Physico-mechanical, thermal and morphological properties of furfuryl alcohol/2-ethylhexyl methacrylate/halloysite nanoclay wood polymer nanocomposites (WPNCs)

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Abstract

In this study, the physical, morphological, mechanical and thermal properties of furfuryl alcohol/2-ethylhexyl methacrylate/halloysite nanoclay wood polymer nanocomposites (FA-co-EHMA-HNC WPNCs) were investigated. FA-co-EHMA-HNC WPNCs were prepared via an impregnation method and the properties of the nanocomposites were characterized through the weight percent gain, Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), three-point flexural test, dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) analysis and moisture absorption test. The weight percent gain in the 50:50
FA-co-EHMA-HNC WPNC was the highest compared with the raw wood (RW) and other WPNCs. The FT-IR results confirmed that polymerization took place in the nanocomposites, especially 50:50 FA-co-EHMA-HNC WPNC, which had a reduced amount of hydroxyl groups. The SEM results revealed that the 50:50 FA-co-EHMA-HNC WPNC had the smoothest and most uniform surface among all of the nanocomposites. The 50:50 FA-co-EHMA-HNC WPNC showed the highest flexural strength and modulus of elasticity. The results revealed that the storage modulus and loss modulus of the FA-co-EHMA-HNC WPNCs were higher and the tan δ of FA-co-EHMA-HNC WPNCs was lower compared with the RW. The FA-co-EHMA-HNC WPNCs exhibited the higher thermal stability in the TGA and DSC analysis. The 50:50 FA-co-EHMA-HNC WPNC exhibited remarkably lower moisture absorption compared with the RW. Overall, this study proved that the ratio 50:50 FA-co-EHMA ratio was the most suitable for introduction in the RW.

Keywords: Nanotechnology, Materials science

1. Introduction

The rapid growth in the demand of resources increases to the importance of their sustainable and efficient resource utilization is proportionally growing (Brown et al., 2011). The constituents of wood include lignin with hemicelluloses, which act as a soft polymer matrix and lignocellulosic fibers, which act as rigid cellulosic microfibrils for reinforcement (Rong et al., 2001). Wood fiber is the most broadly used reinforcement in composite materials. However, wood is a hygroscopic material that adsorbs the surrounding moisture (Ramage et al., 2017). Besides, wood is an organic material that can be easily deteriorated by the fungi attack. Due to the sustainable applications of wood materials, it is important to improve the wood properties through polymer impregnation. Therefore, the introduction of a polymer matrix into wood cells to fabricate wood polymer nanocomposites (WPNCs) which has been widely used for many applications.

Wood polymer nanocomposites (WPNCs) are thermoplastic polymers that have attracted both researchers and industrialists because of their environmental friendliness (Markarian, 2005). WPNCs product show good durability in wet environments due to the hydrophobic polymer matrix, which allows for wood to be substituted with WPNCs in outdoor applications (Cheung et al., 2009). These products can be manufactured easily and rapidly using forming techniques that are typical of thermoplastic polymers (Zini and Scandola, 2011). The growing usage of renewable resources helps to counter various environmental problems caused by climate change and biodiversity threats (Lenzen et al., 2012).

Furfuryl alcohol (FA) is a monomer that improves the mechanical and thermal properties of the nanocomposites compared to pure FA (Ahmad et al., 2013).
Besides, the incorporation of modified clay-FA into wood results in better mechanical properties and lower water uptake into nanocomposites compared with raw wood (RW) (Hazarika and Maji, 2013). FA is a multi-functional polymer with a high possibility of polymerization and crosslinking. The alcohol groups of FAs are reactable and the rings within the polymers can be opened for further reaction. Due to this, the introduction of FA managed can reduce the hygroscopicity of the wood samples, which resulted in better mechanical properties than in RW (Schneider et al., 2009). Therefore, FA could be chosen to be applied in WPNCs.

The compound 2-ethylhexyl methacrylate (EHMA) is a monomer with a gelling nature that is usually used in biomedical applications (Karlsson and Gatenholm, 1996; Ende and Peppas, 1997). Research has shown that the combination of poly (EHMA) and methyl methacrylate in wood cellulose improves the functional properties for biomedical applications (Sharma and Chauhan, 2009).

