

Algae-based bioplastic used in food packaging and biomedical applications

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Abstract

Bioplastics is a form of plastic derived from renewable biomass sources, such as plants, microorganisms; bacteria, fungi and algae. There advantages of bioplastics were reducing dependence on normal plastic obtained from fossil fuels, non-toxic materials, help in recycling process, production with low energy level consumption, environment friendly and can be decomposed by soil microorganisms without releasing any contaminants. Production of bioplastics from algae is one of the modern trends that outperform the old methods that use plants in production. This superiority comes from the fact that algae are highly productive compared to plants and live in a wide environmental range and do not need arable land to grow. Bioplastics produced from algae can be develop mainly after the production of algal biofuels, either through the production of ethanol by fermentation, which can be converted to ethylene (raw material for a large number of plastics) or through the production of biodiesel, where carbohydrates are extracted from algae after oil extraction. In this review a simplified idea of the studies that took place in the last decade, which used algae in the production of bioplastics presented and the different effects of its production methods, which are reflected in its properties and nature. Focus was placed on studies dealing with bioplastics used in food packaging and biomedical purposes

Keywords: Bioplastic- Biopolymer-algae- carrageenan- Alginate

Introduction

The basis for the formation of bioplastics is the use of materials that have one of the following characteristics, a material of biological origin, subject to biodegradation or compostable. Bioplastics consist of two main components, which are polymers and additives that are added to improve their properties. There are different environments in which biological decomposition occurs, such as decomposition in the soil or in the aquatic environment, and its decomposition is affected by sunlight radiation. There are three main routes for production of bioplastic illustrated by ^[1] as follow,

1. Make minor modifications to the natural polymer without prejudice to the composition of its main component, which consists of sugars and proteins.
2. 2- Biomass conversion through two successive steps, the first of which is monomer production such as lactic acid, followed by polymerization of these monomers by

chemical or biochemical formation such as polylactic acid (PLA).

3. 3. Production of a polymeric material directly in microorganisms by using molecular biology technique through transferring the gene responsible for producing PHA from bacteria to plants or algae.

1. The first component of plastic (Polymers)

The polymer is a large molecule (macromolecules) composed of many repeated subunits. The types of polymers were illustrated in Fig. 1. Polysaccharides (natural polymers) used in food packaging applications mostly extracted from different bio-resources; animals (Chitin and Chitosan), Plants (Starch, Galactomannans, Cellulose), Algae (Carrageenan, alginate and agar), Microorganisms (Pullulan, Gellan Gum, Xanthan Gum, FucoPol)

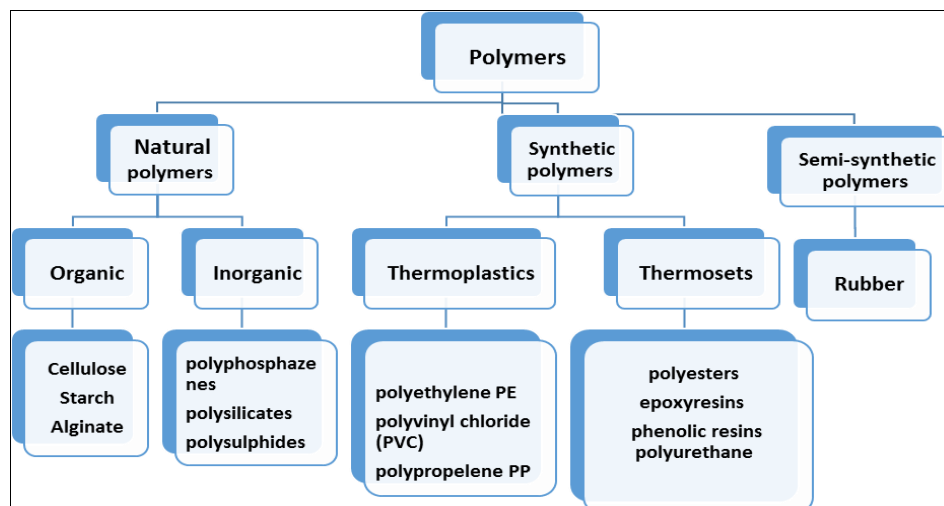


Fig 1: The types of polymers

The second component was the additives

Improving the properties of the polymer (mechanical, physical or chemical) requires the increment of some compounds, called additives, the most widely used of which were Plasticizers (improving the flexibility or decrease the viscosity of materials), Antioxidants (improve the long-term thermal stability of plastics), Lubricants (protect against wear, lower the temperature of material parts, and reduce surface stress), Slip agents (reducing the adhesion and surface coefficient of polymer friction) and heat stabilizers (preventing thermal degradation of polymers).

