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Biodegradable Plastic and Film Production from Seaweeds

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Abstract: To evaluate potential bioplastic and biofilm production from seaweeds, alginate which is known as seaweed hydrocolloid and it is extracted from brown seaweeds was used as a basic material to produce bioplastic for this experiment. A colorimetric analysis of the plastic or the film indicated that the concentration of alginate directly interferes with the color difference, tending slightly yellow when alginate added. The plastic presented low opacity, below 13%, with no significant effect of the different alginate attributions on the material's transparency. The thickness of the plastic produced was directly proportional to the concentration of alginate diluted in the solution, with the addition of 0.50 g being produced in plastics with a thickness of 0.02 mm, while the addition of 5.00 g obtained 0.11 mm. The maximum elongation distance until the plastic breaks does not show differences when subjected to tension, with an average distance of 2.12 ± 1.03 mm, regardless of those analyzed. However, it was possible to observe that the tensile force for breaking the plastic with a concentration of 0.50g was 0.61 ± 0.16 kg, while at a concentration of 2.75g and 5.00g values were five times greater, 3.30 ± 1.24 kg and 3.54 ± 1.10 kg, respectively. The use of seaweed polymer has a great potential for manufacturing various types of biodegradable bioplastics or biofilms. With these properties, the concentration of 2.75g could form a very resistant film, being capable of many ecologically friendly applications in various packaging, for example for biscuits, sachets and seasonings and in developing carrier bags and plastic bottles.

Keywords: biodegrable; bioplastic; biofilm; seaweed hydrocolloids; algal phycocolloids; alginate

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1 Introduction

Nowadays, people have become dependent on petroleum-plastic because it is used in many products such as pharmaceutical materials, packaging, 3D modeling, home appliances, electronics and so on. Although petroleum-based plastics are the main cause of plastic pollution, it takes thousands of years for these plastics to degrade and disappear from nature (Chae and An 2018). For this reason, it is obvious that the use of biodegradable plastics produced from natural resources is of great importance in terms of both human health and environmental sustainability. The use of bioplastics; They have many benefits such as they deteriorate more quickly in nature, are not toxic, provide energy savings during production, require less space for the wastes produced, reduce fossil fuel consumption and reduce the amount of greenhouse gases emitted. Bioplastics are now recognized as a promising approach to solving plastic pollution (Porta 2019). Bioplastics that must be produced from renewable materials; It can be produced from raw materials such as polysaccharides, proteins and lipids, but also corn, potatoes, vegetable oils, food waste, grain products, etc. They can also be produced from many biomaterials. Today, the main types are starch-based, followed by polylactic acid (PLA), poly-3-hydroxybutyrate (PHB), polyamide 11 (PA 11) and organic polyethylene (PE) (Satti and Shah 2020). Today, some bio-based plastics with short-term biodegradability are used in a variety of packaging, medical/pharmaceutical materials and agricultural products industries. The global market for bio-based plastics is estimated to be 2.11 million tons in 2018 and may increase to 2.62 million tons by 2023 (European bioplastics 2018).

Biodegradable and edible materials from plants and animals, including peptides, polysaccharides, and lipids, are profitable alternatives to synthetic packaging films (Sevindik et al. 2017; Umaraw et al. 2020). Bioplastics are derived from renewable resources. Unlike petroleum-derived plastics, which both create a high greenhouse gas effect and consume natural resources, they are sustainable materials. Many varieties have biodegradable properties. Unlike petroleum-based plastics, which continue to pollute the nature for hundreds or even thousands of years and may contain toxic substances, bioplastics prevent environmental pollution after completing their useful life, preventing environmental pollution and do not leave harmful and toxic substances behind. The bad effects of additives such as BPA, PVC, Phthalate, Styren, which can be found in products made of petroleum-based plastics, on human health are revealed by new researches. Bioplastics obtained from natural and biological sources are safer for the environment and human health as they may not contain harmful petroleum chemicals (Umaraw et al. 2020).