Clay acts as a crosslinking agent that enhances the morphological, tensile and flexural properties of the WPNCs (Hazarika and Maji, 2014). Freeze-dried FA-clay nanocomposites can enhance the mechanical properties and thermal stability (Wang et al., 2016).

There is very little research work that has been reported on FA-based WPNCs and EHMA-based WPNCs, especially with the combination of FA and EHMA in WPNCs. Therefore, the aim of this study was to fabricate furfuryl alcohol/2-ethylhexyl methacrylate/halloysite nanoclay (FA-co-EHMA-HNC) WPNCs via an impregnation technique and to investigate the effect of different ratios of the polymer matrix on the physical, mechanical, morphological and thermal properties of WPNCs. The prepared WPNCs are important to both academics and industrialists, and are expected to be used building materials in exterior or interior applications (Rahman et al., 2015).

2. Experimental

2.1. Materials

*Sindora glabra* wood was obtained from Forest Farm, Sarawak, Malaysia. All the wood samples were cut to dimensions of 30 cm x 2 cm x 1 cm. To ensure the wood was well modified, the chemicals namely FA, EHMA, benzoyl peroxide and halloysite nanoclay (HNC) used. HNC was supplied by Sigma Aldrich (USA) with a diameter of 30 to 70 nm and length was in between 1 and 3 μm. The chemicals FA, EHMA and benzoyl peroxide, all these chemicals were supplied by Merck Millipore (USA).
2.2. Methods

2.2.1. Introduction of furfuryl alcohol/2-ethylhexyl methacrylate/halloysite nanoclay (FA-co-EHMA-HNC) into raw wood (RW)

FA, EHMA and HNC were combined in the presence of benzoyl peroxide, which acted as an initiator in the reaction to form the WPNCs. FA, EHMA and HNC were mixed at different ratios, as shown in Table 1. The impregnated wood-formed WPNCs were fully covered with aluminium foil. The covered WPNCs were autoclaved for 15 minutes to complete the reaction.

2.2.2. Impregnation of the FA-co-EHMA-HNC in raw wood

Four specimens were made for each ratio and all of the samples were weighted according to ASTM D1037 before the experiment. The mixtures were poured into a vacuum drying oven at 0.1 bar and dried for 1 h. The excess solution was removed from the wood samples with tissue paper after impregnation. The modified wood samples were wrapped with aluminium foil to prevent the moisture from entering the samples. All of the wrapped samples were kept in an oven at 100 °C for 24 h to ensure that the wood samples were well polymerized by FA-co-EHMA-HNC. The aluminium foil was removed from the polymerized wood samples and dried at 105 °C to achieve a constant weight. The weight percent gain (WPG) of all of the samples was calculated using Eq. (1),

\[
WPG = \frac{W_f - W_o}{W_o} \times 100\%
\]

where

\[W_f = \text{oven-dried weight of the WPNCs after modification (g)},\]

\[W_o = \text{oven-dried weight of RW before modification (g)}.\]

Table 1. Preparation of the polymer system with different ratios.

| Volume of furfuryl alcohol (FA) (mL) | Volume of 2-ethylhexyl methacrylate (EHMA) (mL) | Amount of halloysite clay (HNC) (g) | Amount of benzoyl peroxide (g) |
|------------------------------------|---------------------------------------------|---------------------------------|-------------------------------|
| 0                                 | 200                                         | 2                               | 5                             |
| 100                                | 100                                         | 2                               | 5                             |
| 140                                | 60                                          | 2                               | 5                             |
| 200                                | 0                                           | 2                               | 5                             |
2.3. Microstructural characterizations

2.3.1. Fourier transform infrared (FT-IR) spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was carried out to measure peak intensities of a sample over a narrow range of wavelength range. FT-IR spectroscopy was run and recorded with a Shimadzu IRAffinity-1 with the Attenuated Total Reflection (ATR) technique. The spectral resolution of this equipment was 12000 spectra while the transmittance range of the scan was 4000 to 600 cm$^{-1}$.

