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ORIGINAL PAPER

Micro Crystalline Bamboo Cellulose Based Seaweed Biodegradable Composite Films for Sustainable Packaging Material

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Abstract
This study is aimed to fabricate and characterize the seaweed- biodegradable films incorporated with varying concentrations of microcrystalline cellulose (MCC) which was extracted from two bamboo sources: *Schizostachyum brachycladum* (BLMCC) and *Gigantochloa scortechinii* (BSMCC). Pure biodegradable seaweed film was directly fabricated from red seaweed (*Kappaphycus alvarezii*). In this demonstrated work, commercial MCC (CMCC), BLMCC and BSMCC were used to reinforce the pure seaweed bio-degradable film at different loading concentrations (0, 1, 3, 5, 7, 10 and 15%) based on the dried-weight of seaweed, for packaging applications. There was substantial improvement in the tensile strength and contact angle values while reduction in the water vapor permeability and elongation at break values with the incorporation of the CMCC, BLMCC and BSMCC into the seaweed pure film matrix, which is highly desirable for the packaging material in the current scenario. The morphology of the fabricated films confirmed that there was good dispersion of the 7% of CMCC, 5% of BLMCC and 3% of BSMCC in the pure seaweed films, which resulted in the enhanced mechanical properties. So far, this is the first report on the microcrystalline cellulose based seaweed films with excellent mechanical properties, which makes them suitable for packaging application. The demonstrated work proved that both BSMCC and BLMCC based seaweed composite films have the huge potential to be used as biodegradable packaging material for wide range of applications.

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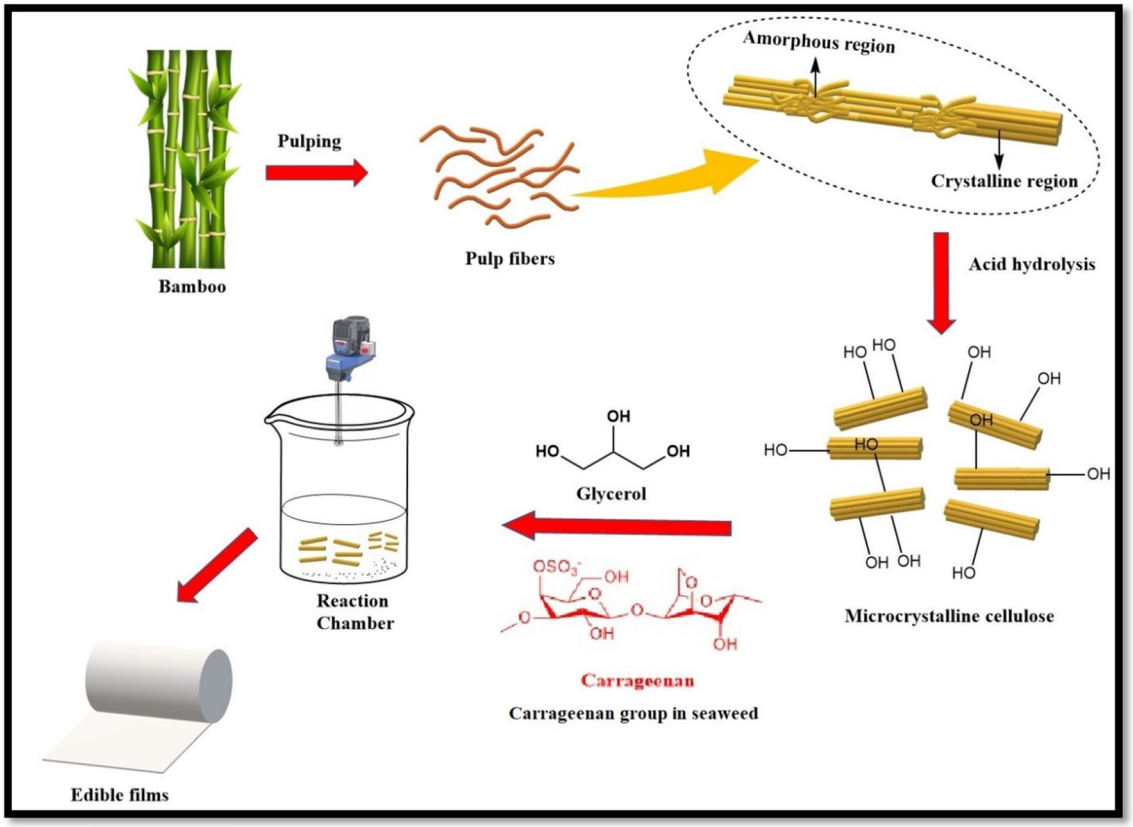
Graphical Abstract



Keywords Eco-friendly · Microcrystalline cellulose · Composite films · Sustainable packaging material

Introduction

Nowadays, the usage of synthetic polymers in daily life results in numerous environmental problems and concerns to the human society. In this context, bio-mass derived polymers have been gained considerable interest in the entire scientific research community due to its abundant availability, eco-friendly nature and sustainability. Seaweed is a sustainable, green, abundant and inexpensive source of polysaccharides biomass. Seaweed-derived polymers, such as agar, alginate and carrageenan have been widely used to form bio-films and their mechanical properties have been widely studied [1–3]. However, the hydrophilic characteristic of seaweed with poor mechanical and water barrier properties has strongly limited their packaging applications. To fix this issue, either raw seaweed or seaweed-derived polymers are always blended and reinforce with other organic and inorganic fillers that are hydrophobic or less hydrophilic to extend their applications. Previous studies have shown that, bio-films could be formed directly from raw seaweed alone or blended with fiber and their results were remarkable and comparable to bio-films formed by seaweed-derived polymers [4, 5].

