Development of Green MMT-modified Hemicelluloses Based Nanocomposite Film with Enhanced Functional and Barrier Properties

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A biocomposite was successfully prepared by blending montmorillonite (MMT)/hemicellulose from oil palm empty fruit bunches (OPEFB) with carboxymethyl cellulose (CMC) through solution casting. The composite was characterized by scanning electron microscopy (SEM), Fourier transmission infrared spectroscopy (FT-IR), and X-ray diffraction (XRD). The results displayed good compatibility between the mixtures of the blended MMT/hemicellulose and CMC due to the hydrogen bonding and electrostatic interaction. There was an improvement in the thermal analysis through their thermogravimetry analysis (TGA), derivative thermogravimetry (DTG), and differential scanning calorimetry (DSC), mechanical properties (tensile strength and tensile modulus), and water vapor permeability (WVP). The best values of tensile strength and tensile modulus of 47.5 MPa and 2.62 MPa, respectively, were obtained from 60H-40CMC-MMT nanocomposite films. The results showed that the mixture of the blended MMT/hemicelluloses and CMC produced a robust nanocomposite film with improved physical and mechanical properties, demonstrating that it is a promising candidate for green packaging applications.

Keywords: Oil palm empty fruit bunch; Montmorillonite; Hemicelluloses; Solution casting; Carboxymethyl cellulose

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INTRODUCTION

Hemicellulose is made of alkali-soluble, biodegradable, biocompatible, natural hetero-polysaccharides that have limited utilization in packaging due to their hygroscopicity and poor mechanical properties (Chen et al. 2016). Global demand for high-barrier food-packaging films was reported to have increased from 2015 to 1.4 million tons in 2017, which is equivalent to USD 230.97 billion. This is expected to rise at a compound growth rate (CAGR) of 7.8% between 2017 and 2027, valued as US$430.08 billion by 2027 (Aldaya et al. 2010). The increase in the demand for green packaging materials, especially in food packaging, is a reflection of changing lifestyles with respect to the convenience and portability of products from the food industry (Nasrabadi et al. 2017). The basic properties that make good packaging materials include chemical properties, heat resistance, odor barrier, puncture resistance, high tensile strength, durability, good surface properties, and low weight, and these factors have contributed to the growing requirements.

of the food industry and retail supply chain (Luqueta et al. 2017). The application of renewable resources such as plant materials in packaging are expected to reduce the dependence on fossil fuel materials for packaging. Of the three principal biopolymers in plants, hemicellulose has received the least attention in terms of application. While cellulose has a unique structure, the term hemicelluloses is used to describe a number of noncrystalline hexose and pentose sugars (Andberg et al. 2016). Hemicelluloses make up 20 to 30% of the total weight of perennial and annual plants; they are abundant polysaccharides with good film forming ability and excellent oxygen and water vapor barrier properties. The composition of hemicellulose depends on the method of its extraction, i.e. by steam, alkali, methanol/water, dimethyl sulfoxide, or microwave (Chaker et al. 2013). Hemicelluloses are often released to the stream during forest operations such as pulping, disposed as an organic waste, burned for energy recovery, or released during fiberboard production, and these materials could be used as renewable resources for packaging materials. Hemicellulose-based films have been used as barrier materials for moisture and oxygen and in the production of polarizing sheets (Creighton et al. 2016). The mechanisms of hemicelluloses reactions as bio-fillers are influenced by the variability in sugar constituents, glycosidic linkages, structure of glycosyl side chains, and the reactive hydroxyl groups at the xylose repeating unit (Reza et al. 2013). These linkages offer various possibilities for region-selective chemical and enzymatic modifications. These and other applications motivate an interest in improving various properties of hemicellulose by blending with other polymeric materials. The abundant hydroxyl groups in hemicelluloses makes it hydrophilic, and it can participate in intermolecular and intramolecular hydrogen bonding. However, hemicellulose-based films are hygroscopic with poor mechanical strength properties (Chen et al. 2016). To overcome these disadvantages, plasticizers such as carboxymethyl cellulose (CMC) and xylitol are often introduced to the composite blend (Chen et al. 2016).

Carboxymethyl cellulose is a cellulose derivative that is prepared through the reaction of alkali cellulose with mono-chloro acetate or its sodium salt in organic medium. It possesses many desirable qualities, such as film forming, emulsification, stabilization of suspensions, water retention, binding, and thickening. Therefore, it is used for many applications such as in medicine, food, textiles, toilet, electrical elements, papermaking, printing, and dyeing. There are many potential applications of CMC in paper coating, textile sizing, and flexible water-soluble packing film due to its high clarity and excellent durability. The mechanical strength properties of a polysaccharide film can be increased by blending with a higher molecular weight polysaccharide that has adhesive properties, such as CMC. It shows amphiphilic characteristics due to the presence of many hydrophilic carboxyl groups (Yu et al. 2014). The most popular bentonites are montmorillonite (MMT), hectorite, and saponite. Of these, MMT is the most widely used clay as nanofiller for CMC modification due to its availability in many localities (Makwana et al. 2018).

