Mechanical and Thermal Characterization of Urea-Formaldehyde Impregnated Wood Polymer Nanocomposites (WPNCs)

M.R. Rahman

Abstract In this study, urea-formaldehyde resin wood polymer nanocomposites (WPNCs) were investigated. All the WPNCs undergo characterizations. The FT-IR spectra confirmed the impregnation of organic urea-formaldehyde into the raw wood. Besides, WPNCs were generally more thermally stable over temperature compared to the raw wood due to the introduction of urea-formaldehyde into the raw wood. From mechanical testing, WPNCs showed higher MOE and MOR for *Eugenia* spp. and *Xylopia* spp., respectively. Besides, WPNCs on *Eugenia* spp. showed higher Young's modulus compared to raw wood and other WPNCs. From the X-ray diffraction patterns, the crystallinity of WPNCs increased with the introduction of urea-formaldehyde resin into raw wood. The SEM micrograph of WPNCs clearly proved that the void space was fully filled with urea-formaldehyde resins and most of the waxy substance was removed. Therefore, urea-formaldehyde-impregnated WPNCs showed significantly effective on *Eugenia* spp., continued by *Xylopia* spp. and *Artocarpus elasticus* wood species.

Keywords Differential scanning calorimetry · Thermal stability · Impregnation · Wood polymer nanocomposites (WPNCs)

1 Introduction

With the advantage of the fibrous nature of wood, wood has been one of the most appropriate and versatile raw materials for various applications. However, the application of wood can be widely applied with some modifications. Polymeric material is one of the materials especially those obtained from renewable resources, namely natural fibers. This material has gained much attention and attraction from

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both researchers and industrialists during the last few years due to environment concerns. Chemical compositions of the wood are highly affected by the properties of the wood fibers. However, all these chemical compositions of the fibers depend on different factors. Few factors, namely geographic location, climate, plant part, and soil conditions are significantly affected by the chemical compositions of wood. In addition, the carbohydrate portion of fiber consists of cellulose and hemicelluloses, and lignocellulosic fibers. From this wood fiber, the percentage of cellulose is the highest which makes them the most abundant natural polymer. Cellulose is usually responsible for the strength of natural fibers. This was due to the specific properties such as high degree of polymerization and linear orientation. Since the past decade, various industries such as the automotive, construction, and packaging industries have shown their great interest in the development of new biocomposites materials.

Borneo Island is one of the regions that is full of natural rainforest. However, this precious wealth of nature is not being exploited for better end products. From the various types of natural wood species, *Eugenia* spp., *Artocarpus rigidus*, *Artocarpus elasticus* and *Xylopia* spp., and the *Koompassia malaccensis* are selected as they have high potential to be used as a reinforcing material in WPNCs.

Therefore, this study was carried out to fabricate WPNCs through the impregnation of urea-formaldehyde resin into five selective wood species as mentioned above. All the WPNCs undergo various characterizations. The expected outcome of this study was the enhanced absorption peak at 1648 cm^{-1} (O=N–), C–H absorption at 1319 cm^{-1} and –C–O– stretching band at 1262 cm^{-1} through FT-IR confirmed the impregnation. Besides, the investigation on TGA and DSC was expected to show that WPNCs had better thermal stability compare to raw wood. Dynamic Young's modulus was expected to prove that WPNCs had higher MOE and MOR value as well as the static Young's modulus. XRD analysis was expected to show higher crystallinity of WPNCs. Moreover, expected outcome from SEM analysis was to show the porous cells of raw wood filled by the urea-formaldehyde as reflected in thermal and mechanical properties.

2 Materials and Methods

2.1 Materials

There were five wood species were collected for this study which was classified as softwood and hardwood. The wood species were used in this study, namely *Eugenia spp., Artocarpus rigidus, Artocarpus elasticus, Xylopia spp*., and *Koompassia malaccensis* respectively. For impregnation, chemicals, namely sodium hydroxide and urea-formaldehyde (Marck, Germany), were used as received. The purity grade of the chemicals was 99%.

2.2 Manufacturing of Wood Polymer Nanocomposites

All the wood samples were oven dried for 24 h and continuously soaked in sodium hydroxide solution for 5 h. The soaking temperature used was 100 °C. Oven-dried wood samples were impregnated with urea-formaldehyde resin to form WPNCs by undergoing a vacuum chamber at 25 °C and 60 cm Hg.

