INFLUENCE OF N, N-DIMETHYLACETAMID ON THE THERMAL AND MECHANICAL PROPERTIES OF POLYMER-FILLED WOOD

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Mercerized wood species were impregnated with N, N-dimethylacetamid. The FT-IR showed enhanced absorption at 1419 cm^{-1}(-C-/CH_3), and the 1267 cm^{-1} (-N-/ CH_3) stretching band confirmed the polymerization reaction. Differential scanning calorimetric analysis indicated that the decomposition temperature of polymer-filled wood gives a higher thermal stability compared to the raw material. Polymer-filled wood yielded higher MOE and MOR compared to the untreated wood. The Young's modulus of *Xylopia Spp Artocarpus Rigidus* and *Eugenia Spp* were significantly different between raw wood and WPC. The increase in the stiffness and the thermal stability of the composites increased due to the crystallinity of polymer-filled wood as indicated by XRD analysis.

Keywords: Tropical wood; DSC; Mechanical properties; Polymer-filled wood

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INTRODUCTION

Wood has been used for many applications because of its excellent characteristics. However, wood also suffers from a number of disadvantages because of its hygroscopic nature. Many studies have been done in order to ameliorate the disadvantageous properties of wood (Bekhta et al. 2003; Boonstra et al. 1998; Gunduz et al. 2008; Korkut et al. 2008; Hamdan et al. 2010; Rahman et al. 2010). Wood polymer composites (WPC) occupy a small but rapidly growing niche in several industries (Simonsen 1996). They are used as replacements for lumber as laminated veneer lumber or medium density fibreboard, millwork, decking, a variety of products in building, in automotives and even in aeroplanes. The market for speciality additives used in natural and wood fibre polymer composites was valued in 2001 at $57 million (Principia Consulting 2002).

Polymers used to produce such composites include phenolic resins, urea-formaldehyde resins, polyurethanes, polyisocynates, acrylates, and methacrylates, both as monomers to impregnate wood or to be used as a binder (Hae 1975; Dotzauer et al. 1991; Michanickl and Boehme 1995; Iwata et al. 2000; Ambrose et al. 1984). The rate of monomer impregnation depends on the density of wood. The density of the wood is increased by the use of monomers to penetrate the cells of wood and fill the voids. The thermal and mechanical strength of wood is similarly increased, but more by chemical bonding of the basic macromolecules of wood. The chemical bonding can be generally achieved by any reactive group for the hydroxyl groups of the wood. Furthermore, combinations of two or more of such monomers may be used (Ellis et al. 1997). Thus, the chemical combination of diacrylates, hydroxyethyl methacrylate, and hexamethylene diisocyanate greatly decreased wetting and penetration of water into the wood (Ellis et al.1997).

In this paper we report on another type of monomer to be used in the preparation of polymer-filled wood, leading to another processing technology. A primary advantage of this monomer is its low cost. On the other hand, the manufactured the polymer-filled wood had high quality compared with our previous work (Rahman et al. 2010). The aim of this work was to obtain a new type of wood polymer composite material with high thermal and mechanical properties.

EXPERIMENTAL

Materials

Five wood species were collected for this study. Among them were the softwoods *Eugenia Spp*, *Artocarpus Rigidus*, *Artocarpus Elasticus*, and *Xylopia Spp*, and the hardwood *Koompassia Malaccensis*. Chemicals used to treat these wood species were 5% NaOH and N,N-Dimethylacetamid (Merck, Germany). The purity grades of these chemicals were 99%.

Specimen Preparation

Five wood species were felled, and each tree was cut into three bolts of 1.2 m length. Each bolt was quarter sawn to produce planks of 4 cm thickness, which were subsequently conditioned to air-dry in a room with relative humidity of 60% and ambient temperature of around 25^{o}C for one month prior to testing. The planks were ripped and machined to 300mm (L) x 20mm (T) x 20mm (R) and 100mm (L) x 25mm (T) x 25mm (R) specimens for the three point bending test, and the compression parallel to grain test. Ten samples were tested for each experiment, with the average value used for the calculations and analysis.

Manufacturing of Treated Wood Composites

Raw wood specimens were soaked in 5% sodium hydroxide solution using an autoclave. The temperature and pressure used were 120°C and 85 kPa, respectively, for 2 hours. Sodium hydroxide soak specimens were then impregnated by 1000 mL N,N-dimethylacetamid using a vacuum chamber at 25^{o}C and 60 cm Hg to convert the mixture into a wood-polymer composite.

FT-IR Spectroscopy Analysis

The infrared spectra of the raw woods and polymer-filled woods were recorded on a Shimadzu Fourier Transform Infrared Spectroscopy (FTIR) 81001 Spectrophotometer. The transmittance range of the scan was 370 to 4000 cm^{-1}.