Bioplastic production

The two main components of plastic are polymers and additives; it is necessary to talk extensively about how to get each of them from biomass to obtained bioplastic.

1. Biopolymers

Biopolymers were obtained from algal biomass can be classified to three types

1.1. Polymers produced by polysaccharides extracted from algae

Now is the time to replace the regular plastic that causes environmental problems with another that is biodegradable, especially biopolymers derived from algae, in the production of bioplastics used in packaging food products or medicines and medical purposes [2]. Some of the polysaccharides found in algae are considered unique types that are found only in algae, and among these types are alginates that are extracted from brown algae and carrageenan that is found in red algae, these two types of polysaccharides are used in bioplastic film formation. Edible films are among the most important types of films. It was found that these films, when made from seaweed polysaccharides, are non-toxic in addition to their ability to decompose. One of its advantages is that it reduces the loss of moisture in food products, and it also prevents spoilage and any microbial contamination [3]. Enhancement of the biofilm (produced from seaweed e.g. *Kappaphycus alvarezii*) properties such as; tensile strength, heat stability and reducing the weakness and fragility of films based on seaweed production by the adding (CaCO₃) and glycerol [4]. Biofilm made from algae to have good tensile properties and long shelf-life rate, the cinnamon extraction oil in concentration of 5% must be added with 3% acetic acid to the biofilm [5]. The most six used polysaccharides (extracted from seaweeds) in biofilm production are as follow,

1.1.1. Carrageenan

Carrageenan is anionic sulfated polysaccharide (22% -35% sulfate groups), extracted from red seaweeds. According to the solubility of carrageenan's in KCl it was categorized into five different types λ , κ , ι , ϵ and μ .

κ -carrageenan properties are excellent for producing gels and membranes. Carrageenan packaging such as edible films, coatings used in food to preserve fresh fruits, Dwivany *et al.*, 2020 showed that treating the fruits with 1.5% carrageenan extend shelf life, reducing moisture loss, and prevent the discoloration.

Comparing the mechanical and physical properties of alginate films by addition of glycerin to *wet alginate* membranes, in which cellulose and carrageenan were used for formation before drying and the Impact of this addition

on the mechanical properties of the conditioned membranes with a moisture content of 57% and 100% was noticed, there is no significant changes occurred in the film properties, while κ -carrageenan slightly affected the physical properties of the film [6], the starch-CMC bioplastics biodegradability did not affected by adding κ -carrageenan [7]. On the other hand, mechanical strength and thermal stability of carrageenan incorporated with cellulose was suitable for food packaging [8].

Edible packaging films formed from κ -carrageenan and, ι -carrageenan need incorporation of plasticizer to improve the moisture barrier and tensile properties, glycerol and sorbitol used to improve the mechanical properties and heat seal strength of κ -carrageenan based film [9].

Carrageenans has another importance other than what was mentioned as edible packaging films, which is its use in different biomedical applications included; drug delivery (applied as; nanoparticles, micro stabilizers, gelling agent and microcapsules), tissue engineering (bone tissue), and wound heading (κ -carrageenan) [10].

1.1.2. Alginate

Alginate can be synthesized from different brown seaweeds and some soil bacteria, it is water-soluble polysaccharide has an anionic character. Biopolymers from Alginate used as food packaging material, in paper industry, pharmaceutical uses, and medical devices, the different mechanical and physical properties of edible alginate films have been studied, such as thickening, heat stability, gel-producing, among others [3].

Some of sodium alginate properties have been modified to make it suitable for food packaging by [11] which using two different methods of CaCl₂ treatment, by direct CaCl₂ addition and the immersion of films into CaCl₂ solutions, and investigated the treatment effects on tensile strength (TS) of the film and water solubility (WS). support of alginate composite (alginate+ starch and sorbitol) films for food packaging, the composite give low moisture environments and degrade in two weeks [12]. The development of biodegradable alginate film have antimicrobial properties and non-toxic for food packaging takes place by addition of calcium [13].