The utilization of organic fillers which derived from cellulosic fibers are excellent candidates for reinforcement purposes in seaweed films due to their abundant, cost effective and eco-friendly nature. Cellulose, a core ingredient for all sources of fibers which chemically made up of linear carbohydrate polymers chains consisting of β-D, 1,4, glucose unit jointed together by glycosidic linkages, is the world most abundant biopolymer because it can find in various sources such as wood, cottons, seeds, algae, tunicates and even bacteria [6, 7]. Cellulose consists of crystalline and amorphous regions. Crystalline phases of cellulose, also called microcrystalline cellulose (MCC) or nanocrystalline cellulose (NCC) depend on their size which could be extracted from the purified cellulosic fibers (pure cellulose) via acid hydrolysis, while their counterparts (amorphous phases) are usually removed and discharged. 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. [8, 9]. It has been used widely in various fields such as pharmaceutical, cosmetic, food, and polymer composite industries as binder, thickeners, stabilizers and reinforcement agent [10]. Many previous studies have been reported about the usage of MCC as reinforcement agents in various biopolymer materials, such as polylactic acid (PLA), polyvinyl alcohol (PVA), thermoplastic starch/polybutylene adipate-co-terephthalate, etc. for making biodegradable films for packaging application [11–14]. Bamboo, which being a fast-growing plant species in the world can potentially be a good option for the future MCC production industry. Previous studies have been proved that, bamboo species like *Muli* bamboo (*Melocanna baccifera*) and *Rawnal bamboo (Dendrocalamus longispathus)* could be potentially utilized for MCC production [15, 16].

In this demonstrated work, two bamboo species, namely *Lemang bamboo (Schizostachyum brachycladum),* and *Semantan bamboo (Gigantochloa scortechinii)* were used to extract MCC. In this context, we here compared the extracted *L. bamboo* MCC (BLMCC) with and extracted *S. bamboo* MCC (BSMCC) as reinforcing material at different loading concentrations in seaweed matrix composite film while compare to commercial MCC (CMCC) reinforced seaweed films that used as references in this work. The demonstrated work proved that both BSMCC and BLMCC based seaweed composite films have the huge potential to use as biodegradable packaging material for wide range of applications.

Materials and Methods

Materials

Edible *Kappaphycus alvarezii* seaweeds were purchased from Green Leaf Synergy Sdn. Bhd. (Tawau, Sabah, Malaysia). Both *S. bamboo* and *L. bamboo* were obtained from locals at Hulu Langat and Taman Melawati Area (Kuala Lumpur, Selangor, Malaysia). The commercial microcrystalline powder (CMCC) was purchased and used for comparison purposes. Glycerol (plasticizers) and all other reagents were of analytical grade and used without further purification.

Extraction of MCC from *Lemang* and *Semantan* Bamboo

The extraction of MCC from bamboo strips could be generally divided into four steps namely pulping, bleaching, isolation of cellulose and acid hydrolysis. About 500 g of bamboo chips (3 × 2 cm; cut with a band saw) were pulped with 23% of sodium hydroxide (NaOH) with 0.1% anthraquinone (additives) at solid to liquid ratio of 1:7 under temperature of 160 °C for 2 h, based on Abdul Khalil et al. [17] method. The obtained bamboo pulp was further bleached to remove all lignin until its turn white based on Suvachittanont and Ratanapan [18] method. The white bleached pulp was further treated with 17.5% sodium hydroxide, NaOH at 80 °C for 1 h to obtain high purity cellulose according to the Pachuau et al. [16] method. Finally, the bamboo cellulose was subjected to acid hydrolysis with 2.5 N hydrochloric acid (HCI) at 100 °C for 30 min with constant agitation with a liquor ratio of 1:25 according to Chuayjuljit et al. [18] method in order to obtain final products of bamboo MCC.

Fabrication of Edible Seaweed/MCC Composite Films

Solvent casting method was employed to fabricate seaweed/MCC composite films based on Abdul Khalil et al. [17]. Four grams of *K. alvarezii* seaweed (finely cut) were dissolved in distilled water (200 ml) with 2 g of glycerol as plasticizer on a beaker. The MCC particles (CMCC, BLMCC and BSMCC) were added into the solution at different loadings (0%, 1%, 3%, 5%, 7%, 10%, 15%) based on the dried weight of seaweed (wt. %). After that, the solution mixture was heated for 1 h at 85–90 °C with constant stirring. Then the hot solution was subjected to settle down at room temperature for 30 min before casting on to a casting tray followed by drying in oven at 35–45 °C. Then, the dried films were peeled off from the tray. In order to maintain the integrity of the films, all dry seaweed/MCC composite films were conditioned in a desiccator at 50% RH before further analysis and testing.

X-ray Diffraction (XRD) Studies

The crystallinity of CMCC, BL-MCC and BS-MCC were determined by XRD (Model Bruker D8 Advance, Germany). The crystallinity of the sample data was collected at 2θ between 5 and 45°. The degree of crystallinity index was calculated based on Eq. (1) described by Das et al. [19], where I_{002} was the counter reading at peak intensity of 2θ angle close to 22° represent the crystalline region and I_{am} was the counter reading at peak intensity of 2θ close to 18° represents the amorphous region of the cellulose.

$$\text{Crystallinity Index } (\%) = \left(I_{200} - I_{am}\right)/I_{200} \times 100 \quad (1)$$

Scanning Electron Micrographs (SEM)

The morphological characteristics of the samples were investigated via scanning electron microscopy SEM EVO MA 10 (Carl- ZEISS, Germany). All samples were dried overnight at 60 °C in an oven before analysis. Then, the samples were mounted on the aluminum stub and further

coated with a layer of gold prior to imaging to enhance their electrical conductivity.

