Effects of Corn Starch and *Kappaphycus alvarezii* Seaweed Blend Concentration on the Optical, Mechanical, and Water Vapor Barrier Properties of Composite Films

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Composite films with different *Kappaphycus alvarezii* seaweed and corn starch concentrations were developed, and the effect of these concentrations on the films' optical, mechanical, and water vapor barrier properties were investigated. The chemical interactions between the two components in the film were verified by chemical composition and Fourier transform infrared (FTIR) spectroscopy investigations. The results showed that the mechanical properties and opacity of the composite films were enhanced with the addition of seaweed. Among the compositions, a composite film with 3% seaweed and 1% starch exhibited the highest tensile strength and elongation at break. The water vapor permeability (WVP) of the composite films linearly increased with the increments of starch and seaweed concentrations. The FTIR analysis also revealed intermolecular interactions between the two components, consistent with the good miscibility of seaweed and starch in the blend. Therefore, different concentrations of the blend of seaweed and starch could be used to tailor a film with certain desired functional properties.

Keywords: Kappaphycus alvarezii Seaweed; Cornstarch; Composite film; Mechanical properties; Optical properties; Water barrier properties

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INTRODUCTION

Composite materials derived from biodegradable polymers, such as polysaccharides, proteins, and lipids, are highly sought by the current research community due to their distinctive features when compared to synthetic polymer materials, *i.e.*, their nontoxicity, biodegradability, and abundant availability (Vieira *et al.* 2011). Starch is one of the most common green plant-originated polysaccharide material. Starch is widely utilized in both food and non-food applications, such as edible packaging, adhesive materials, textile sizing, and cosmetic products, due to its easily obtainable, abundantly available, cheap, biodegradable, and biocompatible qualities (Lafargue *et al.* 2007). Starch is essentially comprised of linear amylose and branched amylopectin. The relative amount of both of these macromolecular components in starch is dependent upon the source of the plant. It is known that cornstarch is composed of 30% amylose and 70% amylopectin. A starch-based polymer known as thermoplastic starch (TPS) can be prepared by heating starch granules in the presence of a plasticizer, commonly water or glycerol. Although starch-based films are transparent, odorless, and oxygen-impermeable, the fact that they are brittle and hydrophilic in nature has restricted their use in many applications (Wu and Zhang 2001). An effective way to overcome these drawbacks is by mixing the films with other natural polymers that have compatible interactions with starch (Poeloengasih *et al.* 2017).

To fulfill the surging demand for natural and renewable materials, biobased polymers from the marine environment, *e.g.*, seaweed, have been receiving plenty of attention recently. Seaweed could be a suitable candidate as a biodegradable polymer because it is made up of bountiful polysaccharides, providing a large array of functional properties such as its gelling ability, recyclability, thermal stability, and effectiveness against health risk (Thakur *et al.* 2017). Alginate, agar, and carrageenan are the most common polysaccharides derived from seaweed that have been utilized as film-forming materials. They have been explored extensively in several fields related to functional food, tissue engineering, drug delivery, and textile sizing applications (Gade *et al.* 2013; Venkatesan *et al.* 2016). However, the extraction process is not environmentally and economically friendly because it requires a high amount of chemical and energy consumption (Abdul Khalil *et al.* 2017b). Moreover, it is believed that pure seaweed also contains other non-polysaccharide compounds that can contribute to the film forming abilities of seaweed, including proteins and lipids (Dawczynski *et al.* 2007). *Kappaphycus alvarezii* is a type of red seaweed that is widely cultivated for the production of the hydrocolloid known as kappa-carrageenan (κ-carrageenan) (Jumaidin *et al.* 2017). Previous studies have reported the feasibility of films developed from native *Kappaphycus alvarezii* seaweed, with or without incorporated fillers, that have attained substantial mechanical strength and other functional properties that are required for several industrial applications (Siah *et al.* 2015; Abdul Khalil *et al.* 2016, 2017a).

Great interest has been focused on binary mixtures of starch- and seaweed-derived polymers over the years, and significant improvement has been reported in the mechanical strength and other properties of starch-based films (Lafargue *et al.* 2007; Wang *et al.* 2011; Abdou and Sorour 2014). To the best of the authors' knowledge, a composite film prepared from starch and native seaweed has not yet been explored. Moreover, the concentration of polymers to be used in the film-forming solution is a considerable factor in estimating an appropriate film fabrication condition for reaching certain desired properties (Galus and Lenart 2013; Wang *et al.* 2013; Ahmed and Ikram 2016). Hence, the aim of the present study is to develop blend films fabricated by cornstarch and *Kappaphycus alvarezii* seaweed, and to study the effects of their concentrations on the film properties in terms of optical, mechanical, and water vapor barrier characteristics. The chemical interactions within the polysaccharide components will also be evaluated based on the chemical composition and FTIR analyses for more comprehensive discussion.

