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Characterization and property investigation of microcrystalline cellulose (MCC) and carboxymethyl cellulose (CMC) filler on the carrageenan-based biocomposite film

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ABSTRACT

Hard capsule has received high demands not only in the pharmaceutical industry but also in food, cosmetics, and personal care applications. Current hard capsule made from gelatin has contributed to the rise of allergy and halal issues. Thus, many researches were looking for alternatives to produce hard capsule from natural and renewable sources such as carrageenan. In this study, carrageenan was incorporated with carboxymethyl cellulose (CMC) and microcrystalline cellulose (MCC) to toughen the carrageenan based biocomposite film and hard capsule. The cellulose filler used was expected to increase the tensile strength and viscosity properties of the carrageenan matrix due to the development of strong hydrogen bonding between the carrageenan and filler. The crystallinity and functional group properties of CMC and MCC were identified via X-ray diffraction (XRD) and Fourier transforms infrared (FTIR) analysis. Then, the hard capsule was prepared by incorporating carrageenan with isovanillin, PEG, alginic acid at different cellulose filler concentrations. The formulation solution was cast for biocomposite film development and dipped for hard capsule development. The tensile strength of the film was analyzed to study the effect of the cellulose filler on the film produced. Crystallinity result shows that CMC is an amorphous while MCC is a crystal, thus CMC has excellent solubility in water compared to MCC. Moreover, film and hard capsule mechanical properties demonstrated that Carra-CMC has the highest tensile strength in comparison to Carra-MCC. Incorporation of CMC in carrageenan biocomposite film shows a significant increment of viscosity up to 50% and the tensile strength up to 37%. The presence of main three functional groups in CMC structure increased the molecular interaction in the carrageenan biocomposite thus improve the film properties. It is predicted that a higher concentration of CMC is required to produce a more stable Carra-CMC biocomposite film and hard capsule.

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1. Introduction

Increasingly modern consumers of dietary supplements seek variety in their choices, and they are looking for products originated from natural-source ingredients concurrent with the awareness and concern on religious perspective, natural food, and vegetarian dietary requirement [1,2]. This preference also leads them to value capsules of plant origin over traditional gelatin capsules which derived from animal by-products. In order to be accepted in the marketplace, plant-based capsules must acquire the same or better properties than gelatin capsules over filling, packaging, and storage processes as well as upon oral administration by consumers. Up to the present time, numerous efforts have been extensively conducted to formulate hard capsule materials with all natural-based ingredients.

Carrageenan, a marine-derived polysaccharide has a potential to form a biopolymer film attributed to its superior gelling and high viscosity properties, which are widely used as a thickening, stabilizing, and suspending agent in the food industry [3–7]. How-

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ever, carrageenan tends to swell and not disintegrate in an aqueous medium. In order to promote the disintegration properties of carrageenan, a crosslinker is introduced in the formulation matrix that binds the polymer chains in the biocomposite physically [8]. In addition, since natural biodegradable polymer usually possesses certain unfavorable physicochemical properties, the carrageenan-based hard capsule exhibited weaker properties of low mechanical strength which restricted its applicability and feasibility in the production [5,9].

A way to solve this issue would be the development of carrageenan biocomposite with the addition of filler as a toughening agent into the formulation matrix to improve the mechanical strength of the hard capsule. There is a great deal of research interest in utilizing cellulose, the most abundant natural polymer, attributed to its excellent mechanical performance as a reinforcement to many feasibilities of application [10]. Abundant of hydrogen bonding giving an advantage on cellulose which increases the potential to create new bonding in carbohydrate polymer [11]. Hydroxypropyl methylcellulose (HPMC) is one of the most notable celluloses employed in the production of capsule shells, replacing the conventional capsules made of gelatin [12]. Even though this kind of capsule is able to meet the requirement and offer some advantages over gelatin capsules, the high cost of raw material and complex production methods giving drawbacks to the HPMC capsule [3,12].

