# Development of Seaweed-based Bamboo Microcrystalline Cellulose Films Intended for Sustainable Food Packaging Applications

D. Hermawan,<sup>a</sup> Tze Kiat Lai,<sup>b</sup> Shima Jafarzadeh,<sup>c</sup> Deepu A. Gopakumar,<sup>b</sup> Hasan. M.,<sup>d</sup> F. A. T. Owolabi,<sup>b</sup> N. A. Sri Aprilia,<sup>e</sup> Samsul Rizal,<sup>f</sup> and H. P. S. Abdul Khalil <sup>b</sup>\*

Seaweed bio-composite films with different proportion of Lemang and Semantan bamboo microcrystalline cellulose (MCC) were fabricated via solvent casting. The seaweed/MCC composite films were flexible, transparent, and slightly yellow. The MCC particles further enhanced mechanical properties and opacity of films. The thermal stability of seaweed films was moderately improved upon addition of bamboo MCC particles. Bamboo MCC was found to be comparable to commercial MCC in reducing the water vapor permeability (WVP), water solubility (WS), and moisture absorption capacity (MSC) of seaweed films. The tensile strength (TS) of seaweed films was increased by 20 to 23% with addition of up to 5% MCC particles. In addition, bamboo MCC efficiently reduced the WVP of seaweed films comparable to commercial MCC particles. The WS of seaweed films was decreased by 10 to 19% with addition of 1% MCC particles loading. Lemang bamboo MCC (SB-MCC) was remarkably reduced the moisture absorption capacity (MAC) of films up to 25% with inclusion of only 1% MCC. Morphological analysis via Scanning Electron Microscopy (SEM) confirmed that there was homogeneous dispersion of MCC particles in the films. MCC particles improved the mechanical, thermal, and optical properties of seaweed films making them more suitable for food packaging applications.

Keywords: Edible seaweed; Bamboo; Microcrystalline cellulose; Thermal stability; Food packaging

Contact information: a: Department of Forest Product, Faculty of Forestry, Kampus IPB, Darmaga, Bogor Agricultural University, Bogor 16001, West Java, Indonesia; b: School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia; c: Food Biopolymer Research Group, Food Technology Division, School of Industrial Technology, University Sains Malaysia, 11800, Penang, Malaysia; d: Chemical Education Department, Universitas Syiah Kuala, Jln. Tgk. Daud Beureueh Darussalam Banda Aceh, 23311 Indonesia; e: Chemical Engineering Department, Universitas Syiah Kuala, Darussalam, 23111 Banda Aceh, Indonesia; f: Mechanical Engineering Department, Universitas Syiah Kuala, Darussalam, Banda Aceh, Indonesia; \*Corresponding author: akhalilhps@gmail.com

# INTRODUCTION

With respect to severe ecological adverse impacts and particularly environmental pollution, it seems vitally important to replace regular petrochemical-plastics with the latest effective, eco-friendly, and biodegradable materials. There has been increasing attention to preparing bio-based products and creative processing technologies that contribute to sustainability and decrease fossil fuel use. Recently biopolymers have gained considerable attention due to their bio-degradable and eco-friendly nature. Nowadays, both polyesters and polysaccharides are the main sources of gaining the regular biodegradable polymers (Jafarzadeh *et al.* 2017).

Seaweed is an affordable source of polysaccharide biomass, which is abundant, sustainable, and green. It is a significant source of natural biopolymer that has been widely used throughout the world. The main derivatives of seaweed (*e.g.* alginate and carrageenan) have been mainly employed in agricultural, cosmetics, packaging, pharmaceuticals, and food due to their impressive phycocolloids, biodegradability, high accessibility, and high organic content (Abdul Khalil *et al.* 2018a). Seaweed phycocolloids are popular for their colloid system either in a gel form or solubilized particles as they have exposure to water. However, they are reported to be naturally hydrophilic. As a result, they develop weak mechanical and water barrier properties. Because of this, those bio-based polymers are usually mixed and strengthened with other fillers in order to promote their applications. It is not feasible that bio-based polymers could fully replace synthetic polymers; however, being biodegradable in nature they could help solve the waste problem which would probably benefit both consumers and manufacturers (Abdul Khalil *et al.* 2012, 2018a).

Fillers obtained from cellulosic fibers are promising for the development of sustainable natural bio-based film due to their abundant, cost effective, and eco-friendly nature. Cellulose is the most popular biopolymer and the key ingredient in all fiber source, and it is chemically formed by linear carbohydrate polymers chains which are comprised of  $\beta$ -D,1,4 glucose unit connected together by glycosidic linkages (Abdul Khalil *et al.* 2012; Abdul Khalil *et al.* 2018a)

Microcrystalline cellulose (MCC) is a naturally occurring substance obtained from purified and partially depolymerized cellulose (Trache *et al.* 2016). Cellulose consists of crystalline and amorphous regions. The latter, is readily hydrolyzed when subjected to strong acid and mechanical forces (Haafiz *et al.* 2013). This odorless, tasteless, and whitish cellulose crystalline powder exhibited strong mechanical properties, low density, less/non-abrasive behavior, high reactivity, renewability and biodegradability compared to other fillers such as silica, glass fibers, carbon black, *etc.* (Ashori and Nourbakhsh 2010; Ibrahim *et al.* 2013). Cellulose crystalline powder is broadly employed in different fields such as cosmetic, pharmaceutical, polymer, and food composite industries as thickeners, binder, reinforcement, and stabilizers agent (Trache *et al.* 2016).

Bamboo is an abundant and fast-growing plant in tropical areas. It is known as a great green source of MCC (microcrystalline cellulose) on the account of its fast-growing nature and affordable cost compared to other wood species. Literature has shown that bamboo species such as *Rawnal* bamboo (*Dendrocalamus longispathus*) and *Muli* bamboo (*Melocanna baccifera*) could be fascinating sources from which to isolate MCC. Thus, there has been a growing research on the development of bamboo-reinforced composites over the last decades (Shojaee-Aliabadi *et al.* 2014).

To the best of our knowledge, there has been limited research on the application of microcrystalline cellulose (MCC) extracted from two bamboo species, namely *Lemang* bamboo (*Schizostachyum brachycladum*), and *Semantan* bamboo (*Gigantochloa scortechinii*) as reinforcing material at different loading concentrations and comparing with commercial microcrystalline cellulose (C-MCC) as a filler for the preparation of films from seaweed. Hence, the objective of present study was to develop seaweed-based films from raw seaweed that incorporated with MCC fillers derived from *Semantan* bamboo MCC (SB-MCC), *Lemang* bamboo MCC (GS-MCC), and commercial microcrystalline cellulose (C-MCC) for potential packaging applications. Moreover, the effect of different bamboo MCC particles loading as compared to C-MCC on mechanical, thermal, morphological, physico-chemical and optical properties of seaweed/MCC composite films were also investigated using several analytical tools including Fourier transformed infrared

spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The overall findings were discussed comprehensively.

