Preparation and characterization of modified and unmodified carrageenan based films

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Abstract. Seaweed is a green, abundantly available, and inexpensive source of polysaccharide that can be obtained from the sea. In this work, seaweed was introduced as a potential raw material for the production of a biopolymer-based film. A seaweed-derived biopolymer, carrageenan, with or without alkali modification was investigated for its physical, mechanical, and water vapor barrier as well as thermal properties. The effects of chemical modification on the properties of carrageenan were also further studied by Fourier Transform Infrared Spectroscopy (FTIR) analysis. Results showed that chemically modified carrageenan film exhibited better thermal stability, water vapor barrier property and less hydrophilic as compared to the native seaweed and unmodified carrageenan films. Nevertheless, its mechanical properties (except elongation at breaks) were among the lowest. FTIR analysis indicated that alkali modification of carrageenan capable of removing the hydroxyl and sulfate ester groups in carrageenan structure and meanwhile, forming 3,6-anhydrogalactose, which could improve the flexibility of the film. Moreover, the heating temperature also significantly impacted the properties of the film. As a result, by using carrageenan as a renewable feedstock with or without chemical modification was shown its feasibility on the production of biopolymer film possessed interesting properties.

1. Introduction
Seaweeds or known as marine macro-algae are multicellular plant-like organisms which generally found living attached to rocks in coastal areas. Since seaweed is abundantly available, able to grow in wide range of environments, cost effective and easy to cultivate in the natural environment as well as harvest year around, they are widely used as a human food source and herbal medicine. Instead of using seaweeds as a food, their excellent carbohydrate content also encouraged the industrial uses of seaweeds as a source of hydrocolloids (i.e. alginate, carrageenan, and agar) in the application for food, pharmaceutical and plastic industries [1].

Carrageenan is one of the seaweed-derived polymers obtained by extraction from red (Rhodophyta) seaweed. It composed of sulfated galactans, which have both gel forming abilities and viscosifying properties [2]. Therefore, it is commonly used as texturizing (or thickening) agents to control the functional properties of aqueous solution in food applications [3]. In general, carrageenan can be classified as Kappa (κ), Iota (ι) and Lambda (λ) according to their sulfate substitution pattern and 3,6-anhydrogalactose content, which affects the gel-forming properties. For kappa carrageenan, its structure consists of 25-30% of sulfate ester group and 28-35% of 3,6-anhydrogalactose while for Iota consists of 28-38% and 25-30% respectively. In Lambda structure have no 3,6-anhydrogalactose and...
contains 32-39% sulfate ester [4]. Since κ-carrageenan exhibits the smallest amount of sulfate esters than others commercial class of carrageenan, it has the least negatively charged, which allows less repulsion for intermolecular hydrogen bonding and thus, is likely to form a strong film with better gelling properties. Moreover, the presence of 3,6-anhydro-galactose in κ-carrageenan capable of reducing the hydrophilicity of the galactose residue and inverting the chair conformation from 1C4 to 4C1, which is also favorable to the gelation properties of carrageenan [5-6]. Therefore, κ-carrageenan possesses a good film-forming ability, which is in agreement with the gelling properties of κ-carrageenan.

Previous studies on carrageenan extracted from Kappaphycus alvarezii in hot water showed that they are mostly composed of strong κ-carrageenans gelling agents, significant amounts of low-molecular-weight galactans with κ-structure, and only small quantities of non-gelling carrageenans and agaroids [7]. However, carrageenan films have shown poor water vapor barrier properties due to the seaweed’s hydrophilic nature [8]. Therefore, several chemical modifications have been proposed to modify the physicochemical properties of carrageenans. Alkali is one of the common and simple solutions used for the extraction of carrageenan as it induces chemical modification that leads to increasing gel strength in the final product [9-10]. Earlier studies on carrageenan are limited mostly to the characterization of the extracted carrageenan properties. There is no study reported on the impact of extraction temperature on the properties of carrageenan film. Hence, the purpose of this study was to develop the carrageenan based film from Kappaphycus alvarezii, in which carrageenan was extracted via aqueous extraction of carrageenan with or without alkali modification, and to determine the characteristics of the developed carrageenan based films. The effects of varied extraction temperature on the properties of unmodified and chemically modified carrageenan based films were also discussed through various characterizations.

