A Review on Algal Biopolymers

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Abstract: Polymers are the most important materials we use in many areas of daily life. Without them humanity could not shape today's world. However, major source of polymeric material is fossil fuels which decrease constantly. Therefore, alternative resources are needed to be discovered especially from biological source for sustainable polymer production. Biopolymers are polymers developed from renewable resources such as plant, animal, bacteria, fungi and algae. They can also be useful in material and many other applications. Algae are one of the most promising organisms in many aspects. Since they grow fast, contain variety of unique value added material and do not compete with food resources, and also they have high bioenergy feedstock potential. In this study, algae are considered as feedstock for biopolymer production and biopolymers derived from algae are investigated. Throughout this study algae derived biopolymers were classified as three types. First type of polymer obtained from algae are natural polymers (polysaccharides, lipids, extracellular polymeric substance). Especially polysaccharides from algae such as alginate and agar are well known for their biotechnological applications. Second type is polyhydroxyalkanoates (PHA) which accumulate in only cyanobacteria. And third type is bio-based polymers polymerized from algae derived monomer, they can have same characteristics with conventional synthetic polymer. This review study will give an idea especially about the algal biopolymers, their resources, properties, structures, application areas, production methods and their future potentials.

Keywords: Algae, natural polymer, biopolymer, lipids, polysaccharides.

1. INTRODUCTION

Algae are alternative renewable sources for biopolymer production, because of their high growth rate, high photosynthetic efficiency and great potential for carbon dioxide fixation [1]. Therefore, variety of biopolymers can be obtained from algae. Basically those are naturally occurring polymers (polysaccharide, lipid, protein), bio-based polymers which are polymerized from algae derived monomer and naturally occurring polyester polyhydroxyalkanoates (PHA) which are accumulated only in cyanobacteria. Each polymer type has different property and application in many areas. For example, PHA and bio-based polymers which are polymerized from algae derived monomer have potential to replace fossil fuel based conventional polymer. And naturally occurring polymer have many applications in medical, pharmaceutical and food industries as a novel material. Therefore, algae derived biopolymer offers sustainable alternative material for many usage areas.

However, the definition of biopolymer is not clear in the literature. There are many terms exist for the concept of biopolymer which have overlapping meanings such as "biodegradable", "bio-based", "compostable", "bioplastic", "renewable polymer" and "green polymer" [2-4]. Mostly biodegradability of polymer constitutes first step for the classification. Also, the term "bioplastic" is often used for the biopolymer. Nevertheless, bioplastic can be biodegradable but this does not mean that the polymer is derived from biological resource. Some of the petroleum based polymers can also be biodegradable such as polycaprolactone (PCL) and poly (butylene succinate) (PBS) [3]. The term bio-based polymer is used for the polymer obtained from renewable resources [2]. However, some bio-based polymers can also be non-biodegradable [2]. Nevertheless, of this contradiction in terms our focus will be polymer obtained from renewable resources.

Mainly, there are three methods to obtain biopolymers from renewable resources; (1) Polymers extracted from biomass (Natural occurring polymers), (2) Polymers produced by microorganism, (3) Polymer synthesized by bio-derivative monomers [2, 3, 5].

Natural polymers are produced by organisms and they are essential polymers for all types of life and synthesized by enzymatic pathway. They are divided into polysaccharides, lipids and proteins, and often obtained by extraction methods. Polymers as second type produced by microorganism, consist of mostly polyhydroxyalkanoates (PHAs) such as poly-3-hydroxybutyrate. PHA is mainly produced by bacteria and blue-green algae (cyanobacteria). This naturally occurring polyester accumulated in this microorganism against stress condition and their production require elaborate culture condition [1-5].

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Polymer synthesized by bio derivative monomers, their monomers are derived from monomers, which are from fatty acids and their derivatives, monomers obtained by digestion of natural polymers such as carbohydrates [4]. Also monomer can be derived from protein which serves as a building block for polymer synthesis. Those monomers are obtained either by chemical, biochemical and thermochemical processes for further polymerization. During polymerization, blending material can be added to enhance polymer properties. Obtained polymer is often called as bioplastic and it has same property with petroleum based conventional polymer. Those polymers either can be bio degradable or non-biodegradable [6].