EXPERIMENTAL

Materials

Corn starch (Bintang Brand, Thye Huat Chan Sdn Bhd., Penang, Malaysia) with a moisture content of 10.11% was used in this study. Dried red seaweed (*K. alvarezii*) was supplied by Green Leaf Synergy Sdn. Bhd. (Tawau, Sabah, Malaysia). Initially, the dried red seaweed was washed with running water to eliminate impurities and dirt. It was then soaked in distilled water for 3 h to allow it to swell and soften. The cleaned red seaweed was cut and chopped into small pieces with a knife and oven-dried at 40 °C for 3 days before storage. Analytical grade glycerol (GLY; Ajax Chemicals Pty. Ltd., Sydney, Australia) was used as the plasticizer.

Methods

Characterization of raw materials

A proximate analysis of corn starch and *K. alvarezii* seaweed were as follow:

- Moisture: Oven desiccation at 100±5°C (AOAC, 934.01)
- Ash: Dry incineration method (AOAC, 930.05)
- Lipid: Soxhlet extraction (AOAC, 991.36)
- Protein: Kjedahl method (ISO 1871,2009 E)
- Carbohydrate: (AOAC,1993)
- Amylose content: Colorimetric method (Juliano 1971; Chrastil 1987)

Fabrication of corn starch/ K. alvarezii seaweed composite films

Corn starch/*K. alvarezii* seaweed composite films were prepared using the solution casting method described by Martins *et al.* (2012) with some modifications. Different concentrations of solute in blend solution were used in this study. *K. alvarezii* seaweed (SE) and corn starch (S) solutions at different concentrations (1 wt%/vol to 3 wt%/vol) were prepared separately by dissolving each in distilled water. The SE solution was prepared by soaking the seaweed particles in distilled water overnight. After soaking, the gelatinized seaweed was formed. Glycerol was added based on 30% of total solid content of the film solution. To prepare blend films, both the SE and S solutions were mixed in proportions of 150 mL each, to obtain a total of 300 mL to form a 1:1 (S:SE) blend solution. Variations of the S/SE blend compositions are presented in Table 1.

Table 1. Composition and Coding of Corn Starch and *K. alvarezii* Seaweed Films

Film Code	Seaweed, SE (wt%/vol)	Starch, S (wt%/vol)
SE1S1	1	1
SE1S2	1	2
SE1S3	1	3
SE2S1	2	1
SE2S2	2	2
SE2S3	2	3
SE3S1	3	1
SE3S2	3	2
SE3S3	3	3

The mixtures of the S and SE solutions were agitated at 250 rpm for 20 min to ensure homogeneous dispersion. Then, the film forming solutions were heated (below 90 °C to avoid degradation) for 30 min with continuous agitation until they were completely dissolved and gelatinized. They were later allowed to cool for 5 min and degassed under vacuum to remove bubbles trapped in the solutions. After cooling, the film forming solutions were filtered using a 1.0 mm pore-size stainless steel sieve to further remove insoluble particles and bubbles. Then, the filtered solution was casted on Teflon-coated plates with 37 × 25.5 cm dimensions. They were oven-dried at 40 °C for 24 h. After being dried, the films were peeled off from the plates.

All of the freshly fabricated films were conditioned prior to subjecting them to further testing for mechanical and water vapor barrier properties in accordance with ASTM D618-61 (1993). All of the films were kept in sealed plastic bags and then stored in desiccators containing saturated sulfuric acid solution at 55% ± 2% RH and 27 °C ± 2 °C for 3 days.

Characterization of the composite films – Optical properties

The color of the samples was evaluated using the Data Color 400 Bench-Top Spectrophotometer (Datacolor International, Lawrenceville, GA, USA) based on the CIE $L^*a^*b^*$ color space system. A specimen was placed on the standard white surface plate to obtain the color coordinates for the parameters of lightness (L^*) = 93.47, redness (a^*) = -0.87, and yellowness (b^*) = 5.31. The measurements were replicated four times to obtain a mean result per sample. The chroma (C^*) and total color difference (ΔE) were obtained from the computerized Datacolor Tools and Datacolor Match software program (Datacolor International, Lawrenceville, GA, USA).

The opacity of the films was determined according to the method described by Martins *et al.* (2011). Samples sized 50 mm × 50 mm were placed on opacity charts. The opacity of the films was identified as the contrast ratio of the result samples on black standard to white standard. Four additional replicated measurements were taken to obtain a mean reading per sample.

Film thickness

The thickness of the blend film was measured using a handheld digimatic micrometer (Mitutoyo Co., Kawasaki, Japan) with a resolution of 0.001 mm. The caliper was recalibrated to zero before each sample was measured. Ten readings were taken at random positions around the samples. The readings were recorded in millimeters (mm) to three decimal places.

