https://doi.org/10.33263/Materials23.433438

ISSN: 2668-5728 https://materials.international

Materials International

Review

Volume 2, Issue 3, Pages 0433-0438
2020

Received: 20.06.2020
Accepted: 1.09.2020
Published: 10.09.2020

Alginic Acid: a Potential Biopolymer from Brown Algae

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Abstract: The increasing rates of environmental issues are forcing industries to rely upon biopolymers rather than synthetic plastics. These biopolymers have the strong ability potential owing to their various physicochemical properties, to become a green solution for environmental attributes in the time to come. However, relatively deficient mechanical and barrier behavior limit the use of these biopolymers. This can be hurdled with the incorporation of suitable other polymers or materials to the matrices of the concerned biopolymer. Alginic acid is a biopolymer that is being widely researched owing to its various physicochemical properties. This paper focuses on a comprehensive discussion on alginic acid from its properties to composites/blends and various applications.

Keywords: biopolymer; alginic acid; composites.

1. Introduction

The growing concern over environmental issues like pollution, waste disposal, and the rules and regulations formulated as a solution to these problems are driving the industries to introduce more environmentally amicable materials for their products. Industries were much dependent on petroleum-based plastics that can harm ecological balance by creating solid waste disposal problems. Polymers are a group of "giant" molecules made up of individual repeating building blocks (monomers) connected together to make long chains. Approximately 140 million tons of petroleum-based polymers are generated worldwide every year. These kinds of synthetic polymers are highly stable that their degradation cycles take infinite time. M. G. Rao *et al.* [1], stated that these kinds of materials remain as such in the soil for a long period of term at the rate of about 8% by weight and 20% by volume of the landfills. Environmental pollution caused by these non-degradable polymers has been identified as a major issue. Also, these materials are mainly derived from non-renewable sources that have a finite limit. There arises research interest in biocompatible materials from renewable sources that can replace materials derived from non-renewable sources. As per J. W. Rhim *et al.* [2], biopolymers or biodegradable plastics are a polymeric system where microorganism assisted degradation takes place. With a proper atmosphere of the appropriate amount of moisture, temperature, and the needed oxygen level, these biopolymers undergo biodegradation, followed by fragmentation or disintegration of the constituent monomers with no dangerous residues. Biodegradation and biorecyclingare considered appealing solutions to remove plastic wastes. Since

Cite This Article: Sreekumar, K.; Bindhu, B. Alginic Acid: a Potential Biopolymer from Brown Algae. Mat Int **2020**, 2, 0433-0438. https://doi.org/10.33263/Materials23.433438

the biopolymers are biodegradable and can be effectively recycled, these materials have become a generally accepted opinion to solve waste disposal problems.

In contrast to synthetic polymers, biopolymers have a distinct structure with a consistently disseminated set of molecular mass and seem to be a long chain of worms or a curled-up string ball under a microscope. One of the major advantages of biopolymers is that they can easily be disposed of as they possess biodegradation property and are compatible with the environment. I. Vroman and L. Tighzert [3] had observed that it is the enzyme activity or chemical deterioration connected with microorganisms that assist the biodegradation. The degradation process takes place, as illustrated in figure 1. Along with the chemical structure of the polymer, degrading environmental conditions like ambient temperature, availability of oxygen, pH, humidity, etc. are the factors that control the degradation.

Biopolymers are now widely used in different industrial purposes. They have been used in a variety of applications such as therapeutic aids, medicines, coatings, food products, and packaging materials. However, relatively deficient mechanical and barrier behavior limit the use of these biopolymers.

