Effect of κ-carrageenan concentration on physical and Mechanical properties of vegetable leather based on kelor leaves (*Moringa oleifera* L.)

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Abstract. The aims of this research were to investigate the effects of κ-carrageenan concentration on the physical and mechanical characteristics of vegetable leather based on *kelor* leaves. This research used non-factorial Completely Randomized Design (CRD), consisting of five treatments of κ-carrageenan concentration ie. 1.00% (K1), 1.25% (K2), 1.50% (K3), 1.75% (K4) and 2.00% (K5). Analysis of physical and mechanical properties (elongation at break, thickness, and solubility) of all treatments were carried out. Morphological properties and functional group identification were conducted from the best treatment. The concentration of κ-carrageenan very significantly affected on thickness and solubility and no significantly affected on the elongation percentage. Morphological tests on the surface of vegetable leather were slightly coarse than edible films from κ-carrageenan. FTIR spectra of vegetable leather had a different absorption band intensity than pure κ-carrageenan. So, it could be concluded that vegetable leather had the potential to be developed commercially.

1. Introduction

Vegetable Leather is a processed product derived from vegetables that are crushed and dried. Vegetable Leather which has a good water content of 10-20%, at less than 0.7, plastic texture, and appearance like skin [1]. The principle of making vegetable leather has many similarities with nori. However, research on vegetable leather is still lacking. The principle of nori processing is currently widely applied in making fruit leather.

Nori is a traditional Japanese food (sea vegetables) made from Phorphyra marine algae (Bangiales, Rhodophyta), in the form of thin sheets (size 0.2 mm arranged 10-20 layers), finely cut in uniform-kizaminori or aonori size), dried or seasoned and toasted nori-ajitsuke nori or okazunori [2]. However, this type of seaweed is very difficult to find in Indonesian waters because seaweed is more suitable to grow in subtropical climate [3]. In the manufacture of commercial nori, seaweed contains carrageenan which has the ability to form a gel so that it can maintain the shape of the nori sheet. Thus, the manufacturing of vegetable leather is also needed for gelling ingredients from carrageenan seaweed.

The purpose of this study was to investigate the effect of carrageenan concentration on physical and mechanical properties ie. elongation at break, Thickness and Solubility. Morphological properties of vegetable leather also investigate using Scanning Electron Microscope instrument. In addition, the
changes and differences between pure carrageenan and after being processed into vegetable leather through a functional group approach were also investigated in this study using FT-IR instruments. Through this research, it is expected to obtain information related to vegetable leather film characters from carrageenan and kelor leaves as a source of protein, so that in the future it can be developed in the food industry.

2. Materials and Method

2.1. Materials

Kelor leaves, sugar and salt were purchased from local market in Kendari, South East Sulawesi, Indonesia. While κ-carrageenan was purchased from Sigma with purity approximately ≥ 99.9%.

2.2. Preparation of fruit leather

15 g Moringa leaves were bleached with water vapour for 5 minutes. Bleaching process using water vapor can maintain vitamin C content, increase β-carotene and protein contents in leaves. This method was able to increase protein content approximately 0.11% [4]. κ-carrageenan according to the treatment variation was put into 100 ml distilled water. Then 0.50 g of salt, 0.30 g of sugar and 100 ml of boiled water were added. The mixture was blended for 1 minute. Then placed in Pyrex glass and dried in oven for ± 15 h at 60°C. Variations of carrageenan used were 1.00% (K1), 1.25% (K2), 1.50% (K3), 1.75% (K4) and 2.00% (K5).

2.3. Elongation at break test

Elongation at break (EAB) were measured using modified digital fruit sclerometer. Film strips (35 x 50 mm) were mounted to a grip of digital fruit sclerometer. The maximum force required to rupture each film was read from the digital display of the device. Elongation at break was calculated by dividing the increase in length of the film strips when the rupture occurred (b) with the initial length of the film strips before loading (a) [5]. EAB was calculated using the formula:

\[
\% \text{Elongation at break} = \frac{b}{a} \times 100\% \tag{1}
\]

2.4. Tickness

Thickness was conducted to determine the robustness of leather made from kelor leaves. Before the measurements are made, 2 x 2 cm sample sheets were prepared and conditioned in the laboratory. Thickness was measured using micrometre screw.

