Seaweed Based Bio Polymeric Film and Their Application: A Review on Hydrocolloid Polysaccharides

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Abstract

The objective of this paper is to discuss the potential of seaweed based polysaccharides as biopolymer in the formulation development and its allied applications. This review is an attempt to describe possible ways to produce environmental friendly bio packaging, bio textile, bio medicinal stuffs that can be at least slightly decomposed to smaller substances by the living organisms from marine algae. The main applications in food packaging and biomedicine are briefly mentioned followed by tentative applications in the domains of packaging, textile, paper and medical textiles which are described. This review also suggests new perspectives for future studies with these polymers.

Keywords: Seaweed; Bio polymer; Biodegradable film; Alginate; Agar; Carrageenan.

1. Introduction

During the last decades, numerous novel compounds have been found from marine (also called the mother of origin of life) organisms as a potential source for the development of pharmaceuticals, food, packaging and textiles that can be applied to improve human wellness. Seaweed refers to several species of marine plants and algae which maybe macroscopic, multicellular that grows in the ocean as well as in rivers, lakes, and other water bodies [1]. Generally, seaweed is plant like organism mostly found in coastal areas. Since the mid-19th century, they are distinguished into four major groups based on pigmentation: Blue algae, Green algae (more than 1800 species), brown algae (about 2000 species) or red algae (over 7200 species) and none are known to be poisonous. Brown and red algae are almost absolutely marine, whereas green algae may common in freshwater (lakes, rivers) and in land-dwelling situation (rocks, houses, wall and tree bark) [2]. Chemical composition of seaweed includes: Water:80-90%, Mineral:7-38%, Carbohydrates:50%, Protein:3-15%(brown algae), 10-48%(red & green algae), Lipid:1-3% [3, 4]. They differ in many ultra-structural and biochemical features including fine structure, storage compounds, composition of cell walls, photosynthetic pigments, ultrastructure of mitosis, presence/absence of flagella, connections between adjacent cells. Having some outstanding characteristics, the versatile marine plants and algae have potential ability to be used for nutrition, biomedicine, bioremediation herbalism, filtration and industrial purposes. Since the early 20th century, however, these biopolymers began to be replaced by synthetic polymers due to their better performance and more reproducible properties, as compared to naturally derived materials [5, 6]. From the last few years, for packaging purpose and for the treatments of humankind, seaweed has become very popular from laboratory to industrial scale [7]. Considering all those factors, sustainable use of seaweeds as biopolymer has now become crucial in this biodegradable era for the growing interest in natural polymers.

2. Seaweed as Biodegradable Polymeric Film

Seaweed as biodegradable polymers has been broadly utilized as a part of bio packaging, food and biomedical applications in terms of their known biocompatibility, bio absorbability and biodegradability and nontoxicity. These polymers can be degradable, either enzymatic association or without enzymatically. Commonly three seaweed-derived hydrocolloids polysaccharides are available in nature that has diversified application as bio polymeric film such as alginate, agar and carrageenan. However, there are others seaweed hydrocolloids polysaccharides, which are less significant like mannitol, fucoidan and funoran [8].

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Red algae *Kappaphycus* and *Betaphycus* are the important sources of carrageenan. *Gracilaria* & *Gelidium* can create gelatin like substances primarily known as agar. Over 7,000 species of red algae, only about 200 live in fresh water. Cell wall of red algae is extracted with water under neutral or alkaline conditions at elevated temperature. Carrageenan is completely biodegradable and has strong binding, gelling and hydrocolloid ability to form polymeric film. They are commonly used ingredient in food, growth medium for microorganisms, smart packaging and for biotechnological applications [8, 9].

Brown algae comprising the class Phaeophyceae, contain alginic acid (alginate) in their cell walls and it may reach 60 m (200 ft.) in length, which is used as an industrial thickening agent in food [10]. Its film forming and binding ability makes it suitable for the use of packaging material and for the use in biomedical application [11, 12].