# EXPERIMENTAL

#### Materials

Edible *Kappaphycus alvarezii* seaweeds were purchased from Green Leaf Synergy Sdn. Bhd. (Tawau, Sabah, Malaysia). Both *Semantan* bamboo and *Lemang* bamboo were obtained from locals at Hulu Langat and Taman Melawati Area (Kuala Lumpur, Selangor, Malaysia). Commercial cellulose microcrystalline powder (cotton linters) supplied by Sigma Aldrich (USA) which denoted as (C-MCC) was used as reference. All the following chemicals used in this study were of analytical grade (AR); sodium hydroxide (NaOH) pellet, hydrochloric acid (HCI) (37 %), and glycerol (plasticizer)

#### Isolation of MCC from Lemang and Semantan bamboo

The MCC isolation from bamboo strips was achieved by processes including pulping, bleaching, and acid hydrolysis. 500 g of bamboo chips (3 x 2 cm) were cut using a band saw; they were then pulped with 23% of sodium hydroxide (NaOH) with 0.1% anthraquinone (additives) at a solid to liquid ratio of 1:7. After that, they were kept at temperature of 160 °C for 2 hours (Abdul Khalil *et al.* 2018a). The obtained bamboo pulps were bleached with 3 g of sodium chlorite and 5% acetic acid for 2 hours at 85°C in order to remove all lignin; during such treatment the material turned white based on the method of Suvachitanont and Ratanapan (2011). Later, 17.5% sodium hydroxide (NaOH) was used to treat the white bleached pulp at 80°C for 1 hour to obtain high purity  $\alpha$ -cellulose on the basis of the Pachuau *et al.* (2014) method. Finally, using the method of Chuayjuljit *et al.* (2010), the bamboo  $\alpha$ -cellulose was exposed to acid hydrolysis with 2.5 N HCI at 100°C for 30 minutes with constant agitation with a liquor ratio of 1:25 in order to yield bamboo microcrystalline cellulose (MCC). The yield of MCC obtained from *Lemang* and *Semantan* bamboo was 82.58% and 83.37%, respectively.

#### Fabrication of edible seaweed/microcrystalline cellulose composite films

Seaweed/MCC composite films were fabricated using a solvent casting method based on (Abdul Khalil *et al.* 2018a). Approximately 4 g (oven-dried weight) of clean raw seaweed were dissolved in distilled water (200 mL) with 2.0 g of glycerol as plasticizer on a heating plate. The MCC particles (C-MCC, SB-MCC and GS-MCC) were added into the solution at different loadings of (0%, 1%, 3%, 5%, 7%, 10%, 15%) based on the dry weight of the seaweed (wt. %). Then, the mixture was heated at 85 °C for about 1 hour with constant stirring in order to obtain a homogeneous solution. Before casting, the hot solution was settled down in room temperature for few minutes before casting into a casting tray (31 cm x 23 cm) and oven-dried overnight in a ventilated oven at 35 to 45 °C. The completely dry seaweed/MCC composite films could be easily peeled off from the plate. All dry seaweed/MCC composite films were straight away conditioned in a desiccator at 50% RH in order to maintain the integrity of the film for further analysis and used.

#### **Characterization of Seaweed Based Bamboo Microcrystalline Cellulose films** *Film thickness*

The thickness values of the neat seaweed and seaweed/MCC composite films were measured with a precision digital micrometer to the nearest 0.001 mm at random positions of each film at room temperature. The film thickness (mm) results were expressed in terms of mean  $\pm$ standard deviation (SD).

# Thermal properties

The residual (%), the maximum temperature ( $T_{max}$ ) of decomposition, and the onset temperature ( $T_{onset}$ ) were measured via Thermogravimetric Analysis (TGA), relying on Mettler-Toledo thermogravimetric analyser model TGA/DSC 1, Switzerland. Roughly 10 mg of films received heat from 30 °C to 800 °C under nitrogen atmosphere at the heating pace of 10 °C/min. The residue was shown as the residual after losing weight at 800 °C in percentage (%). The melting enthalpy, melting temperature ( $T_m$ ), and the onset of melting temperature ( $T_{onset}$ ) were determined using a Perkin-Elmer Differential Scanning Calorimeter (DSC) model 6, Switzerland. Nearly 10 mg of films were chopped into small pieces and packed in aluminum pans. The empty pan was considered as reference. The heating process of the films ranged from 30 °C to 350 °C under nitrogen atmosphere at the scanning rate of 10 °C/min.

## Structural analysis – Fourier transform infrared (FTIR)

An FTIR spectrophotometer (Perkin-Elmer, PC1600, USA) was used to determine the chemical functional groups in attenuated total reflectance (ATR) mode. The absorbance spectrum produced in the range between 400 and 4000 cm<sup>-1</sup> for each film was documented. Prior to FTIR analysis, the prepared films were cut in the size of 2 cm× 2 cm; they then were oven-dried at 60 °C for 24 h.

# Water solubility (WS)

The method of Jafarzadeh *et al.* (2018) was slightly modified in order to determine the water solubility (WS) of seaweed composite film. Three sample specimens (30 x 30 mm) were cut, weighed, and conditioned in a desiccator with silica gel for 3 days. After that, the pre-weight samples were soaked in a beaker that contained 80 mL of distilled water. The samples were constantly agitated (100 rpm) for 1 hour at room temperature. After immersion, the left-over pieces of film were filtered using filter paper (Whatman No 1) before being dried in an oven at 60 °C until the constant dry weight was reached. The sample's WS was measured based on Eq.1, where  $M_i$  is the initial dry weight of the film and  $M_f$  is the final dried weight of the film after immersion.

WS (%) = 
$$\frac{(M_i - M_f)}{(M_f)} \times 100\%$$
 (1)

# Moisture absorption capacity (MAC)

The method of Ghanbarzadeh and Almasi (2011) was slightly modified in order to measure the moisture absorption of seaweed composite film. Initially a 30 x 30 mm square sample was dried at 105 °C in an oven with constant weight in order to determine the film's moisture uptake. Being weighed, the film sample was placed in a desiccator which contained distilled water at room temperature. After 48 hours, the conditioned samples were taken away from the desiccator and weighed straightaway. The samples' moisture absorptions were measured on the basis of Eq. 2, where  $W_f$  stand for the film sample weight

after being exposed to 100% RH after 48 hours, and  $W_i$  stands for the sample's initial weight. All determinations were carried out in triplicate.

MAC (%) = 
$$\frac{(W_f - W_i)}{W_i} \ge 100$$
 (2)

## Color and opacity properties

The surface color of the film was measured using a chroma meter based on the CIE  $L^*$ ,  $a^*$ ,  $b^*$  color system, where  $L^*$  describes lightness (ranging from black to white),  $a^*$  and  $b^*$  describe the chromatic coordinates (ranging from -a: greenness, -b: blueness, +a: redness, +b: yellowness). The film sample was placed on the surface of a white standard background ( $L^*=93.33$ ,  $a^*=-0.89$ ,  $b^*=5.48$ ). The measurements were carried out 3 times to gain a mean result per sample. Color difference ( $\Delta E$ ) was determined based on Eq. 3, where  $L^*$ ,  $a^*$ , and  $b^*$  are the color parameter values of the standard, and values shown as L, a, and b are the color parameter values of the sample.

$$\Delta E = \sqrt{(L * -L)^2 + (a * -a)^2 + (b * -b)^2}$$
(3)

#### Morphological properties of film

The surfaces morphology of MCC particles and seaweed/MCC composite films were determined by means of scanning electron microscopy SEM EVO MA 10 (Carl-ZEISS, Germany). First, all samples were prepared by oven-dried overnight at 60 °C prior to testing. Before SEM examination, all samples were taped to the SEM pin holder with double-sided carbon adhesive tape. Then, the samples were coated with a thin layer of gold prior to imaging in order to intensify their electrical conductivity (Abdul Khalil *et al.* 2018a). The surface morphology of composite films were analyzed using 500 x magnifications at scale 300  $\mu$ m, while the surface morphology of MCC particles were analyzed using 1000 x magnifications at scale 100  $\mu$ m, with 10 to 20 kV accelerated voltage.

#### Mechanical properties of film

The mechanical properties of composite films were evaluated using a miniature tensile tester MT 1175 (Dia-Stron Instruments, UK) at room temperature based on the ASTM D882-02 (2002) standard with small modification. Composite films were cut to 1 cm x 15 cm and were conditioned at 50% RH for a week before all analyses. Tensile strength (TS), Young's modulus (YM), and elongation (E) were determined according to the standard with initial grips separation of 100 mm at applied test speed of 100 mm/min. At least five replicates were performed for each sample to obtain the mean values.