Low cost of cellulose-based material such as microcrystalline cellulose (MCC) and carboxymethyl cellulose (CMC) with highly abundant sources offer great advantages over HPMC [13,14] . MCC is purified, partially depolymerized cellulose which is prepared by treating alpha-cellulose, mostly produced from wood pulp, with mineral acids [15]. Meanwhile, CMC is a water-soluble, anionic polysaccharide of cellulose derivative which is prepared by the reaction of monochloroacetic acid with alkali cellulose [16]. These celluloses are incorporated in the formulation of orally taken products to increase their mechanical properties by the involvement of hydrogen bonding interaction [5]. Both MCC and CMC have been approved to be used in food products since they are non-toxic, non-allergenic, and biocompatible [13,17–19]. In addition, the incorporation of MCC and CMC also improves the biodegradability of the biocomposite film, thus reduce the time taken for the film to degrade in the solvent, as being investigated in preparation of natural rubber latex film and poly(lactic acid) film [20,21].

The incorporation of cellulosic fibers in the formulation matrix has been a focus in numerous studies, intending to improve the mechanical properties of the materials. Li et al. (2015) investigated the effects of MCC content on the mechanical properties of MCC-reinforced soy protein isolate (SPI)-gelatin (MSG) film. They reported that the tensile strength of the composite film was improved about 3.5 times with the incorporation of 3.5% MCC compared to the film without MCC, inducing a relatively better film with good mechanical properties [22]. Hermawan et al. (2019) reported the improvement on the tensile strength of seaweed film by 20 to 23% with the incorporation of MCC up to 5%, which is possibly due to strong hydrogen bonding between MCC and seaweed matrix leading to compatibility and favorable dispersion of MCC fillers in the matrix [23]. In the case of CMC, it is proven to increase the tensile strength and ductility of the sodium alginate-chitosan composite film since CMC has an internal sugar ring structure, which provides a good skeleton effect as a composite structure, thus improving the internal structural stability of the composite film [24]. Similar results on the enhancement of mechanical strength are also reported with the study of kefiran-CMC film [13], corn and cassava starch-CMC film [25], and sago starch-CMC film [26], which ascribed the good intermolecular interaction between the film-forming components.

To the best of our knowledge, limited number of research examining the use of MCC and CMC in the formulation of carrageenan-based biocomposite is carried on as a reinforcement filler for the development of the hard capsule. Hence, this study focused on the effect of CMC and MCC incorporation in the carrageenan-based biocomposite with the aim to toughen the film and hard capsule. The crystallinity of the cellulose fillers is presumably affecting the physical and chemical properties of the biocomposite. The concentration of filler needs to be optimized to produce hard capsules with good dispersion of cellulose particles. While, the addition of cellulose as a filler is expected to increase the tensile strength and viscosity properties of the carrageenan matrix by creating strong hydrogen bonding between the carrageenan and the filler, thus improving the mechanical strength of the biocomposite film and the hard capsule.

2. Methodology

2.1. Materials

Refined carrageenan was obtained by CV Simpul Agro Globalindo, Indonesia. Food-grade crosslinker namely isovanillin, alginic acid, microcrystalline cellulose (MCC), and carboxymethyl cellulose (CMC) were supplied from Sigma-Aldrich, USA. Meanwhile. polyethylene glycol (PEG) as a plasticizer was obtained from Merck, Germany. All the raw materials used in this work were food grade materials.

2.2. Raw material characterization

Reinforcing fillers which are MCC and CMC have undergone phase identification analysis via crystallinity analysis and functional group determination.

For XRD using Rigaku Miniflex X-Ray Diffractometer (Miniflex II, USA), carrageenan powder was set on a sample holder to make sure all the samples exposed to the same X-ray exposure. With a wavelength of 1.54 Å, the sample was exposed to X-ray radiation using Cukα radiation filtered by a Ni filter, generated at 30 kV and 15 mA, and over a 2θ angle range of 5-50°. The crystallinity index (CrI) was calculated based on XRD peak height method published by Segal et al (1959), using the following Equation (1), where I_{002} refers to the maximum intensity of the peak corresponding to plane having the miller indices 002 (2θ = 22.3), while I_{am} is the minimal intensity of diffraction of the amorphous phase at 2θ = 34.5° [27]:

$$I_{cr} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

Meanwhile, for FTIR analysis, Perkin Elmer ATR-FTIR Spectrometer (Frontier, USA) was operated with the spectra in the range of 400 to 4000 cm^{-1}. A total of 16–32 scans were acquired at 0.15 s/scan with spectra resolution of 2–4 cm^{-1}. Meanwhile, the time step of spectral measurement was analyzed at 2.4–19.2 s/spectrum. The spectra were analyzed using OMNIC software.