Alginates can be used in different biomedical applications. Structurally modified alginates were suitable for using in wound healing, drug delivery and also as fillers. Alginate is now a day widely used as haemostatic agent. Since alginate fiber in the nano-form have more surface area and good absorbency, it could be well used as wound dressing material suiting to accidental bleeding from wounds and cuts [14]. Alginate wound dressings has a great benefit in reducing bacterial due to its absorbance of excess wound fluids [15]. New alginate formed by modifications showed difference in structures, functions, physical and mechanical properties and used in tissue healing, wound healing, and new bone regeneration as reported by [16].

In pharmaceutical application Alginate used as capsule material instead of gelatin, or cellulose for hard capsules [17]. Alginate microbeads (AMB) used for curcumin encapsulation to facilitate passage through the stomach area without degradation, because it suffers from deterioration by self-oxidation in the biological medium, this method makes good control for releasing of substance in the intestinal area to help in maximum absorption [18].

1.1.3 Fucooidan

Fucooidans are sulfate polysaccharides extracted from brown algae, the polymer backbone consists mainly of fucose and showed different biological activities such as; antitumor, antiviral and anti-inflammatory, the bioactive effects of it attributed to molecular weight and sulfation degree, and highly dependent on the source, harvesting method and time, and methods used in extraction. ^[19].

Chitosan is used as antimicrobial polymers, formation of the composite (chitosan–fucooidan) nanoparticles and their interactions also Quantitative analysis for its production studied by ^[20], Different studies made on the preparation methods, characterization, and evaluating the composite of chitosan/fucooidan nanoparticles as drug encapsulation, for antibiotics delivery, pulmonary delivery and also for bone tissue engineering ^[21, 22]. *In vitro* biological activity of Chitosan–fucooidan composite were studied for bone tissue engineering, drug encapsulation and cellular uptake ^[23].

Nanoparticles of fucooidan alone used as a coating biomaterial and drug delivery system showed an *In vitro* anticancer activity against fibroblast cell lines, osteosarcoma, while combination of fucooidan and chitosan active on prostate and breast cancer, on the other hand chitosan nanoparticles applied also as oral drug delivery. ^[24, 25, 26].

1.1.4 Cellulose

Cellulose is used as a major bioplastic in various applications such as medical and biomedical applications due to its safe, non-toxic and stable composition. It has also been studied in the pharmaceutical fields ^[27]. The alkaline extraction of less purified cellulose fractions from three different brown seaweed species showed that the obtained films have excellent mechanical properties in addition to the high purity of cellulose in them and noted it to use as food packaging films ^[28].

1.1.5 Agar

Agar is commonly used in microbiological media. It has excellent gelling power. The two extraction methods of agar were, alkali and photo bleaching.

Synthesis of agar based bioplastic film, depend on the extraction method from different red seaweed. Specially, bioplastic films made of agar (AG), with other polysaccharides tested for the possibility of using it as an edible packaging, the composite edible film composed of starch and agar has good mechanical properties and can be used in coating ^[29].

1.1.6 Ulvan

Ulvan is the main hydrocolloid carbohydrates of the cell wall in *Ulva lactuca*. The mechanical properties of Ulvan film is poor due to their ability to absorb water with high rate and swelling, there are several strategies can be made to improve its mechanical properties, such as mixed ulvan with other polymers ^[30], also by incorporation of the seaweed (thallus as a whole) or only seaweed extracts in the ulvan bioplastic film used in production of food packaging, according to the presence of antimicrobial activity in these seaweed it can decrease foodborne pathogens presence, in the same time increasing the food shelf –life ^[2]. The method of using the whole algal biomass has advantages, the most important of which is saving time, effort, and raw materials that can be used in preparing extracts as mentioned by ^[31].

1.2 Chemically synthesized polymer from bio monomers

Poly(lactic acid) (PLA); it is a polymer synthesized by heating lactic acid monomers under vacuum while removing the condensed water. PLA used in packaging of sensitive food products, it is too fragile, therefore it should be strengthening with additives.