Mechanical Properties

The tensile strength (TS), elongation at break (E) was determined at room temperature based on ASTM standard method [20], with slight modification using Dia-Stron Miniature Tensile Tester equipped with adequate tensile test attachments. Rectangular strips with equal dimensions of (10 mm × 150 mm) were cut from individually prepared composite film using a utility knife. Rectangular strips of 10 × 150 mm were conditioned in desiccator for 48 h at 23 °C and 50% RH before testing. Initial grip separation was set at 100 mm and applied test speed was fixed at 100 mm/min. The TS (MPa) was determined by dividing the maximum load (N) by the initial cross section area (mm^2) of the films. The E (%) was determined by dividing the extension at the rupture of the film by the initial length of the film (100 mm) multiplied by 100 percent. The toughness was determined by the area under stress–strain curve. The young's modulus (YM) was determined based on ASTM standard method [20] by drawing a tangent to the initial linear portion of the stress–strain curve, selecting any point on this tangent and dividing the stress by the corresponding strain, whereby stress equivalent to (forces/cross-sectional area); while strain equivalent to (extension length/original length). The result was expressed in gigapascals (GPa).

Contact Angle Studies of Fabricated Composite Films

The contact angle (CA) of water on the film surface was measured using CA analyzer (KSV CAM 101; KSV Instruments Ltd., Finland) at room temperature. A water drop of 6 µl was placed on the surfaces of film using a micro syringe. All film samples were placed on the movable sample stage leveled horizontally before measurement. The CA was measured on both sides (left and right) of the drop and their values were averaged. For each film sample, at least 5 measurements were taken, and their results were averaged.

Water Vapor Permeability (WVP)

Water vapor transmission rate (WVTR) of film was determined at a temperature of 23 °C under 50% relative humidity (RH) according to Ma et al. [21] method. Then, the WVP ($gm/m^2sPa \times 10^{-10}$) of the films was calculated using the Eq. (2) where, WVTR was the measured water vapor transmission rate ($g/s/m^2$) through a film, t was the mean film thickness (m), S was the saturation vapor pressure (2808 Pa) at a temperature 23 °C, R_1 was the relative humidity at vapor source, and R_2 was the relative humidity at vapor sink.

$$WVP = (WVTR \times t) / S(R_1 - R_2) \quad (2)$$

Soil Burial Test

All the film samples (30 mm × 30 mm) from different formulation were weighed for determination of initial weight (M_0) before buried in the container under 5 cm of soil with a relative humidity (RH) of soil of 30–50% at room temperature. The soil was injected with water once per 2–3 days to keep the soil moisturized and the microorganism active. At various time intervals within 7 days, samples were taken from the container, gently cleaned and dried to constant weight at 40–50 °C for 24 h and conditioned inside desiccator at 50% RH and 9.19% equilibrium moisture content (EMC) before weighed. The percentage weight loss of the sample was calculate based on the Eq. (3), suggested by Tan et al. [22], where M_0 was the initial mass of the films before the test, and M_f was the residue mass of the films after the test.

$$\text{Weight loss } (\%) = (M_0 - M_f) / (M_0) \times 100\% \quad (3)$$

Results and Discussion

Morphology Studies of *L. bamboo* MCC (BLMCC) and *S. bamboo* MCC (BSMCC)

In this study, two types of MCC were extracted from two different species of bamboo, namely *L. bamboo (Schizostachyum brachycladum),* and *S. bamboo (Gigantochloa scortechinii)* and were used as reinforcement fillers in the seaweed polymer matrix. The extracted BSMCC (*S. bamboo*) and BLMCC (*L. bamboo)* were white in colour, tasteless and odorless, with neutral pH, like commercial-MCC (CMCC) as shown in Fig. 1a–c.

Figure 1d–f show the SEM images of CMCC, BLMCC and BSMCC respectively. From this Fig. 1e and f, can be clearly seen that, both BLMCC and BSMCC displayed irregular rod shape with rough surfaces which was comparable with Pachuau et al. [16] and they observed the similar morphological pattern of MCC from *Muli* and *Rawnal* bamboo [15]. From Fig. 1d, it was observed that, the CMCC were agglomerated into larger particles with rougher surface when compared to the BLMCC and BSMCC. The morphological difference between extracted bamboo (BLMCC and BSMCC) and CMCC were might be due to the difference in the source of raw materials and the method of MCC extraction [16].

XRD Studies of *L. bamboo* MCC (BLMCC) and *S. bamboo* MCC (BSMCC)

Figure 2 shows the XRD patterns of CMCC, BSMCC and BLMCC. Segal method was used to determine the