3. Alginate

3.1. Source and Properties

Alginate acid and its salts [Ca, Mg, Na & K] are abundantly present in brown algae that is quite abundant in nature and occurs both as a structural component in marine algae & making up as much as 40% of the dry weight [13, 14]. Alginates were discovered by a British Pharmacist, E.C.C. Stanford; commercial production started in 1929 [15]. Annual production of alginates in the world is about 30,000 tones; 30% of this is utilized by the food industry while the rest is used in industrial, dental, pharmaceutical industry [16, 17]. Alginates are linear, unbranched copolymers composed of monomers of β-D Mannuronic acid (M) and α-l guluronic acid(G) residues joined together by [1-4] glycoside linkages. Depending on seaweed source, extraction and harvest time are arranged in an asymmetrical pattern of varying proportions of GG, MG and MM blocks [18]. Alginate that is commercially...
available is typically extracted from brown algae (Phaeophyceae), including Laminaria japonica, Laminaria hyperborea, Macrocystis pyrifera, Ecklonia maxima, Laminaria digitata and Ascophyllum nodosum and Lessonia nigrescens especially by aqueous alkali solutions treatment, typically with NaOH [19, 20]. The extract is then filtered and purified in order to produce water-soluble sodium alginate powder [21].

**Figure-3. Sodium alginate extraction procedure [22]**

Sodium alginates is soluble in cold water, forming viscous, colloidal solution but insoluble in alcohol, hydro alcoholic solutions, organic solvents viz. ether, and in acids. Calcium alginate, is however, practically insoluble in water and organic solvents [23]. If Ca²⁺ ions can be removed degradation of a Ca²⁺ cross-linked alginate gel can happen [24]. Biocompatibility, biodegradability, non-toxicity and immunogenicity properties of this polymer materials has made it versatile for usage in food, packaging, biomedical application, paper industry, textiles and medical textiles [25]. They are appealing film-forming compounds because of its thickening, stabilizing, suspending, gel-producing functional properties [26].

### 3.2. Applications

Alginate are widely used as additives in jams, jellies, ice-creams etc. as it is capable of stabilizing, viscosifying, emulsifying solutions [27]. Alginate film is being used as beverage additive for stabilization and to prevent moisture loss of meat during storage [28, 29]. Fayaz et Al showed incorporation of silver nanoparticles in alginate film for vegetable and fruit preservation [30]. ALG have been investigated as taste masking agents. Calcium complexed alginate mixed with starch was proposed to get high water retention in paper coating and to improve crumpling and resistance of paper [31]. In textile industry, alginate is favorably being used as thickener for the paste that contain dye [32]. In biomedical field, alginate are considered as favorable candidates in chubbiness and type 2 diabetes treatment as they are inhibitor of glucose transporters and glucose intestinal absorption rate [33]. Cheap, hydrophilic, non-staining, pleasant odor and taste and effective use in the presence of saliva, self-life of alginate, makes it suitable for application in dental impression materials [34]. Study revealed that alginate combined with chitosan and Ag (silver) nano-particles can form excellent antibacterial wound dressing as they are breathable, non-allergic, bacteriostatic, anti-viral, fungistatic, non-toxic, high absorbent, biocompatible and have good mechanical properties [35]. Modern dressings from alginate i.e. Algicell™ (Derma Sciences) AlgiSite M™ (Smith & Nephew), Comfeel Plus™ (Coloplast), Kaltostat™ (Convatec), provide a moist wound environment and facilitate wound healing [21]. Alginate gels have been widely explored over the past several decades for their potential approach in tissue engineering, tissue regeneration, cell adhesion and cell migration behavior [37, 38]. Alginate polymers have been extensively studied for prolonged or controlled release drug delivery systems [39]. AlgiMatrix prepared of pharmaceutical-grade alginate have been able to entrap cell into the porous structure in an anti-cancer based study [40]. After the pore is filled with alginate solution, formation of in-situ hydrogel enables fast cell immobilization [41]. It is clearly inferring that owing to unique properties, the utilization & new usage of alginate is swelling day by day.
4. Agar
4.1. Source and Properties
Agar-agar, is a Malayan word obtained by the discovered by Minoya Tarazaemon in 1658 in Japan, from marine algae *Gelidium corneum* and made its chemical analysis. It is a phycocolloid extracted from the cell wall of a group of red algae (Rhodophyceae) including *Gelidium* and *Gracilaria* [42]. *Gelidium* is the preferred source for agar production. Agar is formed by a mixture of two polysaccharides named agarose and agarpectin with agarose making up about 70% of the mixture [43]. It is proved that agarose is responsible for gelling properties whereas agarpectin is responsible for thickening properties [44]. Being a sulfuric acid ester of a linear galactan, agar is soluble in hot water but insoluble in cold water. Agar refers to neutral polysaccharide with repeated D-galactose and 3,6-anhydro-L-galactose units joined by β-1,3- and α-1,4-glycosidic bonds, respectively [45] with possible occurrence of sulphate, methoxyl, and/or pyruvate substituents at various positions in the polysaccharide chain [46]. Agar from *Gelidium* has melting & gelling temperature between 80-90°C and 28-31°C whereas agar extracted from *Gracilaria* has gelling and melting temperatures between 29-42°C and 76-92°C respectively. Agar in red algal cell wall is believed to provide resistance to pathogens [47].