Despite the various literature reports on the fabricated hemicellulose based biodegradable films, practical applications of hemicelluloses films have been severely limited. Zhao and coworkers (2015) further reported that, combination of hemicellulose and plasticizer based nanocomposite films often aimed to ensure enhanced functional properties has rarely been investigated. The aim of this study is to prepare high performance green hemicelluloses based nanocomposite film from the blend of montmorillonite (MMT)/hemicellulose from oil palm empty fruit bunches (OPEFB) with carboxyl methyl cellulose (CMC). To date, packaging film from extracted hemicelluloses from oil palm empty fruit bunches (OPEFB) fortified with montmorillonite has not been

reported with respect to film forming and barrier characterization. The present study developed and characterized eco-friendly biodegradable film from waste OPEFB with improved functional and good barrier properties for low to moderate relative humidity applications.

EXPERIMENTAL

Materials
The raw materials used to produce the nanocomposite films were carboxymethyl cellulose (Drex-Chem (M) Sdn. Bhd., Petaling Jaya, Selangor, Malaysia) and organo-modified montmorillonite (Nanocor Inc., Arlington Heights IL, USA). Hemicellulose from oil palm empty fruit bunch (OPEFB) was supplied by United Oil Palm Sdn Bhd, Nibong Tebal, Penang, Malaysia.

Hemicellulose Extraction from of Oil Palm Empty Fruit Bunch
Alkaline extraction was performed as described by Wanrosli et al. (2004) with the modification of using NaOH instead of KOH. The hemicellulose extraction was conducted at the biomass to alkaline ratio of 1:10 (wt:vol). The total weight of 5 g OPEFB was placed in a beaker with 50 mL of 1.0 M NaOH. The beaker was heated at 40 °C on a magnetic stirrer for 4 h at 400 rpm. The mixture was refrigerated for 24 h at 4 °C. The supernatant was collected, and hemicellulose was precipitated by adding ethanol.

Hemicelluloses Based Film Preparation
This process was repeated two times. The extracted hemicellulose was separated from residue by filtration. The hemicellulose-based composites were reconstituted with 20%, 40%, 60%, or 80% hemicelluloses, which were denoted as 20H-80CMC, 40H-60CMC, 60H-40CMC, and 80H-20CMC, respectively, where 100CMC was used as the control (Table 1).

Table 1. Formulation for Nanocomposite Film

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hemicellulose (%)</th>
<th>CMC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100CMC</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>20H-80CMC-MMT</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>40H-60CMC-MMT</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>60H-40CMC-MMT</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>80H-20CMC-MMT</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

Note: To produce nanocomposite film, 2% of MMT was added to the blend film.

Initially, a distilled water solution of hemicelluloses was transferred into a beaker, followed by additional of CMC, at 90 °C for 30 min under moderate agitation as shown in Table 1. Finally, the film solution was transferred into poly-acrylic plates and drying in an oven (Mermet, Germany) at 45 ± 0.5 °C and relative humidity of 60% for 36 h to obtain a film of uniform thickness. All of the produced films were placed inside a desiccator containing silica-gel prior to analysis.
Characterization

Film thickness

Film thickness was measured using a hand-held micrometer (Mitutoyo, Tokyo, Japan) to the nearest 0.001 mm at twelve different locations, and the average value was obtained. The thickness was used in the calculations for film water vapor permeability and mechanical properties of the films.

Contact angle analysis

Contact angles were measured to study the surface hydrophobicity of the films. The contact angle analysis was determined using a Drop Shape Analyzer DSA100 goniometer (Kruss GmbH, Hamburg, Germany), which is a universal, high-quality instrument for analyzing wetting and coating processes. The wettability test was carried out using water, where 10 μL of water was dropped manually using a micropipette onto the surface of the particleboard. The image of the droplet was recorded using video camera for 60 s. Five replicates were used for the determination of contact angle for each liquid.

Fourier transform infrared analysis (FTIR)

Fourier transform infrared (FTIR) spectroscopy of hemicelluloses film from blend of CMC, MMT, and OPEFB and nanocomposite were measured directly using a Nicolet Avatar Model 360 spectrometer Fourier transform infrared spectrometer (Thermo Nicolet Corporation, Madison, WI, USA). FT-IR spectra were recorded in the spectra range from 4000 to 400 cm⁻¹. The spectra were recorded in the absorbance mode at from 4000 to 400 cm⁻¹ by FTIR analysis immediately afterward.