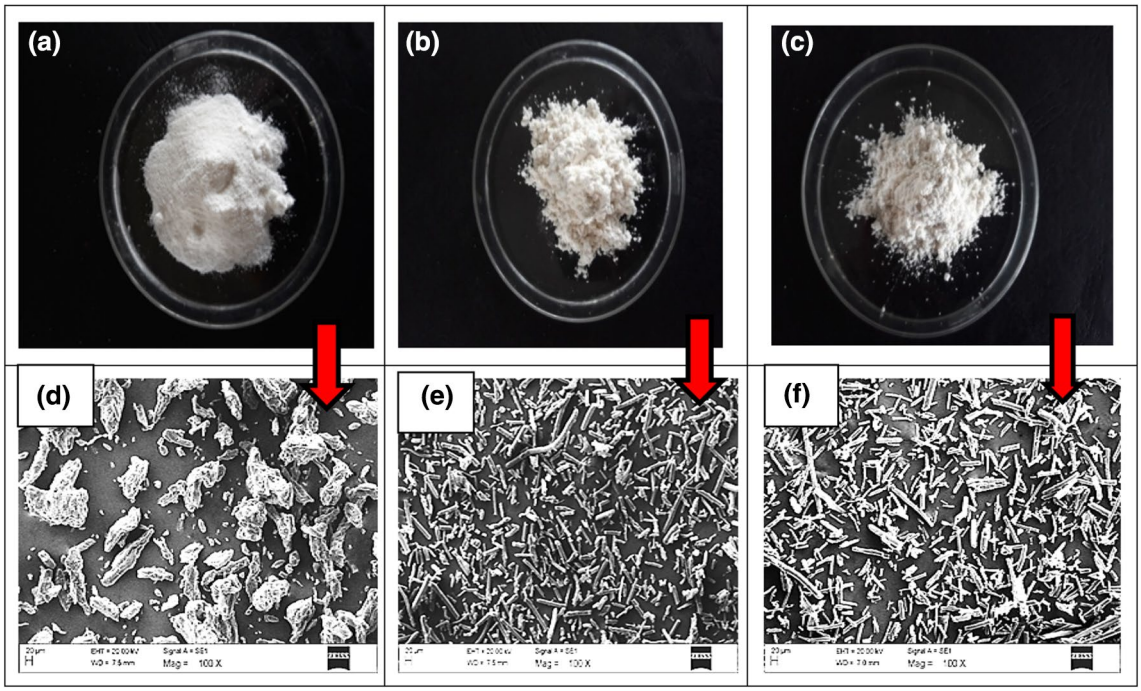


Fig. 1 Digital images of **a** CMCC, **b** BLMCC, **c** BSMCC and SEM images of **d** CMCC, **e** BLMCC, **f** BSMCC

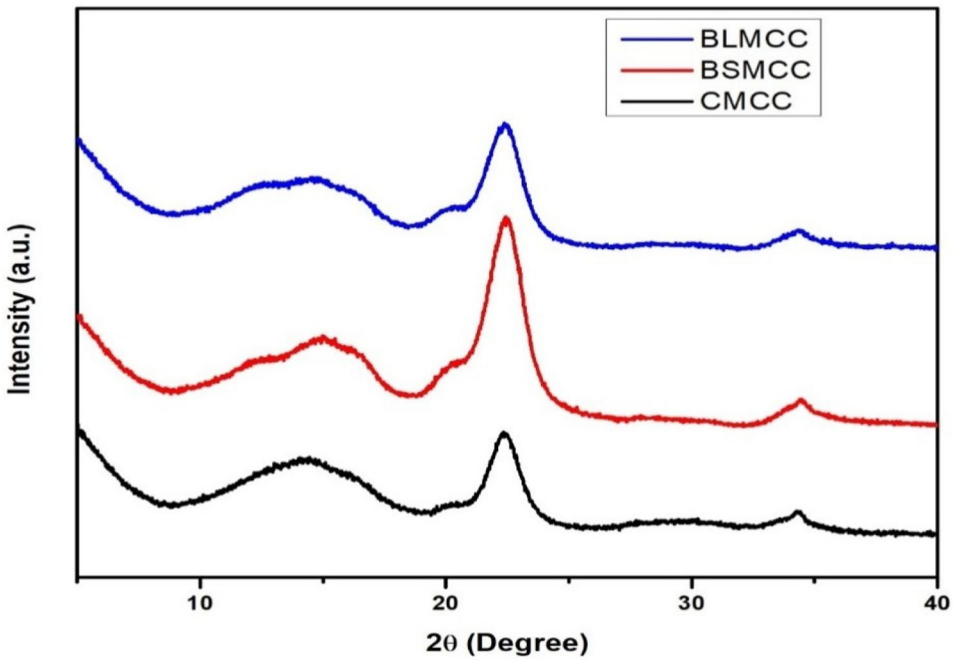


Fig. 2 XRD patterns of CMCC, BSMCC and BLMCC

crystallinity index (CrI) of the CMCC, BSMCC and BLMCC from the given Eq. 4 [19, 23]

$$\mathrm{CrI} = \left[\left(\mathrm{I}_{200} - \mathrm{I}_{\mathrm{AM}}\right)/\mathrm{I}_{200}\right] \times 100 \quad (4)$$

where, CrI denotes the relative degree of crystallinity, I_{200} is the maximum intensities of the 200-lattice diffraction at $2\theta = 22.18°$, and I_{AM} is the intensity of diffraction at $2\theta = 15.36°$. I_{200} represents both crystalline and amorphous regions, while I_{AM} represents only the amorphous portion. The obtained crystallinity index of CMCC, BSMCC and BLMCC were 56.37, 71.82 and 63.18% respectively. The differences in the crystallinity index might be due to the

difference of MCC sources and their processing method. It is worth to mentioned that, the extracted MCC from both bamboo showed higher crystallinity than commercial CMCC. Despite that, in Fig. 2 all samples exhibited a major crystalline peak at around $2\theta = 22°$, which typically represents the cellulose I structure, indicating that the crystal integrity has been maintained [24].

Fracture Morphology Studies of Seaweed/MCC Composite Films

Figure 3 shows the fracture morphology of seaweed composite films incorporated with 3% BSMCC, 5% BLMCC and 7% CMCC particles. From the Fig. 3, the pure seaweed film exhibited smoother and compact surfaces than all MCC reinforced films. But, upon the addition of different proportion and types of MCC, the film fracture surfaces became rougher and exhibited ranged waves as shown in Fig. 3b–d. The pure seaweed exhibited smoother surface and brittle in nature. As a result, the tensile strength (TS) and Young's modulus (YM) were found lower in pure seaweed films as compared to MCC reinforced seaweed composite films as given in the Table 1. However, the incorporation of MCC into the seaweed matrix resulted in the formation of voids, which is shown in Fig. 3b–d.

From Fig. 3b, seaweed +7% CMCC composite film, it was very evident about the void and cavity formation which resulted in the lower tensile strength (31.02 ± 2.51 MPa) compared to seaweed + 5% BLMCC (41.87 ± 1.86 MPa) and seaweed + 3% BSMCC (39.09 ± 2.53 MPa) as given in the Table 1. These observations were similar to Abdul Khalil et al. [5] with the addition of oil palm shells (OPS) nanofillers into the seaweed matrix.