#### Water vapor permeability (WVP) of film

The water vapor transmission rate (WVTR) of film sample was determined gravimetrically at 23 °C under 50% RH conditions using polypropylene cups in accordance with the method of Ma *et al.* (2016) with small modification. Then, the WVP (g.m/m<sup>2</sup>.s.Pa x 10<sup>-10</sup>) of the films was calculated using the Eq. 4 where WVTR is the measured water vapor transmission rate (g/s/m<sup>2</sup>) through a film, *t* is the mean film thickness (m), *S* is the saturation vapor pressure (2808 Pa) at a temperature 23°C,  $R_1$  is the relative humidity at vapor source, and  $R_2$  is the relative humidity at the vapor sink.

$$WVP = (WVTR \times t) / [S(R_1 - R_2)]$$
(4)

# **RESULTS AND DISCUSSION**

## Thickness

Thickness values of seaweed films incorporated with MCC particles at different amount are shown in Table 1. The thickness of neat seaweed film increased when MCC particles levels increased. Films containing 7% MCC particles exhibited higher thickness in comparison with neat seaweed film. The thickness of neat seaweed film was 0.076 mm, and it gradually increased from 0.088 to 0.102 mm during the incorporation of 7% of different types of MCC particles. The result was possibly due to the increase of solid content of film and type of the cellulose crystal particles (Shankar and Rhim 2016). The bulky structure of MCC particles might also expand the interstitial spacing between the polymer chains within the seaweed film matrix, which eventually created a less compact structure and consequently increased the film thickness. Further, similar studies were reported about the thickness of agar film, which was increased linearly with increase in their content of crystalline cellulose (Reddy and Rhim 2014; Shankar and Rhim 2016).

# **Color and Opacity of Film**

Color and transparency are essential parameters in many applications, especially in food packaging, where visual inspection of the contents is of key relevance and could influence the opinion of consumers. Visually, the seaweed composite films prepared through solvent casting method were homogeneous and yellowish in color. Table 1 shows the surface color properties and the total color difference ( $\Delta E$ ), opacity of the composite films. Colour and opacity test are common to assess the colour tone and opacity of a film by light-transmittance. The parameter  $L^*$  represents the lightness,  $a^*$  represents the greenness-redness, where the red and green directions were denoted by a positive and a negative  $a^*$ , and correspondingly,  $b^*$  represents the blue-yellowness of the films, where blue was indicated by negative b values and yellow indicated by positive values. As shown in Table 1, the *L*-values were slightly decreased after incorporation of all MCC particles but remained between 87.57 and 90.94 without drastic changes. It can be observed that the neat film reached the highest lightness  $(L^*)$ . In other words, the neat seaweed film was brighter compared to all other seaweed-based films. Reddy and Rhim (2014) reported similar findings upon addition of cellulose nanocrystals (CNC) into the agar film. Seaweedbased films incorporated with MCC particles showed higher values in greenness and vellowness, and the values kept increasing upon the addition of MCC particles from 1% to 7%. Based on Table 1, the total color differences ( $\Delta E$ ) tended to increase due to the incorporation of different types and proportion of MCC particles. Shankar and Rhim (2016) obtained almost similar results, upon addition of MCC particles into agar film.

Opacity is an established measurement to determine the relative transparency of a film. A high value of opacity indicates that the specimens have low transparency or a more opaque nature (Abdollahi *et al.*, 2013). Opacity measurement is an important factor in film applications, especially in food packaging because it control the penetration of sunlight, fluorescent light, or incandescent light across the films; such penetration can cause deterioration, leading to discoloration and nutrient-loss due to the food due to photodegradation (Abdul Khalil *et al.* 2018b). As shown in Table 1, the opacity of neat seaweed film was  $15.05\pm0.45$  and tended to increase gradually upon addition of MCC particles. In this study, the opacity values of seaweed/MCC composite films were in the range from 14.37 to 18.37. Besides, the seaweed film incorporated with GS-MCC particles indicated slightly higher opacity than SB-MCC and C-MCC particles/seaweed composite films. The

increased opacity (reduced transparency) upon addition of MCC particles was probably due to the diffuse reflection of light by MCC particles. The particle size of MCC is higher than the wavelength of light, so one can expect the scattering of light by MCC.

Film	L	-а	+b	$\Delta E$	0	<i>T</i> /mm
СТ	90.94±0.31 <sup>i</sup>	-0.87±0.07 <sup>a</sup>	10.79±0.73 <sup>a</sup>	5.82±0.78 <sup>a</sup>	15.05±0.45 <sup>abc</sup>	0.076±0.003 <sup>a</sup>
С						
1%	90.19±0.22 <sup>ghi</sup>	-0.84±0.02 <sup>a</sup>	11.70±0.22 <sup>ab</sup>	7.00±0.31 <sup>abc</sup>	14.37±0.32 <sup>a</sup>	0.081±0.006 <sup>ab</sup>
3%	90.11±0.29 <sup>fghi</sup>	-0.72±0.02 <sup>abc</sup>	12.67±0.21 <sup>abc</sup>	7.84±0.26 <sup>abc</sup>	14.55±0.21 <sup>ab</sup>	0.083±0.010 <sup>abc</sup>
5%	89.82±0.03 <sup>fghi</sup>	-0.71±0.01 <sup>abc</sup>	13.63±0.03 <sup>bcde</sup>	8.91±0.02 <sup>bcde</sup>	15.37±0.40 <sup>abcd</sup>	0.089±0.015 <sup>abcde</sup>
7%	88.68±1.28 <sup>bcde</sup>	-0.62±0.28 <sup>abcde</sup>	16.43±2.63 <sup>fgh</sup>	11.91±2.93 <sup>fghi</sup>	15.84±0.59 <sup>abcde</sup>	0.091±0.005 <sup>abcde</sup>
SB						
1%	89.92±0.35 <sup>fghi</sup>	-0.74±0.09 <sup>ab</sup>	12.88±0.50 <sup>abcd</sup>	8.14±0.61 <sup>abcd</sup>	15.39±0.09 <sup>abcd</sup>	0.081±0.019 <sup>ab</sup>
3%	89.73±0.12 <sup>efgh</sup>	-0.72±0.04 <sup>abc</sup>	13.44±0.19 <sup>bcde</sup>	8.74±0.21 <sup>bcde</sup>	16.25±0.49 <sup>abcde</sup>	0.093±0.014 <sup>abcde</sup>
5%	87.69±0.34 <sup>ab</sup>	-0.37±0.04 <sup>ef</sup>	18.38±0.66 <sup>hi</sup>	14.08±0.74 <sup>ij</sup>	16.95±0.83 <sup>cdef</sup>	0.098±0.002 <sup>bcde</sup>
7%	87.27±0.19 <sup>a</sup>	-0.27±0.09 <sup>f</sup>	19.09±0.59 <sup>i</sup>	14.92±0.61 <sup>j</sup>	17.10±0.62 <sup>def</sup>	0.102±0.003 <sup>cde</sup>
GS						
1%	90.52±0.42 <sup>hi</sup>	-0.82±0.03 <sup>a</sup>	11.53±0.26 <sup>ab</sup>	6.68±0.41 <sup>ab</sup>	15.11±0.18 <sup>abcd</sup>	0.078±0.002 <sup>a</sup>
3%	89.00±0.73 <sup>cdef</sup>	-0.64±0.17 <sup>abcde</sup>	15.36±0.81 <sup>efg</sup>	10.79±1.03 <sup>efgh</sup>	15.59±0.35 <sup>abcde</sup>	0.081±0.001 <sup>ab</sup>
5%	88.27±0.20 <sup>abc</sup>	-0.52±0.10 <sup>bcdef</sup>	16.60±0.76 <sup>fgh</sup>	12.22±0.77 <sup>ghi</sup>	16.75±0.63 <sup>cdef</sup>	0.085±0.004 <sup>abcd</sup>
7%	87.57±0.54 <sup>ab</sup>	-0.33±0.13 <sup>f</sup>	18.05±1.43 <sup>hi</sup>	13.84±1.52 <sup>ij</sup>	18.37±1.05 <sup>fgh</sup>	0.088±0.002 <sup>abcd</sup>

|--|

Note: *L*: Lightness; -*a*: greenness; +*b*: yellowness;  $\Delta E$ : color differences; CT: Control; C: C-MCC; SB: SB-MCC; GS: GS-MCC; O: opacity; *T*: thickness; Mean ±SD values with the different superscript letter in the same column indicate that they are significantly different (p < 0.05).