2. NATURAL POLYMERS EXTRACTED FROM ALGAL BIOMASS

2.1. Algal Polysaccharides

The world's surface encompasses more than 70% water, and the vast diversity of marine organisms offers a rich source of natural products such as polysaccharides. Polysaccharides have been an arising material in biomedical applications because of the fact that they are functionally active, water soluble and biodegradable. Marine algae contain a large amount of polysaccharides. These are cell wall structural polysaccharides, mucopolysaccharides and storage polysaccharides [7]. The main polysaccharides in green algae seaweeds are ulnas, sulfuric acid polysaccharides, xylan and sulfated galactans; those in red seaweeds are xylan, carrageenan, fucoidan, water-soluble sulfated galactan, porphyran and mucopolysaccharides [8, 9]; and those in brown seaweeds are alginic acid, fucoidan, laminarin and sargassan. They are sulfated polysaccharides. Sulfated polysaccharides are known to possess some biological activities with the inclusion of anticoagulant, antiviral, anticancer and immunoinflammatory [7].

2.1.1. Alginate

Alginate is a polysaccharide which is obtained from cell wall of brown algae (*Phaeophyceae*). The acid form is a linear polyuronic one and referred to as alginic acid. Alginate is both a biopolymer and a polyelectrolyte [7]. Alginate is now known to be a whole family of linear co-polymers containing blocks of (1,4)-linked β-D-mannuronate (M) and α-L-guluronate (G) residues. The blocks are composed of consecutive G residues (GGGGGG), consecutive M residues (MMMMMM), and alternating M and G residues (GMGMGM). Alginates extracted from different sources differ in M and G contents as well as the length of each block, and more than 200 different alginates are currently being manufactured [10].

An extraction method of alginate is that 100 g algae are ground and left in a 0.1 M hydrogen chloride (HCl) solution overnight. Then, it is washed in 1 L of 1% sodium carbonate (Na_2CO_3) solution, stirred and filtered. The filtrate is collected and precipitated with IsPrOH in three volumes of residue. The resulting gel is dried and milled [11].

2.1.2. Laminarin

The principal storage polysaccharides of brown seaweeds are laminarin and representing up to 35% of the algal dry weight [6]. It is a linear polysaccharide constituted by 25-50 glucose units. M and G are two types of laminarin chains depending upon the reducing end. M chains end with 1-O-substituted D-mannitol, whereas G chains end with glucose as the reducing end [12]. For laminar extraction, 85% ethanol is applied at 23°C and 70°C to separate the pigment and proteins from the milled algae. Then it is centrifuged. The solvent and pellet are separated from each other by vacuum filtration with a filter paper. The separated pellet is treated with 2% $CaCl_2$ at 70°C and centrifuged. Thus, alginates as well as fucoidan and laminarin are precipitated. The fucoidan is separated from the resulting pellet with 0.01 M HCl solution at pH 2 and 70°C and then centrifuged again. The pellet obtained after centrifugation is subjected to 3% Na_2CO_3 at 70°C for alginate extraction and centrifuged again. Last product is laminarin [11].

2.1.3. Fucoidan

Fucoidans are a group of polysaccharides (fucans) essentially composed of sulfated L-fucose with less than 10% of other monosaccharides. It is a ramified sulfated polysaccharide [7]. The low molecular fucoidan (LMF) is more bioavailable than high molecular fucoidan (HMF) [12]. Fucoidan extraction from macroalgae is carried out in hot water followed by precipitation with organic solvents or salts. The process has three crucial steps: milling seaweeds, extraction/purification (which involves several, extensive extractions with aqueous and acidic solutions and includes calcium to promote the alginate precipitation), and drying/careful storage [7].

2.1.4 Carrageenan

Carrageenan is one of the major constituents of red seaweed cell wall representing 30–75% of the algal dry weight. They are linear hydrophilic polysaccharides which have 3-linked β -D-galactopyranose (G-units) and 4-linked α-D-galactopyranose (D-units) or 4-linked 3,6-anhydro-α-D-galactopyranose (DA-units) as alternating units with additional sulphate group [13]. The number and position of sulphate groups in the repeating galactose units allow the classification of carrageenan in three main commercially relevant families, namely, kappa (k), iota (i), and lambda (l). The chemical reactivity of carrageenan is mainly because of the sulfate groups, and its structural diversity justifies its wide application [7, 13].

In extraction process, the algae are collected, dried quickly and then baled to protect its freshness. The dried algae are mechanically ground, sieved to remove foreign matter such as sand and salt, and thoroughly washed to improve quality. A two-stage treatment process is applied for the disposal of cellulosic materials. First, the dissolved carrageenan mixture is centrifuged to remove the cellulosic particles. Following this, filtration is applied to separate smaller particles and the solution is concentrated by evaporation and removal of water. The carrageenan is then recovered by one of the two process methods. The first method is to deposit the carrageenan solution in the potassium chloride solution. This application increases the gelation temperature and thus allows the filtrate to gel immediately. The gel is then frozen and compressed to remove excess water during thawing. In the other method, the concentrated carrageenan solution is precipitated in isopropyl alcohol. As the carrageenan is not soluble in alcohol, it becomes a clot (coagulum) between alcohol and water. This clot is compacted to remove the liquid content and is vacuum dried to remove the alcohol completely. The drying process is completed on a drying strip and the dried coagulum is milled and blended [11].

