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Physicochemical properties of edible alginate film from Malaysian *Sargassum polycystum* C. Agardh

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ABSTRACT

The edible brown seaweed, *Sargassum polycystum* was harvested from the coastal region of Malaysia. This study introduces the preparation of *S. polycystum* alginate through the external (protocol A) and internal (protocol B) gelation methods with 1% and 3% calcium chloride solutions. The physicochemical characteristics of the films such as transparency, internal viscosity, solubility, swelling index and chemical structure were studied. Results indicated that the films cross-linked with Ca^{2+} through Protocol A resulted in uneven films with rough surface compared to Protocol B that produced film with a uniform surface. Additionally, Protocol B with 0.5% glycerol produced films that was flexible and slightly soluble (7.11%) with the shape and integrity maintained. The ^{1}H-NMR analysis estimated the mannuronic: guluronic (M: G) ratio of the film as 0.733 and thus, confirming the characteristics of the alginate gel as less viscous but rigid. Comparatively, the commercial alginate of the *Laminarian* species showed a lower M: G ratio of 0.351 that resulted in a highly viscous gel. Besides that, the FTIR analysis showed that glycerol at increasing concentrations reduces the intensity of the absorption band at 3451.0 cm^{-1} (stretching vibrations of O–H). This indicated that the strong intermolecular bonds between the alginate polymer were reduced and thus, improved the flexibility of the films.

1. Introduction

Over the years, the reliance of consumers on products derived from fossil fuels such as plastics has caused damage to the Earth with 91% of them remained in wasteland and not recycled (Geyer et al., 2017). The United States alone discard about 33.6 million tons each year with only 6.5% recycled and 7.7% combusted in waste-to-energy facilities (Sharuddin et al., 2016). Therefore, there is an urgency to find an alternative material that is cheap, safe and biodegradable to accommodate the current demand of plastic for various applications.

There are over 400 species of *Sargassum* species distributed in the warm and temperate waters of Indo-West Pacific region, which include Malaysia, China, Japan, Indonesia and Australia (Noiraksar and Ajisaka, 2008). The sodium alginate (NaAlg) is a type of polysaccharide that is found abundantly in the cell wall of brown seaweed and consists of homo-polymeric blocks of (1 − 4) -linked β-D-mannuronate (M) and α-L-guluronate (G) that are covalently linked (Venkatesan et al., 2014). Their arrangements may differ across the seaweed species and the ratios of monomer affect the physicochemical properties of alginate (Fertah et al., 2017). Due to the non-toxic property of NaAlg, they are widely reported for various industrial applications, mainly in food, pharmaceutical and chemical industries as thickening, gelling or stabilizing agents (Choi et al., 2009). Currently, there is an increasing demand for safe food package that are eco-friendly and thus, the NaAlg films meet those requirements because they effectively bio-degrade over time with a 90% loss in weight after 35 days (Deepa et al., 2016) and 92% at the end of 80-days (Solak and Dyankova, 2014).

The alginate is compatible to form films with di- and tri-valent elements such as calcium, magnesium and ferrous ion (Cazón et al., 2017). The complex formed between the association of ions and the M and G residues, results in a stable and a three-dimensional network that resembles an “egg-box” model (Tavassoli-Kafrani et al., 2016). Thus, these cross-linked structures have shown improvements in the water barrier, mechanical resistance, cohesiveness and stiffness properties (Cazón et al., 2017). Even though, external gelation is the most common method employed for fast cross-linking of the polymer, however, this results in a localized gelling area that unfortunately compromises the uniformity and quality of films (Al-Remawi, 2012).

Plasticizer is a group of low molecular weight compound that can be added to polymers to provide plasticity to otherwise rigid and fragile polymers (Vieira et al., 2011). For plasticizing hydrophilic biopolymer-based films, especially for the food and pharmaceutical industry, the type of plasticizers used are polyols such as glycerol, sorbitol, mannitol and xylitol (Siepmann et al., 1998). Plasticizer has been commonly used

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to reduce the brittleness and increase the flexibility of the films which normally take place during handling and storage (Antoniou et al., 2014). However, it was reported that films incorporated with glycerol or sorbitol as plasticizers has shown to reduce their mechanical properties such as tensile strength and elongation at break (Sanyang et al., 2015). This study aims to investigate the effects of different concentrations of glycerol and gelation methods with calcium chloride on the structure and the chemical properties of the *S. polycystum* alginate edible films. In addition to the antioxidant properties of the edible films (Sellimi et al., 2015), this could serve as an alternative material that could provide additional health benefits when consumed. Thus, the NaAlg from *S. polycystum* harvested from Malaysia would add economic value to marine seaweeds of this part of the world.

2. Materials and methods

2.1. Sample collection and preparation

The S. polycystum samples were collected from Teluk Kemang, Port Dickson, Malaysia. The samples were rinsed with 0.1% NaCl solution to remove dirt and epiphytes. Then, the samples were air dried and powdered prior to analysis.

