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Preparation and characterization of red seaweed/calcium carbonate composite films

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Abstract. This study aims to evaluate the influence of inorganic filler on the properties of seaweed-based film. Seaweed composite films were prepared from raw red seaweed (Kappaphycus alvarezii) in the presence of glycerol with the incorporation of calcium carbonate (CaCO3). Solution casting technique was used to form films and dried at 40 °C in the ventilation oven for 24 hours. The effects of different CaCO3 concentrations [0.5%, 1.0%, 1.5%, 2.0% (wt. %)] on the physical, mechanical, and thermal properties were determined. Molecular interaction between the functional groups of red seaweed and CaCO3 was examined through Fourier transform infrared spectroscopy (FTIR). The obtained result demonstrated that the addition of CaCO3 improved the neat seaweed film properties in terms of tensile strength, hydrophobicity, thermal properties and reduced the problem of brittleness encountered in seaweed-based film. However, excessive loading of CaCO3 had led to weaker film properties. Raw red seaweed and CaCO3 has shown compatibility through the analyses of FTIR, thermal, and mechanical of the composite films.

1. Introduction

Seaweed is an essential resource of natural biopolymer that has been used in a vast range of applications worldwide. The main derivatives of seaweed such as alginate and carrageenan have been applied broadly in the field of cosmetic, packaging, pharmaceutical, food and agricultural industry owning to their availability, high organic content, impressive phycocolloids, biodegradability, good gas barrier and mechanical properties [1]. Seaweed phycocolloids are well known to form colloid system either in a gel form or solubilized particles in the presence of water. However, they are hydrophilic in nature. Thus they are usually poor in mechanical properties, water barrier properties and thermal stability [2]. In order to alleviate such drawbacks, biopolymer materials can be reinforced by fillers, blending with other biopolymer materials or through chemical modification to form effective interlocks with the hydroxyl group [3]. Reinforcement fillers in the form of organic and inorganic have been identified in the previous works. Examples of organic reinforcement fillers that had been used to incorporate into sulphated seaweed based matrix were cellulose nanocrystalline (NCC) [5], oil palm shell nanoparticles (OPS) [6], cellullosic pulp fiber [7] while inorganic reinforcement fillers were montmorillonite (MMT) [8-9], silver nanoparticles (AgNPs) [8], zinc oxide (ZnONPs), and copper oxide (CuONPs) nanoparticles [10].

Among the fillers, CaCO3 is one of the most common reinforcing fillers in composite material for paper, rubber, concrete and plastic industries due to its natural abundance, cost-effectiveness, non-toxicity, and non-abrasiveness [11]. Calcium carbonate is normally obtained from carbonatite-lava, stalactites, stalagmites, sketetons, eggshells or shells of marine animals. It can also be obtained from...
excavating carbonate containing rock [12]. In the recent years, CaCO₃ is widely utilized as reinforcing filler to biopolymers such as poly (lactic acid), chitosan, starch, gluten and polycaprolactum to develop nanotables, hydrogel, microcapsules and composite films with enhanced physical, mechanical and thermal properties [11-13].

Raw seaweed was selected as a matrix in this work since the previous study done by Siah et al (2015) had demonstrated the feasibility of using raw seaweed to develop edible film without derivatives extraction [1]. Film properties can be further improved by incorporating filler or other biopolymer materials. This study aimed to fabricate composite films using raw red seaweed as the matrix and CaCO₃ as reinforcing filler. It also highlights the influence of using CaCO₃ towards physicochemical, mechanical and thermal properties of the red seaweed-based films. Although studies on developing composite films subjected to biopolymer as a matrix have been done extensively, no study has been explored for the fabrication of raw red seaweed/CaCO₃ composite films thus far.

2. Experimental

2.1. Materials and film fabrication
Films were prepared using solution casting method. 4 g of red seaweed, *Kappaphycus alvarezii* from Tawau, Sabah, Malaysia was used to form film by dissolving in 200 ml of distilled water in the presence of 2g glycerol, functioned as a plasticizer to improve film’s flexibility and reduce film brittleness. Precipitate calcium carbonate with different loadings [0.5, 1, 1.5, 2 (wt. %)] was added to the solution and heated to 90 °C for an hour to allow full gelatinization. The solution was degassed in a vacuum oven and cooled it to room temperature. After that, it was poured unto a casting plate with the diameter of 20 cm and dried in the oven at 40 °C for 24 hours. All dried films were conditioned in a chamber at 50 % RH prior to film characterization.

