular weight of 3.5-3.8x10^5 g/mol and MFI of 20 g/10 min, supplied by Titan Petchem (M) Sdn Bhd, Malaysia, were used as the matrix.

Wood sawdust was dried in an oven at 60°C for 48 h 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 1 h effective treatment time.

FTIR-ATR spectra of heat treated and untreated wood flour were recorded using an FTIR spectrometer (Spotlight 400, Perkin Elmer, USA) combined with a universal ATR accessory at a resolution of 4 cm^{-1} for 64 scans in the range of 650-4,000 cm^{-1}.

LDPE, untreated and the heat treated wood flours were pre-mixed in different compositions in 200 g portions at 20% and 37% 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 pelletised. Extruded pellets were oven dried at 80°C for 24 h and stored in sealed plastic bags over silica gel in desiccators for injection moulding.

The pellets were injection moulded into tensile test pieces using the BOY 55M (Germany) injection moulding machine at a barrel temperature of between 150°C and 155°C, an injection pressure of 100-120 bars and mould 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/$W_{UN/37}$	63	37	-
LDPE/$W_{180/20}$	80	20	180
LDPE/$W_{180/37}$	60	37	180
LDPE/$W_{200/20}$	80	20	200
LDPE/$W_{200/37}$	60	37	200

The outdoor weathering test was conducted according to ASTM D1435 [6]. Specimens were attached to a rack with a rack holder and adjusted to face the equator at an angle of 45°. The rack was placed in an open area free from being overshadowed by other objects. Specimens were exposed to all environmental conditions such as rain, sunlight, wind, etc from April 1st to December 31st 2011 at the University of Malaya main campus geographically located at latitude of 03˚ 07′ North of the Equator and longitude 101˚ 39′ East of the Prime Meridian. At the end of the test period, samples were collected, wiped clean and left to dry in air for 24 h at room temperature before mechanical tests were conducted to determine the extent of properties degradation. The mean temperature and total rainfall in University of Malaya, Kuala Lumpur, Malaysia was compiled for each month according to the data obtained from Malaysian Meteorological Agency and presented in Table 2.

Tensile tests were carried out at room temperature on dry as moulded and outdoor exposed 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 [7] 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 values of at least six reproducible results 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 [8]. Dry as moulded and outdoor exposed 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 cross-head speed of 1.28 mm/min. Ten samples were tested and the average values of at least six reproducible results was recorded

Table 2. University of Malaya weather data for the period from April to December 2011 [9].

Month	Mean relative humidity (%)	Mean rainfall (mm)	Mean temperature (°C)	
			Day	Night
April	85.5	10.4	28.2	25.5
May	80.2	9.7	28.8	26.2
June	81.4	4.7	27.4	26.6
July	79.6	3.5	27.9	26.4
August	83.0	9.2	28.3	25.8
September	84.1	8.1	27.7	25.8
October	85.5	9.2	27.7	25.3
November	86.6	5.5	27.5	25.1
December	84.8	8.0	27.3	25.2

Results and Discussions

Fourier transform infrared analysis. The FTIR spectra of heat treated and untreated wood flour are presented in Fig 1. The spectra look similar as all the samples exhibited characteristic signals of lignocellulosics. A broad peak of cellulose hydroxyl groups (O-H) appeared at 3,335 cm^{-1} and another peak at 1,733 cm^{-1}, which is indicative of C=O aldehyde groups of hemicelluloses and lignin [10].

Despite the similarity in the spectra, a decrease in the intensity of the O-H absorption band at 3,335 cm^{-1} is observed in the heat treated wood samples with the wood sample treated at 200˚C showing a profound decrease. This suggests that the O-H group content in the heat treated wood is reduced after subjecting the wood flour to high temperature. This decrease occurs as a result of the elimination of O-H groups from the less ordered cellulose structure [11]. Such observation has been attributed to the decreased hydrophilicity of heat treated wood by reduction of the potential bonding sites for water [12].