Algal species are recognized as a potential raw material for bio-based plastics due to their rapid growth rate and extensive environmental tolerance (Venkatesan et al. 2016; Mathiot et al. 2019). Seaweed (or, macroalgae) (*Kappaphycus alvarezii* (Doty) Doty ex Silva) films can be used as sachets or pouches, renewable cups, plastic bags, containers and more (Siah et al. 2015).

Macroalgae derivatives called alginate, carrageenan and agar exhibit interesting film-forming properties, including plastics, and have negligible lignin content. Seaweed hydrocolloids are of great interest in the food industry due to their different functional properties (Yarnpakdee et al. 2015). Agar as a hydrophilic gel; It is the first phycocolloid used in food, pharmaceutical, cosmetic and biotechnological applications due to its ideal physical and chemical properties such as gelling, thickening, stabilizing and cryoprotective effects, high biodegradability and large water holding capacity (Guerrero et al. 2014; Sevindik et al. 2017). Red seaweed polysaccharides generally consist of agar, carrageenan, cellulose, fluoride starch, xylan, mannan and porphyra. Red algae are frequently used in film production. This is because they have film-forming polysaccharides such as carrageenan (*Kappaphycus* sp. and *Eucheuma* sp.) and agar (*Gelidium* sp. and *Gracilaria* sp.). Agar is a polysaccharide that can be found in some families of red seaweed (Rhodophyceae), usually *Gracilariaceae* and *Gelidiaceae*. Agar consists of two main components, agarose and agaropectin (Arvizu-Higuera et al. 2008). Red seaweeds are widely used in many applications such as food, agriculture, cosmetics, biomedical application. Agar was first used in the fields of food, biotechnology and pharmaceutical applications before being used as a raw material in bioplastic film production (Phan et al. 2009). Phan et al. (2009) stated that agar-based films have low moisture content, transparent, strong and flexible properties. In addition to these properties, heat seal ability makes agar-based films good practice for the food packaging industry.

Table 1 Green extraction methods for macroalgae (Lim et al. 2021).

Production methods	**Principle**	**Advantage (+)** **Disadvantage (-)**
Enzyme-assisted extraction	Enzymes such as protease and carbohydrase break down the cell wall and release algal polymers.	+High efficiency, environmentally friendly, wide chemical selectivity -Slow process, expensive enzyme
Microwave-assisted extraction	Microwave irradiation raises the temperature and penetrates the cell wall to release the polymers into the solvent.	+Fast process, high yield, low solvent consumption, scalable -High equipment cost, explosion risk, solvent must be polar and non-volatile
Extraction by photo-bleaching	Sunlight is used to remove pigment through photolysis, where the sulphate content of polymers is reduced.	+ Environmentally friendly, chemical-free, improves the quality of extracts, improves efficiency - Affected by weather conditions, causing chemical changes in samples
Reactive extrusion	Mixing, shearing, heating are used to initiate chemical reactions, homogenize and melt materials to form a polymer.	+ Fast and continuous processing, low solvent consumption, expandable - High equipment cost can cause thermal degradation of seaweed
Pressure solvent extraction	The high pressure and solvent temperature below the boiling point (subcritical zone) are used to extract the polymers in a short time.	+ Green solvent and low consumption, efficient, fast process, simple steps -High equipment cost can cause thermal degradation of seaweed
Supercritical fluid extraction	The solvent (usually CO_2 or H_2O) is at the critical temperature and pressure for polymer extraction.	+ Eco-friendly, fast process, high purity extracts, cheap and recyclable solvent - High equipment cost, operation cost and energy consumption, big volume problem
Ultrasound-assisted extraction	Sound waves of more than 20 kHz penetrate the solvent within the cell wall and generate cavitation bubbles to remove polymers.	+ Fast process, low solvent and energy consumption, high efficiency, waste-free, simple steps, easy scale-up - High equipment cost, narrow solvent selectivity