2.3 Microstructural Characterizations

The fabricated WPNCs were characterization using the Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD), Thermogravimetric Analysis (TGA), differential scanning calorimetric testing (DSC), Scanning Electron Microscopy analysis (SEM), free-free flexural vibration testing, three-point bending test, and compression parallel to grain testing.

3 Result and Discussion

3.1 FT-IR

Fourier Transform Infrared Spectroscopy (FT-IR) spectra of raw wood and WPNCs were shown in Fig. 1. The basic structure for most of the wood samples was OH stretching at 4000–3300 cm^{-1} and C–H stretching in methyl and methylene groups at 3000–2800 cm^{-1}. Besides, Owen and Thomas (1989) showed that strong broad superposition with sharp and discrete absorptions could be observed in the region from 1750 to 1000 cm^{-1}. The absorption band at 1508 cm^{-1} was detected due to the degradation of lignin while the absorption located at 1734 cm^{-1} was caused by hemicelluloses. C=O stretch in non-conjugated ketones, carbonyls, and ester groups were clearly proven through Fig. 1. In addition, the region between 1800 and 1100 cm^{-1} was assigned to the main components from wood, namely cellulose, hemicelluloses, and lignin.

Both absorbance values and shapes of the bands as well as their location showed clear difference as shown in Fig. 1. The less xylan content in softwood was evidenced by a carbonyl band at 1734 cm^{-1} especially for chemically modified wood. The peak at 1734 cm^{-1} was clearly this being shifted to a lower wave number value at 1648 cm^{-1}. Through the enhanced absorption peak at 1648 cm^{-1} that was representing O=N– groups, C–H absorption at 1319 cm^{-1} and –C–O– stretching band at 1262 cm^{-1}, this confirmed the impregnation of urea-formaldehyde into raw wood to improve the properties of WPNCs.

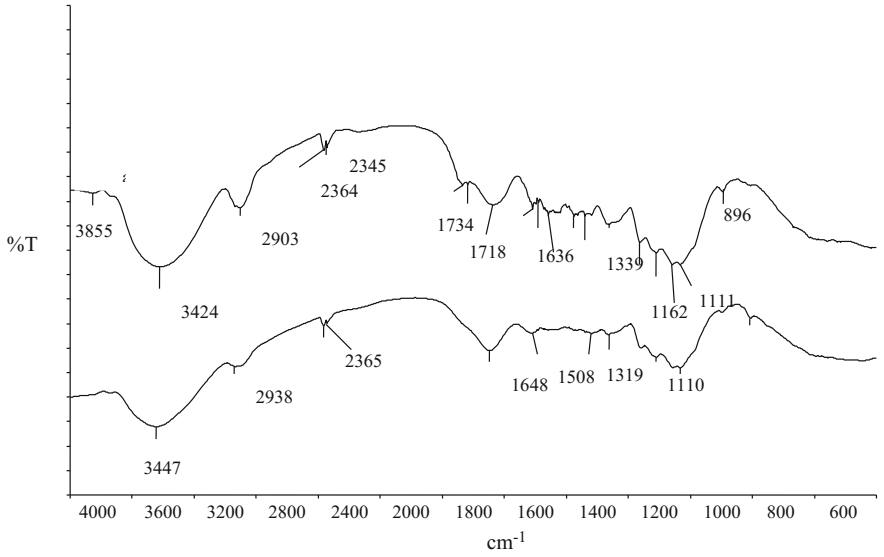

Fig. 1 IR spectrum of **a** raw wood and **b** WPNCs

3.2 TGA

Through Thermogravimetric Analysis (TGA), one of the common behaviors that the raw wood sample undergo was dehydration process, where approximately 5–8% of adsorbed water was removed. Based on the research work of Wielage et al. (1999), there was no degradation up to 160 °C. However, the thermal stability above this temperature gradually decreased as the thermal decomposition took place. The thermogravimetric curves for raw wood and WPNCs were obtained by dynamic scans and presented in Fig. 2a–e.

To ensure all the fabricated WPNCs performed well in many applications, thermal stability is a very important parameter to be investigated. There were few major chemical components, namely cellulose, hemicellulose, lignin, and extractives where all these components degraded at different temperatures. This was because different wood composition degraded at different temperatures, and thus, different degradation profiles were performed. Cellulose, as major percentage in the wood materials, was highly crystalline that created cellulose to become more thermally stable. On the other hand, the minor percentage, namely hemicelluloses and lignin were amorphous and these components started to degrade before cellulose (Autio and Miettinen 1970). This proved that hemicelluloses and lignin were the least thermally stable wood components, due to the presence of acetyl groups (Bourgois et al. 1989).