2.2. Extraction of sodium alginate and phytochemical analysis

The dried and powdered seaweed was soaked in 0.2 M hydrochloric acid at room temperature for 24 h. Subsequently, the residues were rinsed with distilled water and agitation for 5 h with 2% sodium carbonate. The extract was filtered, precipitated with ethanol (99%) to obtain a final concentration of 70%. The sample was rinsed with ethanol to a final concentration of 50% and this step was repeated twice, followed by methanol (99%) and acetone (99%). To access the purity of the crude polysaccharide samples, the presence of phytochemicals; terpenoids, cardiac glycosides, phenolics, flavonoids, saponins, alkaloids, and tannins were analysed based on the methods of Harbone (1973).

2.3. pH

The pH of sample was measured with a pH meter (Eutech Instruments P700, USA).

2.4. Antioxidant assays

Briefly, 600 μL of 0.16 mM DPPH$^{\bullet}$ (2,2-diphenyl-1-picrylhydrazyl) solution was added to 400 μL of 1% alginate sample and incubated in the dark at 37 °C for 30 min and the absorbance of the mixture was read at 540 nm. The DPPH value was expressed as μM Trolox equivalent (TE) per gram extract.

2.5. Preparation of sodium alginate films

1% sodium alginate solution was prepared by dissolving 5 g of powdered alginate in 500 mL of distilled water and stirred overnight to ensure homogeneity. Then, 100 mL of NaAlg solution was separated into 5 different Falcon tubes and glycerol was added at concentrations of 0.1%, 0.5%, 1.0%, 1.5% and control (without glycerol), respectively. The NaAlg was then subjected to 2 different gelation methods (protocol A and protocol B) with both, 1% and 3% $CaCl_2$ solutions.

2.6. Intrinsic viscosity

The viscosity of 1% NaAlg samples at different glycerol concentrations prior to treatments with $CaCl_2$ solutions were measured using DV2TLVTJ0 viscometer (Brookfield). The viscometer was operated with spindle no. 62 with mixing speed of 100 rpm and the results were recorded every 30 s. The intrinsic viscosity values were expressed as Pa s^{-1}.

2.7. External gelation method

Ten milliliters of alginate solutions with different glycerol concentrations (0.1%, 0.5%, 1.0%, 1.5%) and control were poured separately into petri-dishes with a diameter of approximately 8 cm and left to dry for 12–16 h in the oven at 50 °C. After drying, the films were transferred into a desiccator to remove moisture and keep them dry until further testing. Then, the dried films were soaked separately in 1% (w/v) and 3% (w/v) $CaCl_2$ solutions for 3 min and rinsed with distilled water before drying them in the oven at 50 °C for 2–3 h.

2.8. Internal gelation method

The 10 mL NaAlg solutions containing glycerol were heated to 70 °C and 1 mL of 1% and 3% $CaCl_2$ solutions were added separately into 100 mL NaAlg solution in a drop-like manner with constant stirring. To ensure equal size of drops of $CaCl_2$ at a consistent rate, a Biuret was used in the dripping process. Then, 10 mL of all the NaAlg samples were transferred to petri-dishes and dried in the oven at 50 °C for 12–16 h.

2.9. Transparency test

The films were cut into small rectangular strips (10 × 20 mm) and placed in a clear cuvette and absorbance readings were taken at 600 nm. The cuvette without the film was used as blank.

2.10. Swelling test

The film pieces (10 × 20 mm) were immersed in distilled water for 30 min. The films were removed and blotted with filter paper to remove excess water. The films were then weighed immediately and the swelling index was calculated as follows:

$$\text{Swelling index (\%)} = (\text{weight after immersion} - \text{weight before immersion}) / (\text{weight before immersion}) \times 100$$

2.11. Solubility test

Pieces of NaAlg films (20 × 30 mm) were cut and weighed to the nearest 1.0×10^{-4} g and placed in Falcon tubes with 50 mL deionized water. The samples were maintained under constant agitation for 30 mins at room temperature (approximately 25 °C). The remaining pieces of film after soaking were filtered through filter paper (Whatman no. 1), followed by oven drying at 50 °C to constant weight. Samples were measured in 3 replicates and the percentage of total soluble matter (% solubility) was calculated as follows:

$$\text{\% of solubility} = (\text{initial dry weight} - \text{final dry weight}) / (\text{initial dry weight}) \times 100$$

2.12. Transparency test

The films were cut into small rectangular strips (10 × 20 mm) and placed in a clear cuvette and absorbance readings were taken at 600 nm. The cuvette without the film was used as blank.

2.13. Fourier transform infrared (FTIR) spectroscopy measurement

Analysis of sodium alginate samples was performed by ATR-FTIR spectrophotometer with absorption region of 650–4000 cm^{-1}. The