Mechanical Properties of Seaweed/MCC Composite Film

Table 1 shows tensile strength (TS), elongation at break (E), young's modulus (YM) and toughness values of pure seaweed films and all MCC reinforced seaweed composite films. It was observed that the pure seaweed film had tensile strength (TS) of 20.06 ± 1.47 MPa. Incorporation of 1% BLMCC, BSMCC and CMCC caused significant improvement of TS, for about 4.79, 5.75 and 3.42%, respectively. From this data, the optimum TS values were observed for 5% BSMCC (43.12 ± 0.86 MPa), 5% BLMCC

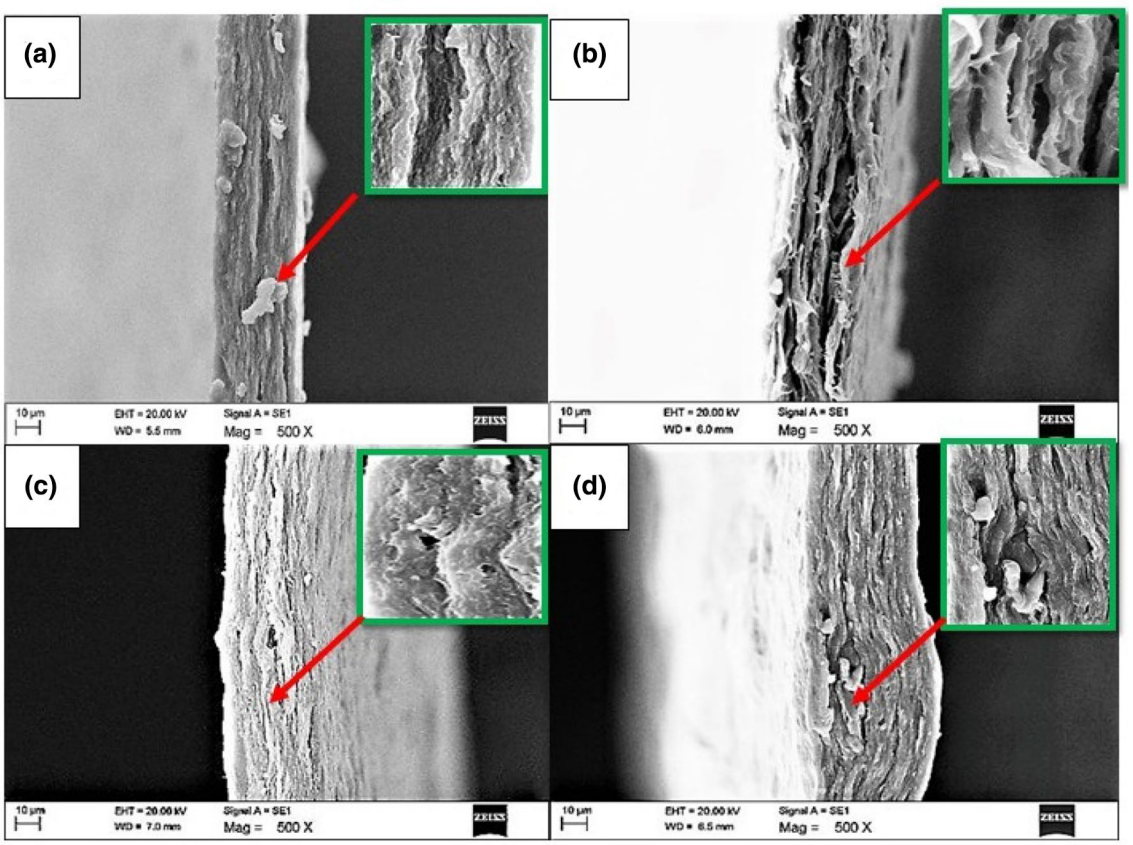


Fig. 3 SEM images of fractured surfaces of **a** pure seaweed film, **b** seaweed + 7% CMCC, **c** seaweed + 5% BLMCC and **d** seaweed + 3% BSMCC

Table 1 Tensile strength, elongation at break and Young's modulus values of pure seaweed films and all MCC reinforced seaweed composite films, Mean ± SD values with the different superscript letter in the same column indicate that they are significantly different ($p < 0.05$)

Samples	TS (MPa)	YM (GPa)	E (%)	Toughness (N)
Pure seaweed films	20.06 ± 1.47^{bcde}	0.111 ± 0.02^{ab}	18.50 ± 3.44^{efgh}	1.33 ± 0.39^{ab}
CMCC				
1%	23.48 ± 2.17^{def}	0.116 ± 0.03^{abc}	18.02 ± 3.33^{efgh}	1.47 ± 0.39^{ab}
3%	28.15 ± 1.57^{gh}	0.144 ± 0.01^{abc}	19.22 ± 2.57^{fgh}	1.58 ± 1.00^{ab}
5%	35.66 ± 6.67^{h}	0.163 ± 0.04^{abcd}	23.14 ± 3.19^{hi}	4.18 ± 1.13^{cde}
7%	31.02 ± 2.51^{h}	0.206 ± 0.10^{cd}	19.28 ± 1.45^{fgh}	4.06 ± 0.88^{cde}
10%	21.71 ± 2.65^{fg}	0.161 ± 0.03^{abcd}	18.90 ± 1.75^{fgh}	0.88 ± 0.19^{ab}
15%	13.69 ± 0.98^{def}	0.144 ± 0.00^{abc}	20.14 ± 1.34^{gh}	0.61 ± 0.09^{a}
BLMCC				
1%	24.85 ± 3.19^{ef}	0.171 ± 0.06^{abcd}	16.74 ± 7.74^{defgh}	1.91 ± 0.76^{ab}
3%	39.00 ± 3.99^{gh}	0.201 ± 0.00^{bcd}	14.32 ± 0.19^{cdefg}	2.59 ± 0.23^{bcd}
5%	41.87 ± 1.86^{h}	0.253 ± 0.07^{d}	27.10 ± 1.52^{i}	4.48 ± 0.42^{e}
7%	35.63 ± 6.58^{ef}	0.176 ± 0.02^{abcd}	19.28 ± 3.48^{fgh}	2.56 ± 0.98^{bcd}
10%	24.87 ± 7.17^{def}	0.135 ± 0.02^{abc}	10.98 ± 2.92^{abcd}	1.59 ± 0.67^{ab}
15%	17.21 ± 2.76^{ab}	0.129 ± 0.02^{abc}	8.73 ± 3.19^{abc}	0.99 ± 0.37^{ab}
BSMCC				
1%	25.81 ± 2.17^{cdef}	0.111 ± 0.02^{ab}	13.44 ± 1.40^{bcdef}	1.44 ± 0.24^{ab}
3%	39.09 ± 2.53^{h}	0.152 ± 0.01^{abc}	12.06 ± 1.81^{abcde}	2.21 ± 0.88^{ab}
5%	43.12 ± 0.86^{ab}	0.131 ± 0.01^{abc}	22.06 ± 2.57^{hi}	4.29 ± 0.43^{de}
7%	40.02 ± 2.31^{bcd}	0.112 ± 0.01^{abc}	8.62 ± 2.25^{abc}	2.42 ± 0.88^{abc}
10%	30.21 ± 3.67^{abc}	0.101 ± 0.02^{a}	7.72 ± 0.39^{ab}	1.01 ± 0.55^{ab}
15%	25.89 ± 1.33^{a}	0.074 ± 0.04^{a}	6.64 ± 1.79^{a}	0.63 ± 0.28^{ab}