DSC analysis

All raw wood and polymer-filled wood samples were analyzed using a Perkin Elmer thermal analyzer. Dynamic scans were made from 0°C to 300°C . All measurements were made under a nitrogen flow (30 mL per min), keeping a constant heating rate of 10 °C per min and using an alumina crucible with a pinhole

Determination of Static Young's Modulus (E_s), Modulus of Elasticity (*MOE*) and Modulus of Rupture (*MOR*)

Determination of E_s, *MOE*, and *MOR* was carried out according to ASTM D-143 (1996). A Shimadzu Universal Testing Machine having a loading capacity of 300kN was used for the test with the cross head speed of 2mm/min. E_s was measured using the uniaxial compression test. The *MOE* and *MOR* were measured using the three point bending method and were calculated using the following equations, respectively,

$$\mathrm{MOE} = \frac{L^3 m}{4bd^3} \tag{1}$$

$$\mathrm{MOR} = \frac{1.5PL}{bh^2} \tag{2}$$

where L = span length of sample, 180 mm
b = width of sample, 20 mm
d = thickness of sample, 20 mm
m = slope of the tangent to the initial line of the force displacement curve
P = the maximum breaking load
h = depth of the beam

XRD Analysis

The X-ray diffraction (XRD) analyses for raw wood and polymer-filled wood were performed with a Rigaku diffractometer (CuK α radiation, λ=0.1546 nm) running at 40 kV and 30 mA.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy Analysis

The IR spectra of raw wood and polymer-filled wood are shown in Fig. 2. The spectrum of the raw wood shows the basic structure that is characteristic of all wood samples, i.e. a strong broad OH stretching (3300-4000 cm^{-1}), C-H stretching in methyl and methylene groups (2800-3000 cm^{-1}), and a strong broad superposition with sharp and discrete absorptions in the region from 1000 to 1750 cm^{-1} (Owen and Thomas.1989). Comparing the spectra of holocellulose and lignin reveals that the absorptions situated at 1508 and1600 cm^{-1} were caused by lignin, and the absorption located at 1734 cm^{-1} was caused by holocellulose; this indicates the C=O stretch in non-conjugated ketones, carbonyls, and ester groups (Owen and Thomas 1989).

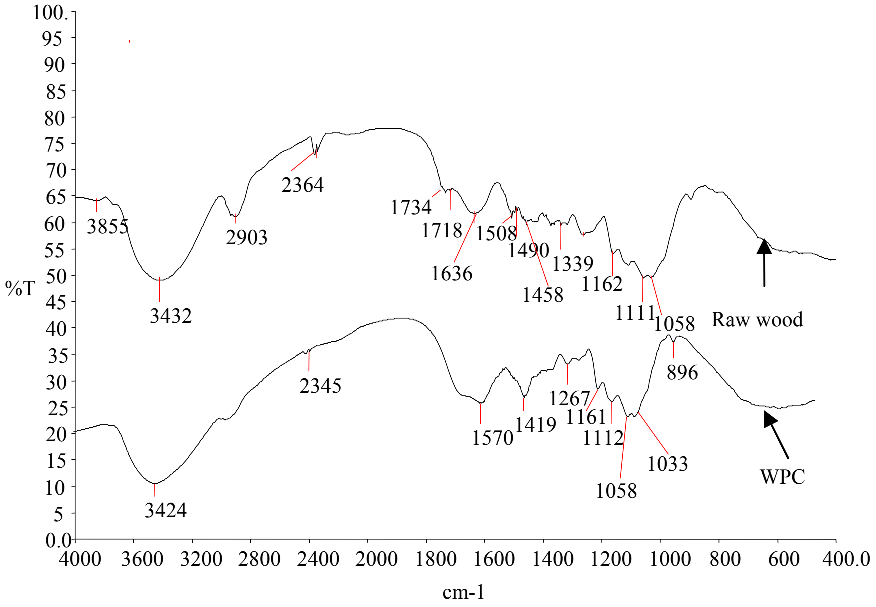

Figure 1. IR spectrum of raw wood and polymer-filled wood

The region between 1800 and 1100 cm^{-1} compares bands assigned to the main components from wood such as cellulose, hemicelluloses, and lignin. Clear differences can be detected in the infrared spectra for raw wood and polymer-filled wood bands and their location.

A decrease in the intensity of the O-H absorption band at 3424 cm^{-1} indicates that the hydroxyl group contents in polymer-filled wood were reduced after mercerization with monomer impregnation. The higher xylan content in raw wood is evidenced by a stronger carbonyl bands at 1734 cm^{-1}, for polymerized wood, this being shifted to a lower wave number value at 1570 cm^{-1}. The absorption at 1419 cm^{-1} (-C-/CH_3) and 1267 cm^{-1} (-N-/ CH_3) stretching band confirmed the polymerization inside the wood cell wall.