2.2. Film characterization

2.2.1. Contact angle measurements. The static water contact angles were carried out using a Contact Angle Analyser (KSV CAM 101; KSV Instruments Ltd., Finland) under ambient conditions. A drop of water (5 μL) was deposited on the surface of the solid films through a syringe. Images of the drop profile were recorded immediately after the water touched the film surface. The contact angle (θ) was calculated and expressed in degrees. The mean values of contact angles from 5 replicate measurements for each sample were calculated.

2.2.2. Film thickness. Film thickness was measured at 10 random positions using a precision digital micrometer (Mitutoyo, Kanagawa, Japan) to the nearest 0.0001 mm and the mean value for each film was determined for tensile calculations.

2.2.3. Mechanical properties. Films thickness was determined using a precision digital micrometer (Mitutoyo, Kanagawa, Japan) to the nearest 0.001 mm prior to the mechanical test. Film samples were cut to 10 cm × 1 cm and were conditioned at 50 % RH for a week before all analyses. Tensile strength (TS), modulus of elasticity (YM) and percentage of elongation (%E) were determined using a tensile tester operated according to ASTM D-882-02 standard with initial grips separation of 100 mm and a cross-head speed of 50 mm/min [14]. At least 5 replicates were performed for each sample to obtain the mean values.

2.2.4. Thermogravimetric Analysis (TGA). A TGA apparatus, Mettler-Toledo thermogravimetric analyzer model TGA/DSC 1 was used to go through thermogravimetric analysis (TGA). Approximately 10 mg for each sample was heated under nitrogen purge from 30 °C to 800 °C at the heating rate of 10°C/min. The residue was at 800 °C was expressed as a residue at weight loss (%).
2.2.5. Fourier Transform Infrared (FTIR) analysis. The analysis was carried out with (Perkin-Elmer) Fourier Transform Infrared (PC1600, USA) in attenuated total reflectance (ATR) mode. Films were dried overnight in the oven at 60°C before performing FTIR analysis. The spectra were recorded in between 500 to 4000 cm⁻¹.

3. Results and discussion

3.1. Contact angle
Surface hydrophobicity and wettability of a fluid on a solid surface were determined by static contact angle measurement using sessile drop technique. Contact angles, \( \theta \), of the neat red seaweed film and red seaweed/ CaCO₃ composite films were illustrated in Figure 1. The contact angle for the neat red seaweed film was 74.37°. A film with the contact angle higher than 65° is normally considered as hydrophobic [15]. In this case, all films including neat red seaweed film were considered hydrophobic despite the hydrophilic nature of seaweed and glycerol as plasticizer. The higher contact angle value achieved by the neat seaweed in the presence of glycerol as a plasticizer could be due to well dispersion of glycerol and the inter- and intra-molecular hydrogen bonding between the hydroxyl groups of red seaweed and glycerol in the matrix [16]. Therefore, this reduced the surface free energy and prevented water penetration through the film. The previous study had shown similar case whereby contact angles increased in the presence of glycerol as a plasticizer [16]. Moreover, it was noticed that contact angle values increased when 0.5 % CaCO₃ was added into the matrix. This indication showed that film hydrophobicity improved with the addition of CaCO₃ as filler. However, the contact angle of the composite films started to decrease from the addition of 1% CaCO₃ onwards. This could be ascribed to excessive addition of CaCO₃ into the matrix which probably caused by agglomeration in the composite films. Previous studies revealed that agglomeration occurred when excessive filler content was loaded in cornstarch films and K-carrageenan films [13, 17]. This phenomenon disrupted the interfacial adhesion between the filler and matrix thus, decreased films contact angles.

![Figure 1. Contact angles of composite films.](image)

3.2 Film thickness
The film thickness is one of the essential parameter used in tensile calculations [6]. The mean value of neat seaweed film thickness was 0.0582 mm while the thickness of the composite films was in the range of 0.0600 to 0.0680 mm as tabulated in ‘Table 1’. The increase of film thickness when CaCO₃ was added could be due to the increase of film dry mass [18]. It was observed that the trend was not consistent with the addition of CaCO₃ increased. This trend was in agreement with the previous study whereby corn starch film reinforced with CaCO₃ nanoparticles exhibited an inconsistent trend with no significant changes in film thickness as the addition of CaCO₃ increased from 0.02% to 0.5% [13].
3.3 Mechanical properties