X-ray diffraction analysis

The X-ray diffraction (XRD) patterns of the hemicelluloses film were obtained on a Philips PW1050 X-pert diffractometer (Radeberg, Germany) using Cu-Kα1 radiation and operation at 40 kV and 25 mA and λ = 1.54 Å. The diffractograms were scanned from 1° to 60° (2θ) in steps of 0.02° using a scanning rate of 0.5°C/min. X-ray diffractograms of hemicelluloses film was carried out for determining the degree of crystalline or amorphous nature of the samples, chemical composition of raw material and particle size. The diffractometer was controlled by a personal computer equipped with X-pert High Score puls Software. 2 g of samples from hemicelluloses nanocomposite film were used prior to analysis.

Water vapor permeability

Water vapor permeability (WVP) of the film sample was measured using ASTM D570-98 (2002). The film sample was mounted on a permeation glass cup (height of 410 mm; width of 450 mm) containing silica gel. The initial weight of the cup together with the film sample and silica gel was recorded before putting in a desiccator containing a beaker of water kept at 25±2°C. The cup was weighed (±0.0001 g) daily for a week, and a plot of weight gained against time was drawn. According to Jouki et al. (2013), the water vapor transmission rate (WVTR) and WVP were calculated using Eqs. 1 and 2,

WVTR = Δm/ΔtA  
WVP= Δm/ΔtA (L/Δp)

where Δm/Δt is the moisture gain weight per time (g/s), A is the exposed surface area of
the film (m²), L is the thickness of the film (mm), and Δp is the difference of partial pressure.

**Tensile Strength**

Film samples of each formulation was uniformly cut into strips (150 mm × 25 mm), and tensile strength (TS), Young’s modulus (E), and elongation at break (EAB) was measured and calculated according to ASTM D882 (2000) using a texture analyzer (Stable Micro Systems TA.XT plus, Surrey, UK). The film strip was clamped between tensile grips with an initial grip separation and test speed set at 100 mm and 0.8 mm s⁻¹, respectively, using a load cell of 30 kg. For each sample, the film was cut, and an average of five measurements was taken to calculate TS, E, and EAB according to the following equations,

\[
TS \text{ (MPa)} = \frac{F_{\text{max}}}{\varnothing} \quad (3)
\]

\[
E \text{ (MPa)} = \left( \frac{F_{\text{max}}}{\varnothing} \right) \times \left( \frac{l_0}{\Delta l} \right) \quad (4)
\]

\[
EAB \text{ (%)} = \left( \frac{\Delta l}{l_0} \right) \times 100 \quad (5)
\]

where \( F_{\text{max}} \) is the maximum load (N), \( \varnothing \) is the cross-sectional area of the film strips (mm²), \( l_0 \) is the initial film length (mm), and \( \Delta l \) is the length of film extension after stretching (mm).

**Scanning Electron Microscopy (SEM)**

The morphology of the blend and nanocomposites film was investigated with a scanning electron microscope (Leo Supra, 50 VP, Carl Ziess, SMT, Radeberg, Germany). Images were obtained under conventional secondary electron imaging. The fracture surfaces of composites obtained from tensile fracture cross sections were sputter-coated with gold prior to microscopy.

**Thermal Analysis**

*Differential scanning calorimetry (DSC)*

A Perkin Elmer Pyris 7 thermal analyzer (Radeberg, Germany) was utilized to determine the melting temperature for hemicellulose film under nitrogen purge at a heating rate of 10 °C/min. Approximately 10 mg of dry sample was transferred into a hermetic aluminum pan and sealed. The sample was placed inside the analyzer with an empty hermetic aluminum pan as reference. The sample was heated at 10°C/min in nitrogen flux from room temperature to 400 °C. The data was recorded continuously over the temperature and time intervals. As the temperature increased, the sample eventually reached its melting temperature (\( T_m \)). The melting process resulted in an endothermic peak in the DSC curve.

*Thermogravimetric analysis (TGA)*

Thermogravimetric analysis was used to evaluate the thermal stability of hemicellulose film specimens. The weight loss of the samples was measured as a function of temperature using a thermogravimetric analyzer (Perkin-Elmer) under nitrogen atmosphere at a flow rate of 20 mL/min. A total of 10 mg of dried sample was heated at 10 °C/min in nitrogen flux from room temperature to 800 °C using Perkin Elmer-YGA7 instrument to obtain individual spectra. The thermogram records the percentage of weight...
loss versus temperature. The mass change of the sample was recorded continuously over the temperature and time intervals. The weight loss of the samples was measured as a function of temperature. This method was described by Owolabi et al. (2017).