Though the present results do not rule out the development of covalent bonds between the N,N-dimethylacetamid and the wood material, it was beyond the scope of the present analysis to determine whether such a reaction occurred. Also, it is not certain whether the reaction conditions were suitable for such a reaction to occur efficiently. However, NaOH reacts with cellulose and reduces the OH groups in the wood component. On the other hand, the monomer N,N-dimethyacetamide plasticized the mercerize wood cell wall (Rahman et al. 2010) and converted it to a more crystalline form, which is reflected in the X-ray analysis.

DSC Analysis

Thermal analysis can be used to determine the moisture content and volatile components present in composites. Since moisture content and volatile components have a deteriorating effect on composites, these studies are of great importance (Herrera-France and Aguilar-Vega 1997). DSC analysis was performed on the raw wood fibres and polymer-filled wood. This was carried out to determine the thermal behaviour of the raw wood and manufactured composites. DSC analysis also enables the identification to be made of chemical activity occurring in the wood fibres as the temperature is increased.

Differential thermal analysis curves of raw wood and polymer-filled wood are shown in Figs. 2(a) to 2(e). The enthalpy and exotherm peaks are shown in Table 1. A broad endotherm observed in the temperature range approximately 50-161°C in both raw wood and polymer-filled wood for all species indicates the presence of water molecules in the fibres. Akita and Kase reported that in cellulose fibres, lignin degrades at a temperature of around 200°C, while the other polysaccharides such as cellulose degrade at higher temperatures. Therefore the second endothermic peaks, which were higher than 200°C, indicate the decomposition temperatures of the cellulose in the fibres. According to the first decomposition temperature, the polymer-filled wood gave a higher value than the raw wood fibre, indicating that it was more thermally stable compared to the raw sample. Sreekala and co-workers (Sreekala et al. 1997) reported that alkali and silane treatment increased the thermal stability of fibres. From Table 1 the crystallization enthalpy (ΔH_c) of all polymer-filled wood samples was higher than raw wood, indicating that polymer-filled wood samples were more crystalline compared with raw samples. This is also reflected in the XRD results.

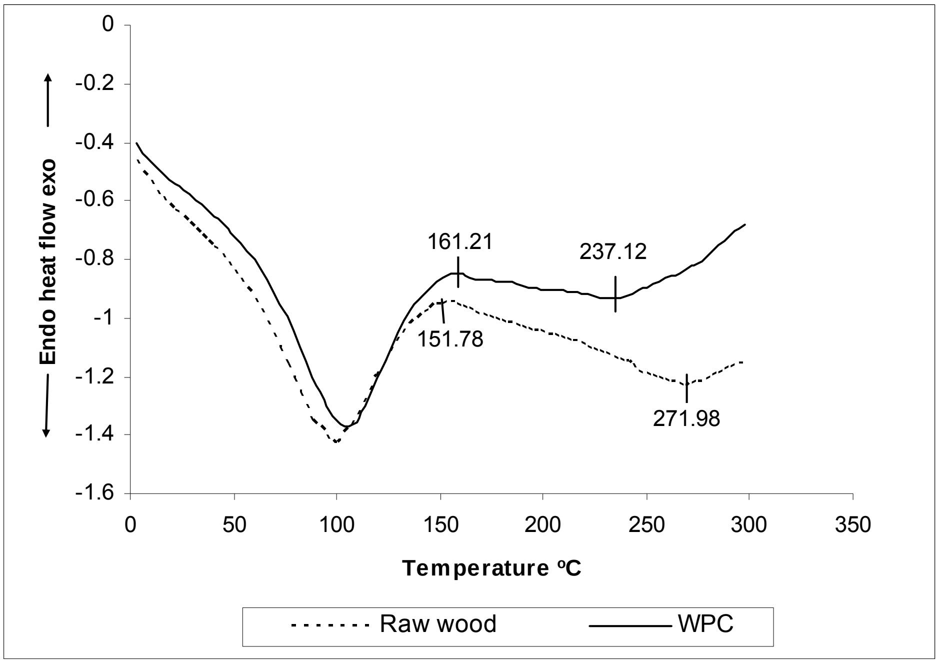

Figure 2(a). DSC thermographs of the *Artocarpus elesticus* raw wood and polymer-filled wood