2. Materials and methods

Dried raw red seaweeds (Kappaphycus alvarezii), which harvested from Sabah, were washed with tap water to remove any impurities found on their surface like salts and sand particles. After cleaned, they were completely soaked in distilled water and left for 5 hours at room temperature. The soaked materials were then cut into small pieces by using a knife. Small pieces of seaweed were distributed in a big plastic tray and then placed inside the oven at 40 °C for 3-4 days. The completely oven-dried samples further stored in air tight container until further use.

2.1. Preparation of seaweed samples

Before extraction, the dried seaweed was pretreated with ethanol and acetone to eliminate the organosoluble fraction and to ease the process of extraction and modification [3]. 25 g of oven-dried (OD) seaweed samples were weighed and then, soaked in 800 ml of distilled water with the mouth of beaker covered with aluminum foil and left overnight at room temperature. The next day, the soaked samples were blended for 15 minutes by using a blender, and later the volume was made up to one liter. Two liters of ethanol was added into the blended solution and left for half an hour. Then, the mixture was stirred simultaneously. After that, the seaweed slurry was filtered twice. The precipitate obtained by filtration was added with acetone until 1000ml and the mixture was stirred simultaneously for half an hour. Again, the seaweed slurry was filtered twice. Finally, the pretreated seaweed sample obtained was oven dried at 40 °C overnight before processing to extraction, modification, and precipitation of carrageenan.

2.2. Pretreatment of seaweed samples

Before extraction, the dried seaweed was pretreated with ethanol and acetone to eliminate the organosoluble fraction and to ease the process of extraction and modification [3]. 25 g of oven-dried (OD) seaweed samples were weighed and then, soaked in 800 ml of distilled water with the mouth of beaker covered with aluminum foil and left overnight at room temperature. The next day, the soaked samples were blended for 15 minutes by using a blender, and later the volume was made up to one
liter. Two liters of ethanol was added into the blended solution and left for half an hour. Then, the mixture was stirred simultaneously. After that, the seaweed slurry was filtered twice. The precipitate obtained by filtration was added with acetone until 1000 ml and the mixture was stirred simultaneously for half an hour. Again, the seaweed slurry was filtered twice. Finally, the pretreated seaweed sample obtained was oven dried at 40 °C overnight before processing to extraction, modification, and precipitation of carrageenan.

2.3. Extraction of carrageenan
All the dried pretreated seaweed was placed in a 2000 ml beaker that containing distilled water (60 mL/g) at pH 7 and stirred until it dispersed in water by using a stirrer machine at 500 rpm for half an hour. The beaker was covered with aluminum foil and then placed in water bath at 60 °C and shaken at 55 rpm for 3 hours. After 3 hours, the beaker was taken out from the water bath. Double volume of ethanol was added to the solution and stirred simultaneously for half an hour. Then, the seaweed slurry was filtered by using a cloth filter and the precipitate was collected by filtration. Next, the obtained extracted carrageenan (precipitate) was placed in a plastic tray and oven dried at 40 °C for 2 days until it dried completely. Lastly, the extracted carrageenan (purified and unmodified carrageenan) was weighed and recorded before processing to the preparation of film. All the above steps for hot water extraction of carrageenan were repeated for a different condition of temperature at 80 °C water bath.