2.3. Carrageenan biocomposite solution, film and hard capsule preparation

Refined carrageenan, crosslinker, reinforcing filler, PEG, and alginic acid were mixed with deionized water in a double jacketed glass reactor. The filler concentrations were varied at 0 wt%, 0.4 wt %, 1.2 wt%, and 2.0 wt%. The sample solution was mechanically stirred at 60 °C for 3 h. After the mixing process, the viscosity of the solution was measured using a Rheometer (Brookfield, Rheo 3000, USA) via a rotational measuring block method, equipped

with LCT 25 4,000,010 geometry. For each test, 16.5 mL of sample solution was transferred to the sample compartment and it was subjected to a speed of 300 revolutions per minute, with 100 MPoints at the temperature of 40 °C. As the sample solution was analyzed in triplicate, the average readings of viscosity were recorded in the units of mPas.

For film casting, 20 mL of the carrageenan biocomposite solution was cast on a stainless steel pan. The solution was dried for 16–18 h at room temperature.

Meanwhile, for hard capsule formation, a size "1″ capsule shell pin bar was dipped in the carrageenan biocomposite solution using self-fabricated capsule dipping machine. The pin bar was dried for 16–18 h at room temperature.

2.4. Carrageenan biocomposite film tensile strength analysis

The tensile strength analysis of 2 cm × 10 cm strips of carrageenan film was conducted in accordance with ASTM D882-12. The biocomposite film was analyzed using CT3 Texture Analyzer (Brookfield, USA) which was fixed with a TA-DGA fixture and 50 kg load cell. TA-DGA protrudes horizontally from the fixture. The test was operated using a target option of "distance" and test mode of "tension". The probe traveled upwards with a target value of 10.0 mm at a speed of 0.50 mm/s until the sample film was pulled apart, and the applied force was recorded.

2.5. Statistical analysis

The viscosity and mechanical analysis were performed in triplicate and the data were presented as means ± standard deviations. One-way analysis of variance (ANOVA) and Duncan's multiple range tests were conducted to determine the significant difference between the tensile strength of Carra-MCC and Carra CMC, with the level of significance set at $p < 0.05$ using IBM SPSS Statistics Version 20 software (SPSS Inc., Chicago, IL) [28].

3. Results and discussion

3.1. Raw material characterization

3.1.1. Crystallinity analysis of cellulose

XRD diffractogram of MCC in Fig. 1(a) shows that there are three diffraction peaks at 2θ of 15.2° (i), 22.3° (ii) and 34.5° (iii). The characteristic peaks confirm the presence of the fingerprints for cellulose crystal planes 101, 002, and 040, respectively [29]. The crystallinity index of the MCC powder is 95.2%. High crystallinity of MCC shows that the powder is insoluble in water.

Meanwhile, the XRD result for CMC in Fig. 1 (a) indicates that a broad peak at 2θ of 20.7° (iv) was due to the presence of small crystallites and imperfect crystals in cellulose granules [16]. During the synthesis of CMC from cellulose through carboxymethylation process, prolong alkaline synthesis led the CMC structure to swell, distort, and uncoiling of the double-helical region [30]. Thus, break up the CMC crystalline structure. Then it leads to the destruction of the crystalline structure of the original cellulose and all characteristics peak for native cellulose has transformed into an amorphous phase. Besides that, the amorphous property causes the CMC to have an excellent solubility as higher solubility represented by lower crystallinity [31].

3.1.2. Functional group determination of cellulose filler

The FTIR absorption peaks at 3375, 2916, and 1638 cm^{-1} in Fig. 1 (b) shows the presence of intramolecular OH stretching, C–H and CH_2 stretching, and OH from absorbed water, respectively in MCC powder. The presence of CH2 symmetric bending and C-O-C asymmetric stretching of β-1, 4-glucosidic linkage are indicated by absorption peaks at 1436 and 1155 cm^{-1} respectively [32]. The absorbance peaks at 1064 and 892 cm^{-1} represent the C-O/C–C stretching and rocking vibration of C–H bend in cellulose [33,34]. The presence of intermolecular OH stretching in the MCC chemical structure is expected to interact with the carrageenan based biocomposite matrix thus increase the tensile strength of carrageenan based biocomposite. Interaction in the carrageenan based biocomposite matrix can be either from sulphate group or hydroxyl group in carrageenan or hydroxyl group in plasticizer.