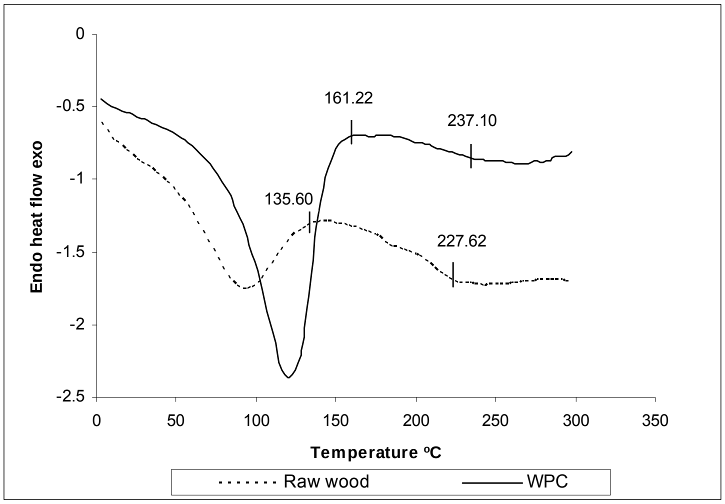

Figure 2(b). DSC thermographs of the *Artocarpus rigidus* raw wood and polymer-filled wood

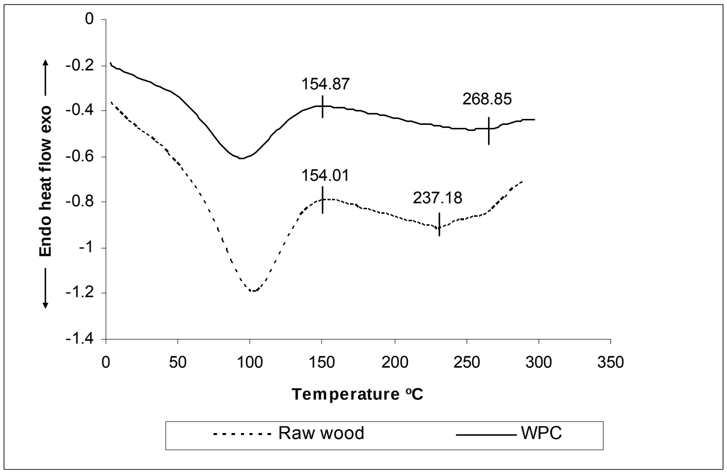

Figure 2(c). DSC thermographs of the *Koompasia malacennis* raw wood and polymer-filled wood

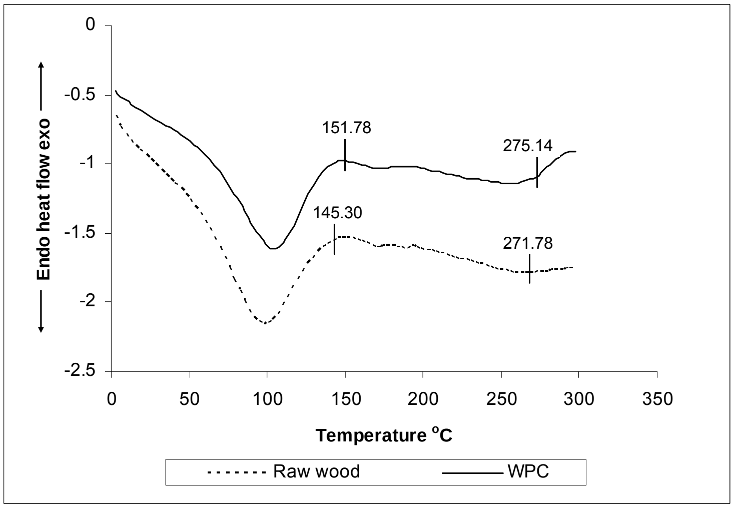

Figure 2(d). DSC thermographs of the *Xylopia spp*. raw wood and polymer-filled wood

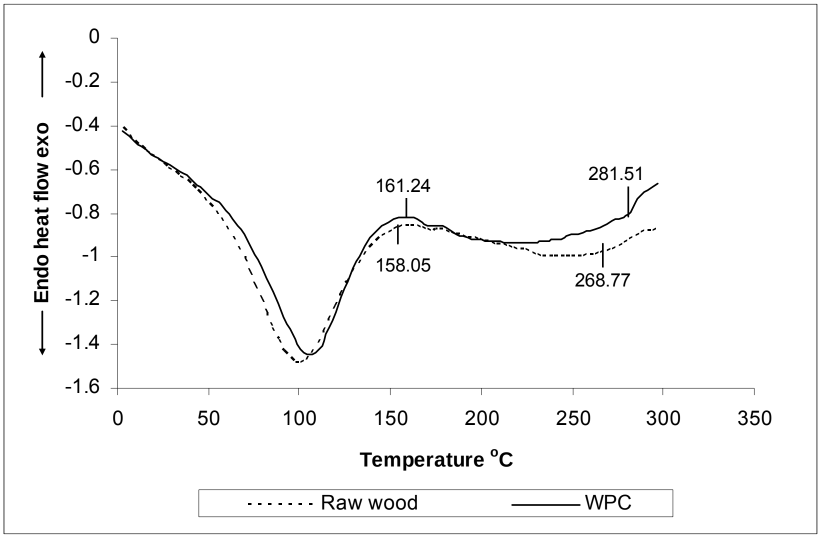

Figure 2(e). DSC thermographs of the *Eugennia spp*. raw wood and polymer-filled wood