(41.87 ± 1.86 MPa) and 5% CMCC (35.66 ± 6.67 MPa). It can be concluded that the all MCC reinforced seaweed composite film showed 17–20% enhancement in the tensile strength when compared to pure seaweed films and this was due to the better dispersion and compatibility of all MCC fillers to seaweed matrix. This better dispersion and compatibility resulted in the efficient and uniform load transfer from the seaweed matrix to the MCC particle network [4, 25]. In this study, bamboo MCC (BLMCC and BSMCC) showed higher TS as compared to CMCC reinforced seaweed films was probably attributed to the high crystallinity of BLMCC of BSMCC compared CMCC as verified by X-RD studies. The obtained crystallinity index of CMCC, BSMCC and BLMCC were 56.37, 71.82 and 63.18% respectively. Among the fabricated composite films, BLMCC reinforced films showed higher TS compared to other composites was due to the higher crystallinity index (71.82%) of BLMCC. Similar results were also found by Huq et al. [26] via using NCC as reinforcement fillers in alginate-based films. Beyond the optimum loading, there was a reduction in the TS, which was due to the agglomeration of MCC fillers in the seaweed matrix at higher loading of MCC fillers.

In this work, the elongation (E) value was found to be 18.50 ± 3.44% for pure seaweed films. The addition of CMCC, tend to increase the E values of seaweed films, and the highest E was found at 5% (23.14 ± 3.19%). In case of BLMCC and BSMCC reinforced seaweed films, the highest E values were observed at 5% of filler loading, correspond to their TS. The obtained E values of 5% BLMCC and BSMCC reinforced films were 27.10 ± 1.52% and 22.06 ± 2.57% respectively. The reason for this enhancement in the E value of 5% BLMCC reinforced films than BSMCC films was due to the less crystalline nature of BLMCC when compared to BSMCC which was confirmed from the crystallinity index values of BSMCC and BLMCC from XRD profiles. The crystalline BSMCC might restrict the motion of polymer chains, which resulted in the decrement in the E values when compared to BLMCC. The addition of BLMCC and BSMCC particles tend to reduce the E of seaweed films at high filler loadings (7–15%). E values were significantly reduced to 8.73 ± 3.19% and 6.64 ± 1.79% by addition of 15% of BLMCC and BSMCC, respectively. Similar work has been reported on agar biopolymer reinforced with crystallized nanocellulose (CNC) and MCC [14, 27]. The glycerol was act as a plasticizer to the films. Preliminary study showed that, seaweed films without/less plasticizer were found brittle and difficult to peel off from the casting surface after drying. In this study, the glycerol could possibly interact with seaweed polymers and thus, enhance the elongation (E) values of the seaweed films. Incorporation of MCC particles at high concentration (7–15%) could probably interrupt the seaweed-glycerol bonding and eventually reduced the flexibility of seaweed films as shown

by drastic decrease of E values in Table 1, especially for BLMCC and BSMCC reinforced seaweed films.

The young's modulus (YM) value of the pure seaweed film was found to be 0.111 ± 0.02 GPa (Table 1). From the Table 1, it is shown that there was substantial improvement in the YM value of the all MCC reinforced seaweed composite films compared to pure seaweed film. This enhancement in YM values were due to enhanced stiffness of the films upon the addition of all MCC fillers into seaweed matrix. These results were comparable with results found by Huq et al. [26] with NCC reinforced in alginate-based biodegradable composite film. Toughness is the ability of a material to absorb energy without fracture and it is the measure of area under the stress- strain curve for the material. From Table 1, the toughness of pure seaweed films was 1.44 ± 0.28 N. Incorporation of 5% CMCC, BLMCC and BSMCC into the seaweed tend to improve their toughness to 4.18 ± 1.13 N, 4.48 ± 0.42 N and 4.29 ± 0.43 N, respectively. Bamboo MCC (BLMCC and BSMCC), even at low concentration (1–5%) showed substantial enhancement in the toughness of seaweed composite films compared to CMCC. Further addition of all MCC particles (7–15%) tend to decrease in the toughness of seaweed composite films, cause the seaweed composite films to be more brittle.