Mechanical properties

The tensile test of the films was conducted using a Miniature Tensile Tester MT1175 (Dia-Stron Instruments, UK) programmed with UvWin1000 software (Dia-Stron Limited Instruments, Hampshire, UK), in accordance with the ASTM D882-02 (2002) standard, conditioned at 58% RH and 28 °C. Ten specimens at the dimensions of 150 mm × 10 mm were cut with a penknife. The conditions set were 100 mm of initial grip separation and 50 mm/min for the crosshead speed. The tensile strength, elongation at break, and Young’s modulus were calculated.

Water vapor barrier property

The water vapor permeability (WVP) of the film samples was determined with a slight modification to the designed technique referred to in the ASTM E96 (1995) standard. Five specimens of each coded film were traced with a knife and cut to a size equal to the mouth diameter of the polypropylene circular cups. Each cup was filled with 20 mL of distilled water, and the specimen sheets were attached and flatly sealed on top with vacuum grease. They were then weighed, and their initial reading was recorded before placement into a controlled chamber conditioned at 50% ± 5% RH and 25 °C ± 2 °C. Weights of the cups were taken every hour for total of 6 h. The line graph of weight changes against time was plotted, and the slope was calculated with $R \leq 0.99$. The water vapor transmission rate

(WVTR) (g/m^2h) was calculated as the slope divided by the exposed surface area. The WVP ($gPa^{-1}s^{-1}m^{-1}$) was calculated according to Eq. 1,

$$WVP = (WVTR \times t) / P \tag{1}$$

where t is the thickness of film (m), $WVTR$ is the water vapor transmission rate (g/m^2h), and P is the partial pressure difference of saturated water vapor across the films (Pa).

Fourier transform infrared (FTIR) spectroscopy

The assessment of main polysaccharides in the seaweed sample was performed using Fourier transform infrared spectroscopy (FTIR). Commercial carrageenan was used as reference material in this study. Approximately 2 mg of the seaweed sample and commercial carrageenan in the form of powder were mixed with potassium bromide (KBr) and pressed into discs. The FTIR spectra of corn starch-*K. alvarezii* seaweed composite films were also studied using infrared spectrometer (Spectrum 8900 IR Spectrometer, Shimadzu, Japan) without the addition of KBr. Spectral measurements were performed in the transmittance mode. The spectra of these samples were measured in the range of 400 to 4000 cm^{-1}.

Statistical analysis

An analysis of variance (ANOVA) was performed to analyze the mean differences, which included the results of mechanical, water vapor permeability, color, and opacity testing of all the specimens. Multiple comparisons of the difference in mean values of all samples were also evaluated using the Tukey test. All of the data were analyzed using SAS (Windows, version 9.0, Cary, NC, USA) software.

RESULTS AND DISCUSSION

Characterization of Raw Materials

The amylose content of corn starch was determined using the colorimetric method according to Juliano (1971) and Chrastil (1987). In this study, the amylose content of corn starch was 19.7%, which was in agreement with the results reported by Yun and Yoon (2010). Moreover, previous studies reported that the amylose content of starch could favor good film properties, wherein it had a high tendency to interact by hydrogen bonds, and thus, it was capable of forming a stiff and strong film (Lafargue *et al*. 2007; López *et al.* 2008).

The chemical compositions of *K. alvarezii* seaweed such as moisture, carbohydrate, protein, fat, and ash are shown in Table 2. In this study, the carbohydrate content of *K. alvarezii* seaweed was 65.2%. A similar finding was also reported by Abd-Rahim *et al.* (2014) and Meinita *et al.* (2012). Moreover, the ash content of *K. alvarezii* seaweed was 11.57%, which was in agreement with data previously published (Abd-Rahim *et al.* 2014; Meinita *et al.* 2012). Furthermore, the low value of protein (3.4%) and fat (1.1%) of *K. alvarezii* seaweed were expected based on previously published reports, which protein and fat were mainly composed at the range of 2.5 to 3.8% and 0.2 to 1.60±0.05%, respectively (Fernando *et al.* 2016). Unlike plants, seaweed is virtually free of structural branched carbohydrate polymers such as lignin and hemicellulose (Masarin *et al.* 2016). However, the percentage of cellulose content is different according to the seaweed species. Siddhanta *et al.* (2009) reported that *K. alvarezii* seaweed contained approximately 2.0% of cellulose, which was relatively low compared to other seaweed species.

Table 2. Chemical Composition of *Kappaphycus alvarezii* Seaweed

Chemical Content	Composition (wt. %)
Moisture	0.89%
Carbohydrate	65.20%
Protein	3.40%
Fat	1.10%
Ash	11.57%

Optical Properties

Figure 1 illustrates that the composite films prepared by corn starch (S) and *K. alvarezii* seaweed (SE) with the solution casting method were visually homogeneous, smooth, and translucent. The films with higher SE content appeared darker and more yellowish. This phenomenon was due to the presence of pigments, including the carotenoids, phaeophytin, and chlorophyll *a* components in seaweed, that capture the light energy and thus provide color to the films (Naguit and Tisera 2009).