Table 1. Crystallization Enthalpy and Exotherm Peaks of Raw Wood and Polymer-Filled Wood

Species	Crystallization Enthalpy ΔH_c (J/gm)		1st Exotherm peaks (°C)	
	Raw wood	WPC	Raw wood	WPC
Artocarpus elesticus	232.10	238.64	151.78	161.21
Artocarpus rigidus	248.64	474.16	135.60	161.22
Koompasia Malacennis	192.86	194.20	154.01	154.87
Xylopia spp.	252.31	323.00	145.30	151.78
Eugennia spp.	248.20	288.78	158.05	161.24

MOE and MOR Measurement

The variation of the MOE and MOR of *Artocarpus elasticus*, *Artocarpus rigidus*, *Xylopia* spp., *Koompassia malaccensis*, and *Eugenia* spp. raw wood and polymer-filled wood are shown in Tables 2 and 3 and Figs. 3 and 4, respectively.

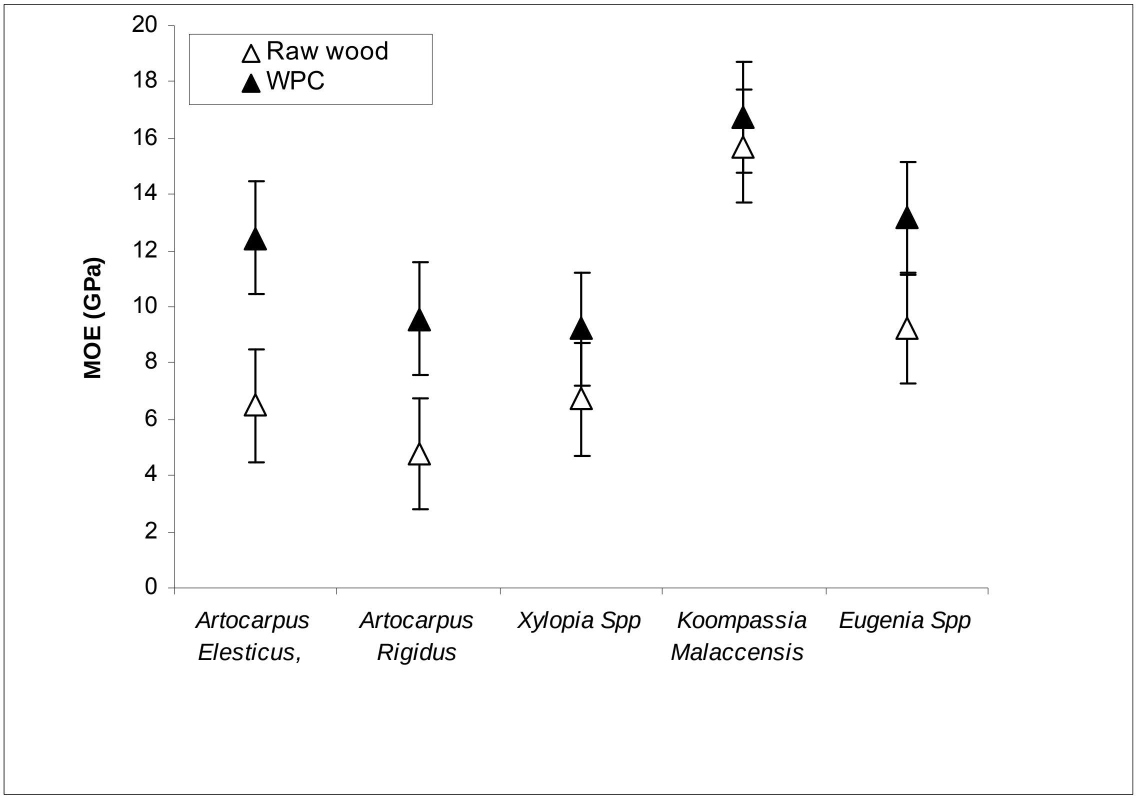

Figure 3. MOE of raw wood and polymer-filled wood

Table 2. *t*-Test Analysis of Raw Wood and Wood Polymer Composites[1]

Treatment	Modulus of elasticity	*t*-test grouping[2]
Raw wood (*Artocarpus Elesticus*)	6.48±0.52	A
PFW[3] (*Artocarpus Elesticus*)	12.44±0.99	B
Raw wood (*Artocarpus Rigidus*)	5.13±0.38	C
PFW (*Artocarpus Rigidus*)	9.56±1.97	D
Raw wood (*Xylopia Spp*)	6.71±0.34	E
PFW (*Xylopia Spp*)	9.23± 1.81	E
Raw wood (*Koompassia Malaccensis*)	15.68± 1.11	F
PFW (*Koompassia Malaccensis*)	16.75± 0.96	F
Raw wood (*Eugenia Spp*)	9.25± 0.37	G
PFW (*Eugenia Spp*)	13.16± 0.41	H

[1] Each value is the average of 10 specimens.