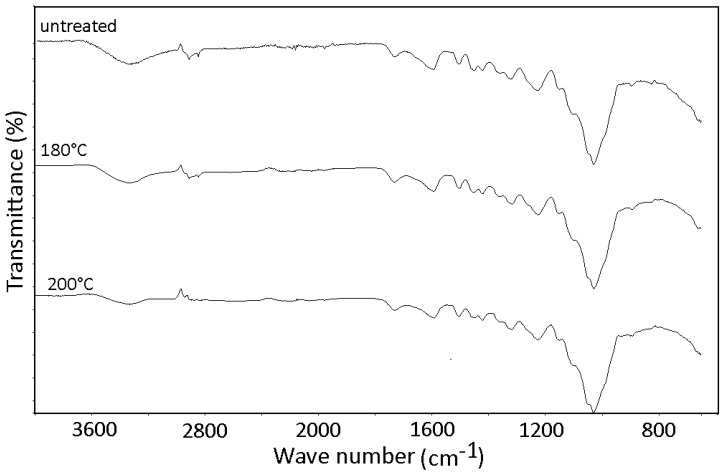

Fig 1**.** FTIR spectra of treated and untreated red balau saw dust.

Physical appearance. Visual assessment of the composites indicates that the dry as moulded specimens appeared dark brown to chocolate in colour depending on the wood content and treatment temperature. However, after exposure for 9 months, the colour changed to light grey with the composites containing higher wood content showing a greater difference in colour and a fibrous appearance due to loss of aesthetic appeal. This must have resulted from the degradation of the wood components by UV radiation. It has been observed that exposure to the outdoor environment affects not only the polymeric material itself but also other components within the matrix. All wood components are susceptible to degradation by UV radiation. However, lignin is responsible for the UV absorption in wood because of the presence of chromophoric functional groups like phenolics, O-H groups, double bonds and carbonyl groups. UV light degrades lignin into water-soluble compounds that are washed from the wood with rain, leaving a cellulose-rich surface with a fibrous appearance [13, 14].

Tensile properties. The tensile modulus of dry as moulded neat LDPE (0.231 GPa) remained relatively the same after exposure to outdoor weathering (0.234 GPa). This indicates that neat LDPE is resistant to degradation by components of the outdoor environment. The chemical structure of LDPE consists of carbon and hydrogen atoms, constituting only C-C and C-H bonds. Since there are no chromophores present, photo-degradation of LDPE will be difficult by UV radiation except when impurities in the form of fillers or other additives are deliberately introduced as in the compounding with wood flour. It should also be mentioned that LDPE can undergo other forms of degradation such as chemical, mechanical or thermal degradation [14]. The tensile properties of unexposed and exposed composites as a function of treatment temperature and wood content are shown in Figs. 2a-c.