2.1.5. Agar

Agar is a mixture of polysaccharides, composed of agarose and agaropectin, with interchangeable structural and functional properties as carrageenan [7]. Agar extraction from algae has following steps in general manner: washing the seaweed to remove the foreign matters, boiling in water to dissolve the agar, filtering, cooling the product to obtain jelly structure. Than the remaining water has been removed with various techniques to obtain the final product [12].

2.1.6. Ulvan

Ulvan are the major constituents of green seaweed cell walls representing 8-29% of the algal dry weight. It is mainly composed of glucose, rhamnose, xylose, glucuronic acid, iduronic acid and sulfate with smaller amounts of mannose, arabinose and galactose. The two major kinds of Ulvan that have been identified are the water-soluble Ulvan and the insoluble cellulose-like material [7]. Ulvan is mostly homogeneously distributed throughout the frond being more predominant within the intercellular space and in the fibrillar wall [14].

3. POLYMERS EXTRACTED FROM CYANOBACTERIA

3.1. Polyhydroxyalkanoates (PHA)

Polyhydroxyalkanoates (PHA) are one of the most promising biopolymer which can be alternative to petroleum based polymer (synthetic polymer). Synthetic polymers have various applications in all areas of industry and variety of daily products. The main properties of synthetic polymers are that they can be shaped easily and have high chemical resistance. However synthetic polymers have an important drawback that their disposal is very difficult since they are nondegradable [15-17]. Polyhydroxyalkanoates are biodegradable biopolymer which have same polymer characteristics with synthetic polymer due to their high molecular weight and other properties like thermoplastic processability and hydrophobicity. Therefore, biodegradability and good material properties of PHAs give PHA very useful characters that they can be used instead of synthetic polymers. However, the production cost of PHA is higher than synthetic polymer. Thus, their applications are limited. New techniques and development are necessary to lower the cost of PHA production [17, 18].

PHA are bio polyesters which can be synthesized and accumulated inside the cell as insoluble granules for energy and carbon storage by various prokaryotic organism. There are two species reported to accumulate PHA; bacteria mostly chemoautotrophic bacteria and cyanobacteria known as blue-green algae. Also, genetically engineered higher plants can produce PHA [17, 19, 20]. Main producers of PHA are bacteria. PHA content in bacteria reachs at most 90% of cell dry weight. Depend on conditions of organism PHA can have different structure up to date 150 different structure, identified most well-known monomers are 3-hydroxypropionate, 3-hydroxybutyrate, 3-hydroxy-valerate, 3-hydroxyhexanoate, 3-hydroxyoctanoate, 3-hydroxydecanoate, 3-hydroxydodecanoate, 3-hydr-oxytetradecanoate and 4-hydroxybutyrate. Within those monomers homopolymers, random copolymers or block copolymers can be formed. This diversity give them various material properties like physical and thermal properties [16, 17]. Also, the type and ratio of monomers namely material properties can be controlled by optimizing culture conditions [20].

PHAs are environmentally friendly plastics and have an application in many areas. Their main advantages are their biodegradability, non-toxicity and material property similarity with conventional plastic. Some applications of PHA; for example, in biomedical industry it can be used as biomedical material as implant, wound dressing, surgical suture or in drug delivery, in tissue engineering application even used as direct drug monomer. Other examples of PHAs are that they can be used as bioplastic for packaging, laminates, film, coating material and consumer goods. Disposable products used in the food industry or it can be used as animal feed, bioenergy source or smart material [16, 2].

3.2. Poly-(Hydroxybutyrate) (PHB)

Apart from bacteria, cyanobacteria are potential host for PHA production. Because cyanobacteria requires minimum nutrient, can fix CO_2 as a sole carbon source. Use of cyanobacteria as PHA producing host has many advantages over bacteria since cyanobacteria use waste CO_2 and sunlight as carbon and energy source. Therefore, cyanobacteria can provide environmentally friendly biopolymer which can be used as bioplastic. However, PHA content is low in percentage cell dry weight to compare with bacteria. The possible reason for low content might be due to larger cell size and thicker cell wall of cyanobacteria restrain downstream processing of PHA extraction [20]. PHB poly-(hydroxybutyrate) is the most abundant PHA which is homopolymer of hydroxybutyrate that presents in various cyanobacteria such *as Chlorogloea fritschii, Spirulina spp., Aphanothece spp., Gloeothece spp*. and *Synechococcus spp. Synechocystis sp, Gloeocapsa sp, Spirulina platensis, Phormidium sp* etc. [17, 18, 19, 21].