2.5. Solubility

The solubility of vegetable leather samples was determined according to the method of Ahmad et al. [6] and Gontard et al. [7]. Solubility test was done using film samples of 3 x 2 cm in size. Samples were dried at 105°C for 24 h and weighed (W1). Each sample was then inserted into a 50 ml centrifuge tube containing 10 ml of distilled water. Samples were stored for 24 h at room temperature and stirred slowly on a periodic basis using a shaker. The solution was filtered, and the residues remained on the filter paper were dried in an oven at 105°C for 24 h after which the samples were weighed to determine the dry matter soluble in water (W2). Solubility was calculated using the formula:

\[
\% \text{Solubility} = \left[ \frac{W2-W1}{W1} \right] \times 100\% \tag{2}
\]
2.6. Scanning electron microscope
The surfaces of vegetable leather were examined by SEM using a JEOL JSM 6480 LV scanning microscope. For cross-sectional observations, the films were cryo-fractured by immersion in liquid nitrogen and stored at 25°C over silica gel. The film samples were mounted on bronze stubs, coated with a gold-palladium alloy and observed using an accelerating voltage of 15 kV.

2.7. Fourier transform infra-red
FTIR spectra of samples were studied using infrared spectrometer (FTIR, Bruker IFS113v). Spectral measurements were performed in the absorbance mode. Each spectrum was recorded at the range of 400-4000 cm\(^{-1}\) with complete 32 scans at a resolution of 4 cm\(^{-1}\) [8].

2.8. Data analysis
The data were analysed by using Analysis of Varian, and the result of the test showed a significant effect on the observation variable, followed by Duncan's Multiple Range Test (DMRT) test at 95% ($\alpha = 0.05$) and 99% $\alpha = 0.01$).

3. Results and Discussion

3.1. Elongation at break
The elongation at break is mechanical properties that closely related to the physical properties of edible films. Edible films and vegetable leather have the same characteristics and functions as food protectors. The elongation at break is quantitative representation of the leather's ability to stretch, which defined as the fraction of the change in material length as the effect of deformation [9]. The results showed that carrageenan concentration had no significant effect on elongation at break in the vegetable leather of kelor leaves. Elongation at break of vegetable leather are K1 = 11.5 ± 0.15%, K2 = 9.5 ± 0.25%, K3 = 9.0 ± 0.53%, K4 = 13.0 ± 0.15% and K5 = 9.5 ± 0.21%. These results are different from those reported by Ariska and Suyatno [10] in making edible films from banana weevil starch using carrageenan concentration of 1; 1.5; 2; 2.5 grams get the result of elongation at break ie. 23.4374%; 17,5884%; 14.2577%; 3.9687%, respectively. The difference in results is very much due to the type of film forming material that will affect the cohesive properties of edible film structures. This is confirmed that the greater the carrageenan mass concentration added, the smaller the extension results. The higher the concentration of carrageenan used, the carrageenan molecule will form a stronger film matrix, so the film becomes less elastic or brittle, and consequently the percentage of extension decreases [10].