RESULTS AND DISCUSSION

Alkali Extraction
The yields of extracted hemicelluloses from OPEFB, which ranged between 23.0 to 29.5%, was in agreement with a similar report by Sun et al. (2000) that extracted hemicelluloses from rice straw. Alkaline-based hemicelluloses extraction is a result of cleavage of ester linkages between lignin and celluloses at the cell wall (Sun et al. 2004). In addition, the α-ether linkage between lignin and hemicelluloses is broken down by alkaline treatment (Palamae et al. 2014). Hemicelluloses can be extracted using potassium hydroxide (KOH) (Haliza et al. 2006); KOH favors the removal of hemicelluloses at higher concentration. Thus, NaOH is preferable as it removes lignin while minimizing the loss of hemicelluloses, which is desirable (Haliza et al. 2006).

Physical Characterization of Hemicelluloses Blend and Nanocomposite Films

Particle size measurement
The suspension of nanocellulose was subjected to zeta potential evaluation and had a mean value of -32.5 ± 1.5 mV. The nanocellulose was considered stable because the absolute value of the zeta potential was higher than 25 mV (Chaturbhuj et al. 2016). The major particle size distribution was approximately 89.5 nm.

Film thickness and optical properties
Table 2 shows thickness and the optical properties (i.e., color), showing the Hunter (L, a, b) color values of nanocomposite films with the different ratios of hemicellulose and different CMC/MMT contents while the sample of the prepared films are shown in Fig 1. Nanocomposite films were at least semitransparent by the virtue of the high L value. The film thickness is pivotal to the water permeability and mechanical properties.

Table 2. Thickness of Nanocomposite Hemicelluloses Films

<table>
<thead>
<tr>
<th>Film</th>
<th>Thickness (mm)</th>
<th>L (Transparency)</th>
<th>a (Redness/Greenness)</th>
<th>b (Yellowness/Blueness)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100CMC-MMT</td>
<td>0.1566 ± 1</td>
<td>97.61 ± 0.99</td>
<td>-3.3 ± 0.05</td>
<td>1.38 ± 0.09</td>
</tr>
<tr>
<td>20H-80CMC-MMT</td>
<td>0.1791 ± 2</td>
<td>0.08 ± 0.01</td>
<td>0.10 ± 0.04</td>
<td>2.74 ± 0.11</td>
</tr>
<tr>
<td>40H-60CMC-MMT</td>
<td>0.1821 ± 1</td>
<td>0.25 ± 0.02</td>
<td>0.28 ± 0.09</td>
<td>4.05 ± 0.12</td>
</tr>
<tr>
<td>60H-40CMC-MMT</td>
<td>0.2043 ± 2</td>
<td>0.08 ± 0.01</td>
<td>0.10 ± 0.04</td>
<td>7.61 ± 0.11</td>
</tr>
<tr>
<td>80H-20CMC-MMT</td>
<td>0.2191 ± 4</td>
<td>0.25 ± 0.02</td>
<td>0.28 ± 0.09</td>
<td>7.89 ± 0.13</td>
</tr>
</tbody>
</table>

The optical properties are very important in films meant for food packaging applications. The thickness of all nanocomposite films under investigations ranged between 0.16 and 0.22 mm while the MMT based pure films without hemicelluloses modification were translucent with the highest luminosity ($L$) value of 97.61 but decreased upon addition of hemicelluloses. Hence the incorporation of hemicelluloses fillers into the methyl cellulose matrix produced less translucent films compared with the MMT-CMC nanocomposite film.

The minor color changes of the nanocomposite films were visible due to the films with added MMT. As shown in Fig. 1, nanocomposite film without the hemicelluloses had better transparency than the blend film, which was because the MMT content of the films was well dispersed and therefore increased some transparency (Kanmani and Rhim 2014).

With an increase in ratio of hemicellulose to CMC/MMT, the $L$-value decreased, while $a$- and $b$-values increased. This result suggested that the introduction of the hemicellulose content directly affected the color of films. This could be attributed to the obstruction of visible wavelength by the increased addition of the hemicelluloses, leading to translucent or opaque films and decreasing the transparency of the films.
Wettability

Contact angles determination has been widely used to determine the wettability of a liquid on a solid surface. The rule of thumb for the study is that a high value of the contact angle $\theta$ indicates a higher cohesive strength within the bulk water hence a weak liquid-solid interaction therefore poor wetting. In contrast, low values of the contact angle $\theta$, with spreading tendencies in solids showing strong liquid-solid interaction. The forces associated with the interaction of water with a surface are greater than the cohesive strength associated with bulk liquid water. The results of the contact angles for all films are shown in Fig. 2, with the highest contact angle of 87% for CMC- blended MMT/hemicellulose film. There were decreases in the contact angle to 54% with least additions of CMC. The highest contact angle recorded for 60HMMT-40CMC was as a result of enhanced hydrophobicity through the combination of blended MMT OPEFB hemicellulose with CMC film, which enhances the contact angle of the CMC- blended MMT/ hemicellulose blend.