The results of tensile strength (TS), Young modulus (YM) and the percentage of elongation (%E) of the composite films were presented in Table 1. Composite films with the addition of 0.5 % CaCO₃ achieved the highest TS and YM while the neat red seaweed film showed the lowest TS and YM among all the films. TS and YM increased when 0.5% of CaCO₃ was added. The increase of TS and YM could be a good indication of miscibility of filler and matrix which was further identified by FTIR-ATR. It was believed that strong intermolecular hydrogen bonding formed between the hydroxyl groups of filler and the matrix, causing the films exhibited high affinity and high TS. Besides, CaCO₃ was able to reduce chain mobility while enhancing macroscopic rigidity of the composite films which resulted in higher TS and YM compared to the neat red seaweed film [13]. However, TS and YM decreased gradually with the addition of 1% CaCO₃ onwards. The decrease could be due to the disruption of the molecular interaction between filler and matrix caused by agglomeration whereby more intra-molecular bonds than inter-molecular bonds were formed between the filler and the matrix [13, 19]. TS and YM in this work were higher compared to the TS and YM of cornstarch films reinforced with CaCO₃ nanoparticles which were 1.83 to 2.24 MPa and 1.92 to 2.41 MPa respectively [13]. This could be attributed to the nature of gelling properties in seaweed due to the functional compound of 3,6-anhydro-D-galactose and D-galactose-4-sulphate [18].

Table 1. Mechanical properties of composite films.

| CaCO₃ loadings (%) | Thickness (mm) | TS (N/mm²) | YM (MPa) | Elongation (%) |
|-------------------|----------------|------------|----------|----------------|
| 0.0               | 0.0582         | 38.32      | 182.87   | 23.26          |
| 0.5               | 0.0648         | 45.37      | 198.22   | 22.84          |
| 1.0               | 0.0680         | 43.76      | 191.11   | 22.96          |
| 1.5               | 0.0600         | 43.24      | 189.09   | 22.82          |
| 2.0               | 0.0650         | 43.23      | 187.05   | 21.40          |

Aside from TS and YM, the percentage of elongation is another important parameter to evaluate film flexibility and stretchability. In this work, the percentage of elongation decreased gradually due to the increase of film rigidity when CaCO₃ was added from 0.5% to 2.0%. Similar cases were found in the study of oil palm shell nanofiller in seaweed-based composite film and nano-CaCO₃ in poly(urethane methacrylate) whereby the elongation decreased as the filler loading increased [6, 11].

3.4 Thermal properties

Thermal properties of the neat red seaweed film and the composite films were evaluated by TGA. T_on (The initial temperature of decomposition), T_max (The maximum temperature of decomposition) and residue after weight loss (%) at 800 °C were determined and tabulated in Table 2. As compared to the neat seaweed film, T_on and T_max shifted to higher values when 0.5% CaCO₃ was added. This could be due to well dispersion of the filler in the red seaweed matrix that led to increase in contact area between the filler and the matrix. Furthermore, there could be the new formation of hydrogen bonds between CaCO₃ and the red seaweed which was further confirmed by FTIR. When stronger intermolecular hydrogen bonds formed between the filler and the matrix, more energy, and higher temperature were required to disorganize the intermolecular interactions between the filler and the matrix thereby, led to higher T_on and T_max [13, 20]. In this work, however, T_on and T_max started to decrease from the addition of 1% CaCO₃ onwards. This could be due to the aggregation of fillers in the matrix that weaken the intermolecular interactions between CaCO₃ and red seaweed thereby, decreased the thermal stability [13]. Similar results were reported on thermal stability of starch/nano CaCO₃ composite films [21]. On the other hand, the residues after weight loss at 800 °C for the composite films increased as the addition of CaCO₃ increased. This finding suggested that the increase
of residue was caused by the content of CaCO$_3$. The increase of residues with the increasing of CaCO$_3$ was also observed in starch/nano CaCO$_3$ composite films which were in accordance with the present work [21].

| CaCO$_3$ loadings (%) | $T_{on}$ | $T_{max}$ | Residue (%) |
|-----------------------|---------|---------|------------|
| 0.0                   | 210.17  | 225.83  | 14.95      |
| 0.5                   | 212.38  | 226.79  | 21.90      |
| 1.0                   | 211.65  | 223.50  | 22.23      |
| 1.5                   | 211.33  | 223.45  | 22.80      |
| 2.0                   | 210.83  | 222.97  | 23.36      |

Table 2. Thermal properties of the composite films.

3.5 FTIR

The interaction between the functional groups of red seaweed and CaCO$_3$ in the presence of glycerol was characterized by FTIR spectroscopy. The miscibility and the effect of molecular interaction between the filler and the matrix can be identified when changes such as shifting, width, and intensity of the spectrum bands were noticed [22].