[2] The same letters are not significantly different at α = 5%

[3] Polymer-filled wood (PFW)

Effects of mercerization with N,N-dimethylacetamid impregnation on the MOE and MOR of the raw wood and polymer-filled wood were investigated. The increment MOE of the *Artocarpus elesticus* and *Artocarpus rigidus* were highest, followed by *Eugenia* spp., *Xylopia* spp., *and Koompassia malaccensis*, respectively. Polymer-filled wood yielded higher MOE compared to raw wood because of the chemical impregnation, which is in accordance with other research (Yildiz et al. 2005; Adams et al. 1970).

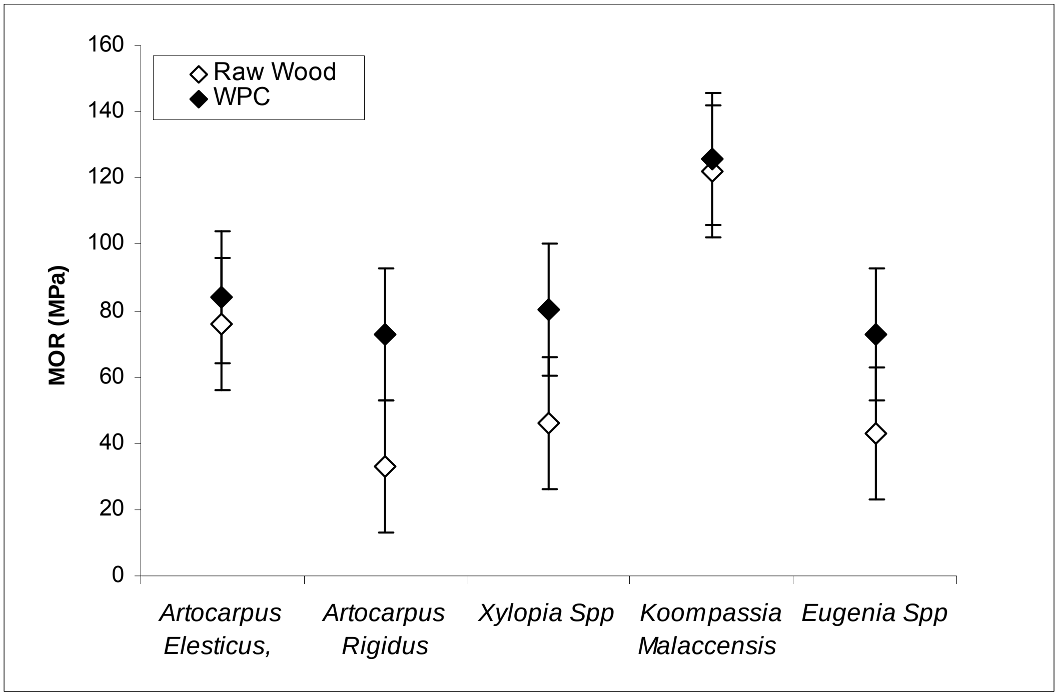

Figure 4. MOR of raw wood and polymer-filled wood

Table 3. *t*-Test Analysis of Untreated Wood and Wood Polymer Composites[1]

Treatment	Modulus of rupture	*t*-test grouping[2]
Raw wood (*Artocarpus elesticus*)	76.17± 3.01	A
PFW[3] (*Artocarpus elesticus*)	83.92± 4.20	A
Raw wood (*Artocarpus rigidus*)	33.02± 3.63	B
WPC (*Artocarpus rigidus*)	73.05± 9.26	C
Raw wood (*Xylopia* spp.)	45.91± 1.36	D
WPC (*Xylopia* spp.)	80.35± 9.01	E
Raw wood (*Koompassia malaccensis*)	22.20± 15.49	F
WPC (*Koompassia malaccensis*)	125.98± 6.77	F
Raw wood (*Eugenia spp.*)	46.10± 3.62	G
WPC (*Eugenia* spp.)	72.8± 4.60	H

[1] Each value is the average of 10 specimens.

[2] The same letters are not significantly different at α =5%

[3] Polymer-filled wood (PFW)

From Table 1, the MOE values of the treated *Artocarpus elasticus, Artocarpus rigidus*, and *Eugenia spp.* were significantly higher than in the case of raw samples. However in *Koompassia malaccensis*, (hardwood) and *Xylopia* spp. there was no significant effect of monomer impregnation because of their hardness.