Fig. 1. Macroscopic visual images of S/SE composite films

Table 2 presents the color attributes of S/SE films. The parameters *L**, *a**, *b**, *C**, and ΔE represent the brightness, degree of greenness-redness, degree of blueness-yellowness, color saturation (or chroma), and total color difference, respectively.

According to Table 2, all of the color parameter results displayed no statistical difference across the increment of S concentration in the blend films. In contrast, the increase of SE concentration reduced the *L** values of the composite films, which were decreased from 91.56 to 89.09. Moreover, the composite films indicated redness (negative values of *a**) and yellowness (positive values of *b**) shading. The increase of SE concentration lowered the values of *a**, but increased the *b** and *C** of the films, indicating the S/SE blend films appeared more yellowish and chromatic. This finding verified that color changes were notably attributable to the SE concentration. The Δ*E* is a measure of the total color difference compared with the standard color plate. Because the Δ*E* was calculated based on delta *L**, *a**, and *b** color differences, the increment values of Δ*E* were also observed with the increase of SE concentration.

Table 3. *L**, *a**, and *b** Color Values, Chroma (*C**), Total Color difference (Δ*E*), and Opacity of the Composite Films

FILM	*L**	*a**	*b**	*C**	*ΔE*	Opacity
SE1S1	91.56 ± 0.13^{c}	-0.96 ± 0.02^{ab}	9.72 ± 0.35^{a}	9.79 ± 0.34^{a}	4.99 ± 0.38^{a}	15.17 ± 0.07^{a}
SE1S2	91.44 ± 0.25^{c}	-0.96 ± 0.02^{ab}	9.23 ± 0.36^{a}	9.88 ± 0.75^{a}	4.04 ± 0.67^{a}	15.24 ± 0.03^{ab}
SE1S3	91.41 ± 0.20^{c}	-1.02 ± 0.02^{ab}	10.01 ± 0.22^{a}	10.14 ± 0.13^{a}	5.05 ± 0.75^{a}	15.29 ± 0.03^{ab}
SE2S1	90.41 ± 0.14^{b}	-0.86 ± 0.05^{bc}	12.32 ± 0.30^{b}	12.35 ± 0.30^{b}	7.47 ± 0.95^{b}	15.35 ± 0.13^{b}
SE2S2	90.33 ± 0.15^{b}	-0.82 ± 0.03^{cd}	12.80 ± 0.35^{bc}	13.07 ± 0.25^{bc}	7.91 ± 0.62^{b}	15.53 ± 0.07^{c}
SE2S3	89.78 ± 0.10^{ab}	-0.78 ± 0.01^{cd}	13.64 ± 0.11^{c}	13.66 ± 0.11^{c}	8.98 ± 0.21^{bc}	15.76 ± 0.03^{d}
SE3S1	89.64 ± 0.06^{ab}	-0.71 ± 0.06^{de}	14.92 ± 0.55^{d}	14.94 ± 0.55^{d}	10.09 ± 0.72^{cd}	15.90 ± 0.06^{d}
SE3S2	89.23 ± 0.61^{a}	-0.61 ± 0.05^{e}	15.08 ± 0.63^{de}	15.10 ± 0.63^{d}	10.13 ± 1.06^{cd}	15.76 ± 0.04^{d}
SE3S3	89.09 ± 0.59^{a}	-0.63 ± 0.08^{e}	15.95 ± 0.45^{d}	16.44 ± 0.19^{e}	11.4 ± 0.96^{d}	16.43 ± 0.07^{e}
Note: a through f represent significantly different values ($p < 0.5$)						

Opacity is also an important measure in film applications, especially packaging, as it controls the incidence of light rays penetrating across the film and protects them against light deterioration sunlight, fluorescent or incandescent light (Martins *et al.* 2011). Exposure to light can bring negative effects to the product such as discoloration, nutrient loss, or off-flavor that lead by photo-degradation. Generally, a higher opacity implies lower transparency. It was observed that the opacity values of blend films increased significantly with SE concentration (Table 3). This phenomenon was due to the content of carotenoids in seaweed capable of absorbing the light wavelengths and meanwhile preventing the light rays from penetrating across the film (Stahl and Sies 2002). Furthermore, the opacity values of the blend films, which ranged from 15.17 to 16.43, were relatively higher than those of the reported film formation using kappa-carrageenan and locust bean gum (Martins *et al.* 2011). Additionally, similar results could also be observed from the results reported by Larotonda (2012), which involved the addition of carrageenan to the starch-based films.