The FTIR-ATR spectra of the neat red seaweed film and the composite films were presented in ‘Figure 2’. Nine characteristics bands were identified and were numbered 1-9. Based on the overall spectra, no obvious differences were observed. This could be due to the small amount of CaCO$_3$ (0.5 to 2 wt%) incorporated into the red seaweed matrix. However, there were slight differences in the shifting of wavenumber (cm$^{-1}$) for certain functional groups as shown in Table 3. Broad and wide peaks noticed at band 1 (3329 cm$^{-1}$) for the neat red seaweed film was assigned to the stretching vibration of hydroxyl (–OH) groups due to the formation of inter- and intra- molecular of hydrogen bonds. The stretching vibration of –OH groups for the composite films (bands 1) shifted to lower frequencies as CaCO$_3$ were added (‘Table 3’). Previous study showed that stronger hydrogen bonds were formed as the wavenumber shifted to lower frequencies [22]. This suggested that stronger hydrogen bonds were formed between the –OH groups of red seaweed and CaCO$_3$ thus, resulted in stronger interaction between the filler and the matrix. This was confirmed by the increase of tensile strength and thermal stability when 0.5% CaCO$_3$ was added.
Figure 2. IR-spectra of neat red seaweed film (control film) and composite films : a) neat red seaweed film (control) b) 0.5%, c) 1.0%, d) 1.5%, e) 2.0% of CaCO₃ loadings.

Table 3. FTIR-ATR spectra of the neat red seaweed film and the composite films.

| CaCO₃ loading content (%) | Wavenumber (cm⁻¹) |
|--------------------------|-------------------|
|                          | Band 1 | Band 2 | Band 3 | Band 4 | Band 5 | Band 6 | Band 7 | Band 8 | Band 9 |
| 0.0                      | 3329   | 2932   | 1647   | 1416   | 1219   | 1030   | 922    | 845    | 732    |
| 0.5                      | 3319   | 2937   | 1645   | 1416   | 1217   | 1034   | 922    | 845    | 700    |
| 1.0                      | 3323   | 2938   | 1645   | 1416   | 1217   | 1032   | 922    | 845    | 700    |
| 1.5                      | 3327   | 2934   | 1647   | 1416   | 1219   | 1032   | 922    | 845    | 700    |
| 2.0                      | 3327   | 2934   | 1647   | 1416   | 1219   | 1032   | 922    | 845    | 700    |

Stretching vibration of long chain alkyl group was identified at bands 2. There was slight shifting in wavenumber from 2932 cm⁻¹ to 2934 cm⁻¹, represents the anti-symmetric stretching of aliphatic C-H and bands 3 at 1647 cm⁻¹ and 1645 cm⁻¹ were attributed to C=O carbonyl stretching and a combination of hydrogen bonding with COO [20]. The shifting of wavenumber indicated that there could be alteration of molecular interaction between red seaweed and CaCO₃. Intense absorption peaks from bands 5 to 7 is common to all polysaccharides due to C-C, C-O stretching of the pyranoid ring and C-O-C stretching of glycosidic bonds. Bands 5 (1219 cm⁻¹, 1217 cm⁻¹) appeared in all films were corresponded to stretching vibration of S=O bond, represents the characteristics of sulphate esters which usually found in carrageenan types [23-24]. Bands 6 at 1030 cm⁻¹, 1034 cm⁻¹, and 1032 cm⁻¹ were assigned to C-C and C-O stretching vibrations. The anomeric region from 950 cm⁻¹ to 700 cm⁻¹ particularly the bands 7 at 922 cm⁻¹ corresponded to 3,6-anhydro-D-galactose and the bands 8 at 845 cm⁻¹ were corresponded to D-galactose-4-sulphate due to the stretching vibration of C-O-C [23-24]. Bands 9 at 732 cm⁻¹ and 700 cm⁻¹ were assigned to the bending of pyranose ring [23].

4. Conclusion

Red seaweed/CaCO₃ composite films were successfully fabricated and characterized based on physicochemical, mechanical and thermal properties. From this work, the composite film with 0.5%
CaCO₃ appeared to exhibit the best physical, mechanical and thermal properties among all composite films. FTIR also revealed good miscibility between seaweed and 0.5% CaCO₃ as –OH groups had shifted to a lower wavenumber, indicating that strong hydrogen bonds formed between seaweed and 0.5% CaCO₃. However, film performance decreased in terms of physical, mechanical and thermal as the addition of CaCO₃ exceeded 0.5%. Therefore, it can be concluded that appropriate loading content of CaCO₃ into the red seaweed matrix is important to fabricate composite films with improved functional properties. The composite films developed can be used as potential packaging material.

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