From Table 1, it is showed that WPNCs had higher decomposition temperature with lower weight loss rate compared to raw wood. In addition, WPNCs had higher activation energy compared to raw wood. It could be summarized that WPNCs were more thermally stable than raw wood in all selective wood species.

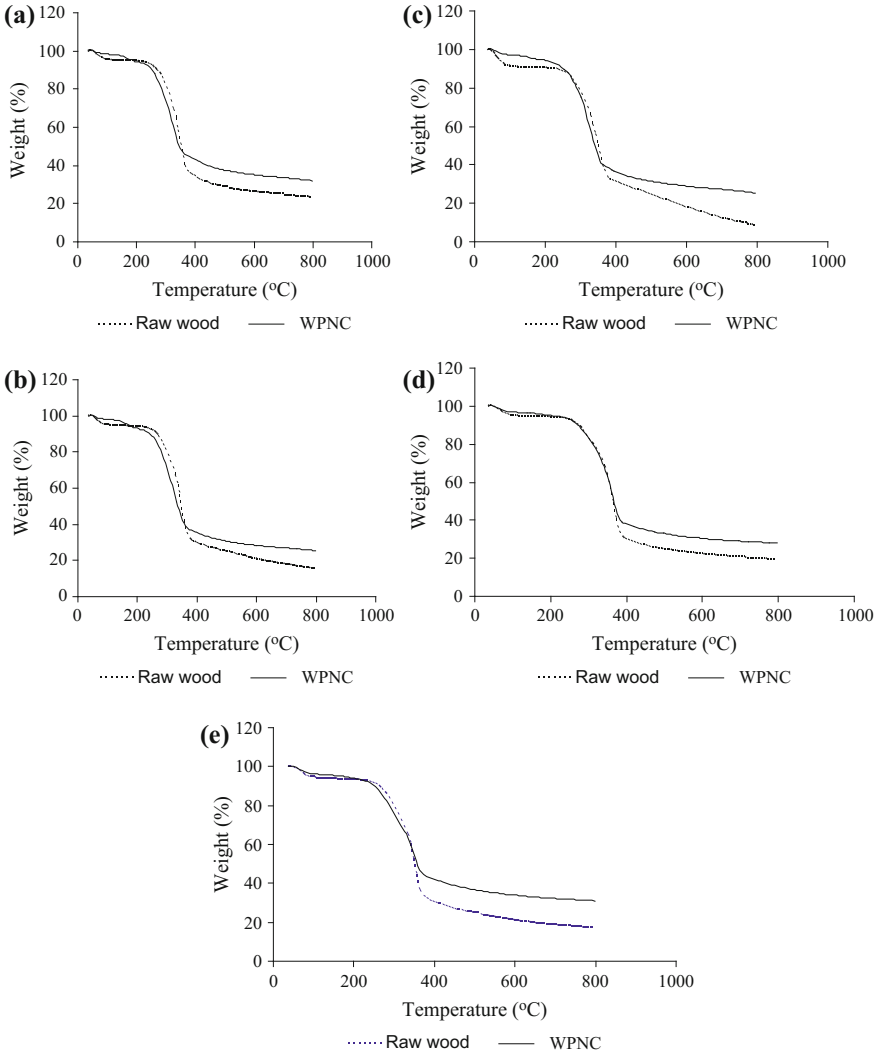

Fig. 2 **a** TGA curve of *Artocarpus elasticus* raw wood and WPNCs, **b** TGA curve of *Artocarpus rigidus* raw wood and WPNCs, **c** TGA curve of *Xylopia* spp. raw wood and WPNCs, **d** TGA curve of *Koompassia malaccensis* raw wood and WPNCs, **e** TGA curve of *Eugenia* spp. raw wood and WPNCs

3.3 DSC

Moisture content and volatile components contained within the raw wood and WPNCs were determined and investigated through differential scanning calorimetry (DSC). These two factors were important as the raw wood would deteriorate and

Table 1 Thermal characteristics of raw wood and WPNCs

Sample		T_i (°C)	T_m (°C)	T_f (°C)	W_{Ti} (%)	W_{Tm} (%)	W_{Tf} (%)	Activation Energy, E_a (J/K)
Artocarpus elasticus	Raw	201	300	419	98.96	64.73	32.67	33.11
	WPNCs	214	356	616	93.89	47.16	34.81	36.08
Artocarpus rigidus	Raw	211	310	388	99.67	56.45	30.63	25.79
	WPNCs	237	332	553	90.61	52.46	31.18	32.28
Xylopia spp.	Raw	212	321	420	98.78	56.15	25.85	27.04
	WPNCs	245	332	632	90.87	55.56	28.16	31.98
Koompassia malaccensis	Raw	212	355	403	98.99	57.91	30.00	16.12
	WPNCs	237	363	545	93.28	52.08	31.51	20.23
Eugenia spp.	Raw	214	340	443	99.77	60.32	27.51	19.17
	WPNCs	237	348	521	92.08	55.68	35.15	22.56

