Effects of Plasticizer and Cinnamon Essential Oil Incorporation on Mechanical and Water Barrier Properties of Semirefined Iota-Carrageenan-based Edible Film

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Abstract. Iota-carrageenan, a water-soluble polymer extracted from red seaweed, Eucheuma denticulatum, showed a high potentiality as a film-forming material. Whilst, one of the essential oils that gained increasing attention is from cinnamon because of its recently observed antimicrobial and antioxidant properties. In this study, mechanical and water barrier properties of semi-refined iota-carrageenan (SRiC)-based edible film incorporated with cinnamon essential oil were evaluated into two stages. Firstly, the effects of sorbitol plasticizer’s concentration (0.5%, 1.0%, 1.5% v/v) on the mechanical and water barrier properties of the SRiC-based edible film (2% w/v) was investigated, and secondly, those of cinnamon essential oil’s incorporation (0.5%, 0.75%, and 1.0% v/v) were evaluated. SRiC (2% w/v) produced with 0.5% (v/v) sorbitol plasticizer addition was selected for the first stage, and 1% (v/v) cinnamon essential oil incorporation on SRiC-based edible film was recommended for the second, suggesting its further utilization in food application.

1. Introduction

Due to increased consumer concerns about food products’ quality and shelf-life, and their awareness of environmental issues, biomaterials utilization to produce biopolymer-based films and coatings has paid off interests [1,2,3,4,5,6]. Biopolymers have been studied regarding their properties to produce edible films that are usually employed as food packaging to avoid deterioration because of physicochemical or textural changes [2,3,7,8]. They are typically developed from renewable resources such as polysaccharides (e.g. starch, alginites, pectin, carrageenans, chitosan/chitin), proteins (e.g. casein, whey, collagen, gelatin, corn, soy, wheat), and lipids (e.g. fat, wax, oil) [2,5,9,10,11].

Iota-carrageenan (ι-carrageenan), a water-soluble polymer from red seaweed (Eucheuma denticulatum) with a linear chain of partially sulfated galactans, has high potentiality as a film-forming material and is utilized individually or as mixed composite blends [5,6,7,12]. Proteins and polysaccharides are used for their mechanical and structural properties, and hydrophobic substances (lipids, essential oils, and emulsifiers) to provide a good moisture barrier [2,9,10,12]. A shorter and cheaper extraction process of the red alga, Eucheuma denticulatum (‘Spinosum’), is applicable in semi-refined iota-carrageenan (SRiC) which is a renewable resource having petroleum-based plastic films’
replacement potential for food applications at a reasonable cost [5,6,7,12]. Moreover, a plasticizer is usually employed to improve brittle carrageenan-based edible films’ mechanical properties. Therefore, sorbitol was used as a plasticizer in this study due to its several advantages, such as retaining moisture and demonstrating stable performance at high temperatures [9,10,13]. Furthermore, essential oils representing hydrophobic materials were used to enhance the films’ barrier properties. Besides its role to inhibit microorganism’s growth and extend food’s shelf-life due to the antimicrobial and antioxidant activities, essential oils are added to edible films’ production for improving their mechanical and barrier properties [10,14]. Edible films utilization with essential oil is a promising preservation technology, for instance, cinnamon essential oil has been incorporated in chitosan coating to maintain the quality of refrigerated rainbow trout and China jujube fruits [15,16]. Cinnamon essential oil has been used previously for evaluating mechanical and barrier properties of semi refined kappa carrageenan edible film [10]. However, as best known, the study on iota-carrageenan-cinnamon essential oil-based edible film is limited. Therefore, this study aimed to develop semi-refined iota-carrageenan-cinnamon essential oil edible film and investigate its mechanical and water barrier properties, including thickness, tensile strength, elongation-at-break, and water vapor transmission rate.

2. Experimental

Semi-refined iota-carrageenan (SRiC) used as the film’s main component was supplied by Galic Artabahari, Co., Ltd. (Cikarang Barat, Indonesia). Sorbitol as a plasticizer was purchased from Brata Chemical store (Surakarta, Indonesia) and cinnamon essential oil was from CV. Orizho (Yogyakarta, Indonesia). Aquadest was used for all sample preparations, and other chemicals were of analytical grade.

This study was divided into two stages, namely the effect of sorbitol plasticizer’s concentration (0.5%, 1.0%, 1.5 % v/v) on the mechanical and water barrier properties of the SRiC-based edible film (2% w/v) was investigated first. Briefly, semi-refined iota-carrageenan (2% w/v) was prepared by dispersing 2 g of its powder under continuous stirring at 65°C for 5 mins, and the concentration was selected based on previous studies [5,12]. Afterwards, 0.5 %, 1.0 %, and 1.5% (v/v) of sorbitol was added in semi-refined iota-carrageenan solution. The various sorbitol concentration was added to determine the best needed for film formation based on its mechanical and water barrier properties. The experimental steps of film preparation at the first stage were conducted based on previous studies [5,12].