2.4. Extraction of carrageenan and alkali modification
Carrageenan from dried pretreated seaweed was extracted and chemically modified using 1M NaOH solution (60 mL/g). First, the mixture in the beaker was stirred at 500 rpm for half hour. Then, the beaker was covered with aluminum foil and then placed in the water bath at 60 °C and shaken at 55 rpm for 3 hours. After 3 hours, the beaker was taken out from water bath and the solution was neutralized to approximately pH7 with HCl (2 M). Then, a double volume of ethanol was added into the solution and stirred with a spatula for half an hour. After that, the seaweed slurry was filtered through a cloth filter and the precipitate was collected by filtration. The obtained alkali extracted carrageenan (precipitate) was placed in a plastic tray and oven dried at 40 °C for 2 days until it dried completely. Finally, the alkali extracted carrageenan (chemically modified carrageenan) was weighed and recorded before processing to the preparation of film. All the above processes for alkaline treatment of carrageenan were repeated for a different condition of a temperature at 80 °C water bath.

2.5. Preparation of native seaweed, unmodified carrageenan and chemically modified carrageenan films
2% (w/v) of unmodified and chemically modified carrageenan solutions were prepared separately by soaking in distilled water overnight and blended for 15 minutes by using a blender (Panasonic MX-895 M). A 33.33% (w/w) concentration of glycerol based on the oven-dried weight of the sample was added to the blended slurry. Next, the mixture was stirred continuously at 500rpm for 4 hours by using a stirrer machine. After stirring for 4 hours, the mixture was transferred into a stainless steel tray with measurement of 32 x 9.5 x 1.5 cm and spread evenly and subsequently left to the oven dried at below 40 °C until dried completely for about 3-4 days. The films were stored in a desiccator with 50% relative humidity for at least 3 days before further characterization.

Moreover, a native seaweed film as a control was also prepared by mixing 2% (w/v) native seaweed solution with glycerol. Then, the mixture was heated to the different temperature (60 °C and 80 °C) in the water bath at 55 rpm for 3 hours and then, followed by drying as mentioned above.

2.6. Characterization of native seaweed, unmodified carrageenan and chemically modified carrageenan films
2.6.1. Film thickness. The thickness of biopolymer films was measured by using a precision electronic micrometer to the nearest 0.001 mm at 5 random locations on each film. The average thickness value for all the films was calculated and used in tensile strength and Young’s Modulus calculations.

2.6.2. Mechanical testing. Mechanical strength and flexibility are basic requirements for a film to resist external stress and maintain its integrity during its application and subsequent shipping or storage. Typically, the mechanical resistance of biopolymer film is studied according to three essential parameters: tensile strength (TS), young’s modulus (YM) and elongation at break (EAB). These parameters are determined based on stress–strain curves according to the norm of the American Society for Testing and Materials (ASTM). TS is defined as the maximum stress that a film can withstand when being stretched or pulled before failure. EAB is the maximum change in the length of a test specimen before breaking.

Tensile testing was conducted for each film specimen using the Miniature tensile Tester MT1175 (Dia-stron Instruments, United Kingdom) programmed with UvWin1000 software, in reference of ASTM D882-02. In tensile testing, at least five film specimens were cut in a rectangular shape with a dimension of 150mm x 2.5mm. The tensile strength, percentage of elongation at break and Young’s Modulus of the film specimens were evaluated based on the generated stress-strain graphs. Each reported data was the mean value of three replicate.

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\text{Tensile Strength, TS (MPa)} = \frac{\text{Maximum load (N)}}{\text{Cross-section area of film (m²)}}
\]  

(1)

\[
\text{Elongation at Break, EAB} (%) = \frac{\text{Final gauge length (mm)} - \text{Initial gauge length (mm)}}{\text{Initial gauge length (mm)}} \times 100
\]  

(2)

\[
\text{Young Modulus (MPa)} = \frac{\text{Maximum load (N) \times Cross-section area of film (m²)}}{\text{Change in length (mm) + initial gauge length (mm)}}
\]  

(3)

2.6.3. Thermal analysis. Thermogravimetric analysis (TGA) was carried out to study the thermal stability or thermal degradation characteristic of the biopolymer films by using Perkin-Elmer TGA6 thermogravimetric analyzer. The film specimen was cut into tiny pieces and each sample had a mass between 8-10 mg. The tiny pieces of the sample were placed in the balance system and heated from 30 °C to 800 °C at a heating rate of 10 °C min\(^{-1}\) under a nitrogen atmosphere to avoid thermo-oxidative reactions.