Meanwhile for CMC powder in Fig. 1 (b), the absorption peaks at 3380 and 2917 cm^{-1} are due to the stretching frequency of OH group and C–H stretching vibration respectively. Meanwhile, the peaks at 1640 and 1457 cm^{-1} are attributed to the stretching vibration of carboxyl group (COO–) and carboxyl groups as salt. The peaks contribute to the presence of carboxymethyl substituent [16,35]. Additionally, the peaks around 1350, 1158, and 892 cm^{-1} indicate to –OH bending vibration, C-O-C stretching and 1,4-β glycoside of cellulose respectively [36,37]. The presence of broad peaks of hydroxyl group and carboxyl group in the CMC structure demonstrates the potential target site for intermolecular interaction between CMC and carrageenan matrix [37].

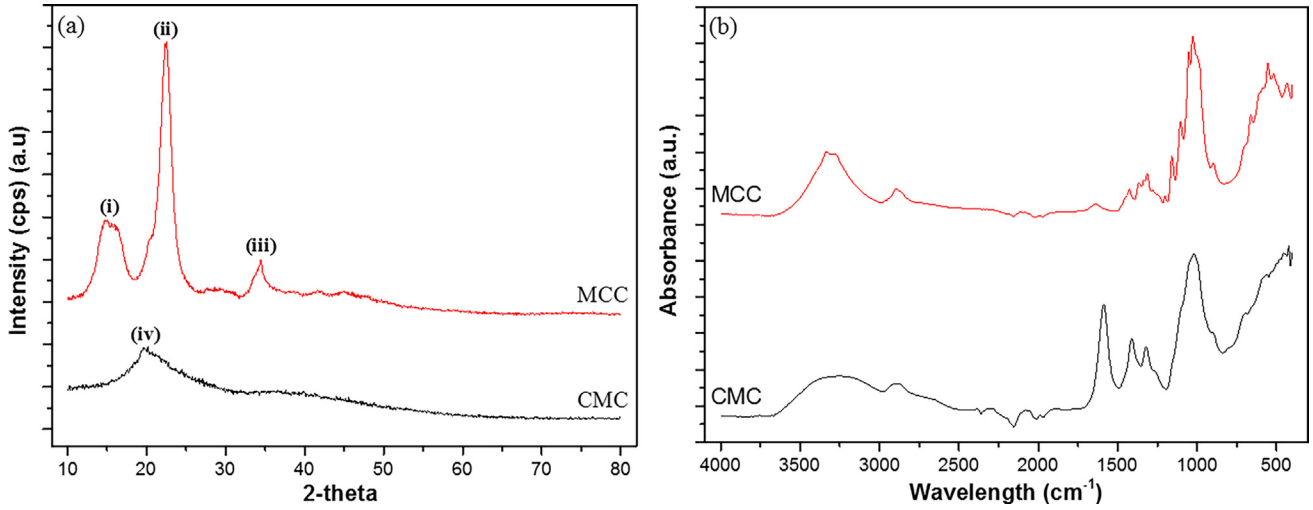

Fig. 1. (a) Crystallinity properties of MCC and CMC toughening agents and (b) Functional group determination of MCC and CMC toughening agents.

3.2. Carrageenan biocomposite film characterization

3.2.1. Functional group determination

The presence of carrageenan can be analyzed based on the FTIR spectra in Fig. 2. The peaks at 925 and 842 cm^{-1} are assigned to C-O of 3,6-anhydrogalactose and C-O-SO4 on galactose-4-sulphate respectively in kappa carrageenan [9,38]. Peaks at 1033 and 1219 cm^{-1} can be attributed to D-galactose-4-sulphate, 3,6-anhydro-D-galactose, glycosidic linkage, and ester sulphate, respectively [39]. Based on the functional groups' presence in the infrared spectrum, it is confirmed that the carrageenan used in this research project is kappa carrageenan. The peaks present in the infrared spectrum are like the standard kappa carrageenan.