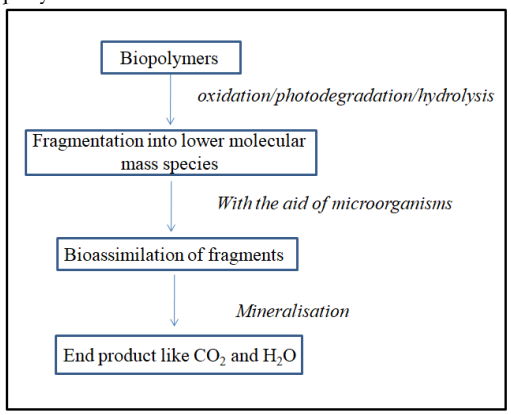

Figure 1. Degradation process of a biopolymer.

Biodegradable plastics and polymers were first introduced in the 1980s. Now the worldwide consumption of biodegradable polymers is 360,000 metric tons and is supposed to rise up to about 550,000 metric tons by 2023. Biopolymers are polymeric biomolecules produced from natural sources either chemically synthesized from biological material or entirely biosynthesized by living organisms. A vast number of biopolymers have been produced or are made in nature at the time of the growth cycle of the organisms.

Biopolymers, its blends, and composites have the potential to become a green solution for environmental attributes in the time to come. According to T N Sun [4], the possibilities of these materials depends on their capability in reducing CO_2 emissions, while fabricating a feasible material with less environmental impact after use and can sustain even without petroleum. As CO_2 is captured during photosynthesis and is released during the degradation process, these materials possess the capacity to reach a neutral carbon process by closing the carbon cycle. Also, these biopolymers can be employed to enhance the performances of various biologically active molecules in a product. They can also be altered to meet different potential applications. Biopolymers are now widely used in the food industries, packaging field, medical field. Osteoconductivity and the excellent mechanical properties due to the highly porous nature make polymer composites a potential substrate for bone tissue engineering. Biodegradable polymer scaffold may provide several benefits for bone tissue engineering, enhanced environment for cell seeding, survival, growth. The upcoming progress and feasibility of polymers and composites from renewable resources are dependent on constant research, particularly in the area of compatibilizing mechanisms, surface modification, and advanced processing techniques. A thorough understanding of these is expected to substitute more and more synthetic plastics from non-renewable sources.

2. Alginic Acid (AA)

AA, also called algin or alginates, are naturally obtained anionic polysaccharides that can be extracted from cell walls of brown algae including, *Macrocystispyrifera, Laminariahyperborea, Ascophyllum nodosum,* and various bacterial strains[5]. As per Davis *et al.* [6], it may be present in both the cell wall matrix and in the mucilage or intercellular material and can constitute between 10% and 40% of the dry weight (untreated) of the algae. Enquist *et al.* [7], had stated that AA composes 30-60% of the total sugars in brown macroalgae. The properties like biodegradability, biocompatibility, non-toxic behavior, and low cost would render AA, an excellent candidate in biological applications. According to toxicological data, AA is safe when used in food. Sodium alginate is one of the most

widely investigated ones among the group of AA in the pharmaceutical and biomedical fields. As a biomaterial, AA possesses a variety of advantageous characteristics, including biocompatibility and non-immunogenicity, which are connected with its hydrophilicity. AA and AA derivative composites have recently been researched as the association of biopolymers and inorganic materials with features that can be explored more for potential aspects.

2.1. Chemical structure of AA.

It is a linear polysaccharide consisting of 1,4-linked β-D-mannuronic acid (M) and 1,4 α-L guluronic acid (G) residues arranged in homogenous (poly-G, poly-M) or heterogeneous (MG) block-like patterns. Benavides *et al.* [8], had described the structure of AA, and it was found out that, in polymer chains, monomers are arranged alternately in GG and MM blocks, together with MG blocks. The G blocks are specifically buckled, while M blocks take the shape of an extended ribbon. A diamond-shaped hole, to which Ca ions can be incorporated, is formed when two G blocks are aligned side by side.