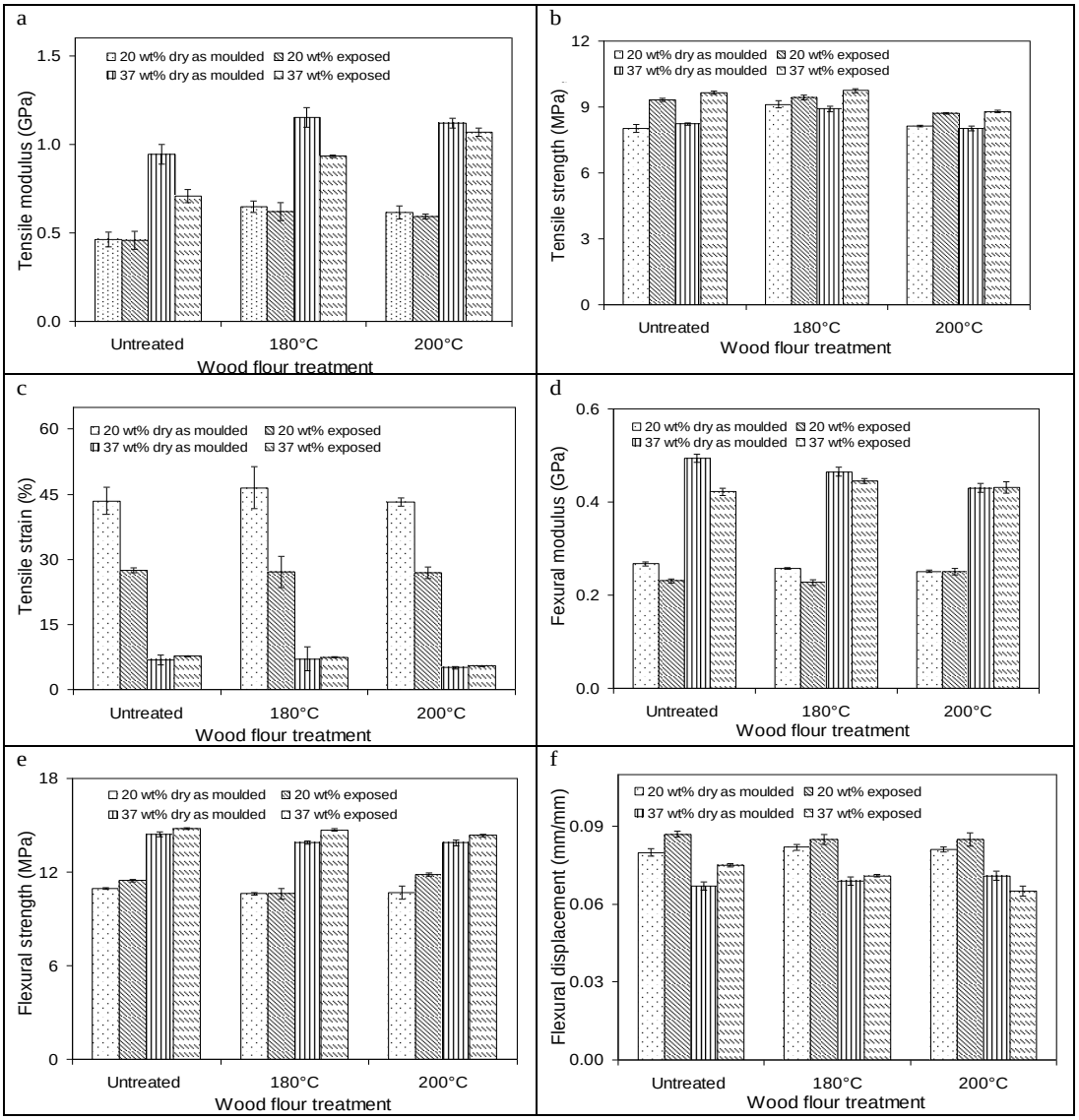

Fig 2.Tensile and flexural properties of outdoor weathered composites made from 20 wt% and 37 wt% untreated and heat treated wood flour.

Tensile modulus increased with wood content for both dry as moulded and outdoor exposed specimens relative to the neat matrix. This is due to the reinforcing effect of the wood particles. However, on exposure to outdoor weathering, the tensile modulus decreased, with the composites filled with 37 wt% wood flour exhibiting a significant drop in modulus values. This is probably due to the deteriorating effect of outdoor environment on the properties of WTC components by photodegradation. It has been reported that changes in mechanical properties of WTC after weathering can be due to changes in the composites surface oxidation, matrix crystallinity changes and interfacial degradation. In addition, wood particles absorb water and swell and the polymer matrix cracks upon UV exposure, resulting in reduced tensile properties. These, in combination, results in a flaky, cracked composites surface with deterioration in mechanical properties [14]. Therefore, the higher the wood content, the higher is the degradation. Heat treated wood composites seems to resist property degradation more than the untreated ones (Fig. 2a). Untreated wood composites showed the highest decrement in tensile modulus (33%) after outdoor exposure. Composites made from wood flour treated at 180°C and 200°C exhibited a decrement to the tune of 23% and 5%, respectively. Reduced hydrophilicity of heat treated wood composites is found because of reduced surface O-H relative to the untreated ones may be responsible for this trend (Fig.1). This has reduced the tendency to absorb water and also, possibly lowered the UV absorption capability.