Fig. 2 (i) represents the infrared spectrum for Carra-MCC biocomposite film. The influence of the network formation was determined by calculating the area under corresponding peaks as shown in Table 1 [40,41]. The result shows that the incorporation of MCC increases the absorbance of hydroxyl group up to 173% from 54.885 to 150.041 cm^{-1}. The result reflects that there is probably intermolecular interaction between the hydroxyl group in MCC with the carrageenan matrix. The intermolecular interaction may be contributed by the presence of sulphate and hydroxyl group in carrageenan. In Carra-MCC2.0, the absorbance of hydroxyl group has reduced to 127.332 cm^{-1} probably due to the agglomeration of MCC that leads to a weak interaction between the functional groups and the carrageenan matrix [42,43]. The tensile strength of Carra-MCC film and solution viscosity can be affected by the increment of the absorbance of the hydroxyl functional groups.

FTIR spectrum in Fig. 2 (ii) shows the FTIR spectrum trend of Carrageenan-CMC biocomposite film, meanwhile Table 2 represents the area under curves of three main functional groups that affect the properties of Carrageenan-CMC biocomposite film. In carrageenan biocomposite, CMC is possible to act as a crosslinker and filler. The sulphate group from carrageenan could crosslink with the hydroxyl group of CMC which will improve the chemical and physical properties of the biocomposite [18]. The area under the graph of hydroxyl group was integrated at the wavelength range from 3000 to 3700 cm^{-1}, stretching vibration of carboxyl group from 1615 to 1700 cm^{-1} and carboxyl groups as salt from 1445 to 1480 cm^{-1} [41,44]. The result shows that, without the incorporation of CMC filler, the area under peak is 54.885 cm^{-1}. Incorporation of CMC increases the hydroxyl group via hydrogen bonding up to 137% from 54.885 to 130.531 cm^{-1} The stretching vibration of carboxyl group increased up to 71% from 8.274 to 14.132, meanwhile the carboxyl group increased up to 51% from 5.239 to 8.451 upon incorporation of 2.0% CMC filler. The results show that the main three functional groups in CMC structure increased the molecular interaction in the carrageenan biocomposite thus improve the film properties. Moreover, changes in functional group properties will lead to improvement in the hard capsule thermal properties [45].

Table 1
Area under peak for hydroxyl group for Carra-MCC film and its biocomposite.

Biocomposite film sample	Area under peak OH (cm^{-1})
Control	54.885
0.4MCC	135.688
1.2MCC	150.041
2.0MCC	127.332

Table 2
Area under peak for hydroxyl group for Carra-CMC film and its biocomposite.

Biocomposite film sample	Area under graph (cm^{-1})		
	Hydroxyl group	Stretching vibration of carboxyl group	Carboxyl groups
Control	54.885	8.274	5.239
0.4CMC	131.596	13.162	6.845
1.2CMC	126.622	14.779	8.364
2.0CMC	130.531	14.132	8.451

3.2.2. Viscosity and tensile strength of carrageenan biocomposite film

Viscosity represents the intermolecular interaction among the carrageenan, crosslinker, cellulose additive, plasticizer, toughening agent, and water in the formulation solution. The viscosity reflects the ability of dipping film formation on the dipping metal bar and film thickness. It is also can be correlated with the homogeneity and uniformity of stirring and tensile strength.

Fig. 3 (i) shows the viscosity and tensile strength of carrageenan based biocomposite solution and film incorporated with MCC. At first stage, the addition of 1.2 w/w% of MCC significantly increases the viscosity but not significant for tensile strength of the biocomposite from 0.982 mPas to 1.36 mPas (viscosity) and 20.95 MPa to 26.89 MPa (tensile strength), respectively. At 2.0% addition of MCC, the viscosities dropped significantly to 1.136 mPas, while tensile strength dropped (but not significant) to 25.78 MPa respectively. The trend reflects the hydroxyl group absorbance from the infrared