![Graph showing contact angles for different film compositions](image)

*Fig. 2. Contact angle of nanocomposite films at (a) 100CMC-MMT, (b) 20HMMT-80CMC, (c) 40HMMT-60CMC, (d) 60HMMT-40CMC and (e) 80HMMT-CMC20

However, the lowest contact angle of 54% recorded for the combination of 80HMMT-CMC20 nanocomposite film could be attributable to the lowest value of the CMC in the nanocomposite formulation, resulting in least hydrophilic specimen. The results can be related to the theory of contact angle measurements, which predicts that if the values of contact angles are low, then the liquid will spread or wet well, while high values indicate poor wetting. This means that 80H-20CMC blend film had the least contact angle of 54% compared with others ratios.

As shown in Table 3, water vapor permeability decreased in the following order: 80H-20CMC > 20H-80CMC > 40H-60CMC > 60H-40CMC > 100CMC. Despite the modification of the CMC with the MMT, the WVP of the film increased with increased hemicelluloses blend due to many hydrophilic carboxyl groups. A similar trend was
reported by Bourtoom and Chinnan (2008). The incorporation of nanocellulose extracted from plant sources should improve the barrier properties of biocomposites because of its nanoscopic structure. However, hemicelluloses have relatively poor water vapor barrier characteristics, which result from their hydrophilicity; hence, high WVP of the nanocomposite film was observed as the proportion of hemicellulose increased (Asem et al. 2018). The moisture uptake is a crucial factor that determines the rate of degradation of a given product.

**Table 3. Water Vapor Permeability of the Hemicelluloses Films**

<table>
<thead>
<tr>
<th>Hemicelluloses Film</th>
<th>Water Vapor Permeability(kg<em>am/m²</em>s*Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100CMC-MMT</td>
<td>1.075 ± 0.08 × 10⁻¹²</td>
</tr>
<tr>
<td>20H-80CMC-MMT</td>
<td>1.150 ± 0.12 × 10⁻¹²</td>
</tr>
<tr>
<td>40H-60CMC-MMT</td>
<td>1.110 ± 0.15 × 10⁻¹²</td>
</tr>
<tr>
<td>60H-40CMC-MMT</td>
<td>1.057 ± 0.21 × 10⁻¹²</td>
</tr>
<tr>
<td>80H-20CMC-MMT</td>
<td>1.220 ± 0.11 × 10⁻¹²</td>
</tr>
</tbody>
</table>

**Physicochemical Analysis of the Biocomposite Films**

The FTIR spectra of the MMT modified hemicelluloses-based nanocomposite films are shown in Fig. 3. The characteristic absorption of the modified hemicelluloses based groups are shown on the IR spectrum peak at 3516 and 3231 cm⁻¹ and corresponded to the -OH stretching bond of the hemicellulose-based composite. The effect of hemicellulose loading in the nanocomposite was monitored in the fingerprint region by the appearance and disappearance of peaks. The new and strong absorption band at 2375 cm⁻¹ confirmed the stretching vibration of the C-H stretching leading to strong compatibility of the composite at higher filler loading. Moreover, peaks at 1727 cm⁻¹ and 1517 cm⁻¹ attributed to carbonyl (C=O) and C=C stretching from CMC, respectively, but disappeared as the hemicellulose addition increased due to the intermolecular rearrangement.

![FTIR spectra of nanocomposite films](image_url)

Fig. 3. FTIR spectra of nanocomposite films at (a) 100CMC-MMT, (b) 20HMMT-80CMC, (c) 40HMMT-60CMC, (d) 60HMMT-40CMC and (e) 80HMMT-CMC20
Peaks in the range of 1000 to 1150 cm\(^{-1}\) were C-O-C and C-O groups from carbohydrates in cellulose (Chen et al. 2016). These changes are attributable to a switch in the intramolecular hydroxyl-hydroxyl bonding to intermolecular hydroxyl-siloxane (Si-O-Si) hydrogen bonding. The peaks lost at 1500 cm\(^{-1}\) from film (c) to (e) indicated asymmetrical COO-stretching of CMC as the hemicelluloses loading increased. Moreover, the frequency of vibration band at 848 cm\(^{-1}\) assigned to the vibration of MMT - CMC, indicated Al-OH bonds formed strong hydrogen bonds via the hydroxyl groups of the hemicelluloses, and CMC interacted with Al on the clay platelet surface, as reported by Attaran et al. (2017).