2.6.4. Contact angle measurement. Static contact angle measurement on the surface of films was performed using a Contact Angle Measurement System, CAM 100/101/200 series Drop Shape Analysis contact angle meter whereby sessile drop technique has been applied. The film specimens were cut into square shape with a dimension of 20mm x 20 mm. A drop of test liquid was uniformly dropped on the film and images were recorded for the 30 s at a speed of 40 frames per second. The images were executed by using KSV Contact Angle Measurement system. Each type of film was repeated for three times and the mean value was calculated.

2.6.5. Water vapor transmission rate (WVTR) analysis. WVTR value of the film specimens was determined according to ASTM E96/E96M-05 method with slight modification. Films free of any defects such as pinholes, air bubbles or cracks were used for WVTR determination. Initially, the internal diameter of the beaker was measured for the calculation of WVTR. Then, the film specimen was sealed on the top of a 100 ml beaker which contained 60ml of distilled water by using a sealing tape and, it was recorded as initial weight. Next, it placed in the desiccator which had been maintained at room temperature and 0% RH. The amount of water transferred through the film and absorbed by the desiccant was determined as the weight loss. Each sample was weighed at an interval of 24 hours until a constant weight loss was obtained. Each type of film was repeated for three times and the mean
value was calculated. The WVTR was expressed in g/m² per day and calculated by the following formula:

\[
\text{WVTR} = \frac{\text{Constant weight loss (g)}}{\text{Area of circular mouth of beaker (m²)}}
\]  

(4)

2.6.6. Fourier Transform Infrared Spectroscopy (FTIR) analysis. FTIR spectra of the biopolymer films were analyzed by using an attenuated total refraction method (ATR) in an IR spectrometer. Film specimens to be analyzed were cut into square shape with a dimension of 10mm x 10mm and then oven dried at 60 °C for overnight. During analysis, the specimen was placed in the zinc selenide ATR cell. Prior to sample collection, a background spectrum was recorded and subtracted from the sample spectra. Infrared spectra of all the film specimens were obtained from Perkin-Elmer FT-IR 1600 spectrometer. A smoothing filter was applied to the spectra without losing peak resolution in order to reduce the apparent noise of the data correlated with Fourier self-convolution.

3. Results and discussion

Seaweeds or known as marine macro-algae are multicellular plant-like organisms which generally found living attached to rocks in coastal areas. Since seaweed is abundantly available, able to grow in wide range of environments, cost effective and easy to cultivate in the natural environment as well as harvest year around, they are widely used as a human food source and herbal medicine. Instead of using seaweeds as a food, their excellent carbohydrate content also encouraged the industrial uses of seaweeds as a source of hydrocolloids (i.e. alginate, carrageenan, and agar) in the application for food, pharmaceutical and plastic industries [1].

3.1. Mechanical testing

According to Table 1, the unmodified carrageenan based film obtained the highest TS and YM, followed by native seaweed and chemically modified carrageenan based films. It was believed that the unmodified carrageenan film possessed strong hydrogen bonding, which was capable of providing more affinity for the higher number of hydrogen bonds formed in the film. On the other hand, modified carrageenan based film attained the lowest TS and YM. This phenomenon was due to some of the hydroxyl and sulfate ester groups were released during alkali modification and thus, reduced the intermolecular hydrogen bonding of the film. Moreover, the removal of sulfate ester group capable of forming 3,6-anhydro-galactose, which was crucial in introduce gelling characteristics in the carrageenan [9]. Therefore, it was believed that the increase in the proportion of 3,6-anhydro-galactose increased the flexibility of the film. Hence, chemically modified carrageenan film obtained the highest value of EAB, as shown in Table 1.