Mechanical Properties

The film thickness is generally an important parameter used to calculate the mechanical and water vapor barrier properties of the films. According to the results presented in Table 4, the thickness of S/SE blend films ranged from 0.0580 mm to 0.1451 mm, depending on the composition of the film forming solution. It was noted that the varying concentration of both S and SE had affected the dry mass of the films, and therefore the films' thicknesses varied (Table 4). The thickness values of the S/SE blend films obtained in this study were close to those of the sago starch/carrageenan film (Poeloengasih *et al.* 2017), neat seaweed film (Siah *et al.* 2015), and starch/gelatin film (Fakhouri *et al.* 2015).

Table 4. Mechanical and Water Vapor Barrier Properties of the Composite Films

Film	Thickness (mm)	TS (MPa)	*E* (%)	YM (%)	WVP (g m^{-1} s^{-1} Pa^{-1})
SE1S1	0.0587 ± 0.0027^{a}	41.37 ± 0.27^{c}	6.50 ± 0.79^{ab}	6.43 ± 0.78^{ef}	1.73E-10 ± 0.08^{a}
SE1S2	0.0730 ± 0.0084^{b}	25.06 ± 0.48^{ab}	8.73 ± 0.06^{ab}	2.87 ± 0.07^{ab}	2.15E-10 ± 0.25^{b}
SE1S3	0.0947 ± 0.0027^{de}	17.73 ± 2.17^{a}	7.13 ± 3.70^{ab}	2.48 ± 0.83^{ab}	2.79E-10 ± 0.08^{cd}
SE2S1	0.0603 ± 0.0034^{a}	42.86 ± 4.84^{c}	6.17 ± 1.34^{ab}	7.06 ± 0.84^{f}	1.77E-10 ± 0.10^{a}
SE2S2	0.0841 ± 0.0032^{c}	28.76 ± 2.77^{ab}	10.57 ± 2.13^{ab}	2.79 ± 0.55^{ab}	2.47E-10 ± 0.09^{c}
SE2S3	0.0870 ± 0.0069^{cd}	24.23 ± 1.06^{ab}	12.67 ± 2.17^{bc}	1.64 ± 0.11^{ab}	2.56E-10 ± 0.02^{cd}
SE3S1	0.0865 ± 0.0012^{cd}	65.73 ± 1.22^{f}	18.40 ± 1.91^{bc}	3.60 ± 0.38^{bc}	2.55E-10 ± 0.03^{cd}
SE3S2	0.1037 ± 0.0049d^{e}	59.96 ± 4.18^{de}	12.83 ± 1.95^{abc}	4.72 ± 0.48^{cd}	3.05E-10 ± 0.14^{de}
SE3S3	0.1451 ± 0.0021^{f}	55.61 ± 3.82^{d}	10.83 ± 1.97^{bc}	5.21 ± 0.70^{de}	4.27E-10 ± 0.06^{f}

Note: a through f represent significantly different values ($p < 0.5$) analyzed by Tukey's Test; TS- tensile strength, *E*- elongation at break, and YM- Young's modulus

To evaluate film stability and resistance to uphold load during storage or usage, the tensile test is a relevant parameter to determine the mechanical properties of biopolymer films, including the tensile strength (TS) and elongation at break (*E*). The TS measures the film's resistance to break, with the presence of cohesion force within the components, whereas *E* accounts for the film flexibility. The TS and *E* values of the S/SE composite films are presented in Table 4. The TS values of the films with 3% SE content were significantly higher compared to the films with 1% or 2% SE content. This can be attributed to the formation of a double helix structure by the carrageenan polymers in *K. alvarezii* seaweed. When there was a high concentration of SE, such polymer formed a more rigid network, resulting in higher tensile strength (Flores *et al.* 2015). However, when the S concentration equaled to or exceeded the SE concentration in the composite film, the mechanical properties, especially the TS, deteriorated (Table 4). It is believed that the addition of starch promoted more intramolecular hydrogen bonding than the formation of intermolecular bonding among the components in the blend (Xu *et al.* 2005).

The elongation at break measures the capacity of film to elongate before it breaks. According to Table 4, the results of E were in the range of 4.67% to 18.40%. Regardless of the seaweed content, the increment of S concentration did not show any significant changes to the E of the composite films. In contrast, regardless of the S concentration, the addition of SE slightly increased the E, which indicated an improvement in flexibility of the composite films. Because seaweed is hygroscopic, the increase of SE concentration in the blend promoted more long linear repeating chains of β-D-galactose and anhydro-galactose that tended to draw more moisture into the matrix, and thus, indirectly created a plasticizing effect to the films (Abdou and Sorour 2014). This finding could be also verified by the results of the Young's Modulus (YM) in Table 4, in which a flexible material has a low YM (Abdul Khalil *et al.* 2017a). A similar phenomenon was also reported in other composite systems, in which the incorporation of a seaweed-derived polymer (*i.e.*, carrageenan) improved the flexibility of polyvinyl alcohol-based film (Kanatt *et al.* 2015).