The best sorbitol plasticizer concentration to produce semi-refined iota-carrageenan film at the first stage was then used in the second. The SRiC-cinnamon essential oil edible film was further developed by incorporating various cinnamon essential oil concentrations (0.5, 0.75, and 1.0 % (v/v)). 2 g SRiC was dissolved in distilled water and heated on a hot plate while stirring using a magnetic stirrer until 65°C. After reaching this temperature, sorbitol plasticizer was added followed by heating until 90°C and maintained for 5 mins. Then, cinnamon essential oil was added (0.5, 0.75, and 1.0 % (v/v)) when the temperature reduced and reached 30°C. Furthermore, the film solution was left and stirred manually for 5 mins for dissolution and dissolved air bubbles produced were naturally removed during stirring. Film-forming solutions were then casted by pouring onto a plastic casting plate and dried in a cabinet dryer at 60 °C for 6 hours. After cooling to room temperature, each dried film was carefully peeled off the casting surface and stored inside a plastic storage box containing silica gel (0% RH) at a temperature of 28 ± 2 °C and a constant relative humidity environment of about 50 % for 24 hours before measurements.

The measurements of thickness, tensile strength, elongation-at-break (EAB), and water vapor transmission rate (WVTR) at the first and second stages were conducted based on previous studies [5,10,12]. The films’s thickness was measured using a digital micrometer (Krisbow, Indonesia) with
0.001 mm accuracy. Five different positions of the samples were randomly measured and the average thickness was calculated. Meanwhile, the tensile strength and EAB were determined with a Universal Testing Machine (Model Zwick I Z0.5, United Kingdom), according to ASTM Standard D882-00 method 2000. Also, the film specimens’ WVTR was measured according to a modified ASTM E96/E96M-05 method 1997 [5,10,12]. A total of 3 samples were tested for each film type, and this study consisted of two replicate measurements. The data were statistically analyzed by one-way analysis of variance (ANOVA) at 0.05 significance level using SPSS Statistics 16 program, and differences in the mean values were determined with Duncan’s Multiple Range Test (DMRT) (p<0.05).

3. Results and Discussion

3.1 Mechanical and Water Barrier Properties of Semi-Refined Iota-Carrageenan (SRiC)-based Edible Film with Sorbitol Plasticizer

| Sorbitol (% ) | Thickness (mm) | Tensile Strength (MPa) | Elongation at break (%) | WVTR (g/m²hour) |
|---------------|----------------|------------------------|--------------------------|-----------------|
| 0.5           | 0.055±0.03     | 11.12±0.12             | 21.14±0.24               | 21.68±0.05      |
| 1.0           | 0.075b±0.02    | 8.95b±0.06             | 32.19b±0.14              | 22.44±0.04      |
| 1.5           | 0.086c±0.02    | 6.30c±0.02             | 43.37b±0.07              | 22.65c±0.01     |

Note: Different letters in the same column indicate significant differences (p<0.05)

Table 1 shows that increasing the sorbitol concentration also increases the edible film’s thickness. The results of SRiC-based edible film thickness measurement with sorbitol concentration variations of 0.5%, 1.0% and 1.5% were 0.055 mm, 0.075 mm, and 0.086 mm, respectively. The highest thickness was obtained with a sorbitol concentration of 1.5%, i.e. 0.086 mm, while the lowest was obtained with 0.5%, i.e. 0.055 mm and there was significant increase (p<0.05). This showed that increased sorbitol concentration had a significant effect on increasing the produced edible film’s thickness. Sorbitol addition is believed to increase the total dissolved solid in film solution, therefore the thickness will be increased [17]. Table 1 shows that the tensile strength of films with various sorbitol plasticizer concentrations [0.5%, 1.0%, and 1.5% (v/v)] ranged from 6.30 to 11.12 MPa. The addition of 0.5% (v/v) sorbitol demonstrated the highest tensile strength’s value compared to other concentrations. The DMRT (significance α = 0.05) analysis showed that iota-carrageenan film’s tensile strength with 0.5% sorbitol was significantly different (p<0.05) from 1.5% concentration, but not different (p>0.05) from 1.0%. The highest tensile strength’s value [0.5% (v/v) sorbitol] in this study is good, because it is in the range of 10-100 MPa [10,17]. According to Table 1, the films’ average EAB with sorbitol concentrations variation ranged from 21.41% to 43.74%. The DMRT (significance α = 0.05) analysis showed that the film’s EAB with 1.5% (v/v) sorbitol concentration was significantly different (p<0.05) from 0.5% (v/v), but not different (p>0.05) from 1.0% (v/v). Plasticizers are added to a polymeric matrix to overcome the film’s brittleness, because they reduce the molecular forces, thereby increasing the film’s flexibility and elongation [10,18,19]. A variety of commonly used polyol-plasticizers, including sorbitol, have been employed to produce edible films, and a small quantity this is easily inserted between polymer chains.
It produces a cross-linker effect that decreased the polymer’s free volume and segmental mobility, hence, decreasing the films’ tensile strength and enhancing their extensibility [19]. In this study, various sorbitol concentrations were incorporated in formulating all films to achieve more-flexible ones. The EAB is good when >50% and bad when <10% [20], while the edible films’ applicable EAB ranged from 1 to 80% [14]. Furthermore, the EAB ranged from 21.41% to 43.74%, suggesting it is quite good. Moreover, the WVTR analysis showed that SRiC-based edible film with 0.5% (v/v) sorbitol addition (21.68 g/m² hour) is the lowest value compared to other concentrations (Table 1.). However, the DMRT results (α = 0.05) showed that various sorbitol plasticizer concentrations used were not significantly different. The edible film’s best water barrier properties were shown by a low WVTR value, which indicated that it adequately resisted water vapor transfer. Conclusively, the best mechanical and water barrier properties for SRiC (2 % w/v) produced in the first stage were observed in a film with 0.5 % (v/v) sorbitol addition. Therefore, this film formula was used for the second stage.