# FTIR characterization of MCC particles and films

From the FTIR spectra, bamboo MCC (SB-MCC and GS-MCC) appeared to be identical to the commercial MCC (C-MCC), as shown in Fig. 1a. Based on the Fig.1a, all MCC particles displayed two major transmittance regions, the first region located at high wavenumber range, which was 2700 cm<sup>-1</sup> to 3500 cm<sup>-1</sup>, while the second region was at low wavenumber range, which was 800 to 2000 cm<sup>-1</sup>, similar to what was reported by Rosa et al. (2012). Depending on materials, the broad band with peaks located from 3300 to 3500 cm<sup>-1</sup> in all spectra were attributed to the hydrogen bonded –OH stretching vibration. Absorbances near 2900 cm<sup>-1</sup> were related to the C-H stretching vibrations (Adel *et al.* 2011; Rosa et al. 2012; Pachuau et al. 2014). A similar peak (1649 cm<sup>-1</sup>) was found in spectrum of all MCC could be due to the bending of water molecules, which is sensitive to the strong interaction between cellulose and water (Rosa et al. 2012). FTIR spectra were obtained after carefully drying process; however, water absorbed in cellulose molecules is very difficult to extract due to the cellulose-water interaction (Adel et al. 2011; Rosa et al. 2012). Similar results had been reported with other sources of MCC (Adel et al. 2011; Rosa et al. 2012; Pachuau et al. 2013, 2014). The absence of absorbances at wavenumbers around 1500 to 1562 cm<sup>-1</sup> and 1700 to 1740 cm<sup>-1</sup>, which is associated with the presence of lignin and hemicellulose for SB-MCC and GS-MCC, indicated that the bamboo MCC produced were of high purity, comparable to commercial-MCC (C-MCC) (Le Troedec et al. 2008; Setu et al. 2014). The disappearances of these peaks in bamboo MCC similar to C-MCC

indicates that most lignin and hemicellulose had been removed during the extraction process of MCC via acid hydrolysis.

The peak found at 1431 cm<sup>-1</sup> for bamboo MCC and C-MCC could probably be associated with asymmetric  $-CH_2$  bending/wagging and CH deformation/vibrations (Adel *et al.* 2011; Pachuau *et al.* 2014). Meanwhile, the peaks that appeared at 1375 cm<sup>-1</sup>, 1371 cm<sup>-1</sup>, and 1369 cm<sup>-1</sup> in C-MCC, SB-MCC, and GS-MCC was probably related to the -CH or C-O bending vibrations in the polysaccharides aromatic rings (Le Troedec *et al.* 2008). Peaks associated with the -C-O-C- stretch of the  $\beta$ -1,4-glycosidic linkage in cellulose was observed at 1165 cm<sup>-1</sup> in C-MCC and 1161 cm<sup>-1</sup> in bamboo MCC respectively. In addition, the peak that appeared at 1060 cm<sup>-1</sup> and 1058 cm<sup>-1</sup> for C-MCC and bamboo MCC was probably due to the  $-CH_2$ -O-CH<sub>2</sub> pyranose ring stretching vibration (Nasution *et al.* 2017). Lastly, the peak observed near wavenumber 896 to 898 cm<sup>-1</sup> for all MCC is assigned to the asymmetric out of plane ring stretching in cellulose due to the  $\beta$ -linkage and also to the amorphous form in the cellulose (Adel *et al.* 2011). Based on Fig.1a, the FTIR spectra observed for bamboo MCC appeared similar to the FTIR spectra shown by C-MCC. The results of FTIR spectra of bamboo MCC were similar and comparable to FTIR results for other species of bamboo reported by Pachuau *et al.* (2013, 2014).



Fig. 1a. FTIR spectra of MCC particles

FTIR analysis is regarded as a reliable and cost-effective analytical tool to identify the polymers, the functional groups, and bonding within the films. Fourier transform infrared spectroscopy (FTIR) spectra of the seaweed, seaweed/MCC composite films, and their functional groups are shown in Fig. 1b. The spectrum of seaweed composite films exhibited various characteristic peaks within the range 500 cm<sup>-1</sup> to 3500 cm<sup>-1</sup>. The broad absorption band in the region 3500 to 3000 cm<sup>-1</sup> indicate stretching and vibration of free, inter-, and intra-hydroxyl (O-H) group bonding (Kanmani and Rhim 2014a). In this study, a peak appeared at 3323 cm<sup>-1</sup> for neat seaweed films; this peak frequency was shifted to higher wavenumber from 3323 to 3331 cm<sup>-1</sup>, depending on MCC particles loading, which probably was related to O-H vibration of crystalline MCC. Moreover, the intensity of the overall O-H band absorbances (3000 to 3500 cm<sup>-1</sup>) increased, due to the formation of hydrogen bonding between –OH groups from the seaweed and MCC within the polymer matrix. Huq *et al.* (2012) has also reported the similar finding with addition of crystalline nanocellulose (NCC) into alginate film matrix.

The characteristic peak at around 2900 cm<sup>-1</sup> possibly can be attributed to the stretching of C-H groups (Shankar *et al.* 2014). Meanwhile, the peaks appeared around 1640 cm<sup>-1</sup> were probably due to stretching vibrations of the conjugated peptide bond formation by amine (NH) and acetone groups (Shankar and Rhim 2016). All composite films also exhibited peaks at 1217 to 1219 cm<sup>-1</sup>, which might due to the stretching of the sulphate group (S=O) of kappa-carrageenan in seaweed (Abdul Khalil *et al.* 2018c; Paşcalău *et al.* 2012) Asymmetric stretching vibration of the S=O bond in the region between 1210 and 1270 cm<sup>-1</sup> has been commonly found in all carrageenan types (Kanmani and Rhim, 2014a). The strong peak appearing at 1031 cm<sup>-1</sup> and 844-912 cm<sup>-1</sup> might attributed to glycosidic linkage (C-O) of 3, 6-anhydro-D-galactose, C-O-S stretching in a (1-3)-D-galactose and C-O-C stretching in 3,6-anhydrogalactose which typically referring to present of carrageenan in seaweed films (Nanaki *et al.* 2010; Sedayu *et al.* 2018). Overall, the neat seaweed film spectra and seaweed/MCC composite films spectra showed a relatively similar pattern of bands indicated the good miscibility of MCC with the seaweed polymer matrix.



Fig. 1b. FTIR spectra of seaweed/MCC biocomposite films

# **Mechanical Properties of the Fabricated Films**

The tensile strength (TS), Young's modulus (YM), and elongation (E) of composite films are presented in Table 2. It was observed that the neat seaweed film (CT) had tensile strength (TS) of  $20.06 \pm 1.47$  MPa, and it increased up to  $40.02 \pm 2.51$  MPa with 5% addition of C-MCC. In case of seaweed/SB-MCC composite films and seaweed/GS-MCC composite films, the TS increased gradually with increased concentration of SB-MCC and GS-MCC particles similar to seaweed/C-MCC composite films. The highest TS (43.12±1.86 MPa) was found at 5% SB-MCC/seaweed composite films, which was slightly higher compared to TS of seaweed/5% GS-MCC composite films (41.87±1.86 MPa) under the same condition. The improvement of TS upon addition of MCC particles could probably be due to strong hydrogen bonding between MCC and seaweed matrix. Moreover, the enhancement in mechanical strength could be also due to compatibility and favorable dispersion of MCC fillers in seaweed matrix (Abdul Khalil et al. 2017; Khan et al. 2012). The elongation (E) measures the flexibility of films before it breaks. It was found that the neat seaweed film had an elongation (E) of  $18.50 \pm 3.44\%$ . The highest E values were found at 5% C-MCC (23.14±3.19%), 5% SB-MCC (22.06±2.57%), and 3% GS-MCC (27.10±1.52%) composite films, corresponding to their TS. A similar elongation pattern corresponding to TS had been reported by (Reddy and Rhim 2014) with addition of crystallized nanocellulose in agar matrix. The young's modulus (YM) measures the degree of stiffness of a film. The young's modulus (YM) of neat seaweed film (CT) was  $0.111\pm0.02$  GPa. From the Table 2, it has shown that there was a substantial increase in the YM values of all MCC reinforced films as compared to neat seaweed film. The improvement of YM was probably due to the enhanced stiffness of films upon addition of MCC particles into seaweed matrix. Similar mechanical performance of crystalline cellulose (i.e. MCC, NCC) has been reported with other biopolymers such as agar (Huq et al. 2012; Shankar and Rhim 2016).