Among the S/SE blend films, the blend film with 3% seaweed and 1% starch (SE3S1) possessed the highest TS and *E* (Table 4). This blend composition showed that the addition of SE induced an improvement in TS and *E* providing that the S content in the blend film was low. This finding was also in agreement with the reported composite film fabricated from carrageenan and starch blend (Abdou and Sorour 2014). Moreover, the overall mechanical results of the S/SE blend films obtained in this work were comparatively close or even better than the ones previously reported, such as those of the film prepared from sago starch and carrageenan (TS: 4.55 MPa to 12.98 MPa and *E*: 3.07% to 18.59%), corn starch and alginate (TS: 40.81 MPa to 63.41 MPa and *E*: 2.84% to 8.64%) and potato starch and agar (TS: 11.76 MPa and *E*: 58.33%) (Wu *et al.* 2009; Wang *et al.* 2011; Poeloengasih *et al.* 2017).

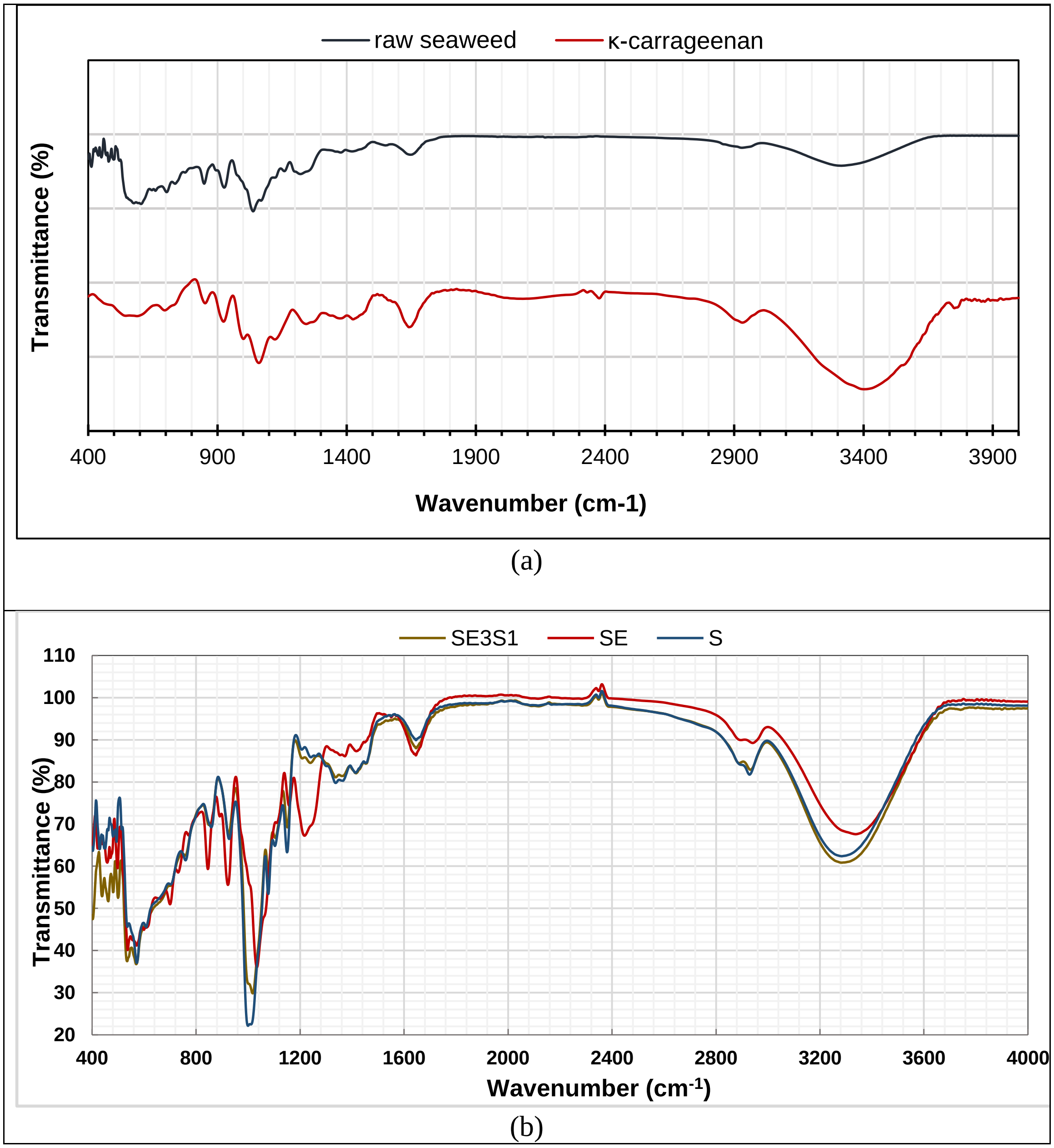
Water Vapor Barrier Property

The WVP commonly depends on both the solubility and diffusibility of water molecules across the film matrix (Ahmed and Ikram 2016). Water vapor barrier properties are of basic importance for packaging or edible coating that are the barrier against moisture transfer across food or surroundings. A low WVP means a good barrier to moisture transfer across the film. The WVP of the S/SE films were investigated by a gravimetric method, and the results are shown in Fig. 3. In this study, the WVP of the films were overall influenced by the linear effects of S and SE concentrations (Table 4), in which the WVP increased in parallel with the increase in S and/or SE concentrations. This phenomenon could be related to the higher number of free hydroxyl groups from S and SE, which might enhance more interaction with the hydrophilic water molecules and thus, result in a significant increase in the permeation rate of water vapor through the blend films. Similar results have been reported on yam starch film and starch/carrageenan film by Mali *et al.* (2004) and Poeloengasih *et al.* (2017), respectively, wherein the polysaccharide film usually exhibited high WVP value due to its hydrophilic character. Moreover, the S/SE composite films exhibiting increased WVP with film thickness were also found in this study (Table 4). This finding was supported by other researchers, in which film thickness could be one of the factors affecting the WVP values (Mali *et al.* 2004; Alves *et al.* 2010).