The molecular structure of AA [9] is shown in figure 2. β-D- Mannuronate and α-L-guluronate residues are available in different proportion, sequence, and molecular weight. As per George and Abraham [10], the composition and extent of the sequences and the molecular weight define the physical behavior of the AA. Leal *et al.* [11] had reported that the content of uronic acid changes with species and tissue types, and partial acid hydrolysis of AAs allows the preparation of fractions enriched in hetero- and homopolymeric blocks. With the increase in the concentration of guluronic content, the strength of the gels also formed increases. Agulhon*et al.* [12], efficiently related this phenomenon to the impressive affinity of the guluronic residues for divalent cations. With AA, there is variation in cation affinity. The guluronic residues stack to form a characteristic egg-box structure.

Bayer *et al.* [13], had observed that the dimerization of the AA chains occurs through the divalent cations, causing junctions between many chains to create a network structure. As per the observations of J Rhim[14], AA being the unique polysaccharide with carboxyl groups present naturally in each constituent residue, posses numerous capabilities to act as functional materials.

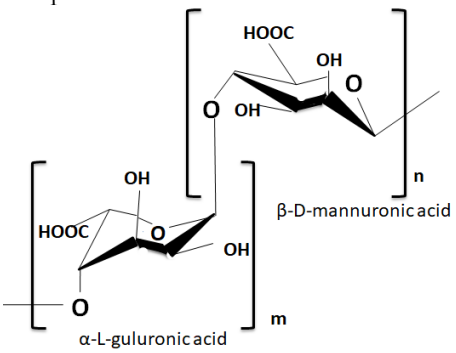

Figure 2. Molecular structure of AA.

2.2. Properties of AA.

AA form cross-linked structures, in a favorable environment with parameters like lenient, without any assistance of heat, oxidants, or organic solvents. With these mild conditions, macro materials like proteins or even cells can be incorporated into the network, without any alteration of the biological activity of the guest materials. According to Bayer *et al.* [13], AA is generally considered biocompatible and non-immunogenic due to its chemical composition. The hydrophilic nature of the AA films, along with the cross-linking process, can be made utilized to improve their water barrier properties, mechanical resistance, cohesiveness, and rigidity. George and Abraham[10] had found that AA, being an anionic polymer with carboxyl end groups, is a good mucoadhesive agent.

3. Alginic Acid Composites

Szekalska*et al.* [5] had studied the extraction of AA. The extraction of alginic acid from brown seaweeds comprises of multistage process, starting with mineral acid treatment on dried raw material, followed by purification, and conversion into water-soluble sodium salt in the presence of calcium carbonate, which is further transformed back into acid or expected salt. Alginic acid has been used in the food industry. Liling*et al.* [15] had studied about cross-linking in AA and found out that cross-linking with Mn^{2+}, Zn^{2+}, and Ca^{2+} had resulted in enhanced tensile strength and light transmission, and these effects can be made used in making agricultural mulching films. The pore size ranging from 5 to 200 nm, makes it a good choice for oral delivery. Olivas and Barbosa[16] had studied the behavior of AA films towards water vapor content and had reported that they show better barrier properties to water vapor on treatment with $CaCl_2$. According to Zaman *et al.* [17], photocuring of sodium alginate with vinyltriethoxysilanewas reported improving tensile properties. Cheong and Zhitomirsky[18] had

reported the development of alginic acid film composites via electrodeposition with hydroxyapatite, TiO_2, and chitosan. The composites showed excellent biocompatibility and bioactivity. Alginic acid fibers have been developed with high sorption properties with potential for textile industries. The hydrophilic nature of alginic acid has an effect on sorption capacity. In the work of Kazem *et al.* [19], it was observed that the hydrophobic nature of the alginate had been improved by the incorporation of octadecyl groups to the backbone of the native alginate. Oregano essential oil incorporated alginate films fabricated by Benavides *et al.* [8] showed enhanced film strength with significant antibacterial activity. According to Bandeira *et al.* [20], alginates, when combined with clay particles, showed high adsorption capacity for heavy metals and dyes molecules. The study reports of Pandi and Viswanathan [21] states that the metal coordination enabled carboxylatedalginic acid shows excellent ability in fluoride removal. Aligned graphene oxide sheets in the alginate matrix were reported by Vilcinskas*et al.* [22] to have the ability to be employed as gas barrier coatings.