2.3.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was carried out to obtain information about surface topography and composition of the sample using a scanning electron microscope (SEM) (JSM-6710F) supplied by JEOL Company Limited, Japan. The FA/EHMA/HN WPNCs were extracted with the dimensions of 5 mm x 5 mm x 5 mm. The specimens were fixed with Karnovsky’s fixative, which was followed by a graded alcohol dehydration series. After the alcohol dehydration process, the specimen was coated with a thin layer of gold and then undergo microscopic viewing. The micrographs were taken at a magnification of 500.

2.3.3. Three-point flexural test

The purpose of the three-point flexural test was to determine the flexural modulus or flexural strength of a sample using an AG-X Plus Series Precision Universal Testers (300 kN Floor Model) supplied by Shimadzu Corporation, Japan. The samples were prepared with the dimensions of 80 mm x 30 mm x 10 mm and analysed according to ASTM D 7900–00 at a cross head speed of 10 mm/min. Four samples were prepared for each composition and average values were determined. The flexural strength ($Q_{fs}$) and modulus of elasticity ($E_m$) were calculated using Eqs. (2) and (3), respectively.

\[
Q_{fs} = \frac{3PL}{2bd^2} \quad (2)
\]

where

P = maximum load on the load-deflection curve (N),

L = support span, 63.7 mm,

b = width of the tested beam, 10 mm,
d = thickness of beam, 4 mm.

\[ E_m = \frac{L^3 m}{4bd^3} \]  

(3)

where

L = support span, 63.7 mm,

m = Slope of the tangent to the initial straight-line portion of the load-deflection curve, N/mm of deflection,

b = width of the tested beam, 10 mm,

d = thickness of beam, 4 mm.

### 2.3.4. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) investigated the effect of the temperature on the storage modulus (log \( E' \)) and loss tangent (tan \( \delta \)) of the FA-co-EHMA-HNC WPNCs using Perkin Elmer dynamic mechanical thermal analyser (PE-DMTA) supplied by Perkin Elmer, the United States of America, which run at a frequency of 10 Hz. This test allowed molecules in the wood to interact with mechanical stress. The specimens with a moisture content of approximately 15% were tested using the dual-cantilever bending mode. The chamber surrounding the specimen was cooled by liquid nitrogen. The system provided a thermal scan at a rate of 2 °C/min from 0 to 200 °C. The Tg was determined from the graph of tan \( \delta \) versus temperature.

### 2.3.5. Thermogravimetric analysis (TGA)

The purpose of the thermogravimetric analysis (TGA) was to detect the physical and chemical properties of a sample as a function of increasing temperature. Five to ten milligrams of a sample were tested using a Thermogravimetric Analyzer (TA Instrument SDT Q600) supplied by TA Instruments, the United States of America. All TGA testing was carried out at a heating rate of 10 °C/min in a nitrogen (N₂) atmosphere with a constant flow rate of 5 mL/min. The sample undergone thermal decomposition over a programmed temperature range of 0 °C to 700 °C. After the decomposition, the final weight loss and temperature were recorded and analyzed.

### 2.3.6. Differential scanning calorimetry (DSC) analysis

Differential scanning calorimetry (DSC) was carried out using a Perkin Elmer thermal analyser in order to investigate the thermal behaviour of a sample. All the measurements were made with a constant N₂ flow rate of 30 mL/min, constant heating rate of 10 °C/min and using an alumina crucible with a pinhole.
2.3.7. Moisture absorption test

The moisture absorption test was carried out on the samples to evaluate the moisture content of the dry weight of a sample and to reduce the moisture to a minimum to enhance the moisture resistance. The test was performed using electronic moisture balance (MOC-120H) supplied by Shimadzu Corporation, Kyoto, Japan at 110 °C for 3 h. All of the wood samples were dried at 25 °C and immersed in distilled water. The FA-co-EHMA-HNC WPNCs were removed from distilled water and placed on a pan to be weighted. The heater lid was closed and the percentage display and the measuring time were observed. The moisture absorbed, \( W_{ab} \) was calculated with Eq. (4),

\[
\text{Moisture absorbed percentage, } W_{ab} (\%) = \frac{W_w - W_d}{W_d} \times 100
\]

where

\( W_{ab} \) = absorbed weight (%),
\( W_w \) = weight of the wet WPNCs,
\( W_d \) = weight of the dry WPNCs.

