Sri Lankan Journal of Applied Sciences Vol.1.1 (2022) 18-30

Biopolymers: Structure, properties, extraction methods and applications

Attanayake N.A.B. [a], Chandrasiri M.T.M.S. [a], Asela A.U. [a], Pitawala H.M.J.C. [a], Senevirathna M.A.S.R. [a, *]
[a], Department of Science and Technology, Uva Wellassa University, Passara Road, Badulla, Sri Lanka, 90000

*** Corresponding author email address**: sandhya.senevirathna@gmail.com

(Received 28th April 2022; accepted 10th August 2022)

Abstract

Polymers are natural or synthetic macromolecules with repeating units. Biopolymers are polymeric materials derived from living organisms. The use of these biopolymers has grown significantly in recent years due to their renewability, abundance, biodegradability, low immunogenicity and other unique properties. This review article is focused on several types of biopolymers such as polysaccharides; cellulose, starch, proteins; collagen, silk, and agar. It will discuss the importance of these polymers, their physical and chemical properties, extraction methods and finally applications of those polymers.

Keywords: Biopolymers, Cellulose, Chitin, Agar, Starch, Collagen, Silk,

1. Introduction

The term polymer is derived from the ancient Greek word “Polus” which means many and “meros” which means parts. Polymers are macromolecules composed of repeating units. Monomers have the ability to react with another molecule of the same type or different type at suitable conditions to form a polymer chain [1]. Their large molecular weights lead to unique physical and mechanical properties including rigidity, viscosity, and the tendency to form glass and semi crystalline structures rather than crystals. Polymers can be considered as important components of highly functional materials in the fields of chemical, electronic, optical, pharmaceutical and medical industries.

Bio polymers is a sub category of polymers which are defined as polymers derived from biological origin. Most of the biopolymers are bio-degradable with the action of micro-organisms, heat or moisture. Therefore, industries tend to move towards biopolymers to avoid the environmental issues comes from conventional synthetic non-degradable polymers.

The main objective of this review is to discuss about structure, properties, extraction methods and applications of biopolymers.

2. Discussion

2.1 Biopolymers

According to the definitions biopolymers are derived from biological origin. Biopolymers can be simply extracted as natural polymers produced in biological systems or chemically synthesised from biological raw materials. Natural polymers are produced by living organisms in nature such as trees, plants, animals, and microorganisms etc. [2]. They are produced within the natural cells by complex metabolic processes [3]. The monomeric units of natural biopolymers are covalently bonded to form the corresponding polymer. Those materials can be degraded by the action of microbial enzymes. [3]. Biopolymers are considered as the most promising materials due to their competitive mechanical properties and biodegradability [4].

There are some major reasons which encourage the use of biopolymers. Industries focusing on biopolymers due to some drawbacks of synthetic polymers including use of non-renewable fossil resources and greenhouse gas emissions during the synthesis, environmental pollution due to non-degradability, and human health impacts [5]. Biopolymers are sustainable since they are composed from living materials [6]. They are carbon neutral and their sources are renewable. Biopolymers can decrease the carbon dioxide levels and carbon emission in the atmosphere. Even though bio-degradation of biopolymers can release carbon dioxide, it will be reabsorbed by the crops grown to use as the source of biopolymer [7]. After the use of particular application, they can be discarded to the environment because they are compostable. Therefore, chances of polluting environment from these compounds are less. These biopolymers reduce the dependency on non-renewable fossil fuels and it will limit the use of fossil fuels [6].

Biopolymers can be used vastly for tissue engineering, medical devices and the pharmaceutical industry, drug delivery, and overall medical applications due to their physio-mechanical properties. Further, they have specific characteristics like wound healing, catalysis of bio-activity, and non-toxicity. Compared to synthetic polymers, many biopolymers are normally better with bodily integration as they also possess more complex structures.

Due to the biodegradable and biocompatible nature, biopolymers can be used to enhance the activity of other biologically active molecules in a product and also can be modified to fit with different potential applications such as bio-based food-packaging applications, food coatings, encapsulation matrices for functional foods, applications in water treatment, biosensor productions and manufacturing storage elements [8]. Further polysaccharide-based materials have been developed in a variety of forms, including films, membranes, fibres, hydrogels, food casing, sponges, and air gels [9].

Synthetic polymers show some unfavourable conditions to both human and the environment. They have various disadvantages like immunogenic rejection and toxicity after degradation. The stability and nondegradable behaviour results in deterioration of the environmental quality due to the synthetic polymer and it has been affected to solid wastes treatment plants [10].

Polynucleotides, polypeptides and polysaccharides are considered as three major categories of natural bio polymers produce by living cells [2]. Polynucleotides such as DNA and RNA, polypeptides including protein, and polysaccharides such as starch, cellulose, glycogen, and chitin play a major role in the ecosphere. They can be extracted and modified for potential applications. Among these biopolymers, cellulose is the most common. It is the most abundant organic compound on this planet. It consists of around 33% of all plant components on Earth.