Samples	TS (MPa)	YM (GPa)	E (%)
СТ	20.06±1.47 <sup>bcde</sup>	0.110±0.02 <sup>ab</sup>	18.50±3.44 <sup>efgh</sup>
С			
1%	23.48±2.17 <sup>def</sup>	0.116±0.03 <sup>abc</sup>	18.02±3.33 <sup>efgh</sup>
3%	28.15±1.57 <sup>gh</sup>	0.144±0.01 <sup>abc</sup>	19.22±2.57 <sup>fgh</sup>
5%	40.02±2.51 <sup>bcd</sup>	0.163±0.04 <sup>abcd</sup>	23.14±3.19 <sup>hi</sup>
7%	31.02±2.51 <sup>h</sup>	0.206±0.10 <sup>cd</sup>	19.28±1.45 <sup>fgh</sup>
SB			
1%	25.81±3.19 <sup>fgh</sup>	0.171±0.06 <sup>abcd</sup>	13.44±1.40 <sup>bcdef</sup>
3%	39.00±3.99 <sup>ij</sup>	0.201±0.00 <sup>bcd</sup>	14.32±0.19 <sup>cdefg</sup>
5%	43.12±1.86 <sup>j</sup>	0.253±0.07 <sup>d</sup>	22.06±2.57 <sup>hi</sup>
7%	35.63±6.58 <sup>ef</sup>	0.176±0.02 <sup>abcd</sup>	10.98±2.92 <sup>abcd</sup>
GS			
1%	25.81±2.17 <sup>cdef</sup>	0.111±0.02 <sup>ab</sup>	16.74±7.74 <sup>defgh</sup>
3%	39.09±2.53 <sup>hij</sup>	0.152±0.01 <sup>abc</sup>	27.10±1.52 <sup>i</sup>
5%	41.87±1.86 <sup>h</sup>	0.131±0.01 <sup>abc</sup>	12.06±1.81 <sup>abcde</sup>
7%	35.66±6.67 <sup>h</sup>	0.112±0.01 <sup>abc</sup>	7.72±0.39 <sup>ab</sup>

Table 2. Mechanica	Properties of	<b>Composite Films</b>
--------------------	---------------	------------------------

Note: CT: Control; C: C-MCC; SB: SB-MCC; GS: GS-MCC; Mean  $\pm$ SD values with the different superscript letter in the same column indicate that they are significantly different (p < 0.05).

# **Thermal Properties of Film**

The thermal stability of seaweed and seaweed/MCC composite films was evaluated by using TGA analysis, and the results are shown in Fig. 2a,b and Table 3.



Fig. 2a TGA curve of seaweed/MCC composite films



Fig. 2b DTG curve of seaweed/MCC composite films

The initial step of decomposition occurred at around 40 to 85 °C (< 100 °C), which was due to removal of moisture from the films (Shankar and Rhim 2016). The second step of thermal decomposition began at around 160 °C and reached a maximum at around 202 °C. These findings might ascribed to the volatilization of glycerol added as a plasticizer (Harnkarnsujarit and Li 2017). Then, the third feature was also major thermal decomposition of composite films, which occurred at around 225 to 257 °C, which can be probably attributed to the thermal decomposition of seaweed, as shown in Fig. 2b and Table 3. These observations were comparable to those of Abdul Khalil *et al.* (2018c), and they showed that the thermal decomposition of seaweed polymer occurred in the range of 210 to 225 °C. Seaweed reinforced with SB-MCC and GS-MCC particles at 3%, 5%, and 7% were observed to be more thermally stable as compared to seaweed/C-MCC composite films, as shown in Fig. 2b and Table 3.

Types	1 <sup>st</sup> (°C)	2 <sup>nd</sup> (°C)	3 <sup>rd</sup> (°C)
of films	(T onset-T max)	(T onset-T max)	(T onset-T max)
N-SE	45.67-62.49	163.31-194.50	230.66-249.33
C-1	47.16-61.33	160.02-178.83	232.82-249.33
C-3	56.40-77.00	170.36-186.67	234.18-257.17
C-5	55.59-77.00	169.70-194.50	235.83-249.33
C-7	61.82-84.83	172.73-186.67	236.79-249.33
SB-1	52.57-77.00	171.35-202.33	239.69-257.17
SB-3	53.98-69.17	173.75-202.33	240.20-257.17
SB-5	43.58-69.17	166.59-194.50	240.71-257.17
SB-7	50.78-69.17	166.32-194.50	245.05-257.17
GS-1	52.21-77.00	171.52-194.50	225.63-233.67
GS-3	61.33-63.13	174.13-194.50	234.14-257.17
GS-5	55.38-77.00	170.30-194.50	235.89-257.17
GS-7	50.61-69.17	172.28-186.67	235.89-257.17
Note: N-SE: Neat seaweed; C: C-MCC; SB: SB-MCC; GS:GS-MCC			

Based on Table 3, the thermal decomposition of neat seaweed film at the third decomposition step was 230.66 to 249.33 °C, and it tended to improve when all MCC particles were added. At 7% C-MCC, SB-MCC, and GS-MCC loading, the thermal decomposition temperature was in the ranges 236.79 to 249.33 °C, 245.05 to 257.17 °C, and 235.89 to 257.17 °C, respectively, which was higher compared to thermal decomposition of the neat seaweed film. Higher thermal decomposition temperature indicated a better thermal stability of the material. In this case, the enhanced thermal stability of the fabricated seaweed based MCC composites films can be attributed to the incorporation of the highly crystalline MCC particles into the seaweed film. Similar properties had been reported by Zarina and Ahmad (2014) with addition of cellulose nanocrystals (CNC) in kappa-carrageenan films. The fourth step decomposition step observed around 300 to 400 °C by TGA analysis as shown in Fig. 2b might be due to the thermal degradation of MCC particles. Shankar and Rhim, (2016) have reported a similar observation with the addition of nanocrystalline cellulose (NCC) and microcrystalline

cellulose (MCC) in an agar film matrix. They found that nanocrystalline cellulose (NCC) and MCC tend to be thermally degraded around 330 to 360 °C.

DSC measurements were performed from 30 °C to 400 °C in order to find the melting temperature of neat seaweed and seaweed/MCC composite films (Fig. 3). Based on Table 4, the melting temperature ( $T_{onset}$ ) of neat seaweed film was 213.4 °C, and it was shifted to higher value as the MCC loading increased from 1 to 7% for all MCC types (C-MCC, SB-MCC, and GS-MCC).