![Figure-4. Structural unit of agar](image)

has great gelling power in an aqueous environment which is stronger than those of any other gel-forming agent [48]. Agar gives gels without flavor and does not need to add reagents to produce gelation such as K (necessary for carrageenans) or Ca (necessary for alginates). At 1.5% concentrated solution agar form gels between 32-43°C and does not melt below 85°C. This is a unique property of agar known as hysteresis property.

![Figure-5. Microscopic structure of agar gel formation](image)

4.2. Applications
Thanking to its biodegradable nature, agar is intensively being used in food and beverages, pharmaceutical, paper, textile and biotechnology industry. In food industry, it is used as additive rather than as nutrient and as a covering agent to prevent dehydration while baking the food material [49]. Moreover, 80% of the globally produced agar is used as gelling, thickening, stabilizing and viscosity controlling agent for jellies, candies and jams, pudding,
stabilizers for canned food, dessert, ice-cream, sauces [50, 51]. In addition to food applications, about 10% of all agar is currently being used as clarifying agent in brewing, binder for deserts, textile and paper making, clarifier, for wine making, aids in making ultra-thin separating film and in paper sizing fabrics [52]. One study showed the usage of agar-based metallic nanoparticles (Fe, Cu, Pd etc.) to remove cationic dyes that can be applied in degradation of noxious dyes from industrial textile wastewater [53]. Jeevan et al showed that crystallized nanocellulose blended with agar can be used as a reinforcing agent for the preparation of bio-nanocomposites that have high potential as biodegradable food packaging materials [54]. Another researcher has experimented that in food packaging application, the addition of NCC improves film mechanical, thermal & water vapor barrier properties though film transparency decreased [55]. Agar has given the research a pool of opportunities to discover new compound and its therapeutics value. Its high gel strength at low concentrations, low viscosity in solution, high transparency in solution, thermo-reversible gel and sharp melting/settling temperatures makes it suitable for usage in biomedical treatment [56]. It can also purify human body as it has binding ability to heavy metals, carcinogens and pesticides and can remove from our body through its cell wall [57]. Agar is also widely used as medium for antibody clone typing of various bacterial virulence antigens [58]. Agar usages in nano engineering have been recently developed for various applications i.e. synthesis of silver nano-particles using agar, with bactericidal effect, may find applications in wound dressing [59]. Meanwhile, impression materials in dentistry, intestinal regulator, excipient in pills, to make salt bridges and gel plugs for use in electrochemistry, as a substrate for precipitin reactions in immunology [60]. Today the invention of new agar-based formulas are widely used as supporting matrices in animal cell culture, drug delivery, tissue engineering, immobilizing agent for enzymes and microorganisms in various biochemical and fermentation industries.

5. Carrageenan
5.1. Source and Properties
Carrageenan is a naturally occurring anionic sulfated linear polysaccharide extracted from red algae specifically from the Rhodophyceae family, consisting of linear-sulfated polysaccharides of D-galactose and 3,6-anhydro-D-galactose (3,6-AG) [61]. This specific type of seaweed is common in the Atlantic Ocean near Europe, Britain and North America. The sulfated polysaccharides are further extracted using dilute alkaline solution. Using of alkali brings chemical changes which leads to increased gel strength in the final product. Carrageenan was discovered by British pharmacist Stanford in year 1862 [3, 49]. It is a complex mixture of five distinct polymers designated as \( \iota \)-, \( \kappa \)-, \( \lambda \)-, \( \mu \)-, and \( \nu \)-carrageenan [62]. Among those, three major types i.e. lambda (\( \lambda \)), kappa (\( \kappa \)), and iota have sulfate contents of 41%, 33%, and 20% respectively. Classification of carrageenan was made based on its solubility in KCl. Compared to \( \lambda \)- and \( \iota \)-carrageenan; \( \kappa \)-carrageenan membranes reveal better mechanical properties [63]. As carrageenan possess different types and compositions, it is most difficult to depict its characteristics [64]. It may lead to whole loss of functionality rapidly at high temperatures and low pH [65]. Carrageenan has a unique property to form a variety of gel textures at room temp:

![Figure-6. Kappa carrageenan](image)
rigid or elastic, tough or tender, heat stable or thermally reversible, clear or turbid, low or high melting/gelling temperatures [66]. Kappa and iota-carrageenan can form gel through crosslinking in the presence of potassium or calcium ions, so it has great potential as a gel-forming material [26]. Iota-carrageenan produces softer, elastic; kappa-carrageenan forms rigid and brittle gels and lambda-carrageenan can’t create gel formation [67].

5.2. Application

Research on carrageenan is increasing steadily from the last decade. In order to meet the new renewable resources for the production of edible and biodegradable material, carrageenan can be used as an interesting alternative to produce edible films and coatings, food and beverages, biopackaging and medicine for biomedical application [68]. Among these different forms of carrageenans, kappa carrageenan is the one most commonly used in industrial applications. Semi refined carrageenan (SRC) for film packaging applications can be produced at a significantly lower cost due to the fewer number of processing steps required in its production. This opaque or colored packaging is widely used in food containers, trays, cups, wraps, and other packaging designed to preserve light- or UV-sensitive products. But pure carrageenan films limit its use for food packaging due to its brittle behavior [69]. Plasticizers like glycerol, non-volatile polyol are therefore typically added to the formulations in to improve their flexibility. For the manufacture of edible film carrageenan obtained from seaweed is being used as one of the cheapest raw materials. Saiful et al. prepared edible film from carrageenan that has been applied for slice apple packaging [70]. The optimized edible films structure was obtained with the carrageenan and palm oil as plasticizer which can maintain vitamin C of 99.853%. Brody and colleagues have also reviewed commercial antimicrobial food packaging materials and structures and their applications [71]. Another promising emerging technology is to apply biopolymer coating i.e. carrageenan-based coating as antimicrobial agent carriers. Cha et al. studied the synergistic effect of antimicrobials and chelating agent (EDTA) in κ-carrageenan-based biopolymer films which showed inhibitory effects against all microorganisms and pathogens [72]. It has been widely utilized in food industry as...
thickening, gelling, stabilizing agent in ice-cream, milk shakes, chocolate milk, processed meat, fruit juices, desserts, cream thickener, sauces, jam, and canned food etc. [73]. Carrageenan as protective barrier can also be used in the food industry in order to prevent the transfer of moisture, gases, flavors or lipids and to maintain food quality and food product shelf-life [74]. If coating with carrageenan is chosen, a controlled respiratory exchange can be established and thus the preservation of fresh fruits and vegetables can be prolonged [75]. Besides nanocomposites with nanoclays or with cellulose nano-whiskers are able to block the light against UV-visible, which is of interest in packaging and membrane applications [76]. The application of carrageenan is also gaining attention in industry as thickeners for tooth paste, cosmetic, lotion, ceramic coatings etc. Recently, the utilization of carrageenan is increasing in other areas, such as drug delivery, tissue engineering, dengue and herpes virus, beads for controlled released system, to reduce cholesterol and lipids levels, suspending agents in antacid, eye drops, suppositories and biosensor applications [77, 78]. Gan and Feng et al. discovered a new injectable biomaterial carrageenan/nano-hydroxyapatite/collagen for bone surgery [79]. Moreover, carrageenan has antitumor and immunomodulation activities, antiviral activity, antioxidant activity, anticoagulant and antithrombotic activities for which it is massively used as drug delivery tool [80, 81].

6. Conclusion

In this review, seaweed based polymeric film has demonstrated numerous advantageous, which is of great potential to food, packaging, medical and high end productions identified with natural insurance and the support of physical wellbeing. The emergence of natural polymers about few decades ago reduced the need for synthetic polymer production at a low cost, thereby producing a positive effect both environmentally and economically by producing highly sustainable, functional and cost-effective products. The promising research trend undertaken in this direction will hopefully lead biodegradable polymers to domain their fields with more simulated properties. In future, seaweed and its derivative blends will be more innovative and multifunctional that can be researched for further development and application.

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