4. POLYMER SYNTHESIZED FROM ALGAE DERIVED MONOMER

So far natural polymer from algae and PHA from cyanobacteria are discussed. Apart from them algal biomass can be utilized by chemical, thermochemical, mechanical and biochemical processes for production of monomer for further polymerization of green bio based polymer. The polymer that is produced from those processes can be biodegradable or nonbiodegradable. They often called as bioplastic which suits the definition of American Society for Testing and Materials ASTM D6866-06, since they are obtained from biological resource [22]. Algal biomass is excellent source for production of various chemicals. With suitable treatment, these chemicals serve as a monomer for polymer production. Currently majority of conventional polymers are polyethylene (PE), polyethylene terephthalate (PET), and polypropylene carbonate (PPC), and their monomer (ethylene, propylene, benzene) derived from fossil fuel [23]. However, there is a huge concern about sustainability of fossil fuel and their non-environmental friendly manner [24]. Therefore, renewable biomass gains importance to become as alternative source to fulfill energy demand and need for valuable chemical to act as monomer for bio based polymer production having theoretically low greenhouse gas emissions [25]. With chemical synthesis, almost all chemical building block of polymer can be produced from biomass and these building blocks have same property of petrochemical counterpart. Those polymers are called 'drop-in' bioplastic [26]. Also, new kind of chemical building block can be produced from biomass which have different property and cannot be synthesized from petrochemicals such as lactic acid [6]. Mainly these polymers, can be produced by converting algal biomass into ethanol by fermentation, which can be used as feedstock for variety of polymer like as polylactide (biodegradable polyester) [2, 27].

As pointed earlier, algal biomass have advantages over first and second generations of biomass since they utilize CO_2 from atmosphere and convert it to carbon source. One of the major advantages of using algal biomass is its potential to reduce biomass cost [6, 23, 24, 27].

However, this process may include many steps and those steps can be different for different kinds of polymer which cannot be economically feasible. Also, polymer production yield is very low to compensate polymer demand. Therefore, it is important to design modest process to fulfill the economic requirement and environmentally friendly manner. On the other hand, biopolymer synthesis researches from biomass are mostly conducted in laboratory scale hence, industrial application is not common. Dongda Zhang *et al*. analyses 20 polymer synthesis pathways from biomass including algal biomass to find most promising pathway and they found that polyethylene (PE) is the most promising polymer since number of reaction step to produce PE is lower than others [23].

Algae contain high amount of carbohydrate, oil and protein. Some species contain high amount of carbohydrate for example red algae that their carbohydrate amount reach up to 75-80% of its dry weight [1]. On the other hand, some microalgae species like as *Phaeodactylum tricornutum* contain high amount of lipid [28]. And some of the species contain high amount of protein (~30–65 %) like as *Scenedesmus spp*. [29]. Therefore, depend on species' different characteristics, chemical building block of polymer can be obtained from algal biomass. In this section, examples of some polymer synthesized from algae derived monomer are investigated.

4.1. Polyester Production

One of the aspects of the obtaining polyester is utilizing macroalgal polysaccharides. Agar is natural polysaccharide and highly reactive. Therefore, it can be converted into 5-hydroxymethylfurfural (HMF). From HMF common polyester building block 2,5-furandicarboxylic acid (FDCA) can be synthesized [1, 30, 31]. And, various polyesters can be produced from FDCA [1].

Another chemical building block is 1,2-propanediol (propylene glycol) which is also used in production of polyester. 1,2-propanediol usually produced from petrochemical can also be obtained biologically from renewable biomass. Microorganisms like bacteria and yeast, known for their ability to produce 1,2-propanediol from fermentable sugar like fucose and rhamnose which are abundant in structure of EPS, which can be used as feedstock [30, 31].

4.2. Polyurethane Production

Protein is highly abundant in some microalgal species. However, as microalgal biomass mostly used for biofuel production the protein present in algae degraded and incorporated into biofuel. On the other hand, it is possible to extract protein from algae and convert it into polyurethane. S. Kumar *et al*. (2008), demonstrate the process pathway. Firstly, algal protein is removed by flash hydrolysis (280°C, 10 s) process. After filtration and freeze drying amino acid residues, peptide are obtained. Then, obtained peptide and amino acid residues are treated with diamine and ethylene. Finally polyol, which is polymerized to polyurethane, is obtained. The main advantage of this process is that remaining residue, containing lipid and algal cell after flash hydrolysis of protein, can be used as feedstock for other application like as biofuel production [29]. Polyurethane is biocompatible polymer which have various applications due to their easiness to modify properties such as coating, adhesive, sealants, adhesives, elastomers and foams [32].