Fig. 3. DSC curve of seaweed/MCC composite films

The melting temperature ( $T_{onset}$ ) for seaweed/C-MCC composite films were between 215.8 °C and 226.2 °C; however seaweed/SB-MCC and seaweed/GS-MCC showed almost similar melting temperature ranges, which were 213.8 °C to 223.8 °C and 219.0 °C to 224.5 °C. At 1% MCC loading, the melting temperature of ( $T_{onset}$ ) for seaweed/C-MCC was 215.8 °C, which is slightly higher than seaweed/SB-MCC composite films (213.8 °C) and much lower than seaweed/GS-MCC composite films (219 °C). Overall, melting temperature of seaweed/MCC composite films were higher than its neat seaweed films. This was due to the strong hydrogen bonding formed between the hydroxyl groups in seaweed polymer matrix and hydroxyl groups in MCC particles. Therefore, higher energy is required for the activation for the melting of seaweed/ MCC composite film. Based on Table 4, the melting enthalpy of neat seaweed (-18.13 J/g) was shifted to higher values (-2.79 to -4.99 J/g) when 7% of different MCC particles were added. This enhancement was due to the chain stiffening action of the MCC particles on the chains of the seaweed polymer matrix.

Types of films	Melting <i>T<sub>onset</sub></i> (°C)	Melting enthalpy $\Delta H_{m}$ (J/g)
N-SE	213.42	-18.13
C-1	215.78	-9.92
C-3	216.49	-8.47
C-5	216.93	-13.36
C-7	226.17	-4.99
SB-1	213.79	-6.73
SB-3	219.29	-5.79
SB-5	222.91	-5.01
SB-7	223.83	-2.79
GS-1	219.00	-10.06
GS-3	223.23	-7.99
GS-5	224.30	-6.49
GS-7	224.51	-4.79

## Table 4. Melting Onset and Melting Enthalpy of Seaweed/MCC Composite Films

Note: N-SE: Neat seaweed; C: C-MCC; SB: SB-MCC; GS:GS-MCC

# Surface Morphology of the Isolated MCC Particles and the Fabricated Composite Films

The SEM images of different types MCC particles are displayed in Fig. 4. As can be observed from the SEM images, both SB-MCC and GS-MCC particles showed similar morphological pattern: irregular rod shape with rough surfaces that were similar to those of MCC particles derived from *Muli* and *Rawnal* bamboo by other researchers (Pachuau *et al.* 2013, 2014).



Fig. 4. Morphological properties of (a) C-MCC, (b) SB-MCC and (c) GS-MCC particles (x 1000 magnification)

PEER-REVIEWED ARTICLE

# bioresources.com



**Fig. 5.** SEM micrographs (x 500 magnifications) of seaweed/MCC composite films incorporated with C-MCC, SB-MCC, and GS-MCC at loading: 0%, 1%, 3%, 5%, and 7% (w/w)

Moreover, both types of bamboo MCC particles also exhibited fibrous morphology, which could be probably inherited from their parent fiber. Conversely, the C-MCC particles, which also commercially available and derived from cotton, was irregular in

shape and rough in surface with more aggregates particles formation, as indicated in Fig. 4(a).

Images of surface morphology of seaweed/MCC composite films are shown in Fig. 5. As shown in Fig. 5, the neat seaweed film exhibited smooth, compact, and homogeneous surfaces. However, with the addition of microcrystalline cellulose (MCC) particles, the seaweed film surface became rougher and uneven, as indicated by circle (see Fig.5). MCC particles were seen to be embedded in the seaweed matrix. Some aggregations of MCC particles were observed present on the film surface, especially when concentration of MCC particles increased. Shankar and Rhim (2016) observed a similar pattern of surface due to addition of MCC particles into the agar matrix.

## Water Vapor Permeability (WVP) of the Fabricated Films

The WVP of the neat seaweed and seaweed/MCC composite films was determined by the gravimetric method, and the results are shown in Table 5. The WVP of neat seaweed (NE-SE) film was  $3.91\pm0.28$  g.m/m<sup>2</sup>.s.Pa, slightly decreased to  $3.82\pm0.84$ ,  $3.30\pm0.76$  and 3.38±0.17g.m/m<sup>2</sup>.s.Pa, respectively when 1% C-MCC, SB-MCC, and GS-MCC particles were incorporated into the seaweed matrix. The high WVP value of NE-SE was probably due to hydrophilic nature of seaweed. The large number of free hydroxyl groups in seaweed might enhance more interaction between seaweed and water molecules and eventually have resulted in an increase of permeation rate of water vapor through the films (Abdul Khalil et al. 2018b). The lowest WVP was obtained at 5% C-MCC, SB-MCC, and GS-MCC loadings, with WVP values of 2.48±1.12, 2.48±0.06, and 2.49±0.37 g.m/m<sup>2</sup>.s.Pa, respectively, which was about 1.43% less than the WVP of neat seaweed (NE-SE) films. The WVP decreased linearly when MCC particles are added up to 5%. Then, it increased slightly with further increases in the loading of MCC particles. However, it still was less than or comparable to the WVP value of NE-SE films. The substantial decrease in WVP of seaweed/MCC composite films may be attributed to the formation of a tortuous path introduced by impervious MCC particles and their good dispersion in the seaweed matrix (Abdollahi et al. 2013). Moreover, the hydrogen bonding interaction between the seaweed matrix and MCC leads to the decrement in the hydroxyl groups which eventually resulted in the low water vapor permeability (Shankar and Rhim 2016). However, the slightly increased of WVP after 5% MCC loading might due to the agglomeration of MCC particles in the seaweed matrix as shown in the SEM analysis. A similar pattern also had been reported by Reddy and Rhim (2014) with addition of crystallized nanocellulose (CNC) to the agar films.

Samples	C-MCC	SB-MCC	GS-MCC	
NE-SE	3.91±0.28 <sup>abcd</sup>			
1% MCC	3.82±0.84 <sup>abcd</sup>	3.30±0.76 <sup>abc</sup>	3.38±0.17 <sup>abc</sup>	
3% MCC	3.23±0.19 <sup>ab</sup>	3.25±0.30 <sup>ab</sup>	2.67±0.16 <sup>a</sup>	
5% MCC	2.48±1.12ª	2.48±0.06 <sup>a</sup>	2.49±0.37 <sup>a</sup>	
7% MCC	3.19±0.09 <sup>ab</sup>	2.66±0.57ª	3.00±0.29 <sup>abc</sup>	
Note: NE-SE: Neat seaweed; Mean $\pm$ SD values with the different superscript letter in the same column indicate that they are significantly different (p < 0.05).				

Table 5. Water Vapor Permeabilit	ty (WVP)	of Composite Films
----------------------------------	----------	--------------------

# bioresources.com

#### Water Solubility of the Fabricated Films

Water solubility of neat seaweed and seaweed/MCC composite films are displayed in Fig. 6. The WS of neat seaweed film was very high  $(95.54 \pm 3.04\%)$ , which is probably due to the hydrophilic nature of seaweed. Moreover, addition of hydrophilic glycerol in order to plasticize the seaweed film might also increase the film solubility in water. A plasticizer such as glycerol can weaken the interaction of seaweed polymer chains by opening more empty space between the chains. These in turn, promotes water diffusion into the matrix and consequently increases the solubility of plasticized seaweed film (Ramos et al. 2013). As shown in Fig. 6, addition of C-MCC, SB-MCC, and GS-MCC particles to the seaweed matrix at low concentration (1% loading) managed to decrease its WS of about 10 to 19%. Then, with further addition of C-MCC, SB-MCC, and GS-MCC (up to 7% loading) into the seaweed film resulted in the decrease of WS to  $72.43\pm4.29\%$ . 74.57±1.25%, and 85.76±1.26%, respectively. Although GS-MCC particles seen to be less efficient in reduced the film WS as compared to C-MCC and SB-MCC particles, still it managed to reduce WS of film up to about 10% lower than WS value of the neat seaweed film. Nevertheless, the decrease in WS of film upon addition of C-MCC and SB-MCC particles also indicated a strong hydrogen bond formation between the hydroxyl groups in MCC particles with hydroxyl groups in seaweed film matrix that resulted in the enhanced stability of seaweed films in water.