In the wood specimens, sodium hydroxide reacted with the cellulose in wood cells, which reduces the water molecules from the wood specimens. During the N,N-dimethylacetamid impregnation with mercerized specimens, wood cell walls couple with monomer and fill the void space in the wood specimens and increase it stiffness.

The MOR also increased after monomer impregnation, in agreement with previous research (Adams et al. 1970). Table 3 indicates that the increment MOR were significantly different for *Artocarpus rigidus, Xylopia* spp., and *Eugenia* spp. raw wood and polymer-filled wood. The increment of MOR for *Artocarpus rigidus* was highest, followed by *Xylopia* spp., *Eugenia* spp., *Artocarpus elesticus*, *and Koompassia malaccensis*, respectively. The value for *Koompassia malaccensis* (hardwood) of raw wood and polymer-filled wood were almost similar, which indicates that monomer impregnation is not effective on hardwood. It is confirmed by our previous work (Rahman et al. 2010).

Static Young's Modulus (E) Measurement

The static Young's modulus was determined from 10 repetitions, as summarized in Fig. 5. The highest increment of E value was observed in *Xylopia* spp., followed by *Artocarpus rigidus, Eugenia* spp., *Artocarpus elesticus*, and *Koompassia malaccensis*, respectively.

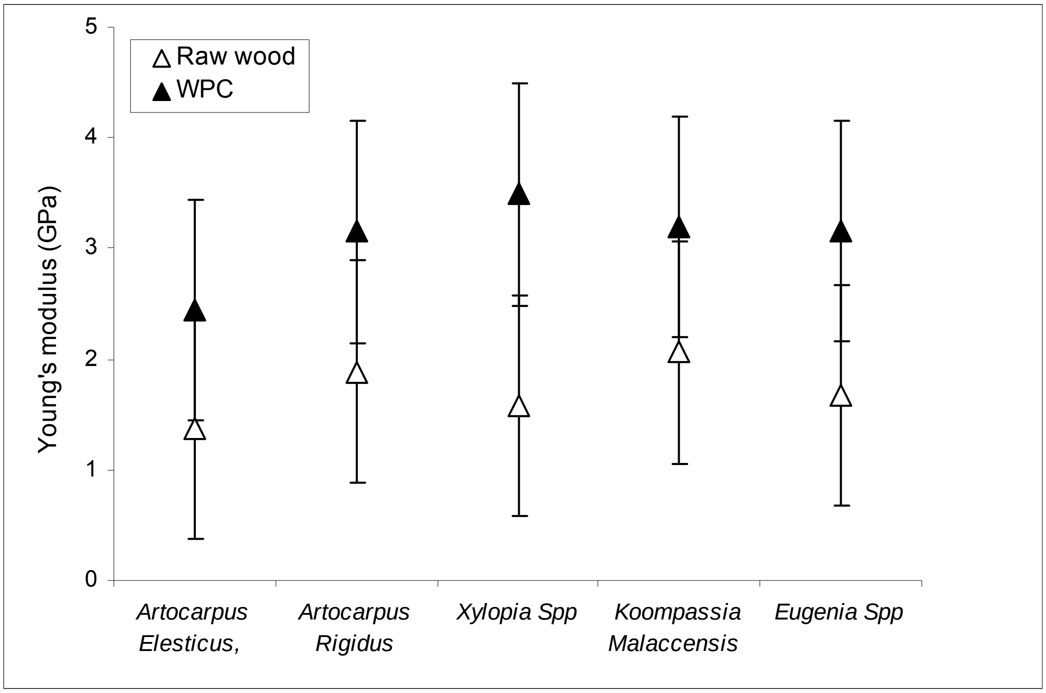

Figure 5. Static Young's modulus raw wood and polymer-filled wood

From Table 4, the increment of Young's modulus for *Xylopia* spp., *Artocarpus rigidus*, and *Eugenia* spp. was significantly different between raw wood and polymer-filled wood. The increment of *E* in polymer-filled wood compared to raw wood was also reported by different researchers (Autio et al. 1970; Hamdan et al. 2010). The monomer impregnation of raw wood plasticization on the cell walls which thickens them, thus greatly increasing their lateral stability.