Elongation at break is categorized as bad if it is less than 10% and very good if it is more than 50%. So, the sample meets the minimum standard is the sample K1 and K4 with the concentration of carrageenan about 11.5% and 13.0%.

| Sample | Elongation at break (%) |
|--------|-------------------------|
| K1     | 11.5±0.15               |
| K2     | 9.5±0.25                |
| K3     | 9.0±0.53                |
| K4     | 13±0.15                 |
| K5     | 9.5±0.21                |

3.2. Thickness
Thickness is one of the physical characteristics of vegetable leather which shows the size of the sheet from the vegetable leather. The test results can be vegetable leather thickness of Moringa leaves are
shown in Table 2. Based on Table 2 shows that the higher the concentration of carrageenan will increase the thickness of vegetable leather. This is because the higher the concentration of the material used, will increase the total solids found in vegetable leather after drying, so that it will produce thicker leather. The mass of carrageenan and the yield of thickness in this study are 1 g = 0.15 (mm); 1.5 g = 0.16 (mm); 2 g = 0.17 (mm); 2.5 g = 0.19 (mm) [10]. Besides being influenced by the constituent components, the thickness of the leather is also influenced by the area of the mild plate and the volume of the film suspension being printed [13]. The thickness of vegetable leather obtained is still relatively good because it is still below the maximum standard of vegetable leather / edible film thickness approximately 0.25 mm [11].

Thickness values can affect the mechanical properties and the value of vegetable leather vapor transmission rate, namely elongation at break. However, the thickness of vegetable leather must be adjusted to the product that will be packaged if it is applied as a food wrapper [10].

Table 2. Thickness of vegetable leather based on kelor leaves with variation of carrageenan concentration.

| Sample | Carrageenan Concentration (%) | Averages of Thickness (mm) | DMRT α 0,01 |
|--------|-------------------------------|---------------------------|-------------|
| K1     | 1.00                          | 0.0150<sup>d</sup>        |             |
| K2     | 1.25                          | 0.0450<sup>c</sup>        | 2 = 0.01390 |
| K3     | 1.50                          | 0.0625<sup>b</sup>        | 3 = 0.01457 |
| K4     | 1.75                          | 0.0750<sup>b</sup>        | 4 = 0.01498 |
| K5     | 2.00                          | 0.0950<sup>a</sup>        | 5 = 0.01527 |

Note: The numbers followed by different letters in the same column differ very significantly at the 99% confidence level.

3.3. Solubility test

Solubility is one of the physical properties of vegetable leather which shows the percentage of dry weight dissolved after immersion in water for 24 h. The solubility of the leather/film is determined by the source of the base material of the film. Vegetable leather polymer-based carrageenan solubility rate is influenced by hydrophilic group bonding materials. The weaker the hydrophilic group bond, the higher of leather solubility. Leather with high solubility indicates that leather resistance to water is lower, and indicates the hydrophilicity of the leather. The results of vegetable leather solubility test can be showed in Table 3.

Vegetable leather with high solubility indicates that the leather is easy to consume. Solubility is a benchmark for a soluble film when it will be consumed and also for the determination of biodegradable film when it will be used or used for packaging [13]. The manufacture of edible film-based carrageenan, the mean percent of solubility ranged from 39.1547% -55.5926% and the best treatment available in edible films that have low solubility [14].

The lowest solubility value indicates that the edible film is best because it plays a role when the film is packaged for edible products. The higher of solubility value, the lower the ability of biodegradable film to have water resistance [15]. The low solubility value in biodegradable film is very good to be used as packaging material. However, in this study the treatment chosen from the solubility analysis is treatment that high solubility (K1) because leather is intended as a packaging that worth eating. If the application of a film is desired as an edible packaging, high solubility is desired. Likewise, if the application of a film to foods with high water content, the film that not dissolved in water is used [16].
Table 3. Solubility of vegetable leather based on kelor leaves.

| Treatment | Carrageenan Concentration (%) | Average of Solubility (%) | DMRT α 0.01 |
|-----------|-------------------------------|---------------------------|-------------|
| K1        | 1.00                          | 72.750\(^a\)              |             |
| K2        | 1.25                          | 54.650\(^b\)              | 2 = 11.86   |
| K3        | 1.50                          | 51.900\(^bc\)             | 3 = 12.44   |
| K4        | 1.75                          | 39.900\(^c\)              | 4 = 12.79   |
| K5        | 2.00                          | 39.950\(^c\)              | 5 = 13.03   |

Note: The numbers followed by different letters in the same column differ very significantly at the 99% confidence level.