Fig. 6. Water solubility of seaweed/MCC composite films

#### Moisture Absorption Capacity (MAC) of Fabricated Films

Moisture absorption capacity (MAC) of neat seaweed and seaweed/MCC composite films was displayed in Fig. 7. The MAC of neat seaweed film was very high with the value of 180%, which can be attributed to the hydrophilic character of seaweed because of its large number of hydroxyl groups (-OH), which increase its ability to bind water. As shown in Fig. 7, at the loading of 1%, MAC of seaweed/MCC composites were reduced to 155%, 173%, and 178% due to incorporation of SB-MCC, GS-MCC, and C-MCC particles, respectively. The MAC of seaweed/MCC composite films was further decreased due to the increase of different types loading of MCC from 1% to 7%. There was an exception in the case of MAC of seaweed film incorporated with C-MCC particles; in

this case there was a plateau at loading 5% and 7%, which was probably due to effective moisture equilibrium has been achieved at that level. Despite that, the reduction of MAC upon addition of different types and proportion of MCC particles in film might due to the formation of intermolecular hydrogen bonding between the hydroxyl groups in MCC and hydroxyl groups in the seaweed polymer matrix. This intermolecular hydrogen bonding reduced the accessible hydroxyl groups in seaweed and eventually reduced the moisture absorptions of the films. Overall, the additions of MCC particles decreased the average moisture absorption compared to the neat seaweed film (without MCC particles). Wilpiszewska and Czech (2014) reported almost similar findings with addition of MCC particles in citric acid modified potato starch film.



Fig. 7. Moisture absorption capacity of seaweed/MCC composite films

# CONCLUSIONS

- 1. A series of seaweed/MCC composite films plasticized with glycerol were successfully developed using a solution casting technique.
- 2. The mechanical properties, thermal stability of seaweed/MCC composite films were improved upon addition of different types and proportion of MCC particles, and the improvement was more pronounce with seaweed/SB-MCC composite films.
- 3. The reduction of water vapor permeability (WVP), water solubility (WS), and moisture absorption capacity (MAC) of the seaweed based MCC films was due to the intermolecular hydrogen bonding between the hydroxyl groups in the MCC and hydroxyl groups in the seaweed polymer matrix, which thereby resulted in the reduction of accessible hydroxyl groups and enhanced stability in water, which usually preferable for most packaging applications.
- 4. SB-MCC and GS-MCC particles were comparable to C-MCC particles in terms of improving mechanical, thermal, and water resistance of hydrophilic seaweed films. The

FTIR analysis revealed possible intermolecular hydrogen bonding between MCC particles and seaweed.

5. Although all fabricated film showed a slightly rough surface morphology upon addition of MCC particles as observed from SEM images, the seaweed films were observed homogeneously interacted with MCC particles, which was due to the uniform dispersion of MCC particles on the surface of the neat seaweed film.

# ACKNOWLEDGMENTS

The authors would like to thank the collaboration between Department of Forest Product, Bogor Agricultural University, Indonesia and School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia that has made this work possible. The authors would like to acknowledge University Sains Malaysia, Penang, for providing the RUI Grant (1001/PTEKIND/814255).

# **REFERENCES CITED**

- Abdollahi, M., Alboofetileh, M., Behrooz, R., Rezaei, M., and Miraki, R. (2013).
  "Reducing water sensitivity of alginate bio-nanocomposite film using cellulose nanoparticles," *International Journal of Biological Macromolecules* 54(1), 166-173. DOI: 10.1016/j.ijbiomac.2012.12.016
- Abdul Khalil, H. P. S, Yap, S. W., Tye, Y. Y., Paridah, Md. T., and Samsul Rizal, M. R. N. F. (2018b). "Effects of corn starch and *Kappaphycus alvarezii* seaweed blend concentration on optical, mechanical and water vapor barrier properties of composite films," *Bioresources* 13(1), 1157-1173. DOI: 10.15376/biores.13.1.1157-1173
- Abdul Khalil, H. P. S., Bhat, A. H., and Ireana Yusra, A. F. (2012). "Green composites from sustainable cellulose nanofibrils: A review," *Carbohydrate Polymers* 87(2), 963-979. DOI: 10.1016/J.CARBPOL.2011.08.078
- Abdul Khalil, H. P. S., Chong, E. W. N., Owolabi, F. A. T., Asniza, M., Tye, Y. Y., Tajarudin, H. A., ... Rizal, S. (2018c). "Microbial-induced CaCO<sub>3</sub> filled seaweedbased film for green plasticulture application," *Journal of Cleaner Production* 199, 150-163. DOI: 10.1016/j.jclepro.2018.07.111
- Abdul Khalil, H. P. S., Lai, T. K., Tye, Y. Y., Paridah, M. T., Fazita, M. R. N., Azniwati, A. A., ... Rizal, S. (2018a). "Preparation and characterization of microcrystalline cellulose from sacred bali bamboo as reinforcing filler in seaweed-based composite film," *Fibers and Polymers* 19(2), 423-434. DOI: 10.1007/s12221-018-7672-71
- Abdul Khalil, H. P. S., Tye, Y. Y., Chow, S. T., Saurabh, C. K., Tahir, P. M., Dungani, R., and Syakir, M. I. (2017). "Cellulosic pulp fiber as reinforcement materials in seaweed-based film," *BioResources* 12(1), 29-42. DOI: 10.15376/biores.12.1.29-42
- Adel, A. M., Abd El-Wahab, Z. H., Ibrahim, A. A., and Al-Shemy, M. T. (2011).
  "Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part II: Physicochemical properties," *Carbohydrate Polymers* 83(2), 676-687. DOI: 10.1016/j.carbpol.2010.08.039
- Ashori, A., and Nourbakhsh, A. (2010). "Performance properties of microcrystalline cellulose as a reinforcing agent in wood plastic composites," *Composites Part B:*