There are mechanical, chemical and biological extraction methods for bioplastic production from macroalgae. Each extraction method has some positive and negative aspects. Answer of the question of which extraction method that should be applied is depending on the type, solvent types, environmental effects, cost, time, amount and preferred properties. Commonly used methods in the production of bioplastics from seaweeds are washing, grinding, drying, alkali, acid neutralization, formaldehyde, hot water, filtration and precipitation (Lim et al. 2021). However, these commonly used methods are not suitable in terms of time, money and efficiency compared to petroleum-based plastics. The cost is high due to the amount of water used, production method, reactants and chemicals. In addition, reactants and chemicals increase the cost as they require hazardous and appropriate waste management (Lim et al. 2021). Seaweed bioplastics with green production methods have great potential when it comes to replacing petroleum-based plastics. Besides being economical and biodegradable, materials are renewable and sustainable, and their synthesis methods can be chemical and hazardous waste-free. There are many green extraction methods for macroalgae, such as enzyme-assisted extraction, microwave-assisted extraction, photo-bleaching extraction, reactive extrusion, pressurized solvent extraction, supercritical fluid extraction, ultrasound-assisted extraction (Table 1) (Lim et al. 2021).

Today, seaweeds are of great interest in applications ranging from food to energy to products such as paper and plastic. This is due to the rich composition of seaweeds. In general, the dry weight of seaweeds contains an average of 50% total carbohydrates, 1-5% lipids, 7-73% minerals for all three groups, while proteins are lower in brown (4-24%) and higher in red and green seaweeds. (8-47%). Some types of seaweed are used to make films. To name a few, *Kappaphycus*, *Eucheuma, Gracilaria, Porphyra, Gelidium, Pterocladia* for red algae, *Ulva, Codium, Enteromorpha* for green algae, and *Macrocystis, Laminaria, Ascophyllum, Lessonia*, *Sargassum* for brown algae. Alginate is a phycocolloid and binary copolymer that can be extracted from brown algae as a raw material for bioplastic (Draget and Taylor, 2011). Alginate is a polysaccharide responsible for 22-44% of the dry weight of most marine brown algae (Li et al. 2019). Notably, alginates can cross-link with cations to form hydrogels or packaging films (Xue et al. 2019).

The general objective of this study is to produce biodegradable bioplastics and biofilms from alginate (or, alginic acid) and in order to reach the mail goal it was to analyze the mechanical, physical and barrier properties of films prepared from alginate to compare to petroleum-plastics.

2 Materials and Method

The preparation of biofilms was performed with three alginate concentrations: 0.50, 2.75 and 5.0 (m/v). Each of these concentrations was diluted in distilled water, with the addition of 2% Glycine dissolved in 150 ml of distilled water. The solutions were kept under stirring for 10 min at room temperature in a bioreactor. After that the temperature rise was raised to 45°C under constant stirring for 20 min. After this homogenization process, 12 g of solution was spread in ten Petri dishes and then dried in an oven at 45°C for 24 h. Dry films were removed from the Petri dish and all film samples were preconditioned for at least 48 h at constant temperature and humidity (25°C and 50% relative humidity) controlled by Sodium Bromide (NaBr).

The thickness (mm) of the films was determined using a digital micrometer at ten random points on the film body. The color and opacity of the films were determined using a colorimeter, using the CIEL*a*b system. The parameters analyzed in this color system are: L (brightness), a* (green and red) and b* (blue and yellow), using the method described by Saberi et al. (2016). Film color was expressed as total color difference (ΔE*), which is calculated according to the program.

The opacity of the films was calculated as the ratio between the opacity of the film superimposed on the black standard (Yblack) and the white standard (Ywhite) detected by the colorimeter, using the methodology described by Thakur et al. (2016). To determine the mechanical properties of the films in a texturometer, it was necessary to cut the films into strips 5 cm long and 25 mm wide. The properties studied were the tensile strength (Kg) and maximum elongation to break (mm) using the methodology described by ASTM (2002). The results of thickness, optical and mechanical properties were submitted to analysis of variance (ANOVA) and means were compared by Tukey test at a 5% significance level.