3. Results and discussion

3.1. Weight percent gain (WPG %)

The WPG values of the RW and FA-co-EHMA-HNC WPNCs are shown in Table 2. The WPG values of the RW, FA-HNC, 50:50 FA-co-EHMA-HNC, 70:30 FA-co-EHMA-HNC and EHMA-HNC WPNCs were 0.376%, 5.267%, 28.655%, 25.132% and 12.959%, respectively. It was due to the characteristics of the polymer matrix characteristics, which impregnated the wood (Makarona et al., 2017). Therefore, it was confirmed that the impregnation of FA-co-EHMA-HNC into the RW improved the mechanical and thermal properties.

3.2. Spectral (FT-IR) analysis

The formation of new chemical bonds between the RW, FA, EHMA, HNC and wood fiber of the FA-co-EHMA-HNC WPNCs and RW as shown in Fig. 1 and Table 3. The RW had several specific peaks such as 3400 cm\(^{-1}\), 2900 cm\(^{-1}\) and 1735 cm\(^{-1}\) which were attributed to the stretching vibrations of –OH, C-H and C=O, respectively. These absorption peaks were significant due to the hydroxyl groups in fiber and carbonyl groups of acetyl ester in the fiber (Ismail et al., 2002). However, the peak at 3400 cm\(^{-1}\) was greatly reduced when the polymer matrix was impregnated well into the RW especially for the 50:50 FA-co-EHMA-HNC and
70:30 FA-co-EHMA-HNC WPNCs. The peak at 1735 cm\(^{-1}\) was shifted towards 1730 cm\(^{-1}\) in the WPNCs due to the fracture of ester carbonyl bonds in the fiber in the impregnation system (Mohd Idrus et al., 2011). In addition, the intensity of the peak at approximately 1350 cm\(^{-1}\), which was attributed to C-O-H stretching vibration, was reduced in WPNCs due to good chemical bond formation between the polymer matrix and hydroxyl groups in the fiber. Therefore, it was concluded that the RW was impregnated well with the FA-co-EHMA-HNC, which reduced the amount of hydroxyl groups in the wood cells. The functional groups of the peaks are summarized in Table 3 and the reaction scheme is shown in Fig. 2. Fig. 2 showed that the FA undergone condensation to form open-ended FA. This was with the EHMA into the wood that contained hydroxyl groups with the 2-ethylhexyl methacrylate to form WPNCs by removing water molecules from the reactions.

Table 2. Average weight percent gain (WPG) of the RW and different ratios of the FA-co-EHMA-HNC WPNCs.

| Sample                  | Average weight before impregnation (g) | Average weight after impregnation (g) | Weight percent gain, WPG (%) |
|-------------------------|----------------------------------------|---------------------------------------|-----------------------------|
| RW                      | 70.756                                 | 71.023                                | 0.376                       |
| FA-HNC WPNCs            | 58.703                                 | 61.967                                | 5.267                       |
| 50:50 FA-co-EHMA-HNC WPNCs | 43.079                               | 60.381                                | 28.655                      |
| 70:30 FA-co-EHMA-HNC WPNCs | 48.479                               | 64.753                                | 25.132                      |
| EHMA-HNC WPNCs          | 46.810                                 | 53.779                                | 12.959                      |

Fig. 1. FT-IR spectra of the (a) RW (b) FA-HNC WPNCs (c) 50:50 FA-co-EHMA-HNC WPNCs (d) 70:30 FA-co-EHMA-HNC WPNCs (e) EHMA-HNC WPNCs.
3.3. SEM analysis

SEM analysis was carried out to examine the compatibility between the wood cell walls and polymer matrix. Fig. 3(a-e) shows the surface morphology of RW and FA-co-EHMA-HNC WPNCs. Major differences were observed in all of the samples as the interfacial bonding of the wood cell-polymer matrix was different. Fig. 3(a) clearly showed the void spaces inside the RW. The detected void spaces were due to the weak fiber-fiber interaction in the wood that would reduce the mechanical and thermal properties. With the impregnation of FA-HNC into the RW, the void spaces were filled with the polymer matrix. However, the surface was not uniform due to the weak interfacial bonding between the FA-HNC and HNC.