3.2 Mechanical and Water Barrier Properties of Semi-Refined Iota-Carrageenan (SRiC)-based Composite Edible Film Incorporated with Cinnamon Essential Oil

| Cinnamon Essential Oil (%) | Thickness (mm) | Tensile Strength (MPa) | Elongation at break (%) | WVTR (g/ m² hour) |
|---------------------------|---------------|------------------------|-------------------------|------------------|
| 0.5                       | 0.060±0.01    | 22.99±0.13             | 9.50±0.04               | 23.61±0.85       |
| 0.75                      | 0.062±0.08    | 20.46±0.07             | 17.16±0.29              | 22.22±0.38       |
| 1.0                       | 0.065±0.05    | 26.00±0.01             | 14.00±0.11              | 21.45±0.63       |

Note: Different letters in the same column indicate significant differences (p<0.05)

According to Table 2, the thicknesses of the SRiC-based composite edible film with sorbitol [0.5% (v/v)] and incorporated cinnamon essential oil [0.5%, 0.75%, and 1.0% (v/v)] were 0.060 mm, 0.062 mm, and 0.065 mm, respectively. This indicated that the concentration is directly proportional to the thickness. Furthermore, the DMRT (sig. α = 0.05) analysis showed that the results were not significantly different for all variations in the oil’s concentration. The tensile strength ranged from 20.46 to 26.00 MPa, where the DMRT results (α = 0.05) showed that the addition of various cinnamon essential oil concentrations was not significantly different. However, tensile strength of SRiC-based composite edible film increased by cinnamon essential oil addition compared to the one without cinnamon essential oil addition as shown in Table 1 (11.12 MPa). The similar result has been observed in the increment concentration of garlic oil added to the alginates’ edible film that caused tensile strength decrease, however, it increased again at a certain concentration [21]. There was a strong interaction between the polymer and essential oil to produce a crosslinking effect that reduced the polymer molecules’ free volume and mobility. This caused the film-shaped sheets’ microstructure to express the film’s structural cohesion. Therefore, increasing the continuity in the polysaccharide network and leading to a decreased percentage of elongation [10,22]. Based on Table 2, the EAB of SRiC-based composite edible films with variations of cinnamon essential oil concentration [0.5, 0.75, and 1.0% (v/v)] were 9.50%, 17.16%,
and 14.00%, respectively. The highest percentage of the film’s EAB was obtained at 0.75% concentration, while the lowest was at 0.5%. This showed cinnamon essential oil’s concentration had no significant effect on the percentage based on statistical analysis using DMRT (significance $\alpha = 0.05$). The presence of essential oils in the film acted as a plasticizer that increased the polymer chains’ flexibility. However, essential oils addition in certain concentrations will make the film network more brittle due to the weak bonds between the compounds [10,23]. Moreover, according to Table 2, WVTR of SRiC-based composite edible film with the 1.0% (v/v) cinnamon essential oil addition (21.45 g/m² hour) was the lowest value compared to other concentrations. DMRT ($\alpha = 0.05$) analysis showed that the film’s WVTR with 1.0% (v/v) cinnamon essential oil was significantly different ($p<0.05$) from 0.5% (v/v), but not different from 0.75% (v/v). Therefore, SRiC-based edible film with the incorporated 1% (v/v) cinnamon essential oil showed promising result for further utilization in food application.

4. Conclusion
The effects of sorbitol plasticizer and cinnamon essential oil addition on the mechanical and water barrier properties of the SRiC-based edible film were evaluated at the first and second stages, respectively. This study showed that the film with 0.5% (v/v) sorbitol addition was the best in the first stage, therefore this film formula was used for the second. Furthermore, 1% (v/v) cinnamon essential oil incorporation to the SRiC-based edible film was the recommended SRiC-based composite edible film for the second stage and future applications.

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