The hydrogen bonds in the MMT-modified hemicelluloses based nanocomposite were strengthened, forming the strong interfacial attachment needed for stress transfer in 60HMMT-40CMC film. Similarly, the dual peak intensity peak appeared at 995 cm\(^{-1}\) (which later disappeared as the hemicelluloses loading increases), and the appearance of low intensity bands at 1700 to 1600 cm\(^{-1}\) were probably due to water present in the amorphous phase (Yeasmin and Mondal 2015). These changes of the IR spectra show the compatibility of both matrix and the filler components participated in the formation of the nanocomposite. Hence, the peak disappearance can be seen in Fig. 3.

**X-ray Diffraction Analysis**

The XRD pattern was performed to quantify the crystalline structure of hemicelluloses-based nanocomposite film as shown in Fig. 4. Composite film (a) shows a typical diffractogram of a CMC-MMT composite with broad diffraction peak at a \(2\theta =12.8^\circ\), \(2\theta = 20.44^\circ\), indicating partially crystalline character. CMC/MMT nanocomposite film with peaks at \(2\theta = 37.8^\circ\) and at \(38.12^\circ\), which decreases as the hemicelluloses loading increases from nanocomposite films (b-e). This is attributable to the fact that hemicellulose-based films are semicrystalline and hygroscopic. X-ray diffraction patterns of all the nanocomposite show weak peaks in the hemicelluloses-based nanocomposite films due to the amorphous nature of the hemicelluloses (Gu and Catchmark 2012). Generally, the peak exhibit different intensity from the pattern due to the number of hemicelluloses increased, the intensity of the peaks decreased.

![X-ray diffractogram for all nanocomposite film](image)

**Fig. 4.** X-ray diffractogram for all nanocomposite film; (a) 100CMC-MMT, (b) 20H-80CMC-MMT, (c) 40H-60CMC-MMT, (d) 60H-40CMC-MMT and (e) 80H-20CMC-MMT
The weak broad peak observed in all nanocomposites hemicelluloses film, suggested that the nano composite film were amorphous. The result further shows that the X-RD pattern of semi-crystalline structure at 2θ value of 39.0° for film (d) could be used to validate the highest tensile strength recorded for film 60H-40CMC-MMT, as discussed earlier. These results suggested that the crystalline structure which was mainly due to the addition of MMT polymer and explained the higher thermal temperature for film 60H-40CMC-MMT. Compatibility of the MMT-modified hemicelluloses-based nanocomposite has been seen from the results of the FTIR, and X-RD to increased strong hydrogen bonding, leading to improved tensile strength with the hemicelluloses loading through the great interaction between the two materials. On the other hand, the intensity of peaks decreased as the amount of hemicellulose increased. These results are in agreement with Migneault et al. (2015) and Adina et al. (2010). The disappearance of X-ray diffraction peaks corresponding to H-MMT-CMC films (a-e) confirms the interaction between two biopolymers. These results are supported by the work of Ju et al. (2015). This phenomenon illustrates the reduction hydrogen bonds between hydroxyls of the anhydroglucose units of cellulose.

**Mechanical Properties of the Nanocomposite Films**

The results for the mechanical properties investigated on the nanocomposite films, including the tensile strength, the tensile modulus, and the elongation at break are shown in Fig. 5.

![Fig. 5. Mechanical properties of the nanocomposite films. (a) Tensile strength and elongation at break; (b) tensile modulus. Within the panels, the samples are indicated by (a) 100CMC-MMT, (b) 20H-80CMC-MMT, (c) 40H-60CMC-MMT, (d) 60H-40CMC-MMT, and (e) 80H-20CMC-MMT](image)