T_m Temperature corresponding to the maximum rate of mass loss
T_i Temperature corresponding to the beginning of the decomposition
T_f Temperature corresponding to the ending of the decomposition
W_{Ti}, $W_{Tm,}$ and W_{Tf} Mass loss at T_i, $T_{m,}$ and T_f

affect the great properties achieved (Herrera et al. 1997). DSC was carried out to determine the thermal behavior of the raw wood and fabricated WPNCs. In addition, DSC analysis also enabled the chemical impregnation to be clearly identified which could be carried out in the raw wood and WPNCs with the increment in temperature.

Figure 3a–e shows the DSC curves of raw wood and WPNCs. Besides, the enthalpy and exotherm peaks were shown in Table 2. From Fig. 3, there was a broad endotherm in the temperature range around 40–150 °C in both raw wood and WPNCs for the five selective wood species-indicated water molecules were presented within the wood fibers. Cellulose fibers especially lignin degraded rapidly at the temperature about 200 °C while the other polysaccharides especially on cellulose degraded at higher temperature (Akita and Kase 1967). Moreover, the temperature at 200 °C and above produced tar with scientific name 1, 6 anhydro-β-D-glucopyranose combined with polymeric materials (Peters and Still 1979). Therefore, the second endothermic peaks of all raw wood and WPNCs increased more than 200 °C temperature. This was due to the decomposition temperatures of the cellulose in the wood fibers. From Fig. 3, it was clearly observed that WPNCs showed a higher endothermic heat flow compared to the raw wood with exceptional on *Koompasia malacennis* and *Eugennia* spp. based on the first decomposition temperature. Sreekala et al. (1997) reported that thermal stability of WPNCs could be greatly enhanced due to the alkali and silane treatment. Table 2 showed that the crystallization enthalpy (ΔH_c) of WPNCs was two times higher compared with raw wood, which could be reflected in the XRD results. From this, it could be concluded that WPNCs were thermally more stable than raw wood on some of the selective wood species.