The WVP values of the blend films varied with the S and SE concentrations. They were in the range of 1.60×10^{-10} $gm^{-1}s^{-1}Pa^{-1}$ to 4.27×10^{-10} $gm^{-1}s^{-1}Pa^{-1}$, which were a similar order of magnitude, or lower than, those of other composite films such as starch/carrageenan film (Poeloengasih *et al.* 2017), starch/gelatin film (Fakhouri *et al.* 2015), agar/kappa-carrageenan/konjac glucomannan film (Rhim *et al.* 2013), alginate-acerola puree reinforced with cellulose whiskers film (Azeredo et *al.* 2012), and chitosan/tapioca starch with potassium sorbate film (Vásconez *et al.* 2009).

FTIR Spectroscopy

In order to identify the main polysaccharides in *K. alvarezii* seaweed, FTIR was used as a tool for the direct identification of the main natural phycocolloids such as κ-carrageenan (Pereira *et al.* 2009; Gómez-Ordóñez and Rupérez, 2011). The FTIR spectra of *K. alvarezii* were compared with those of commercial κ-carrageenan in Fig. 2(a).



(a)

(b)

Fig. 2. FTIR spectra of (a) K. alvarezii seaweed and commercial κ-carrageenan powder and (b) cornstarch (S) film, seaweed (SE) film, and cornstarch/seaweed composite film (SE3S1)

The spectra of native *K. alvarezii* showed the main features of commercial κ-carrageenan, for which a strong Raman band at approximately 850 to 853 cm^{-1} and 924 to

932 cm^{-1} were assigned to the presence of D-galactose-4-sulphate and 3,6-anhydro-D-galactose, respectively. Moreover, the bands at 1236 to 1244 cm^{-1} corresponded to the sulfate ester stretching of κ-carrageenan backbone. Therefore, these functional groups indicated the presence of carrageenan in *K. alvarezii*. Hence, κ-carrageenan was the major polysaccharide component in SE contributed to intermolecular interaction in the film.

According to Figure 2(b), the presence of functional groups and the interaction within the components in S/SE composite films was detected by FTIR spectroscopy. The FTIR spectra can be used to detect changes of the chemical groups of the molecules including shifting of the absorption band and peak intensity (Wanchoo and Sharma 2003). Generally, these interactions signify good miscibility of the components in the polymer blend (Xu *et al.* 2007). The IR spectra of SE, S and S/SE films are presented in Fig. 2. The changes within the S and SE in the blend (as the SE3S1 film with highest tensile results was selected) were observed by comparing to the FTIR spectra of blank S and SE films. According to Fig. 2, the broad absorption band within 310 cm^{-1} to 3500 cm^{-1} displayed the stretching vibration of the hydroxyl group. Moreover, FTIR spectra at around 280 cm^{-1} to 3000 cm^{-1} indicated the –CH stretching (Cerqueira *et al.* 2011), and within the range of 70 cm^{-1} to 1400 cm^{-1} associated with the functional groups of carbohydrates in the polysaccharide components (Martins *et al.* 2012).