3.4. Scanning electron microscope
Characterization using SEM aimed to see the morphology structure of edible films. The vegetable leather analysed was K1 treatment. The results of micrograph characterization using SEM can be seen in Figure 1. This is in contrast to the more delicate edible films of κ-carrageenan and the results study on the edible seaweed surface morphology of the *Kappaphycus alvarezii*, it was observed that the films showed homogeneous, uniform and continuous, surface without cracking and porous structure [16]. The surface of the film becomes flatter/smooter and soft due to the addition of the starch, the smaller the ratio of glycerol: starch, the chances for the formation of small cracks on the surface of the film are smaller [17]. Film from sago starch: fish gelatine produces a smoother surface in the ratio of the starch: gelatine greater [18]. While in this study did not use starch.

Besides being caused by the addition of starch, the coarse film surface is also caused by the addition of protein. Protein-added pectin films showed that the surface of the protein-free pectin film was relatively smoother and flatter than the surface of the protein-added pectin film, which was coarse, dense and brittle with irregular particles spread evenly. So, it is assumed that the rough film surface in the study can also be caused by protein from kelor leaves. [19]. The addition of κ-carrageenan cannot reduce the presence of cracks, so the surface appearance is not compact [20].

![Figure 1](image1.png)

*Figure 1.* SEM image of (a) vegetable leather from kelor leaves (K1: 1.00%) and (b) edible film of κ-Carrageenan, 1000x magnification.
3.5. Fourier transformation—infra red
FT-IR analysis aims to identify functional groups and compounds contained in vegetable leather by comparing them with carrageenan. FT-IR spectra in vegetable leather and carrageenan are presented in Figure 2.

![FT-IR spectra of (a) Carrageenan and (b) Vegetable leather of kelor leaves.](image)

FT-IR spectrum results obtained were comparisons of kappa-carrageenan absorption bands and vegetable leather the best treatment from organoleptic test (K1). Based on this identification it can be seen that the functional group modification occurs due to the interaction of compounds in vegetable leather and physical modifications occur due to mixing with kelor leaves. The FTIR spectrum of kappa carrageenan showed absorption bands at 1210-1260 cm\(^{-1}\) (S = O ester sulphate group), 1010 - 1080 cm\(^{-1}\) (glyosidic), 928-933 cm\(^{-1}\) (3,-6-anhydro-D-galactose) and 840-850 cm\(^{-1}\) (D-galactose-4-sulphate) [21]. In the sample (a) there is a peak of the absorption band 1041 cm\(^{-1}\) and in the sample (b) the peak of the absorption band is not obtained. This is due to a slight difference in the structure and arrangement of molecules, so that the distribution of absorption peaks changes. Absorption band in vegetable leather at 1068 cm\(^{-1}\).

The addition of several components (Kelor, Sugar and Salt) in sample (b) causes the shift of the O-H band uptake at wave number at 3427 cm\(^{-1}\). This causes the O-H bond to be shorter, which will cause the bond energy to be higher. This causes the peak to narrow and a shift towards the higher wave numbers. The FT-IR test results showed that the spectra of samples (a) and (b) are similarly shown with no apparent peak shift significantly. This is presumably due to the decrease of functional groups in vegetable leather caused by the duration of heating process, apart from the effect of absorption of functional groups of kelor leaves mixed in vegetable leather [22].

4. Conclusions
The addition of carrageenan concentration in the process of making vegetable leather had significant effect on the assessment of physical and mechanical properties. The higher of carrageenan concentration increased the thickness and decreased the level of solubility and not significantly affect on elongation at break. FT-IR test results in vegetable leather showed the intensity of uptake of different compounds with carrageenan compounds as standard. However, many tests still need to be done for vegetable leather products in their use as edible films.

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