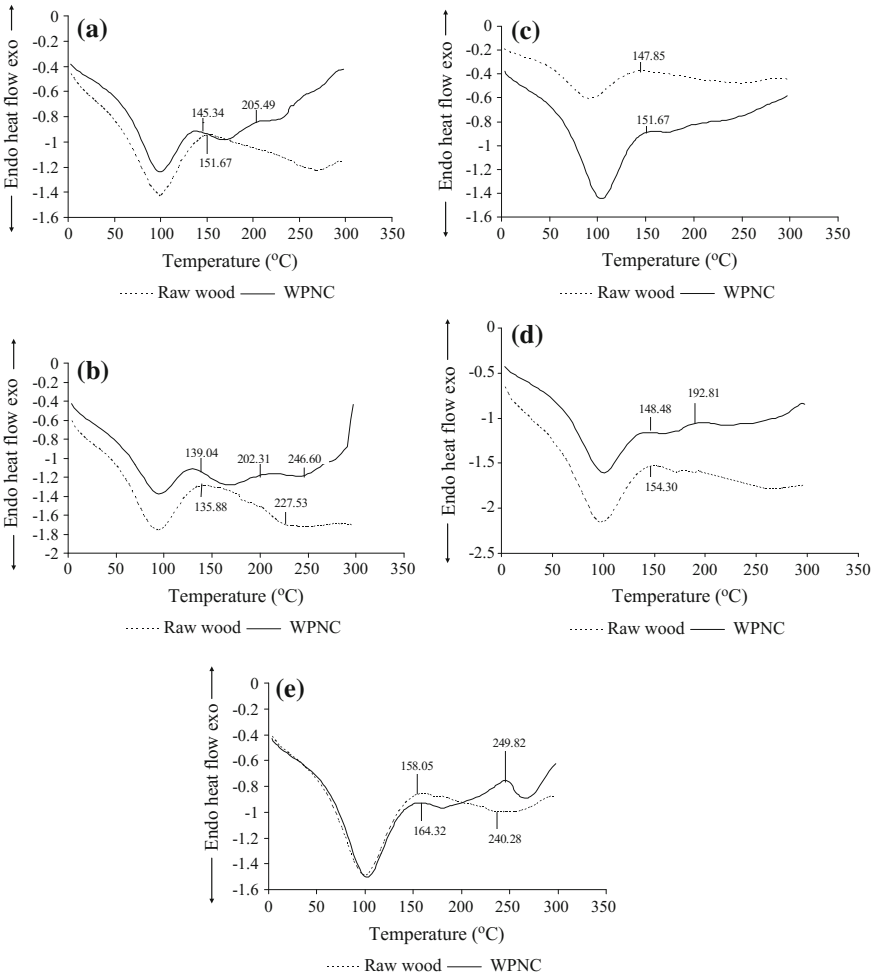

Fig. 3 **a** DSC thermographs of the *Artocarpus elasticus* raw wood and WPNCs, **b** DSC thermographs of the *Artocarpus rigidus* raw wood and WPNCs, **c** DSC thermographs of the *Koompasia malacennis* raw wood and WPNCs, **d** DSC thermographs of the *Xylopia* spp. raw wood and WPNCs, **e** DSC thermographs of the *Eugennia* spp. raw wood and WPNCs

Table 2 Crystallization enthalpy and exotherm peaks of raw wood and WPNC

Species	Crystallization enthalpy ΔH_c (J/gm)		1st Exotherm peaks (°C)	
	Raw wood	WPNC	Raw wood	WPNC
Artocarpus elasticus	126.39	233.10	151.78	145.35
Artocarpus rigidus	124.91	248.64	135.60	139.04
Koompasia malacennis	192.86	224.60	147.85	151.67
Xylopia spp.	192.29	323.00	145.30	151.78
Eugennia spp.	231.27	290.78	158.05	164.32

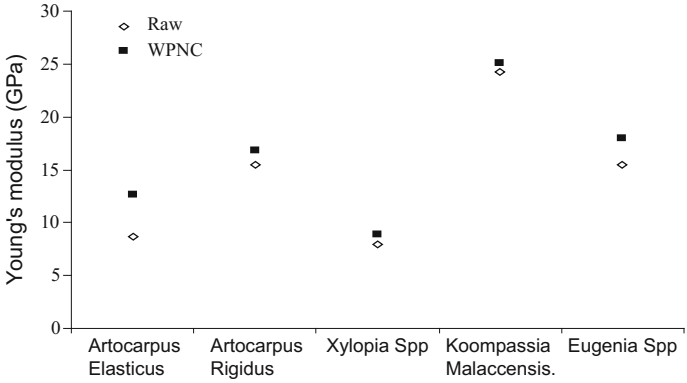

Fig. 4 E_d of raw wood, WPNCs for all species

3.4 Dynamic Young's Modulus Measurement

Figure 4 presented the dynamic Young's modulus of raw wood and WPNC through free-free flexural vibration testing system. All the results were based on ten specimens that were used for each wood species prepared. Through urea-formaldehyde impregnation, Young's modulus of WPNCs was increased which was according to the other researcher (Hamdan et al. 2010). Besides, Young's modulus of WPNCs on *Artocarpus elasticus*, *Artocarpus rigidus,* and *Eugenia* spp. was significantly higher than raw wood. On the other hand, Young's modulus of *Koompassia malaccensis* and *Xylopia* spp. was slightly higher among all the wood species due to their hardness. From Table 1, the activation energy was greatly increased due to the urea-formaldehyde impregnation. However, only WPNCs on *Artocarpus elasticus*, *Artocarpus rigidus,* and *Eugenia* spp., respectively, showed significant changes in elastic properties.

3.5 MOE and MOR Measurement

Both modulus of elasticity (MOE) and modulus of rupture (MOR) of raw wood and WPNCs were shown in Tables 3 and 4 as well as Figs. 5 and 6, respectively. MOE and MOR were investigated on the impregnation of urea-formaldehyde resin on the selective wood species. WPNCs on *Eugenia* spp. and *Artocarpus elasticus* were highest followed by, *Artocarpus rigidus, Xylopia* spp., and *Koompassia malaccensis*, respectively. WPNCs yielded higher MOE mainly due to the impregnation of resin into raw wood, which was in accordance with other researchers (Adams et al. 1970; Yildiz et al. 2005).