AA/poly(1-vinylimidazole) composites, developed by Kartal*et al.* [23], showed excellent temperature resistance with reasonable operational stability. These composites showed capability for immobilizing tyrosinase. The composites developed by Aranda and Darder[24] in which zein and alginate have been combined to form a new matrix that has the potential to encapsulate drugs. In semi dilute solution, intermolecular hydrophobic interactions of long alkyl chains result in the development of physical hydrogels, which can then be reinforced by the addition of calcium chloride. Further, it was inferred that the combination of calcium bridges and intermolecular hydrophobic interaction results in improved gel strength with better stability. Alginate/pectin matrices synthesized by Islan *et al.* [25] via ionotropic gelation using calcium as crosslinker containing ciprofloxacin showed a fast antibiotic release associated with the matrix disaggregation. The composite comprised of alginate, 2-acrylamido-2-methylpropanoesulfonic acid, and montmorillonite was fabricated by Yadav and Rhee[26] through graft polymerization, and the resultant showed super absorbent nature. Alginate coated chitosan nanoparticles have been developed as a delivery carrier for an oral DNA vaccine by Z Liu *et al.* [27]. In another work, Chae *et al.* [28] had synthesized hydroxyapatite/alginate nanocomposites fibrous scaffolds that suites bone tissue regeneration. As per the reports of Sand *et al.* [29], the graft copolymer of N-vinylformamide with alginic acid synthesized by free radical polymerization showed flocculation property. Kavas *et al.* [30] observed that the iron oxide nanoparticles coated with alginic acid/polyvinylimidizole showed the potential to use as electrostatic materials and electromagnetic shielding materials.

3.1. Applications of AA based materials.

AA is one of the extensively researched biopolymers for the separation of metal ions from aqueous media due to its biodegradability, immunogenicity, and capability to form gels with numerous cross-linking agents[31]. Water-insoluble, heat-stable strong gels formed upon gelation of AA with divalent cations can be used in the food industry, drug delivery system biotechnology, and pharmacy. They can excel over the conventional synthetic polymers due to their ability to form strong gels in aqueous media, and they are non-toxic, with low cost-free availability and good biodegradability characteristics. According to Barbetta*et al.* [32], AA based materials are also used as adsorbents for the removal of heavy metals and organic impurities from the polluted system. Due to its nontoxicity, unique tissue compatibility, and biodegradability, AA has been investigated widely in tissue engineering, including the regeneration of skin, cartilage, bone, liver, and cardiac tissue. Sreekumar *et al.*[33] had developed PLA/AA/ MoS_2 thin films, which, has the potential to be used as packaging materials. Bayer *et al.* [13], had observed that AA and its composites are also used for macromolecular imprinting. Zaman and Beg [17] had discussed various applications of AA, and it was found that AA has been explored to fabricate biodegradable or edible films because of its unique colloidal behavior, such as thickening, stabilizing, suspending, film-forming, gel producing, and emulsion stabilizing properties.

4. Conclusions

Biopolymers are presumed to bring revolutions in different industries owing to their nature-friendly properties. One of the major advantages of biopolymers is that they

can easily be disposed of as they possess biodegradation property and are compatible with the environment. Alginic acid is a much-anticipated biopolymer with unique physiochemical properties and adaptable biological activities that pioneer among the biomaterials that are being researched for different fields of applications like biomedical and pharmaceutical applications. The blends and composites based on alginic acid had gained wide attention to find applications in different fields with enhanced properties. These composites and blend of alginates indeed would sustain the industries both economically and ecologically.

Funding

This research received no external funding.

Acknowledgments

The authors declare no acknowledgments.

Conflicts of Interest

The authors declare no conflict of interest.

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