Table 3. Summary of the functional groups in the FA-co-EHMA-HNC WPNCs.

| Functional groups detected | Peak (cm$^{-1}$) |
|---------------------------|-----------------|
| -OH                       | 3400 cm$^{-1}$  |
| C-H                       | 2900 cm$^{-1}$  |
| C=O                       | 1735 cm$^{-1}$, 1730 cm$^{-1}$ |
| C-O-H                     | 1350 cm$^{-1}$  |

Table 3. Summary of the functional groups in the FA-co-EHMA-HNC WPNCs.

Fig. 2. Proposed schematic reaction diagram of the condensation of FA and the reaction of FA, EHMA and HNC.
wood fiber. Fig. 3(c) showed a smooth and uniform surface for the 50:50 FA-co-EHMA-HNC WPNCs (Rahman et al., 2015). A strong interfacial bond between the wood fiber and FA-co-EHMA-HNC was formed, which reduced the amount of hydroxyl groups in the wood fiber (Liew et al., 2016). The surface in Fig. 3(d) was fully covered due to the impregnation of 70:30 FA-co-EHMA-HNC. However, the surface was not as smooth as Fig. 3(c) due to the different ratio led to a different reorganization of the polymer matrix chains (Ndiaye and Tidjani, 2014). Fig. 3(e) showed a non-uniform surface with some void spaces for the FA-co-EHMA-HNC WPNCs. This could have been due to the poor adhesion of the EHMA-HNC into the wood cell walls (Sheshmani et al., 2010). Therefore, the SEM results confirmed the improvement of the interfacial bonding between the polymer matrix and wood
fiber by the impregnation method, especially for the FA-co-EHMA-HNC WPNCs by impregnation method, which contributed to better mechanical and thermal properties.

3.4. Three-point flexural test

The mechanical properties of the RW and WPNCs are shown in Figs. 4 and 5 respectively. The flexural strength increased with the incorporation of different ratios of polymer matrix. The flexural strength of the WPNCs was increased approximately 8 to 20% higher compared with the RW. This was due to the less agglomeration on the polymer matrix on the surface of the WPNCs (Ismail et al., 2001). Besides, hydrogen bonds that formed between the FA-co-EHMA-HNC and hydroxyl groups from the RW led to better adhesion at the fiber-matrix interface and thus, the flexural strength of the WPNCs was improved. Low flexural strength
was detected in the RW due to the abundance of hydroxyl groups on the surface (Lu et al., 2005).

The modulus of elasticity of the RW and FA-co-EHMA-HNC WPNCs are presented in Fig. 5. The WPNCs showed higher modulus of elasticity compared with the RW due to the better interactions between the polymer matrix and wood cell walls. Besides, the impregnation of FA-co-EHMA-HNC into the RW increased the modulus of elasticity due to the inclusion of rigid matrix particles in the RW. The better interfacial bonding of WPNCs reduced the interfacial stress concentration, which led to a better modulus of elasticity (Cao et al., 2011). Therefore, the 50:50 FA-co-EHMA-HNC WPNCs showed the highest flexural strength and modulus of elasticity compared with the RW and other WPNCs.

3.5. DMTA

DMTA was carried out to study the storage modulus (E’), loss modulus (E’”) and damping behaviour (tan δ). There were three stages observed, namely the glassy, transition region and rubbery regions (Komadan et al., 2007). Fig. 6 showed the storage modulus of RW and FA-co-EHMA-HNC WPNCs decreased over the temperature range. The value of storage modulus represents the stiffness of the WPNCs. It was significant that the changes in the storage modulus were lower in the glass transition region due to the semi-crystalline nature of the FA-co-EHMA-HNC. The crystallinity of both the RW and WPNCs was reduced as the storage modulus decreased with increased in temperature and then finally levelled off at high temperatures. The polymer matrix component was greatly affected the storage modulus over the temperature range (Quintens et al., 1990). All of the WPNCs showed a transition at 120 °C, whereas the transition of the RW occurred at 100 °C due to the combination of FA, along with EHMA and HNC (Hamdan et al., 2010).
This confirmed that the $E'$ values for the WPNCs were greatly improved over the temperature range compared with the RW.