Table 3 summarized the MOE of raw wood and WPNCs. The result showed that WPNCs on *Artocarpus elasticus, Eugenia* spp., and *Xylopia* spp. were significantly

Table 3 *t*-test analysis of raw wood and wood polymer nanocomposites[a]

Treatment	Modulus of elasticity	*t*-test grouping[b]
Raw wood (*Artocarpus elasticus*)	6.48 ± 0.52	A
WPNCs (*Artocarpus elasticus*)	11.66 ± 0.60	B
Raw wood (*Artocarpus rigidus*)	5.13 ± 0.38	C
WPNCs (*Artocarpus rigidus*)	10.53 ± 2.60	D
Raw wood (*Xylopia* spp.)	6.71 ± 0.34	E
WPNCs (*Xylopia* spp.)	11.83 ± 0.67	E
Raw wood (*Koompassia malaccensis*)	15.68 ± 1.11	F
WPNCs (*Koompassia malaccensis*)	19.58 ± 2.58	F
Raw wood (*Eugenia* spp.)	9.25 ± 0.37	G
WPNCs (*Eugenia* spp.)	20.70 ± 0.83	H

[a]Each value is the average of 10 specimens
[b]The same letters are not significantly different at $\alpha = 5\%$

higher compared to raw wood. However, WPNCs on *Koompassia malaccensis* (hardwood) showed no significant effect due to its hardness.

Sodium hydroxide reacted with the cellulose in wood cells by reducing the water molecules from the raw wood. Wood cell walls plasticized with urea-formaldehyde resin to fill the void space in the raw wood to increase its stiffness during the impregnation process. With this, the MOE of all WPNCs was higher than raw wood as shown in Fig. 5.

Besides MOE, MOR of WPNCs especially on *Eugenia* spp. was significantly increased after the impregnation of urea-formaldehyde resin. Figure 6 shows that all the WPNCs showed higher MOR compared to raw wood which agreed with previous research (Adams et al. 1970). Table 4 indicates that the MOR of raw wood and WPNCs on *Xylopia* spp. and *Eugenia* spp. were significantly different. The

Table 4 *t*-test analysis of raw wood and wood polymer nanocomposites[a]

Treatment	Modulus of elasticity	*t*-test grouping[b]
Raw wood (*Artocarpus elasticus*)	76.17 ± 3.01	A
WPNCs (*Artocarpus elasticus*)	85.09 ± 3.44	A
Raw wood (*Artocarpus rigidus*)	33.02 ± 3.63	B
WPNCs (*Artocarpus rigidus*)	53.42 ± 11.72	B
Raw wood (*Xylopia* spp.)	45.91 ± 1.36	C
WPNCs (*Xylopia* spp.)	88.11 ± 3.78	D
Raw wood (*Koompassia malaccensis*)	122.20 ± 15.49	E
WPNCs (*Koompassia malaccensis*)	125.43 ± 24.36	E
Raw wood (*Eugenia* spp.)	46.10 ± 3.62	F
WPNCs (*Eugenia* spp.)	107.78 ± 13.44	G

[a]Each value is the average of 10 specimens
[b]The same letters are not significantly different at $\alpha = 5\%$