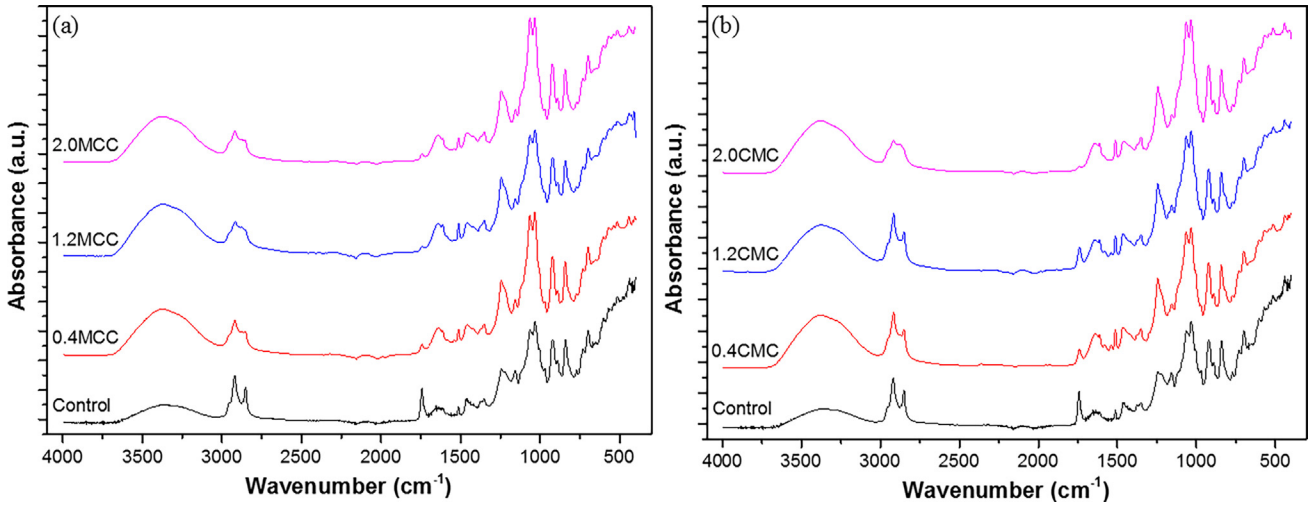

Fig. 2. Functional group determination of (a) Carrageenan-MCC and (b) Carrageenan-CMC biocomposite films at different concentration of toughening agents.

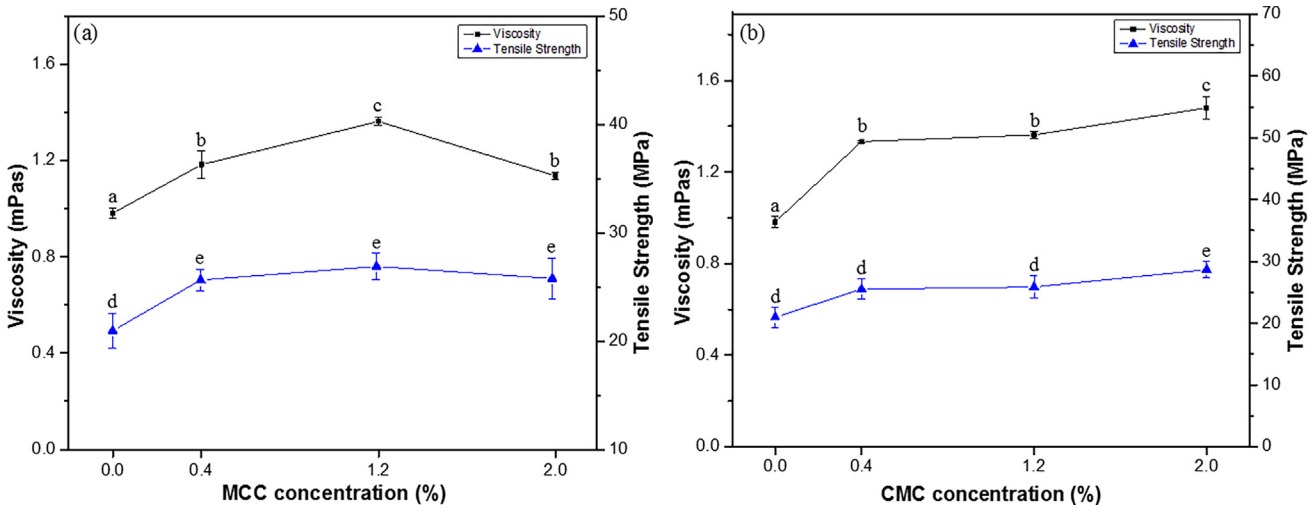

Fig. 3. Viscosity of biocomposite solution and tensile strength of biocomposite film of (a) Carrageenan-MCC and (b) Carrageenan-CMC at different concentration of toughening agents. Same letters in the same point are not significant ($p > 0.05$).

spectroscopy in Fig. 2 (i). At Carra-1.2MCC, the absorbance of hydroxyl group is the highest which reflects the strong intermolecular interaction of MCC in the carrageenan matrix thus produce a high tensile strength of sample film. Meanwhile, the absorbance of hydroxyl group in Carra-2.0MCC samples is lower which shows lower intermolecular interaction thus produce lower film tensile strength.