Regarding the mechanical properties of hemicelluloses-based films, hydrogen bond cross-linking happens at drying temperature in the oven (Palamae et al. 2017). This has a noticeable effect on the tensile strength and elongation of the films. There was an improvement in both the tensile strength and the tensile modulus with increased hemicelluloses loading up to 60H-40CMC-MMT, as indicated in Fig. 5. This is attributable to the increase in the electrostatic interactions resulting in the compatibility of the materials with the presence of MMT, which allowed good interfacial interaction. With 60H-40CMC-MMT loading, the tensile strength and tensile modulus reached the maximum value, which was 47.53 MPa and 2.62 MPa, respectively, as a result of good interaction between the filler and the matrix (Palamae et al. 2017). This interaction is an indication of strong electrostatic interactions, which allowed good interfacial interaction resulting in better
stress transfer between the filler particles and the matrix and consequently, enhanced the tensile strength of the composite. The addition of hemicelluloses up to 80% decreased the tensile strength of the nanocomposite film, which is an indication of poor adhesion between fiber and matrix due to the lack of transfer of stress from the matrix to the fiber material. Further increases in hemicelluloses loading resulted in a gradual decrease in the mechanical properties of the nanocomposite film. This is attributable to the inability of the 80H-20CMC-MMT nanocomposite film to transfer the load during tensile loading (Inácio et al. 2017), resulting in lower tensile strength and tensile modulus. This observation was in agreement with previous research on modifying hemicelluloses film (Chen et al. 2016). However, elongation at break of the composite film decreased with the increase in hemicelluloses loading.

![Fig. 6. Tensile fracture surface images of nanocomposite films; (a) 100CMC-MMT, (b) 20H-80CMC-MMT, (c) 40H-60CMC-MMT, (d) 60H-40CMC-MMT and (e) 80H-20CMC-MMT](image)

The steady decreases in the elongation at break with increasing hemicellulose loading (Fig. 5a) is attributed to low elongation at break of natural fiber. Furthermore, the stiffness and brittleness of the nanocomposite as the hemicellulose load increased resulted in the decrease in elongation at break. This observation is similar to the a previous report (Inácio et al. 2017).
Scanning Electron Microscopy

SEM images of the nanocomposite at various hemicelluloses loadings are shown in Fig. 6 at 500× magnification. The images show very good dispersal of the filler in the matrix. The surface images show that despite the configuration, the filler-matrix materials contributed positively to the enhancement of the mechanical strength of the composite. The presence of MMT on the surface of hemicelluloses embedded with the CMC matrix improved the surface morphology of the CMC-MMT composite. The presence of MMT enhances the compatibility of the hemicelluloses fillers, which resulted in improved fiber matrix interface hence increased mechanical strength properties. Despite the lack of filler coagulations in the nanocomposite, the presence of interfacial fractures in the SEM image at the sample Film 80H-20CMC-MMT would have contributed to the mechanical strength failure resulting in the lowest value of both the tensile strength and tensile modulus.

Thermal Analysis

*Differential scanning calorimetry (DSC)*

DSC was used to study the phase transition of the hemicelluloses based biopolymer without any change in mass. DSC measures the heat flow with increasing temperature, with respect to the glass transition temperature ($T_g$) and melting temperature ($T_m$) of the nanocomposite films. The DSC data were taken from the first heating cycle and is presented in Fig. 7.

![DSC curve](image)

*Fig. 7. DSC curve of all nanocomposite film; (a) 100CMC, (b) 20H-80CMC, (c) 40H-60CMC, (d) 60H-40CMC and (e) 80H-20CMC*

The glass transition temperature ($T_g$) of the prepared nanocomposite was compared with other nano-composite films from different sources, as presented in Table 4. All samples showed a small endothermic peak at 100 °C, which was related to removal of moisture when the samples were heated. It reflects the hydrophilic nature of respective polymer (Inácio et al. 2018). The melting temperature $T_m$ of native hemicelluloses was between 200 °C and 250 °C, but it changed upon hemicelluloses modification to between 250 °C and 290 °C. This is in line with a study by Stefani et al. (2005), which reported that...
the lignocellulosic material decomposed thermochemically between 150 °C and 500 °C: hemicelluloses mainly between 150 °C and 350 °C, cellulose between 275 °C and 350 °C, and lignin between 250 °C and 500 °C.

Table 4. Comparison of the Glass Transition Temperature of Hemicellulose Films

<table>
<thead>
<tr>
<th>Hemicellulose sources</th>
<th>$T_g$ (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beechwood</td>
<td>133</td>
<td>Moine et al. (2004)</td>
</tr>
<tr>
<td>Softwood kraft</td>
<td>158</td>
<td>Laine et al. (2016)</td>
</tr>
<tr>
<td>OPEFB</td>
<td>183 to 188</td>
<td>Measured</td>
</tr>
</tbody>
</table>

This change indicates good compatibility between the MMT-modified hemicelluloses based nanocomposite. However, at high hemicelluloses loading into the matrix, there was decreased film performance in terms of physical, mechanical, and thermal stability. The glass transition temperature ($T_g$) and the thermal degradation properties are important measures of polymers, as they can predict the thermal performance of the material. Theoretically, increased molecular weight or cross-linking increases the strength and the glass transition temperature of any given polymer (Palamae et al. 2017). It is therefore likely that the molecular weight of hemicelluloses affects the properties of the produced material. The DSC results showed an increase in the $T_g$ value of 15 °C for the nanocomposite sample. The addition of MMT led to increased mechanical and thermal properties in hemicelluloses nanocomposite film. This could be due to two different reasons: (1) increased stability due to the increased molecular weight beyond the assumed molecular weight of the hemicelluloses and (2) linkages that are created between the aromatic units, causing reduced mobility of the polymer chains (Hassan and Badri 2016).