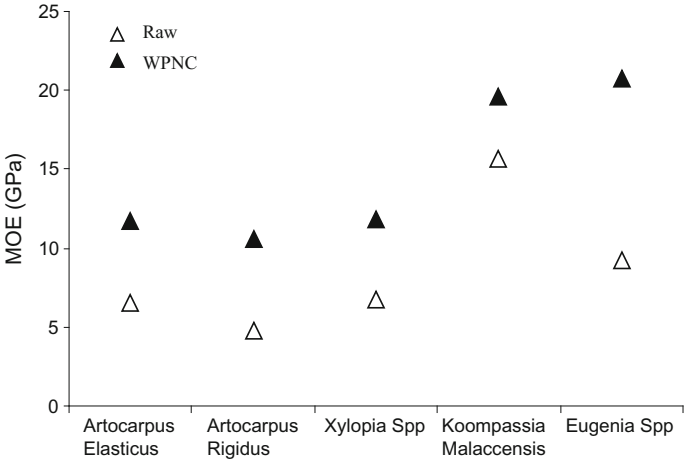

Fig. 5 MOE of raw wood and WPNCs

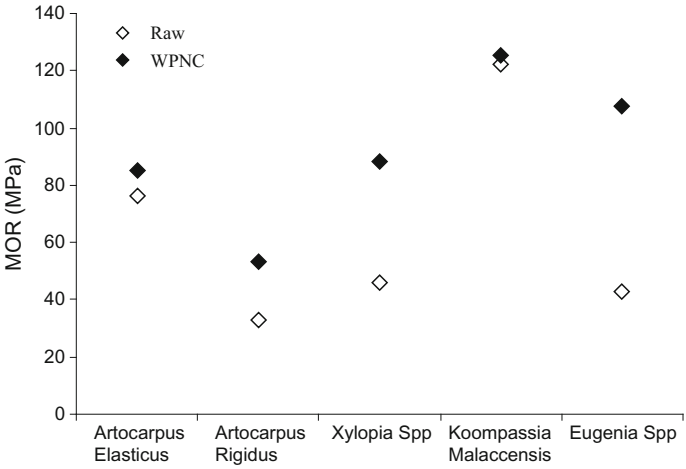

Fig. 6 MOR of raw wood and WPNCs

increment of MOR for WPNCs on *Eugenia* spp. was the highest followed by *Xylopia* spp., *Artocarpus rigidus*, *Artocarpus elasticus,* and *Koompassia malaccensis*, respectively. However, the value on raw wood and WPNCs for *Koompassia malaccensis* (hardwood) was almost similar which proved that the impregnation of urea-formaldehyde resin into hardwood was not effective as confirmed by our previous work (Rahman et al. 2010).

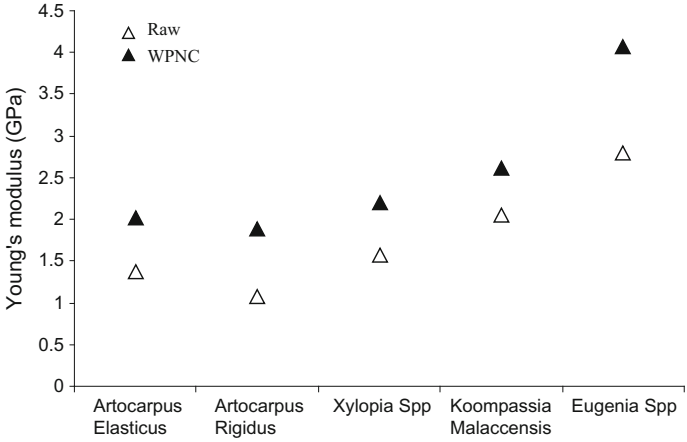

Fig. 7 Static Young's modulus of raw wood and WPNCs

3.6 *Static Young's Modulus (*E*) Measurement*

Figure 7 shows the static Young's modulus of raw wood and WPNCs which were determined from 10 repetitions. WPNCs of *Eugenia* spp. followed by *Artocarpus rigidus*, *Artocarpus elasticus*, *Xylopia* spp., *and Koompassia malaccensis*, respectively showed the highest increment of E value. Besides, Table 5 shows Young's modulus of WPNCs for *Eugenia* spp. was significantly different from raw wood. Rahman et al. (2010) proved that WPNCs showed higher increment of *E* in WPNCs compared to raw wood. This characterization confirmed that the introduction of urea-formaldehyde resin plasticized on the wood cell walls as well as greatly increased their lateral stability.

Table 5 *t*-test analysis of raw wood and wood polymer nanocomposites[a]

Treatment	Static Young's modulus	*t*-test grouping[b]
Raw wood (*Artocarpus elasticus*)	1.36 ± 0.23	A
WPNCs (*Artocarpus elasticus*)	2.01 ± 0.37	A
Raw wood (*Artocarpus rigidus*)	1.88 ± 0.58	B
WPNCs (*Artocarpus rigidus*)	1.07 ± 0.07	B
Raw wood (*Xylopia* spp.)	1.57 ± 0.39	C
WPNCs (*Xylopia* spp.)	2.19 ± 0.25	C
Raw wood (*Koompassia malaccensis*)	2.05 ± 0.18	D
WPNCs (*Koompassia malaccensis*)	2.60 ± 0.49	D
Raw wood (*Eugenia* spp.)	1.67 ± 0.60	E
WPNCs (*Eugenia* spp.)	4.06 ± 0.79	E

[a]Each value is the average of 10 specimens
[b]The same letters are not significantly different at $\alpha = 5\%$