Strangely, the tensile strength of the composites increased with exposure to outdoor weathering (Fig. 2b). A decrease in strength is expected because the composites are supposed to have aged from out door exposure. However, this is not the case in the present investigations. It has been suggested that starch filled polyethylene undergo a small increase in tensile strength in the very early stages of degradation due to increased cross-linking as cleaved molecules, possibly resulting from radical formation as a result of UV radiation from sunlight, relax into more stable configurations [15]. It is possible that the duration of exposure in this study is not enough to have resulted in depreciation of tensile strength. This result is also corroborated with the findings of [16] who observed an increase in tensile strength during the initial period of exposing talc/calcium carbonate filled polypropylene composites to tropical outdoor environment for six months. It has been observed that predicting a polymer's useful life is difficult because its mechanical properties can be a nonlinear function of aging time. Thus, extrapolation of short-term behaviour may not be an accurate predictor of long-term behaviour [17]. As with the dry as moulded specimens, composites from wood flour treated at 180°C presents the highest strength values.

Tensile strain decreases with wood content as a result of the embrittlement of the matrix by the fillers (Fig. 2c). A further decrement is observed with exposure. Depolymerisation, surface cracking and increase in crystallinity may be responsible for this trend [16]. However, no correlation could be made between the tensile strain and treatment temperature in relations to outdoor exposure.

Flexural properties. The flexural properties of the composites are presented in Figs 2d-f. The flexural modulus improves with wood content for the different categories of composites studied (Fig. 2d). This is observed to be a result of the reinforcing effect of the fillers, which is able to transfer stress from the stiff fillers to the matrix. On exposure to outdoor weathering, the flexural modulus decreases with exposure for all compositions. Deterioration due to outdoor exposure could be responsible for this trend. Again, the rate of decrease was higher in untreated wood composites than the heat treated ones. The possibility of better interfacial adhesion between the wood fillers and the matrix in composites made from heat treated wood flour may be responsible for this behaviour.

Fig. 2e presents the flexural strength of exposed and unexposed composites. Flexural strength increased with wood content for the different categories of composites studied. In addition, a slight increase in flexural strength is observed with outdoor exposure, indicating retention of flexural strength after weathering. The increment is higher in composites made from heat treated wood relative to the untreated wood composites. The same reasons adduced for the increase in tensile strength could also be applied in this case.

The flexural displacement of weathered and unweathered compsites is presented in Fig. 2f. It can be seen that the flexural displacement decreased with wood content. Also, flexural displacement reduced with heat treatment with composites made from untreated wood showing the highest values. It is expected that with better compatibility in heat treated wood composites, stiffening of the composites results, thereby leading to reduced flexural displacement in this category of composites. However, within the same wood content and heat treatment, the flexural displacement increased marginally with outdoor weathering. Surface crazing and cracks developed on the surface of the composites as a result of outdoor exposure could be responsible for this behaviour. Composites made from wood treated at 200°C deviated from this general trend at 37 wt% wood content.

Conclusion

All the composites studied shows a change in colour, fading from dark brown to light grey on exposure to outdoor environment as an indication of the degradation of wood components by UV radiation. Tensile modulus reduces with outdoor exposure as a result of the deteriorating effect of outdoor environment on the composite's properties by photodegradation. However, composites made from heat treated wood flour show more resistance to the elements of the outdoor environment than the untreated counterparts. Conversely, tensile strength increases marginally with outdoor exposure due to increased cross-linking as cleaved molecules, resulting from free radicals generated by the action of UV radiation from sunlight, relax into more stable configurations during the period of this investigation. Tensile strain decreases generally on exposure.

Flexural modulus deteriorated with out door exposure, with the untreated wood composites showing higher rate of deterioration. By contrast, flexural strength increases marginally for all the composites studied with the heat treated wood composites exhibiting a higher retention rate than the untreated ones. Flexural displacement is also found to be higher in samples exposed to the outdoor environment. From these findings, it can be concluded that heat treatment of wood flour enhances the properties of WTC with the ability to retain mechanical properties after exposure to harsh outdoor environment.

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