Fig. 7 shows the variation of the damping behaviour (tan $\delta$) with temperature for the RW and WPNCs. The damping behavior was the highest when the samples were in the transition region. Both the glassy and rubbery regions showed low tan $\delta$ values as the molecular movement was frozen and free to move around, respectively (Komadan et al., 2007). The WPNCs had a lower damping variation compared with the RW due to the rubbery nature of the WPNCs. Besides, the removal of stress in the RW caused more permanent deformation and thus produced higher tan $\delta$ values. The FA-co-EHMA-HNC impregnation caused a shift of the tan $\delta$ to a higher temperature, which proved there was an increase in the relaxation temperature. This was caused by certain restorative forces within the wood cell walls in the rubbery state (Hamdan et al., 2010).

Fig. 7. Tangent $\delta$ versus temperature of the RW and different ratios of the FA-co-EHMA-HNC WPNCs.

Fig. 8. TGA curves of the RW and different ratios of the FA-co-EHMA-HNC WPNCs.
Overall, the storage modulus and loss modulus increased with a reduction in the damping behaviour of the WPNCs due to the significant changes in the molecular motion in the transition region.

3.6. TGA

The TGA curves of the RW, FA-HNC, 50:50 FA-co-EHMA-HNC, 70:30 FA-co-EHMA-HNC WPNCs are shown in Fig. 8. The TGA curves showed that the decomposition of the RW and FA-co-EHMA-HNC WPNCs occurred in three stages. The first stage occurred within the temperature range of 0 °C to 200 °C. The second stage of thermal degradation started at 200 °C and ended at 350 °C. Fiber was decomposed during this stage. The third stage was occurred over the temperature range of 350 °C to 450 °C and was associated with the decomposition of the wood cell walls (Hasnan et al., 2016). From Fig. 8, the weight loss percentage from the thermal degradation below 400 °C was lower for all of the WPNCs compared with RW. However, the weight loss of the WPNCs was much higher than the RW for the temperature range of 400 °C to 600 °C. This indicated that the WPNCs had a higher thermal stability than the RW due to the better interfacial adhesion of the FA-co-EHMA-HNC in the wood cell walls. Besides, the polymer matrix-cell wall interaction was remarkably stronger compared with the fiber-fiber interaction (Dato’ Hasnan et al., 2016).

Table 4 shows the thermal characteristics such as initial temperature ($T_i$), maximum rate loss temperature ($T_m$) and final decomposition temperature ($T_f$) as well as the activation energy. The Arrhenius equation was used to determine the

| Sample                      | $T_i$ (°C) | $T_m$ (°C) | $T_f$ (°C) | $W_{T_i}$ (%) | $W_{T_m}$ (%) | $W_{T_f}$ (%) | $E_a$ (kJ/mol) |
|-----------------------------|------------|------------|------------|---------------|---------------|---------------|---------------|
| RW                          | 84.0       | 360.0      | 456.0      | 96.3          | 51.1          | 13.1          | 1120.9        |
| FA-HNC WPNCs                | 78.0       | 360.0      | 468.0      | 96.1          | 51.6          | 18.8          | 1399.9        |
| 50:50 FA-co-EHMA-HNC WPNCs  | 78.0       | 360.0      | 486.0      | 96.4          | 57.3          | 22.9          | 2211.9        |
| 70:30 FA-co-EHMA-HNC WPNCs  | 78.0       | 360.0      | 480.0      | 96.2          | 53.0          | 23.1          | 2021.6        |
| EHMA-HNC WPNCs              | 78.0       | 360.0      | 468.0      | 96.1          | 51.7          | 21.9          | 1701.0        |

*a* Temperature corresponding to the beginning of decomposition.

*b* Temperature corresponding to the maximum rate of mass loss.

*c* Temperature corresponding to the end of decomposition.

*d* Mass loss at the temperature corresponding to the beginning of decomposition.

*e* Mass loss at the temperature corresponding to the maximum rate of mass loss.