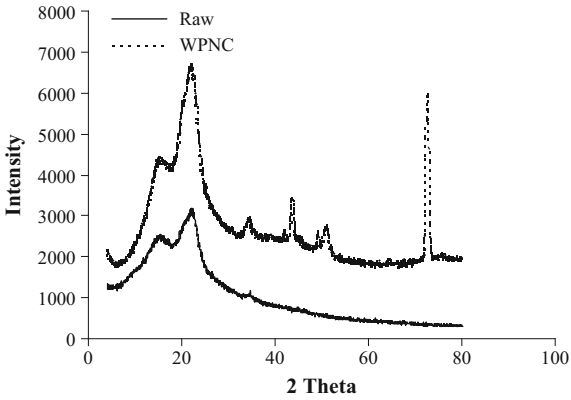

Fig. 8 X-ray diffraction of raw wood and WPNCs

3.7 XRD Analysis

Figure 8 shows the X-ray diffraction patterns of raw wood and WPNCs. From Fig. 8, raw wood only showed one well-defined 2θ peak at 22.0° which was corresponded to cellulose (Stamm 1964). On the other hand, WPNCs exhibited five broad 2θ peaks at 43.67°, 49.14°, 50.97°, 72.59°, and 75.73°. All these peaks were due to the incorporation of urea-formaldehyde resin into raw wood through impregnation. According to Stamm (1964), the crystallinity of WPNCs was greatly affected by the chemical modification of lignocellulosic materials. The urea-formaldehyde resin firstly reacted with the chain ended on the surface of crystallites. This occurred because the resins could not diffuse into the crystalline region which resulted in the opening of some of the hydrogen-bonded cellulose chains. From this, it showed that the mercerization removed the raw wood fiber's amorphous constituents upon impregnation of resin which increased the crystallinity of WPNCs.

3.8 SEM

SEM micrographs of raw wood and WPNCs were analyzed as shown in Fig. 9. Figure 9a shows the surface morphology of raw wood which consisted of many small void space. From Fig. 9b, the introduction of urea-formaldehyde resin into raw wood filled all the void space. This showed that the impregnation of urea-formaldehyde resin into raw wood increased the activation energy, crystallization enthalpy, and final decomposition temperature. Besides, WPNCs showed smooth surfaces with the waxy substance removed from the raw wood which was confirmed by our previous work (Rahman et al. 2010).

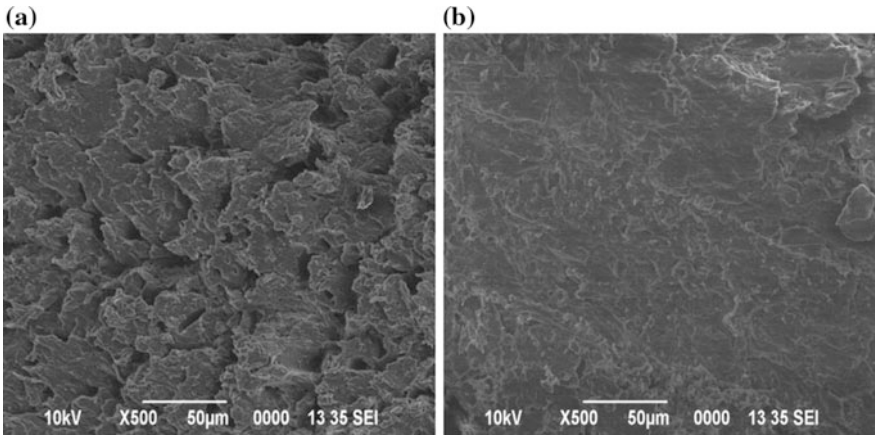

Fig. 9 Scanning Electron Microscopy of **a** raw wood and **b** WPNC

4 Conclusion

In this study, urea-formaldehyde resin WPNCs were fabricated and investigated through different characterizations. From FT-IR spectra, the impregnation of organic urea-formaldehyde resin into raw wood enhanced few peaks at 1648 cm^{-1} (O=N–), C–H absorption at 1319 cm^{-1} and –C–O– stretching band at 1262 cm^{-1}. These peaks confirmed the impregnation of WPNCs. Besides, WPNCs were more thermally stable over temperature range compared to raw wood through the well impregnation of urea-formaldehyde resin WPNCs. In addition, WPNCs showed higher MOE, MOR and stiffness of the WPNC were significantly increased compared to raw wood on *Eugenia* spp. and *Xylopia* spp., respectively. Besides, Young's modulus of *Eugenia* spp. was significantly higher for WPNCs. The X-ray diffraction patterns confirmed that the crystallinity of WPNCs was increased with polymer resin loading. From SEM micrograph, the surface morphology of WPNCs was smooth as the void space was filled by urea-formaldehyde resin to remove the waxy substance. It could be proven that urea-formaldehyde resin was significantly effective on *Eugenia* spp., continued with *Xylopia* spp. and *Artocarpus elasticus* wood species, respectively.

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