*Engineering* 41(7), 578-581. DOI: 10.1016/J.COMPOSITESB.2010.05.004

- Chuayjuljit, S., Su-uthai, S., and Charuchinda, S. (2010). "Poly(vinyl chloride) film filled with microcrystalline cellulose prepared from cotton fabric waste: Properties and biodegradability study," *Waste Management & Research* 28(2), 109-117. DOI: 10.1177/0734242X09339324
- Ghanbarzadeh, B., and Almasi, H. (2011). "Physical properties of edible emulsified films based on carboxymethyl cellulose and oleic acid," *International Journal of Biological Macromolecules* 48(1), 44-49. DOI: 10.1016/j.ijbiomac.2010.09.014
- Harnkarnsujarit, N., and Li, Y. (2017). "Structure-property modification of microcrystalline cellulose film using agar and propylene glycol alginate," *Journal of Applied Polymer Science* 134(47), 45533. DOI: 10.1002/app.45533
- Haafiz, M. K. M., Hassan, A., Zakaria, Z., Inuwa, I. M., Islam, M. S., and Jawaid, M. (2013). "Properties of polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose," *Carbohydrate Polymers* 98(1), 139-145. DOI: 10.1016/j.carbpol.2013.05.069
- Huq, T., Salmieri, S., Khan, A., Khan, R. A., Le Tien, C., Riedl, B., Fraschini, C., Bouchard, J., Calderon-Uribe, J., Kamal, M. R., and Lacroix, M. (2012).
  "Nanocrystalline cellulose (NCC) reinforced alginate based biodegradable nanocomposite film," *Carbohydrate Polymers* 90(4), 1757-1763. DOI: 10.1016/J.CARBPOL.2012.07.065
- Ibrahim, M. M., El-Zawawy, W. K., Jüttke, Y., Koschella, A., and Heinze, T. (2013).
  "Cellulose and microcrystalline cellulose from rice straw and banana plant waste: Preparation and characterization," *Cellulose* 20(5), 2403-2416. DOI: 10.1007/s10570-013-9992-5
- Jafarzadeh, S., Alias, A. K., Ariffin, F., and Mahmud, S. (2018). "Physico-mechanical and microstructural properties of semolina flour films as influenced by different sorbitol/glycerol concentrations," *International Journal of Food Properties* 21(1), 983-995. DOI: 10.1080/10942912.2018.1474056
- Jafarzadeh, S., Ariffin, F., Mahmud, S., Alias, A. K., Hosseini, S. F., and Ahmad, M. (2017). "Improving the physical and protective functions of semolina films by embedding a blend nanofillers (ZnO-nr and nano-kaolin)," *Food Packaging and Shelf Life* 12, 66-75. DOI: 10.1016/J.FPSL.2017.03.001
- Kanmani, P., and Rhim, J. W. (2014a). "Development and characterization of carrageenan/grapefruit seed extract composite films for active packaging," *International Journal of Biological Macromolecules* DOI: 10.1016/j.ijbiomac.2014.05.011
- Kanmani, P., and Rhim, J. W. (2014b). "Properties and characterization of bionanocomposite films prepared with various biopolymers and ZnO nanoparticles," *Carbohydrate Polymers* 106, 190-199. DOI: 10.1016/j.carbpol.2014.02.007
- Khan, A., Khan, R. A., Salmieri, S., Le Tien, C., Riedl, B., Bouchard, J., Chauve, G., Tan, V., Kamal, M. R., and Lacroix, M. (2012). "Mechanical and barrier properties of nanocrystalline cellulose reinforced chitosan based nanocomposite films," *Carbohydrate Polymers* 90(4), 1601-1608. DOI: 10.1016/j.carbpol.2012.07.037
- Le Troedec, M., Sedan, D., Peyratout, C., Bonnet, J. P., Smith, A., Guinebretiere, R., Gloaguen, R., and Krausz, P. (2008). "Influence of various chemical treatments on the composition and structure of hemp fibres," *Composites Part A: Applied Science and Manufacturing* 39(3), 514-522. DOI: 10.1016/J.COMPOSITESA.2007.12.001
- Ma, Z., Ma, Y., Qin, L., Liu, J., and Su, H. (2016). "Preparation and characteristics of

biodegradable mulching films based on fermentation industry wastes," *International Biodeterioration & Biodegradation* 111, 54-61. DOI: 10.1016/j.ibiod.2016.04.024

- Nanaki, S., Karavas, E., Kalantzi, L., and Bikiaris, D. (2010). "Miscibility study of carrageenan blends and evaluation of their effectiveness as sustained release carriers," *Carbohydrate Polymers* 79(4), 1157-1167. DOI: 10.1016/J.CARBPOL.2009.10.067
- Nasution, H., Yurnaliza, Veronicha, Irmadani, and Sitompul, S. (2017). "Preparation and characterization of cellulose microcrystalline (MCC) from fiber of empty fruit bunch palm oil," *IOP Conference Series: Materials Science and Engineering* 180(1), 012007. DOI: 10.1088/1757-899X/180/1/012007
- Pachuau, L., Malsawmtluangi, C., Nath, N. K., Ramdinsangi, H., Vanlalfakawma, D. C., and Tripathi, S. K. (2013). "Physicochemical and functional characterization of microcrystalline cellulose from bamboo (*Dendrocalamus longispathus*)," *International Journal of PharmTech Research* 5(4), 1561-1571.
- Pachuau, L., Vanlalfakawma, D. C., Tripathi, S. K., and Lalhlenmawia, H. (2014). "Muli bamboo (*Melocanna baccifera*) as a new source of microcrystalline cellulose," *Journal of Applied Pharmaceutical Science* 4(11), 87-94. DOI: 10.7324/JAPS.2014.41115
- Paşcalău, V., Popescu, V., Popescu, G. L., Dudescu, M. C., Borodi, G., Dinescu, A., Perhaita, I., and Paul, M. (2012). "The alginate/k-carrageenan ratio's influence on the properties of the cross-linked composite films," *Journal of Alloys and Compounds* 536, S418-S423. DOI: 10.1016/J.JALLCOM.2011.12.026
- Ramos, Ó. L., Reinas, I., Silva, S. I., Fernandes, J. C., Cerqueira, M. A., Pereira, R. N., Vicente, A. A., Pocas, M. F., Pintado, M. E., and Malcata, F. X. (2013). "Effect of whey protein purity and glycerol content upon physical properties of edible films manufactured therefrom," *Food Hydrocolloids* 30(1), 110-122. DOI: 10.1016/j.foodhyd.2012.05.001
- Reddy, J. P., and Rhim, J. W. (2014). "Characterization of bionanocomposite films prepared with agar and paper-mulberry pulp nanocellulose," *Carbohydrate Polymers* 110, 480-488. DOI: 10.1016/J.CARBPOL.2014.04.056
- Rosa, S. M. L., Rehman, N., de Miranda, M. I. G., Nachtigall, S. M. B., and Bica, C. I. D. (2012). "Chlorine-free extraction of cellulose from rice husk and whisker isolation," *Carbohydrate Polymers* 87(2), 1131-1138. DOI: 10.1016/J.CARBPOL.2011.08.084
- Sedayu, B. B., Cran, M. J., and Bigger, S. W. (2018). "Characterization of semi-refined carrageenan-based film for primary food packaging purposes," *Journal of Polymers and the Environment* 26(9), 3754-3761. DOI: 10.1007/s10924-018-1255-y
- Setu, M. N. I., Mia, M. Y., Lubna, N. J., and Chowdhury, A. A. (2014). "Preparation of microcrystalline cellulose from cotton and its evaluation as direct compressible excipient in the formulation of naproxen tablets," *Dhaka University Journal of Pharmaceutical Sciences* 13(2), 187-192. DOI: 10.3329/dujps.v13i2.21899
- Shankar, S., and Rhim, J. W. (2016). "Preparation of nanocellulose from microcrystalline cellulose: The effect on the performance and properties of agar-based composite films," *Carbohydrate Polymers* 135, 18-26. DOI: 10.1016/J.CARBPOL.2015.08.082
- Shojaee-Aliabadi, S., Mohammadifar, M. A., Hosseini, H., Mohammadi, A., Ghasemlou, M., Hosseini, S. M., Haghshenas, M., and Khaksar, R. (2014). "Characterization of nanobiocomposite kappa-carrageenan film with *Zataria multiflora* essential oil and nanoclay," *International Journal of Biological Macromolecules* 69, 282-289. DOI: 10.1016/j.ijbiomac.2014.05.015

- Suvachitanont, S., and Ratanapan, P. (2011). "Evaluation of microcrystalline cellulose from corn cob for development to the pharmaceutical industry," *TIChE International Conference* 45, 3-8.
- Trache, D., Hussin, M. H., Hui Chuin, C. T., Sabar, S., Fazita, M. R. N. R. N., Taiwo, O. F. A., and Haafiz, M. K. K. M. M. (2016). "Microcrystalline cellulose: Isolation, characterization and bio-composites application—A review," *International Journal of Biological Macromolecules* 93(September), 789-804. DOI: 10.1016/j.ijbiomac.2016.09.056
- Wilpiszewska, K., and Czech, Z. (2014). "Citric acid modified potato starch films containing microcrystalline cellulose reinforcement Properties and application," *Starch Stärke* 66(7–8), 660-667. DOI: 10.1002/star.201300093
- Zarina, S., and Ahmad, I. (2014). "Biodegradable composite films based on κcarrageenan reinforced by cellulose nanocrystal from kenaf fibers," *BioResources*, 10(1), 256-271. DOI: 10.15376/biores.10.1.256-271

Article submitted: December 19, 2018; Peer review completed: February 17, 2019; Revised version received: February 26, 2019; Accepted: March 1, 2019: Published: March 7, 2019. DOI: 10.15376/biores.14.2.3389-3410

Hermawan et al. (2019). "Seaweed-MCC films," **BioResources** 14(2), 3389-3410.