Fig. 3 (ii) shows the viscosity and tensile strength of Carra-CMC film and its composite. Carrageenan solution incorporated with CMC shows that the viscosity increases significantly from control sample (0%) to 2.0 w/w%, from 0.982 mPas to 1.48 mPas. The tensile strength of Carra-CMC films is also increased but not significant from 20.95 MPa (control) to 28.61 MPa (1.2 w/w%). Furthermore, at 2.0 w/w% of CMC addition, the tensile strength is significantly increased. It is predicted that higher concentration of CMC is required to produce more stable Carra-CMC hard capsule. Increment of tensile strength in film is correlated with the increasing degree of substitution value in CMC. A study reported that the substituent of carboxymethyl group in CMC lead to an increase in intermolecular force between the composite chains [46]. The statement is proven by the increment of functional groups in infrared spectroscopy in Fig. 2 (ii). Moreover, the internal sugar ring structure in CMC provides a good skeleton effect to the carrageenan biocomposite structure, thus improve the internal structural stability and increase the tensile strength [24].

3.2.3. Physical appearance of carrageenan biocomposite hard capsule

Based on this work, a good range of viscosity for hard capsule solution is from 1.00 to 1.20 mPas. As the viscosity is low, it will lead to inability to form a stable shape of biocomposite hard capsule. Meanwhile, the best hard capsule is evaluated based on the mechanical strength property of the hard capsule.

The physical appearance of Carra-MCC hard capsules is shown in Fig. 4. Carra-1.2MCC is the best hard capsule but most of them

Fig. 4. Physical appearance of Carrageenan-MCC and Carrageenan-CMC hard capsules at different concentration of toughening agents. Circles indicate the dented area of hard capsule.

are dented due to low viscosity that leads to low tensile strength of sample film as highlighted in the previous section. The surface of Carra-MCC hard capsule is not smooth because the MCC is just dispersed in the water instead of dissolved due to its low solubility, as proven by XRD analysis.

The physical appearance of hard capsules for Carra-CMC is also presented in Fig. 4. Based on the physical evaluation, the best hard capsule is Carra-CMC2.0. The low viscosity of the formulation solution leads to inability of dipping process and formation of dented hard capsule due to the low film thickness. The results show that CMC which is an amorphous solid is a better cellulose filler in comparison to MCC, a high crystallinity solid [18,47]. As an amorphous filler, CMC dissolves in water solvent thus produce a smooth surface film. Meanwhile, MCC as a crystal solid did not dissolve in water thus the filler remains on the film surface after mixing and drying thus lead to a formation of rough layer [48]. However, at a lower amount of filler, the mechanical strength of Carrageenan-MCC film is comparable to Carrageenan-CMC film. This shows that MCC has a great potential as a filler to be applied in biocomposite development. As an alternative, the MCC size could be reduced to nano size via chemical or mechanical approach to reduce the crystallinity index.

4. Conclusion

Incorporation of cellulose filler is an ideal solution to increase the mechanical strength of carrageenan film and hard capsule. From the extension comparison and evaluation of CMC and MCC filler, mechanical strength properties are an important aim of the desired properties to develop hard capsule products. The film and hard capsule mechanical properties demonstrated that Carra-CMC has the highest tensile strength in comparison to Carra-MCC. Besides, the incorporation of 2.0% of CMC increases the absorbance of hydroxyl group up to 137% in the FTIR spectrum. This proves that the incorporation of CMC in carrageenan effectively increases the hydroxyl bonding, stretching vibration of carboxyl group, and carboxyl groups in biocomposite matrix, thus increases the viscosity, intermolecular interaction, and film tensile strength. Moreover, MCC has a great potential to be applied in the carrageenan biocomposite film except for the crystallinity, insolubility, and agglomeration issue. At a low concentration of MCC, the mechanical strength of the biocomposite is comparable to the Carrageenan-CMC biocomposite film.

CRediT authorship contribution statement

Mohd Aiman Hamdan: Conceptualization, Formal analysis, Investigation, Writing - original draft. **Nur Amalina Ramli:** Visualization, Writing - original draft. **Nor Amira Othman:** Methodology. **Khairatun Najwa Mohd Amin:** Supervision, Writing - review & editing. **Fatmawati Adam:** Supervision, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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