Interestingly, the TS and YM of three different seaweed-based films were improved at low treatment (or extraction) temperature (60 °C), whereas EAB of these films was increased when treatment was conducted at elevated temperature (80 °C). The previous study reported that treatment or extraction temperature affected gel strength, which was higher when carrageenan was extracted at high temperature of about 80 °C. In contrast, the gel viscosity increased when the extraction temperature achieved 60 °C, and at higher temperatures this variable decreased due to the degradation of biopolymer [7]. Therefore, these findings verified that temperature significantly affected the mechanical properties of the films (Table 1).

Table 1. Mechanical properties, contact angle and WVTR of native seaweed, unmodified carrageenan and modified carrageenan based films.

| Film specimens          | Temperature (°C) | Tensile strength (MPa) | Young's Modulus (MPa) | Elongation at break (%) | Contact angle (°) | WVTR (g/m²/day) |
|-------------------------|------------------|------------------------|-----------------------|-------------------------|------------------|-----------------|
| Native seaweed          | without          | 78.3                   | 751.9                 | 8.6                     | 61.9             | 683.91          |
3.2. Wettability analysis

The contact angle measurement was used to determine the surface hydrophobicity and wettability properties of biopolymer films. Generally, high contact angle indicated film surface with hydrophobic character. Or in other words, low contact angles corresponded to high wettability, whereas large contact angles corresponded to low wettability. Based on the results presented in Table 1, native seaweed film prepared without undergone heating process obtained the lowest value of contact angle (61.9°) due to the hydrophilic nature of seaweed. Nevertheless, the increase of contact angle was observed when the native seaweed underwent the heating process. Therefore, these findings verified that temperature significantly affected the wettability of the film, in which heating could reduce the hydrophilic nature of seaweed and form better gel strength, as discussed earlier.

According to Table 1, the contact angle of all films was increased with the increase of heating (or extraction) temperature. This phenomenon might be due to the removal of hydroxyl and sulfate ester groups at elevated temperature, which then resulted in increasing surface hydrophobicity of biopolymer film. This could be further verified by the analysis of FTIR. Therefore, 80 °C was a maximum temperature to increase the hydrophobic character of the film in the case of this study. Among the films, the alkali modified carrageenan based film obtained the highest value of contact angle. Previous study reported that κ-carrageenan capable of undergoing cyclization in the presence of 1 M sodium hydroxide at 80 °C, in which sulfate ester groups (very hydrophilic) were removed for the formation of 3,6-anhydro-bridge that could lead to a reduction of hydrophilicity of film [9]. Thus, the alkali modified carrageenan based film exhibited hydrophobic surface with low wettability, in comparison to other films.

3.3. Water vapor transmission rate (WVTR) analysis

Permeability is the contribution of diffusivity and solubility through the solid matrix, whereby in this research it was measured as water vapor transmission rate. WVTR is a method to measure the ease of moisture to penetrate and pass through a material [11]. The water vapor transmission of the carrageenan based film can be influenced by several factors such as the structure of polymer matrix, glycerol as plasticizer and surface wettability properties [12-13].