3 Results and Discussion

The colorimetric analysis of the film indicated that the concentration of alginate directly interferes with the color difference, tending slightly to yellow when alginate is added. The optical properties of coloring can be seen in Table 1. The film had low opacity, below 13%, and the effect of different alginate concentrations on the material's transparency was not significant. The thickness of the film produced was directly proportional to the concentration of diluted alginate in the solution, with the addition of 0.50g resulting in films with a thickness of 0.02 mm, while the addition of 5.00g obtained 0.11 mm. The maximum elongation distance until the film breaks did not show significant differences when subjected to tension, with an average distance of 2.12 ± 1.03 mm, regardless of the concentrations analyzed. However, it was possible to observe that the tensile force for breaking the film with a concentration of 0.50g was 0.61 ± 0.16 kg, while at the concentration of 2.75g and 5.00g it obtained values five times greater, 3.30 ± 1.24 kg and 3.54 ± 1.10 kg, respectively. The mechanical properties and opacity of the produced films can be seen in Figure 1 and Picture 1 shows different packages prepared by the bio-plastics/bio-films produced by macroalgal alginates.

Table 1 The table shows the values obtained from the optical analysis, as follows: L*: luminosity; a*: green and red; b*: blue and yellow; ΔE: total color difference.

Alginate (%)	L*	a*	b*	ΔE
0.5	96.50 ±0.17 [a]	-0.49 ±0.08 [a]	3.95 ±0.34 [a]	2.45 ±0.20 [a]
2.75	94.78 ±0.70 [b]	-0.98 ±0.13 [a]	8.44 ±0.23 [b]	6.89 ±0.61 [b]
5	93.09 ±0.57 [c]	-1.05 ±0.19 [a]	12.43 ±0.43 [c]	11.53 ±0.52 [c]

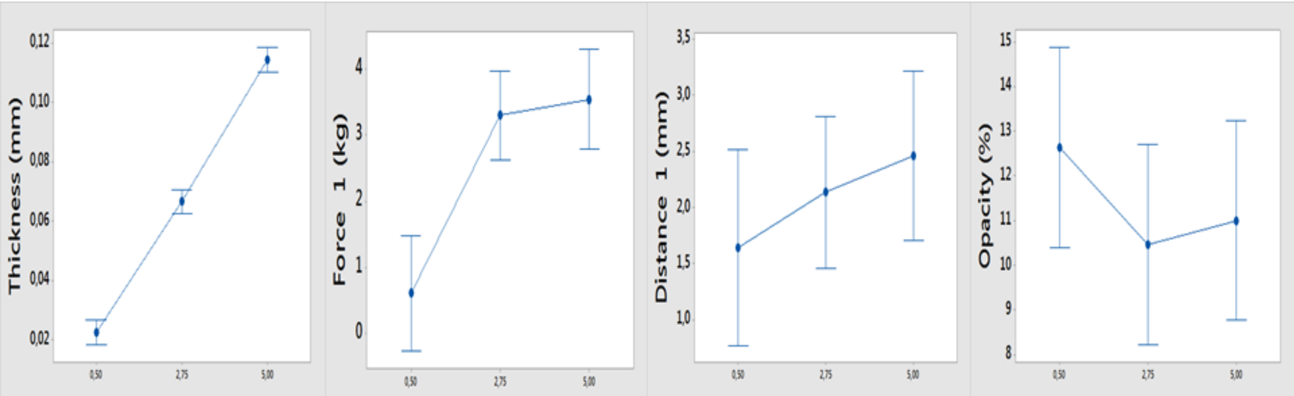

Fig. 1 Optical and mechanical properties the bio-plastic/bio-film produced from alginate.