**Thermogravimetric analysis**

TGA measures the thermal stability of material by determining the mass loss with increasing temperature. Thermogravimetric analysis and the DTG profile of the nanopolymer films are shown in Figs. 8 and 9, respectively. Thermal stability can be expressed in the terms of the initial decomposition temperature (Wang et al. 2017), the temperature at onset of the decomposition, and residual content, as listed in Table 5 in conjunction with the result in Fig. 9.

Figure 8 shows the thermal stability of the nanocomposite obtained through TGA under nitrogen atmosphere. The first stage of decomposition, which is equivalent to 5% mass loss, was assigned to the evaporation of water (Garcia-Maraver et al. 2015). The temperature of 10% weight loss $T_{10}$ of the films 100CMC-MMT, 20HMMT-80CMC, 40HMMT-60CMC, 60HMMT-40CMC, and 80HMMT-20CMC occurred at 243 °C, 246 °C, 248 °C, 254 °C, and 282 °C, respectively. These results are in accord with earlier reports on hemicellulose-based film of 283 °C from aspen wood (Liu et al. 2011), 292 °C from ryegrass leaves (Liu et al. 2006), and 228 °C from wheat straw (Azeredo et al. 2015). The thermal degradation temperatures ($T_{20\%}$, $T_{50\%}$), maximum degradation temperatures ($T_{\text{max}}$), and residual weight at 700 °C that corresponds to the char residue are listed in Table 5. Notably, the $T_{\text{max}}$ of this study was between 300 and 304 °C, which was similar to Chen et al. (2016) with lesser residue at 700 °C. However, the hemicellulose-based film showed improvement in $T_{\text{max}}$ compared with CMC-MMT film.

In the case of polymer nanocomposites, the improvement in thermal stability could be attributed to uniform dispersion of nanofiller in the matrix. A similar conclusion was drawn from other studies (Benhamou et al. 2015).
Fig. 8. TGA of nanocomposite films; (a) 100CMC-MMT, (b) 20HMMT-80CMC, (c) 40HMMT-60CMC, (d) 60HMMT-40CMC and (e) 80HMMT-20CMC

Fig. 9. DTG of nanocomposite films; (a) 100CMC, (b) 20H-80CMC, (c) 40H-60CMC, (d) 60H-40CMC and (e) 80H-20CMC
**Table 5.** Thermal Properties of Hemicelluloses Based Nanocomposite Films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Degradation Temperature (°C)</th>
<th>Residual Weight (%) at 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{20}$</td>
<td>$T_{50}$</td>
</tr>
<tr>
<td>100CMC</td>
<td>241</td>
<td>291</td>
</tr>
<tr>
<td>20H-80CMC</td>
<td>262</td>
<td>280</td>
</tr>
<tr>
<td>40H-60CMC</td>
<td>194</td>
<td>279</td>
</tr>
<tr>
<td>60H-40CMC</td>
<td>194</td>
<td>279</td>
</tr>
<tr>
<td>80H-20CMC</td>
<td>147</td>
<td>263</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

1. Eco-friendly nanocomposite films were successfully prepared from the combination of the CMC and premixed MMT/hemicellulose with particle size of 89.5 nm, resulting in good barrier properties for low to moderate relative humidity applications.
2. The 60H-40CMC-MMT nanocomposite film gave the best physico-chemical, mechanical, thermal, and barrier properties, while greater hemicelluloses loading gave a poor result.
3. The SEM and FTIR studies confirmed the compatibility of the blended materials.
4. A uniform dispersion of fillers was expected for film 60H-40CMC-MMT due to the interlayer spacing of the MMT, leading to more intercalation, which in turn increased the tensile strength of the nanocomposites film.
5. The nanocomposite film showed high transparency, good thermal behavior, and poor water vapor permeability with the hemicelluloses loading.
6. The rate of weight loss was dependent on the hemicelluloses content, whereby the weight loss increased with additional hemicelluloses.
7. The result shows that the 2% MMT inclusion in the composite formulation was able to improve the functional properties of the hemicellulose-based nanocomposite films, hence reducing the water vapor permeability.

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