*f* Mass loss at the temperature corresponding to the end of decomposition.
activation energy (Chanmal and Jog, 2008). The higher activation energy implies a higher thermal stability. It was found that the activation energy of the 50:50 FA-co-EHMA-HNC WPNCs was significantly higher, followed by the 70:30 FA-co-EHMA-HNC, EHMA-HNC, FA-HNC WPNCs and RW. The impregnation of FA-co-EHMA-HNC increased the thermal stability because the particles of the polymer matrix filled the voids in the wood cell walls, which resulted in the WPNCs having a better surface (Kumari, 2008). Therefore, impregnated wood performed had a better thermal stability than the RW.

3.7. DSC analysis

The DSC thermograms of the RW and WPNCs with different ratios are shown in Fig. 9. The DSC analysis was carried out to determine the thermal behavior of the RW and WPNCs. Besides, the chemical activity that occurred within the RW and WPNCs was identified. The results showed that the chemical reaction changed over the temperature range. However, the properties have been affected due to the moisture content in the wood (Tay et al., 2016). There were two noticeable stages of thermal decomposition that occurred between 50 °C and 200 °C.

Fig. 9 shows that broad endotherms were observed in the temperature range of 50 to 200 °C due to the presence of water molecules in the wood cell walls. Above 200 °C, it was clearly indicated the decomposition of cellulose in the wood cell walls was clearly observed (Akita and Kase, 1967).

All of the first endotherm peaks were detected at approximately 60 °C. The second endotherm peak of RW, FA-HNC, 50:50 FA-co-EHMA-HNC, 0:30 FA-co-EHMA-HNC and EHMA-HNC WPNCs occurred at 210 °C, 190 °C, 160 °C, 160 °C and 150 °C, respectively. From the second decomposition temperature, it was
significantly indicated that the WPNCs were more thermally stable compared with the RW. The second decomposition stage of the RW and WPNCs differed widely as the wood cell walls contained large amounts of hemicellulose that could be decomposed at approximately 170 °C. As shown in Table 5, the WPNCs showed higher bond dissociation enthalpy, which proved the WPNCs had a higher crystallinity compared with the RW. This was due to the good impregnation of the polymer matrix into wood cell walls (Sulaiman et al., 2013). Overall, the WPNCs, especially the 50:50 FA-co-EHMA-HNC WPNCs, had the highest thermal stability, which was reflected in the TGA results.

### 3.8. Moisture absorption analysis

The moisture absorption of the RW and FA-co-EHMA-HNC WPNCs as a function of the heating time is shown in Fig. 10. It was very clear that the moisture absorption decreased as different ratios of the polymer matrix were introduced into the RW. The RW was highly hydrophilic in nature. The incorporation of the FA-co-EHMA-HNC polymer matrix into the wood fiber decreased the rate of moisture sorption ability by breaking the hydrogen bonds in the moisture to form new chemical bonds between the free hydrogen molecules and the polymer matrix (Cao...
et al., 2011). As the amount of polymer matrix increased, the number of hydrogen bonds between the moisture was greatly reduced. The impregnation of the polymer matrix into the RW filled up most of the voids, which led to a lower accumulation of moisture at the interface between the wood fiber and the polymer matrix (Jacob et al., 2005). Therefore, the 50:50 FA-co-EHMA-HNC WPNCs showed the lowest moisture absorption percentage among all of the WPNCs and RW.

4. Conclusions

From the present study, it was clearly proved that the WPNCs performed better than the RW after the impregnation of FA-co-EHMA-HNC in terms of physical, mechanical, morphological and thermal properties. It was confirmed that the 50:50 FA-co-EHMA-HNC WPNCs showed the highest weight percent gain with the lowest amount of hydroxyl group in FT-IR. Besides, this WPNCs provided a smoother morphology with the highest flexural strength, modulus of elasticity, storage modulus and loss modulus with lower tan δ. The 50:50 FA-co-EHMA-HNC WPNCs exhibited the highest thermal stability with the lowest moisture absorption. This study proved that the impregnation of different percentages of polymer matrix into the RW produced different effects. Therefore, RW should be modified through impregnation, which gradually reduced the hydroxyl groups and improved the decay resistance of the RW.

Declarations

Author contribution statement

Md. Rezaur Rahman: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Sinin Hamdan: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Josephine Chang Hui Lai: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Mohammad Jawaid, Fahmi A. bin Md Yusof: Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.
Additional information

No additional information is available for this paper.

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