Fig. 2 Different packages prepared by the bio-plastics/bio-films produced by the alginate.

The results of this present study shows that it is possible to produce degredable bioplastics and biofilms from seaweeds that is similar results to previous studies of Doh et al. (2020) who developed marine algal biopolymer film from 2 different brown macroalgae (*Laminaria japonica* and *Sargassum natants*).

In this present study, a film-forming solution was prepared with supernatan occuring after acid-base pre-treatment and marine algal polymer film was obtained using a bulk evaporation method. And, optical and mechanical properties were studied to determine its liability as a packaging subtrate. The result of these properties showed similarities to the findings of Sudhakar et al (2020) who developed and characterized the bioplastic film obtained from red seaweed (*K alvarezii*). In their study, the red seaweed *K. alvarezii* was used for the production of bioplastic film. The ratio of plasticizer polyethylene glycol (PEG) to seaweed biomass was optimized and a thin bioplastic film with higher tensile strength was produced. The resulting films were characterized by their thickness, tensile strength, color (L, a, b), elongation at break (EAB), water vapor transmission rate (WVTR) and oxygen transmission rate (OTR). TG-DSC, AFM, SEM and FTIR spectroscopy analysis were performed to evaluate the composition, phase transitions and chemical reaction capabilities of the film. Bioplastic film from 4% (whole seaweed) *K. alvarezii* showed better physical and mechanical properties, while TG-DSC, FTIR and AFM showed similar bioplastic properties at all concentrations. A decrease in OTR was observed against the decreasing wall thickness of the film. And, Sudhakar et al (2020) also suggested that seaweed is a potential alternative source for bioplastic production that could reduce the use of non-degradable plastics.

4 Conclusion

Seaweed is a leading source of polysaccharides, with properly established extraction processes allowing it to be used in a variety of fields. All types of biopolymers derived from seaweed has gained popularity in recent years. This is due to its abundance, water solubility, and outstanding film-forming abilities. And, remarkable developments in improving the properties of seaweed-based films have been described in many studies in the literature. And, there are many research opportunities to explore regarding the improvement of material properties.

Alginate (or, Alginic acid) is derived from brown algae and is a promising natural polymer. There are many studies emphasized the innovative method in the preparation, characterization and performance of seaweed-based films as food packaging by the researchers. Among the polysaccharides obtained from brown algae, Alginate has recently gained notoriety for its excellent film-forming ability. Alginate is an anionic sulfated polysaccharide classified together with carrageenan and agar for use as food additives according to European Union legislation. In light of this, numerous recent studies have demonstrated the production of sustainable, active and smart edible films based on this polysaccharide.

The use of seaweed polymer has a great potential for manufacturing several types of biodegradable films and the present study results suggest that seaweed is a potential alternative source for bioplastic production that could reduce the use of non-degradable plastics. With optical and mechanical properties obtained in this study, we suggest to use the concentration of 2.75 g could form a very resistant film, capable of being applied in different packages, for example, for biscuits, sachets and seasonings. I the further studies on bioplastics and biofilms produced from algae by using different additives are needed to obtain different mechanical and optical properties in order to reach other useful niches. The properties and characterization of seaweed bioplastic film are used to make a comparison with petroleum-based plastic. Properties and characterization data of bioplastics are generally categorized as physical, optical, mechanical, morphological, thermal, antioxidant, antibacterial and biodegradable. Physical properties include thickness, solubility, water vapor permeability (WVP), water vapor transmission rate (WVTR), and moisture content of the films. Optical properties include transparency, opacity, and light transmittance. Mechanical properties include tensile strength, elongation at break, and Young's Modulus. Morphology study Fourier transform infrared (FTIR) spectroscopy, Field Emission Scanning Electron Microscopy (FESEM or SEM), Atomic force microscopy (AFM), and X-ray diffraction analysis (XRD) can be done with Thermal properties include Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

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Conflict of interest disclosure:

No conflict of interest was declared by the authors.

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