Production of PLA may be from green seaweeds such as *Ulva* sp., the environmental impact of lactic acid production from *Ulva* sp. was estimated by ^[32], which found that electricity consumption during seaweed cultivation is the main hotspot, the process of production included *Ulva* spp cultivation, solubilization of thallus sugars, sugars fermentation to lactic acid and finally collecting lactic acid (precursor of polylactic acid) from fermentation broth. poly(lactic) acid prepared as matrix and various algae (red, brown and green) as filler ^[33], algae also used as a filler to increase degradation rate of PLA and decrease the cost for increasing the flexibility, epoxidized palm oil was added as plasticizer. Plasticized PLA with 3% algae loading exhibit the best properties (thermal, mechanical and morphological) ^[34].

PLA-cellulosic nanomaterial production depending on critical factors illustrated by ^[35]. PLA can be used as an antimicrobial packaging by incorporation of plant extracts such as essential oils, plant enzymes and metals ^[36].

1.3 Polymers produced by fermentation processes using microorganisms (polyhydroxyalkanoates)

Polyhydroxyalkanoates (PHAs) synthesized by more than 300 different microorganisms, according to chain length it classified into short, medium, and long chain, they differ in their mechanical and heat stability properties.

The PHA biosynthesis in the different microorganisms could be improved by molecular genetics technique by introducing PHA synthase gene to organisms to increase the percentage of PHA in cell because the normal content was only about 5 percent of cell dry weight.

1.3.1 Polyhydroxybutyrate (PHB)

Polyhydroxybutyrate (PHB) is a short-chain PHA produced by several microorganisms. When production of PHA takes place under photoautotrophic conditions Polyhydroxybutyrate (PHB) was produced, so that cyanobacteria and micro algae are the most microorganisms produced it. The mechanical and physical properties of PHB are close to those of polypropylene and polyethylene and can be compared with them, so it represented as one of the most promising bioplastics ^[37].

The various cultivation conditions of algae species such as N percentage, P content, light intensity and exposure time, have an impact on the capability of *Nostoc muscorum* and *Synechocystis* sp. to produce PHB, ^[38, 39]. Sodium acetate concentration in the culture of microalgae combined with N and P deficiency effects and phosphate content increased the production of PHB from different algal species ^[40].

The highest PHB was detected in *Nostoc muscorum* (6.44% w/w of dry cells) while, the lowest percentage 0.51% was obtained in *Spirulina platensis*, whereas *Cylindrospermum* sp., *Oscillatoria* sp. and *Plectonema* sp. have not any PHB production from 23 screened cyanobacteria strains As recorded by ^[41].

Highlight on the new trend which depend on using exogenous carbon sources in microalgae cultures with reduction in the use of nutritional sources to produce PHB,

the maximum concentration PHB extracted from *Chlorella fusca* 3.7 % (w w⁻¹) exogenous substrate cultivation in culture with 75 % NaNO₃ and D-xylose at 20 mg L⁻¹ addition [42].

2. Additives

During manufacture or during processing of biopolymers some additives are incorporated for improving its properties; mechanical, physical or chemical. additives such as plasticizers, antioxidants, lubricants, thermal stabilizers and others

Additives are also added to provide the necessary protection to polymer from degradation by abiotic factors (light, heat, etc.) or bacteria (biotic factor). dialdehyde starch film showed better moisture content, solubility and tensile strength against the film produced in the presence of silica [43].

Types of additives,

2.1 Plasticizers

Plasticizers are the common polymer additives used in bioplastic manufactures such as phthalate esters used in PVC products, plasticizers improved the flexibility, durability and stretch ability of polymeric films. The medical devices for enteral nutrition, made of PVC must be tested to estimate that devices free from phthalate and determine the plasticizers that have the potential to pass into the patient's body to avoid any effect of these substances that may cause danger to the patient's health [44].

Glucose esters represent a promising option as a green PVC capable of overcoming some environmental phthalates problems along with palm oil epoxide (EPO) which has led to improved mechanical properties of biopolymers and increased flexibility [45, 46].

2.2 Antioxidants,

Antioxidants additives reduce the biopolymer thermo-oxidative degradation when exposed to high temperatures, UV, infrared heating. and microwave, specially, in food packaging. [47]. The most commonly used antioxidants in

plastic food packaging were Arylamines, also Phenolics, carvacrol, thymol, cinnamaldehyde, and finally limonene additives are used as antioxidants [48].