According to Fig. 2 and Table 5, the neat SE film presented a dominant absorption band at 1217 cm^{-1}, 922 cm^{-1}, and 845 cm^{-1}, that was associated with the S=O bond of the sulfate ester groups, C-O and C-C vibration of 3,6-anhydrogalactose, and D-galactose-4-sulfate, respectively (Freitas *et al.* 2008; Distantina *et al.* 2013). Both functional groups of 3,6-anhydro-D-galactose and D-galactose-4-sulfate are the main compounds that provide the gelling ability and mechanical support to seaweed's structure (Pereira *et al.* 2013). The presence of pigments that gave yellowness to seaweed also were displayed in the current work's FTIR spectra within the range of 400 nm to 650 nm (Limantara and Brotosudarmo 2015). This observation also verified the obtained results in optical properties, as discussed earlier. Other peaks included the $-CH_3$ stretching at 2940 cm^{-1}, C=O group at 1640 cm^{-1} and 1366 cm^{-1}, and glycosidic linkage stretching at 1034 cm^{-1} that also were characteristic of the seaweed film. The chemical structure of protein also existed in the FTIR spectra of seaweed film in this study located at 698 cm^{-1}, which revealed the stretching of N-H bending and 571 cm^{-1} stretching of the phosphate group (Kumar and Singh 2008). Furthermore, the IR bands in FTIR spectra of S films according to a few pieces of literature are indicated in Fig. 2 and Table 5: 1078 cm^{-1}, 1150 cm^{-1}, and 999 cm^{-1}, attributed by the stretching of the C-O group, and 573 cm^{-1}, 760 cm^{-1}, 858 cm^{-1}, and 928 cm^{-1} that characterized the stretching vibration of the entire an-hydro-glucose ring, 1648 cm^{-1} featured in the presence of water in S, stretching of C-H responded at 2928 cm^{-1}, and also a broad brand at 3283 cm^{-1} due to stretching vibration of free, intermolecular, or intramolecular –OH groups (Fang *et al.* 2004; Chi *et al.* 2008).

For the S/SE composite film, a decrease in IR band intensities of starch film at 573 cm^{-1} and 1150 cm^{-1} was observed when starch was blended with seaweed. Similarly, it was observed that the intensity of the seaweed characteristic bands at 845 cm^{-1}, 922 cm^{-1}, 1034 cm^{-1}, and 1217 cm^{-1} were decreased in the composite film (Fig. 2). Moreover, chemical interaction within the components could also be detected by the shift of peak of the characteristic bands (Wanchoo and Sharma 2003). The –OH and CO- interactions that corresponded to the shifting of peak of both S and SE components showed a pattern commonly displayed in a reported miscible blend (Martins *et al.* 2012).

Table 5. FTIR Band Assignments in Starch Film and Seaweed Film

Seaweed (SE)	
Wavenumber (cm^{-1})	**Groups**
422, 600	Chlorophyll a, carotenoid, and phaeophytin pigments
571	Phosphate groups
700	N-H bending
845	-O-$SO_3$of D-galactose-4 sulfate
922	C-O-C vibration of 3,6- anyhydro-galactose
1034	C-O and C-C stretching of pyranose ring
1217	S=O bond of sulfate ester groups
1366, 1640	Carbonyl groups stretching
2936	Free CH_3 groups
3337	Free OH, SO2, and NH groups
Starch (S)	
Wavenumber (cm^{-1})	**Groups**
573, 760, 858, 928	Anhydro-glucose ring stretching vibration
999, 1078, 1150	C-O stretching
1648	Water
2928	C-H stretching
3283	Free, intermolecular, or intramolecular -OH groups stretching vibration

The shifts of peaks could be observed in the S/SE blend film at the feature bands: 1034 cm^{-1} shifted to 1030 cm^{-1} that was associated with C-O and C-C stretching of glycosidic linkage in SE, and 1648 cm^{-1} shifted to 1643 cm^{-1} that could be related to the interaction of OH group of water in starch that shifted from 1648 cm^{-1} to 1643 cm^{-1} (Fig. 2 and Table 5). In addition, other shifted peaks for both SE and S from 1034 cm^{-1} (SE film) to 1030 cm^{-1} (S/SE film), and from 999 cm^{-1} (starch film) to 1030 cm^{-1} (S/SE film) were due to the interactions of C-O and C-C within both components. Hence, this analysis revealed the changes in S/SE blend films' optical, mechanical, and water barrier properties.

CONCLUSIONS

1. A series of *Kappaphycus alvarezii* seaweed/corn starch composite films plasticized with glycerol were successfully developed using a solution casting technique.
2. Composite films with different concentrations of seaweed and starch showed a noticeable impact on the optical, mechanical, and water vapor barrier properties of the films.
3. The optical and mechanical properties of the starch/seaweed composite films were mainly affected by the seaweed concentration. In contrast, the water vapor permeability of the composite films increased linearly with the increase in concentration of starch and seaweed.
4. Seaweed could induce an increase in mechanical strength and flexibility of the starch/seaweed composite films provided that a low starch concentration was applied.

5. The FTIR results revealed good miscibility between the seaweed and starch in the composite film driven by their intermolecular interactions.
6. Findings from this study could be contributed as an approach to optimize film compositions for desired properties based on different biopolymer concentrations in the blend.

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