According to Table 1, it could be observed that the value of WVTR decreased with the increasing of the contact angle of all film. Since the native seaweed film prepared without undergone heating process obtained the lowest value of contact angle as mentioned earlier, it WVTR was the highest (683.91 g/m²/day) among other films. This finding revealed that the water vapor was easy to diffuse through the film due to the hydrophilic character of native seaweed. In contrast, the decrease of WVTR was noted when film prepared by heating the native seaweed at 60 °C and 80 °C. Similar to others characterization studies, these finding also validated that temperature also significantly affected the WVTR of the film, in which heating would reduce the hydrophilic nature of seaweed and enhance hydrophobic characteristic of the film. Among the films, alkali modified carrageenan based films prepared at 80°C of extraction temperature attained the lowest value of WVTR. Since alkali could induce a chemical modification that improved the gel strength of the film due to the formation of anhydro linkage, the chemically modified carrageenan film became less hydrophilic. The water vapor diffusion across the film was reduced and thus, lowered the WVTR.
3.4. Thermal analysis – Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed to evaluate the thermal degradation of native seaweed, unmodified carrageenan and chemically modified carrageenan films at high temperature. TGA usually analyzed the materials that possessed either mass loss or gain due to the decomposition, oxidation or loss of volatiles like moisture. Figure 1 shows the weight decreasing pattern of all films caused by thermal decomposition. For native seaweed films, TGA thermograms illustrated that there were four significant stages of weight loss, whereas there were only three stages of weight loss for unmodified and modified carrageenan films.

Figure 1. TG curves of native seaweed, unmodified carrageenan and chemically modified carrageenan based films.

Initially, the first stage of weight loss for all the films occurred in the temperature range of 60-100 °C (Figure 1). This phenomenon was due to evaporation of adsorbed water molecules trapped within the film matrix, which existed in H-bonded form with -OH groups of the galactose units along the polymer chain [14-15]. The weight losses at this stage for all native seaweed, unmodified carrageenan, and chemically modified carrageenan films were 20-22%, 19-20% and 16-17%, respectively. Native seaweed film attained the highest reduction in weight because of its hydrophilic nature which led to high water adsorption. In contrast, modified carrageenan film showed the lowest weight loss among the film. This phenomenon was probably due to the removal of –OH groups during alkali modification and thus, it could be further validated by FTIR and wettability tests.

In the second stage, all the films showed tremendously weigh losses along with different thermal degradation temperature, in which the native seaweed, unmodified carrageenan, and chemically modified carrageenan films achieved total weight losses of 21-25%, 46-50% and 58-61% at 130-180 °C, 200-240 °C, and 240-300 °C, respectively (Figure 1). This stage took place was due to the degradation of glycerol and initial decomposition of seaweed polymers [16, 17]. Furthermore, in the third stage, the weight losses of all films were further decreased, wherein native seaweed, unmodified carrageenan, and chemically modified carrageenan films achieved weight losses of 30-47%, 73-75% and 70-73% at 200-235 °C, 350-380 °C and 390-430 °C, respectively (Figure 1). This stage took place most probably related to the thermal degradation of seaweed or carrageenan polysaccharide chains [18, 19].

Based on the respective results from the second stage and third stage, the thermal degradation temperature was increased after extraction and modification of carrageenan. This revealed that the high temperature of thermal degradation resulted in the better thermal stability of the films prepared...
from unmodified and modified carrageenan. The unmodified and modified carrageenan films showed higher degradation temperature than native seaweed films as purification of carrageenan could lead to the removal of other thermally sensitive impurities like proteins, lipids, and etc. Furthermore, more hydrogen bonds formed in purified carrageenan films than native seaweed films which might also contribute towards the better thermal stability of the films [20, 21]. Nevertheless, modified carrageenan films were more thermally stable than unmodified carrageenan films. This was possibly caused by the presence of more charged groups (SO$_3^-$) in unmodified carrageenan molecules than modified one did. After alkali modification, the formation of anhydro linkages indicated the reduction of charged groups in the modified carrageenan molecules. This finding was in agreement with the reported study from Villetti et al [22], which neutral polysaccharides showed higher thermal resistance than the charged polysaccharides.