Table 4. *t*-Test Analysis of Untreated Wood and Polymer-Filled Wood[1]

Treatment	Static Young's modulus	*t*-test grouping[2]
Raw wood (*Artocarpus elesticus*)	1.36± 0.23	A
PFW (*Artocarpus elesticus*)	2.43± 0.51	A
Raw wood (*Artocarpus rigidus*)	1.88± 0.58	C
PFW (*Artocarpus rigidus*)	3.14± 1.11	D
Raw wood (*Xylopia* spp.)	1.57± 0.39	E
PFW (*Xylopia* spp.)	3.48± 0.37	F
Raw wood (*Koompassia malaccensis*)	2.05± 0.18	E
PFW (*Koompassia malaccensis*)	3.19± 0.31	E
Raw wood (*Eugenia* spp.)	1.67± 0.60	G
PFW (*Eugenia* spp.)	3.16± 0.75	H

[1] Each value is the average of 10 specimens.
[2] The same letters are not significantly different at α =5%
[3] Polymer-filled wood (PFW)

XRD Analysis

The X-ray diffraction patterns of raw wood fibre and polymer-filled wood are given in Fig. 6. As seen in Fig. 6, the patterns of raw wood fibre exhibited only one well defined 2θ peak at 22.62°, which is due to cellulose (Yi et al. 2009). By contrast, the polymer-filled wood exhibited four broad 2θ peaks at 26.45°, 49.21°, 51.17°, and 72.64°, which are due to increasing polymerization.

The effect of chemical modification of lignocellulosic materials on their crystallinity also has been investigated (Yi et al. 2009). The reagent first reacts with the chain ends on the surface of crystallites, as it cannot diffuse into the crystalline region, resulting in the opening of some of the hydrogen-bonded cellulose chains. It was clear from the study that the mercerization with monomer impregnation increased the crystallinity of polymer-filled wood, which is due to an increased removal of the fiber's amorphous constituents.

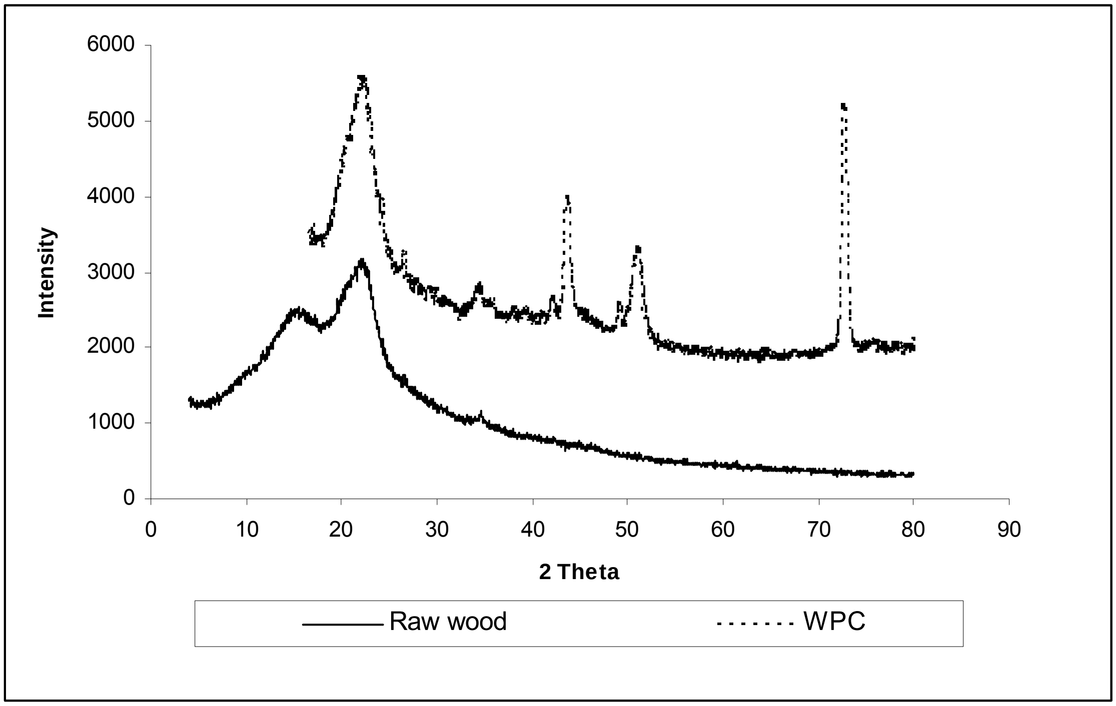

Figure 6. X-ray diffraction of raw wood and polymer-filled wood

CONCLUSIONS

According to the experimental results, FT-IR spectra indicate the occurrence of chemical impregnation of wood by the monomer N,N-dimethylacetamid. The enhanced absorption at the 1419 cm^{-1}(-C-/CH$_3$) and 1267 cm^{-1} (-N-/ CH$_3$) stretching bands confirmed the polymerization reaction. The wood polymer composites were thermally more stable at certain temperature ranges during this study. The MOE and MOR of polymer-filled wood were significantly increased for *Artocarpus elasticus, Artocarpus rigidus*, and *Eugenia* spp., respectively. The Young's modulus of *Xylopia* spp., *Artocarpus rigidus*, and *Eugenia* spp. were significantly different between raw wood and polymer-filled wood. The X-ray diffraction patterns indicate polymer-filled wood samples were more crystalline compared with raw wood.

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