4.3. Thermomechanical Polymerization of Microalgal Biomass

Another approach is using thermomechanical polymerization technique. It is possible to use microalgae as a raw material to produce polymer which is also biodegradable. *Spirulina* and *Chlorella* microalgae are mostly used since they contain high amount of protein (e.g. dried *spirulina* contain 51-71% and *chlorella* contain 51-58% protein) [22, 33]. The process of thermomechanical molding is usually done with addition of plasticizer such as glycerol to increase mechanical properties of polymer such as increasing viscoelastic properties of polymer, and also blending with polyethylene enhances mechanical properties of polymer [22, 33, 34]. Throughout the thermomechanical molding, heat and pressure are applied which lead to formation of new intermolecular bonds, and addition of plasticizer stabilizes the three-dimensional structure [22].

Also, apart from thermomechanical polymerization polysaccharide from macro and microalgae such as carrageenan's are polymerized with addition of reinforcement material to improve their mechanical and thermal properties. S. A. Rodriguez *et al*. showed production of nanocomposite material from Carrageenan [35]. Furthermore, M. Nizar Machmud *et al*. (2013) use red algae *Eucheuma Cottonii* directly as a raw material to produce polymer with filtration technique and with addition of plasticizer [36].

There are many commercial attempts to produce bioplastic from algae. To do this few companies aimed to produce biopolymer from thermochemical processing of microalgae. These are; Algix and Algaeplast. Algix produces algae based bioplastic resin pellets [37]. Another attempt is project SPLASH (Sustainable Polymers from Algae Sugars and Hydrocarbons) which is funded by EU. The aim of the project is to develop process to convert algal biomass into biopolymer and plastic product and enhance cooperation with business and researcher [26, 38].

Table 1: SWOT Analysis for Algal Biopolymers

Strengths	• Biopolymers obtained from algae have potential to replace fossil fuel based polymers. • They have sustainable and bioeconomical approach. • Algae provide alternative, cheap, sustainable resource for biopolymer production because of their high growth rate, without need of arable land and lack of competition with food resources. • Algal biopolymer production is a new market. • With biopolymer production, CO_2 can be utilized from the environment. • Biopolymers with different characteristics and properties can be obtained from different algae species (e.g. therapeutic property, high mechanical property). • Produced biopolymers can be biodegradable or non-biodegradable both of them have their own advantages.
Weaknesses	• Biopolymer production cost is still high mainly due to complex production process. • Biopolymer production yield is low to fulfill the polymer demand in the market. • Information present in literature is not very enough for production of biopolymer from algae. • Controlling monomer composition of biopolymer is relatively difficult. • Accumulation or secretion of desired product from microalgae need stress condition which also decrease cell growth rate. • Some difficulties in commercially algae production.
Opportunities	• Novel bio composite polymers can be produced with blending of algal biopolymer or biomass with another polymer. • Some algae species can also grow in waste water with designing suitable process, so that both waste water is disposed and a useful product is obtained. • Biorefinery approach for algae utilization provides to lower production cost with zerowaste concept. • Algae species are prone to genetically engineering modification which let high yielded biopolymer. • International investments and collobrations are possible to enhance algal biopolymer production, • New job oppurtunities for algal biopolymer production are available. • New patents for algal biopolymer production are available.
Threats	• Weakness of algal biopolymer may prevent their further commercialization. • Very low cost of fossil fuel based polymers prevents awareness of necessity to find and use alternative sources for biopolymer production.

The polymer produced from algae have advantages and disadvantages over conventional polymers which demonstrated on SWOT analysis (Table **1**). Therefore, further researches and projects are needed to reveal more information about algal biomass production and feasible process to convert this biomass into various biopolymer for different kind of applications.

CONCLUSIONS

Algae are used as food, feed and fertilizer sources, and feedstocks for biofuel production. They can be also utilized in waste water treatment applications and in production of therapeutic and value added chemicals for industry. Nowadays, they are considered as third generation feedstock since they have many advantages over first and second generation feedstocks such as their high growth rate, noncompetitiveness with food, need of less area for growth, fixation of CO_2 from environment and lack of having recalcitrant compartment like lignin, and they are more suitable for mainly biofuel and bioderived polymer productions. In conclusion, by means of this review, the types of algal biopolymers and many different processes to produce commercial bio-based polymers from algal biomass were presented to give point of view for using sustainable and renewable sources.

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