According to Figure 1, there was a fourth stage could be observed only in the thermal analyses of native seaweed films. It occurred at the temperature ranged from 250-400°C with a total weight loss of 69-77%. This might be due to the degradation of some components such as proteins, lipid or minerals that could be found in native seaweed films. Besides, the weight loss gradually rose until reaching the temperature around 760 °C (Figure 1). This progressive decrement in weight was attributed to the further breakage of sub-products in the film matrix from the third or fourth stage. The char residues contributed by native seaweed films were ranged from 20% to 23% by weight, while for unmodified and modified carrageenan film were ranged from 17% to 19% by weight. The high amount of residue left in native seaweed films was most probably attributed from the residual of lipids, proteins or minerals.

3.5. Fourier Transform Infrared Spectroscopy (FTIR) analysis

Infrared spectroscopy is a rapid and non-destructive technique that is widely used to characterize different polysaccharides and to determine the presence of various functional groups. When chemical groups interact at the molecular level, changes can be investigated by FTIR spectra through the shifting of absorption bands. The FTIR spectra of native seaweed, unmodified carrageenan, and modified carrageenan based films are shown in Figure 2.

As it would be expected, after the extraction and modification process, the FTIR spectra were changed. According to the results of FTIR, all the spectra revealed a broad band ranging between 3100 and 3600 cm$^{-1}$, which was attributed to O-H stretching vibration from the hydroxyl group of polysaccharides which correspond to the hydrophilic character of seaweed. While, the broad band around 2800-3000 cm$^{-1}$ was attributed to C-H stretching vibration [23]. Since native seaweed undergone heating process showed an increase in the percentage of transmittances, this information showed that heating process could remove some of the hydroxyl group from the seaweed (Figure 2). Nevertheless, no obvious changes in the IR spectra of hydroxyl group were observed for extraction temperature of 60 °C and 80 °C, wherein the native seaweed, unmodified carrageenan and modified carrageenan films prepared at 60 °C and 80 °C were 3329.14 cm$^{-1}$, 3332.99 cm$^{-1}$, and 3325.28 cm$^{-1}$.

FTIR spectra of film specimens showed the high intensity of band in the region of 750-1300cm$^{-1}$ that corresponding to the carbohydrates region (Figure 2). A very strong absorption band in the region of 1210-1260 cm$^{-1}$ was observed. This is due to the presence of S=O bond of sulfate ester groups. Moreover, the IR bands at around 840-850 cm$^{-1}$ showed the presence of C-O-SO$_3$ of D-galactose-4-sulfate [3]. According to Figure 2, the peak of S=O bond was shifted from 1219.01 cm$^{-1}$ (unmodified carrageenan film) to 1222.87 cm$^{-1}$ (modified carrageenan film), whereas the peak of C-O-SO$_3$ was shifted from 844.82 cm$^{-1}$ (unmodified carrageenan film) to 848.68 cm$^{-1}$ (modified carrageenan film). This phenomenon was due to the removal of some sulfate ester groups and thus, formation of 3,6-anhydro linkage, which it was depicted by an IR band around 922 cm$^{-1}$ that corresponding to the C-O bond of 3,6-anhydro-D-galactose [3]. Hence, this analysis revealed the changes in native seaweed, unmodified carrageenan and modified carrageenan based films mechanical, thermal and water barrier properties.
Figure 2. FTIR spectra of native seaweed, unmodified carrageenan and modified carrageenan based films.

4. Conclusion
Native seaweed, unmodified carrageenan, and alkali modified carrageenan based films showed differences in physicochemical, mechanical and water vapor barrier as well as thermal properties. Unmodified carrageenan was suitable to produce biopolymer films with the best mechanical properties which exhibited high tensile strength and Young’s modulus; while modified carrageenan was suitable to produce biopolymer films with the best thermal stability and hydrophobic properties. Moreover, varying of extraction temperature also lead to significant changes in the properties of the film, wherein the increase of temperature reduced the tensile strength and Young’s modulus, but improved the elongation at break and hydrophobicity agreed with the results of contact angle and WVTR. Therefore, it was believed that chemical modification of carrageenan could enhance all the properties of film provided that an appropriate extraction temperature was selected.

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