Surface Hydrophobicity of Seaweed/MCC Composite Film

The pure seaweed film exhibited the water contact angle of 41.35 ± 0.73°, which indicates the hydrophilic nature of the seaweed due to the presence of hydrophilic hydroxyl groups. Incorporation of different types of MCC resulted in the reduction of film hydrophilicity as shown in the Table 2. Incorporation of 1% MCC cause significant reduction in film hydrophilicity of ($p < 0.05$), especially with BLMCC reinforced seaweed films which was about 8%. The contact angle of seaweed films had enhanced from 41.35° to 68.12 ± 0.02° with addition of 5% BLMCC. Both BSMCC and CMCC also showed enhancement of contact angle ($p < 0.05$) compared to their pure seaweed films when level of MCC loading was increased. This might be due to the formation of more intermolecular hydrogen bonding between –OH groups of seaweed polysaccharides and MCC which resulted in the reduction of free available hydroxyl groups thereby resulted in the reduction of hydrophilicity of the film. Almost similar results had been observed by Balakrishnan et al. [28] with cellulose nanofiber reinforced starch film. From this, it could be concluded that the incorporation of MCC fillers into seaweed film reduced the hydrophilicity of the seaweed film. This facilitated the reduction in the water vapor permeability, which is highly desirable for the packaging application.

Water Vapor Permeability (WVP) of Seaweed/MCC Composite Film

The water vapor permeability of different types MCC loading seaweed composite films was measured under constant conditions at 23 °C and 50% relative humidity (RH). The pure seaweed films had a high WVP (3.91 ± 0.28 gm/m^2sPa × 10^{-10}) due to its hydrophilic nature. The results showed that the addition of different types of MCC showed significant different ($p < 0.05$) on WVP values as compared to pure seaweed films. As given the Table 3, MCC fillers reinforced seaweed composite films showed reduction in the water vapor permeability compared to pure seaweed film. This decrease in the WVP of the seaweed/MCC composite film was due to the formation of tortuous path by the MCC particles in the seaweed matrix, which hinders the water vapor permeability [18, 28]. The tortuous path formation was due to the well dispersion of MCC particles in the pure seaweed matrix. However, at higher loadings of MCC particles, it shown that the WVP values have a reversed trend due to the agglomeration of MCC particles that prevents the formation of torturous path. Almost similar results were reported by Shankar and Rhim [14] where they used both MCC and NCC as reinforcement fillers in the agar polymer

Table 2 Water contact angle measurements of pure seaweed films and all MCC reinforced seaweed bio-composites films

Samples	CMCC	BLMCC	BSMCC
Pure seaweed films		41.35 ± 0.73^{b}	
1%	40.98 ± 0.13^{b}	49.31 ± 0.09^{e}	43.25 ± 0.85^{c}
3%	47.86 ± 0.26^{c}	56.19 ± 0.63^{j}	50.79 ± 0.05^{fg}
5%	59.79 ± 0.19^{ef}	68.12 ± 0.02^{m}	66.24 ± 0.08^{l}
7%	46.34 ± 0.31^{k}	54.67 ± 0.47^{c}	52.79 ± 0.06^{i}
10%	41.53 ± 0.03^{d}	49.86 ± 0.36^{ef}	47.98 ± 0.11^{hi}
15%	38.51 ± 0.89^{a}	46.84 ± 0.13^{f}	44.96 ± 0.54^{gh}

Mean ± standard deviation (SD) (°) values followed by different superscript letter in the same column indicate significantly different ($p < 0.05$)

Table 3 Effect of microcrystalline cellulose on water vapor permeability (WVP) of seaweed/MCC biocomposites films

Samples	CMCC	BLMCC	BSMCC
Pure seaweed film		3.91 ± 0.28^{abcd}	
1% MCC	3.82 ± 0.84^{abcd}	3.30 ± 0.76^{abc}	3.00 ± 0.29^{abc}
3% MCC	3.19 ± 0.09^{ab}	2.67 ± 0.57^{a}	2.37 ± 0.16^{a}
5% MCC	2.98 ± 1.12^{a}	2.46 ± 0.06^{a}	2.16 ± 0.37^{a}
7% MCC	3.77 ± 0.15^{a}	3.25 ± 0.30^{ab}	2.95 ± 0.17^{abc}
10% MCC	4.75 ± 0.46^{ab}	4.23 ± 0.21^{bcd}	3.93 ± 0.61^{cd}
15% MCC	5.44 ± 0.19^{ab}	4.92 ± 0.49^{d}	4.62 ± 0.47^{d}

Mean ± standard deviation (SD) (g.m/m^2.s.Pa x 10^{-10}) values followed by different superscript letter in the same column indicate significantly different ($p < 0.05$)

matrix. They reported that, NCC was more efficient to reduce the WVP than MCC.

Soil Burial Test of Seaweed/MCC Composite Film

Figure 4 shows the photos of before and after the soil burial test of seaweed/MCC composites films for a period of one month. In Fig. 4, sample that highlighted in red is pure seaweed films. Moreover, each set of the MCC/seaweed composite film was represented by a different colour, namely black (seaweed/CMCC), yellow (seaweed/BLMCC) and blue (seaweed/BSMCC). From Fig. 4, it shows that before the test, the seaweed/MCC film exhibited relative clear and smooth surfaces with the regular square shape. It was clearly evident from Table 4 that, the pure seaweed films were started to shrink and degraded after 7 days, which resulted in the weight loss of 37.04 ± 8.8%. The weight loss of pure seaweed films was more prominent after 14 days, which was 52.62 ± 7.3%. The hydrophilic nature of seaweed could probably account for the increased weight loss in pure seaweed films. Meanwhile, the weight loss of 30.64–51.62%, 26.35–48.08% and 33.83–50.34% were exhibited by the CMCC reinforced seaweed films, BLMCC reinforced seaweed films and BSMCC reinforced seaweed films, respectively from 7 to 14 days burial time as shown in Table 4. The weight loss found in MCC reinforced seaweed films were less prominent compared to pure seaweed films could probably due to the high crystallinity of MCC and strong hydrogen interaction between MCC particles and seaweed matrix which enhanced the rigidity of the fabricated seaweed/MCC composite films. Eventually after 1 month, all the films have undergone more shrinkage, cracks and the color change from yellowish to dark with more weight loss as shown in Table 4 and Fig. 4.