2.3 Lubricants,

Friction obtained from movement of object against another object reduced by using lubricants, it decreases the temperatures of the materials, Emissions of CO₂ from biolubricants is about a third less than for fossil-based lubricants. Vegetable oils considered as one of the cheapest material, used to produce biodegradable lubricants. In recent years, plastic greases that have a high ability to biodegrade were used, and it would be preferable if these greases were from used frying oils [49].

Table 1: Biolubricants production (European commission, 2018)

Year	Production cost (USD)
2013	3.255 million
2025	5.150 million
2030	6.200 million

2.4 Slip agents

The polymer surface coefficient of friction can be significantly decreased by using fatty acid amides, including 1st and 2nd amides, which represent the most slip agents used, it reduced melt viscosity and also give the polymer more antistatic properties. The most common used slip agents are erucamide, oleamide, waxes, fatty acid esters and zinc stearate [46].

2.5 Heat stabilizers

The deterioration of polymers occurs for several reasons, including exposure to temperatures, which necessitates the use of some compounds as heat stabilizers to be responsible for preventing this deterioration [50]. Stabilizers divided into two groups; primary stabilizers such as mixed metal salt mixture, organic tin compounds, and also lead compounds. On the other hand, the secondary heat stabilizers that are widely used are, organic alkyl compounds, epoxy compounds, and beta diketones.

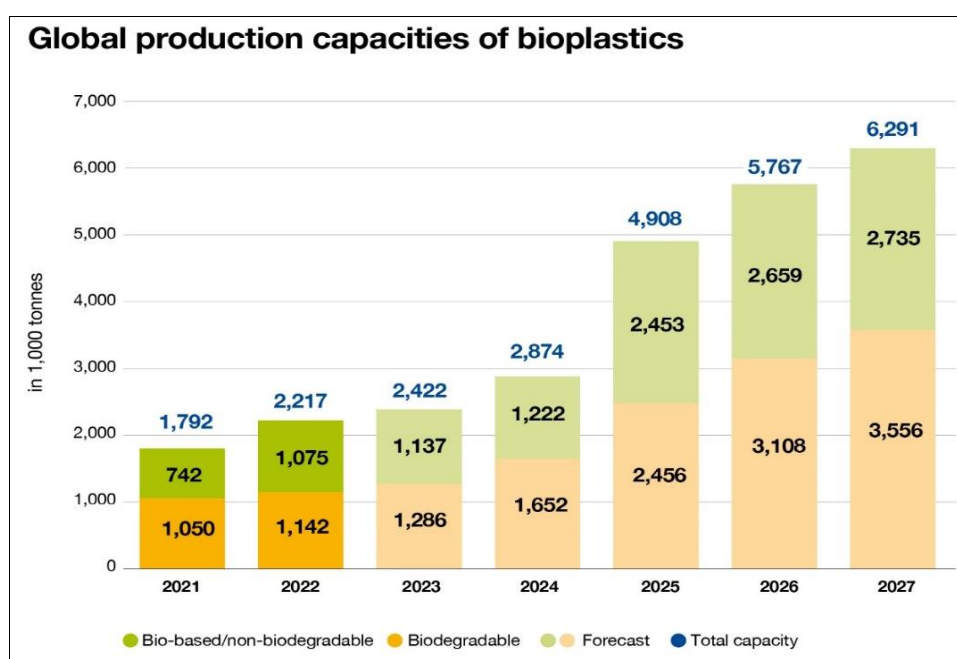


Fig 2

Conclusion

The increasing demand for biodegradable materials (environmentally friendly and non-toxic) in the food industry prompted all interested scientists and researchers on the one hand, and industrialists on the other, to search for alternatives to traditional plastic materials, which take hundreds of years to decompose. In this review, some studies that dealt with this topic were reviewed. These studies illustrated the significant role that algae, whether microalgae or macroalgae, can play in the production of biodegradable plastics.

Bioplastic that consist of a material derived 100% from algae are not yet available and require further studies to make innovative developments. This can happen in several ways, including the use of biotechnology techniques that achieve sustainability in algae bioplastics. Among these technologies are genetic engineering, new technologies for fermentation and extraction of polysaccharides from cells, and nanotechnologies that in turn enhance the nutritional properties of foods through additives, nano-nutrients, and nano-delivery systems.

Active compounds encapsulation by an edible polymer made from algae if it Micro type and nano-type helps to control and keep these compounds from being broken down and released in the places and conditions that contribute to their maximum utilization.

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