Table 4 The weight loss of seaweed/MCC films after different degradation time by soil burial test

Samples	Weight loss (%)		
Days	7	14	1 month
Pure seaweed film	37.04 ± 8.8	52.62 ± 7.3	58.54 ± 7.4
1% CMCC	33.27 ± 21	38.60 ± 25	42.19 ± 22
3% CMCC	40.67 ± 4.8	51.62 ± 4.1	54.64 ± 2.4
5% CMCC	42.28 ± 4.9	44.73 ± 5.1	49.61 ± 3.0
7% CMCC	38.89 ± 3.1	42.72 ± 2.4	47.10 ± 2.6
10% CMCC	30.64 ± 5.6	35.76 ± 7.2	41.40 ± 4.3
15% CMCC	35.76 ± 4.0	42.19 ± 3.4	46.58 ± 5.4
1% BLMCC	34.85 ± 18	48.08 ± 5.2	52.65 ± 3.9
3% BLMCC	34.05 ± 19	47.42 ± 16	58.65 ± 4.8
5% BLMCC	35.65 ± 3.2	40.96 ± 7.2	45.81 ± 2.0
7% BLMCC	40.86 ± 3.9	44.92 ± 5.6	49.60 ± 7.9
10% BLMCC	26.35 ± 18	38.89 ± 7.1	44.67 ± 2.9
15% BLMCC	34.69 ± 8.1	47.89 ± 3.3	55.69 ± 6.8
1% BSMCC	45.96 ± 7.0	49.10 ± 7.6	56.53 ± 0.7
3%BSMCC	39.25 ± 13	46.67 ± 9.3	54.02 ± 1.4
5% BSMCC	33.83 ± 8.6	49.44 ± 3.1	52.47 ± 5.4
7% BSMCC	40.30 ± 6.4	48.24 ± 5.9	50.59 ± 6.8
10% BSMCC	41.94 ± 7.2	49.43 ± 6.0	53.08 ± 8.5
15% BSMCC	37.21 ± 5.1	50.34 ± 2.9	57.49 ± 4.4

In this study, no significant changed were observed with addition of different loading and types of MCC particles to the seaweed films. All fabricated seaweed/MCC composite films tend to undergo rapid biodegradation during the test. Both seaweed and MCC fillers are bio-degradable polymers and thereby prone to microbial attack during the soil burial test. It can be concluded that, all fabricated MCC reinforced seaweed composite films are excellent candidates for packaging materials for dry stuff such as tea bag, sachet,

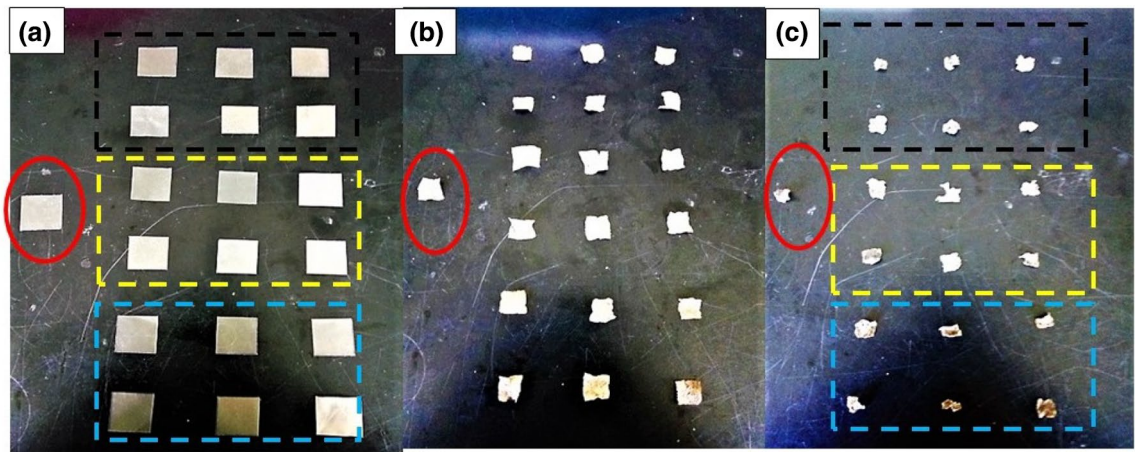


Fig. 4 Digital images of soil burial bio-degradability test of MCC reinforced seaweed composite films **a** before biodegradation test, **b** after 14 days of test and **c** after 1 month of test

food wrapper due to their biodegradable nature with good mechanical properties and low water vapor permeability.

Conclusions

Commercial MCC (CMCC), BLMCC and BSMCC were used to reinforce the pure seaweed biodegradable film at different loading concentrations (0, 1, 3, 5, 7, 10 and 15%) based on the dried-weight of seaweed, for packaging applications. All fabricated MCC based seaweed composite films showed substantial improvement in the mechanical and reduction of water vapour permeability, which is highly desirable for the sustainable packaging application in the current scenario. The incorporation of all MCC fillers into seaweed matrix polymer resulted in the enhancement of water contact angle, for CMCC 5%, BLMCC 5% and BSMCC 5% seaweed composite films; it was 66.24°, 68.12° and 59.79° respectively.

This clearly indicates that the addition of all MCC fillers reduced the hydrophilicity of the seaweed matrix film, to some extent. The water vapour permeability of the fabricated films was reduced due to the formation of tortuous path by the MCC particles in the seaweed matrix, which hinders the water vapor permeability. So far, this is the first report on the MCC based seaweed films with excellent mechanical properties, which makes them suitable for packaging application. It can be concluded that, both demonstrated BSMCC and BLMCC based seaweed composite films have the huge potential to be used as biodegradable packaging material for wide range of applications.

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