2.2 Cellulose and its derivatives

Structure and properties of cellulose

Cellulose is the most important structural component of the cell walls of plants and it can be defined as central component in the plant cell walls. Cellulose presents in a wide variety of other living species such as algae, fungi, bacteria, and in some sea animals such as tunicates also [11]. Tunicates are the only known animals which have the ability of biosynthesizing cellulose.

From the current point of view, cellulose is the most common organic polymer, representing about $1.5 * 10^{12}$ tons of the total annual biomass production, and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products. The structure of cellulose is an unbranched, natural polymer composed of repeating glucose units $(C_6H_{10}O_5)_n$ linked together by $\beta\ (1 \rightarrow 4)$ glycosidic bonds [12,13]. It is considered as the most profuse organic material and polysaccharide on Earth.

The hydroxyl groups which are on the glucose molecules form hydrogen bonds with oxygen atoms of another cellulose molecule and it holds the chains in place and hence giving high tensile strength to the fibres. Due to that reason unlike starch or glycogen, these cellulose chains do not undergo any coiling or helix formation or branching. Instead of that, these chains are arranged parallel to each other. This results in the formation of stable and strong cellulose microfibrils. The cellulose microfibrils are extremely tough and inflexible due to the presence of hydrogen bonds. In plant cell walls, multiple chains have bonded together to form microfibrils.

Cellulose nanofibers are a type of flexible, elongated, cross-linked nanocellulose that can be extracted from cellulose fibres by using mechanical treatment. It is also known as nano fibrillated cellulose [14].

Cellulose is insoluble in water and in most organic solvents. It is a chiral and biodegradable polymer with a rigid linear structure. Cellulose is a semi-crystalline material which is consisting of four types of allomorphs of cellulose such as I, II, III, and IV [15]. The main sources of cellulose are bio-waste and residues from various foods. There are some useful derivatives which can be obtained from cellulose.

Extraction of cellulose

There are several ways to extract cellulose from plants. Cellulose can be extracted from plant fibres after several steps such as alkalization, bleaching, and acid hydrolysis processes [16].

Cellulose has been extracted from Areca empty fruits by Ranganagowda et al. [16]. Washed and dried fibres were dewaxed with ethyl alcohol followed by delignification and bleaching to collect the cellulose [16].

Cellulose has also been extracted from rice husks [17]. As the first step, alkali treatment with NaOH is performed to purify cellulose by removing lignin and hemicellulose from rice husk fibres. After the alkali treatment, the bleaching process is done by refluxing with a buffer solution of acetic acid, aqueous chlorite (1.7 wt%) and distilled water. Bleached sample is then acid hydrolysed with sulphuric acid. [17].

Applications of cellulose

Cellulose and its derivatives are widely used in biomedical applications, food packaging industry, textile industry, paper production etc. [18]. They are extensively used in such applications because cellulose has attractive properties such as biocompatibility, mechanical strength, low production cost, abundance, sustainable resources, nontoxicity, chemical and morphological controllability [19].

In biomedical applications cellulose nano fibrils have been used in hydrogel preparation for several applications, such as wound dressing, tissue engineering scaffolding and drug delivery [20]. For biomedical applications, it is essential to assess the biological compatibility of substances and to verify their interactions with cells, especially if the fluid is to be in contact with living tissue and not to have any cytotoxic or other side effects. For tissue engineering, cellulose acts as an additive or as a primary scaffold material and that should have mechanical properties matching real tissues and promote porous structures for scaffolds. There are several cellulose derivatives used in tissue engineering. The most commonly used ones are the cellulose acetate, hydroxypropyl cellulose, cellulose sulphate, carboxymethyl cellulose and methyl cellulose [21].

The use of cellulosic materials as reinforcement in bio composites is a new trend due to their ability to enhance properties. For example, cellulosic fibres have recently been demonstrated to enhance the formidability of bio composite scaffolds due to unique structure in bone tissue engineering applications [15]. In addition, the micro-fibrillar cellulose surface area is significantly increased and its interfibrillar hydrogen bonds facilitate network building.

Conventional cellulose and its derivatives such as cellulose ether, cellulose ester and oxycellulose are widely used in various drug delivery systems. Cellulose ethers are used as important excipients in the pharmaceutical industry when designing matrix tablets [22]. Cellulose esters are another derivative of cellulose and it is widely used in the preparation of closed tablets with microporous membranes for continuous drug delivery [19]. Cellulose esters are non-toxic and do not cause gastrointestinal absorption. They also benefit from extensive evidence that the human stomach lacks the cellulose enzymes that cause abnormal stability in body use [23]. Oxycellulose can be used as a release modifying agent, enter sorbent, carrier, and/or a mucoadhesive polymer for the drug tablet to support haemostasis and tissue healing in modern drug delivery systems [24].

In the food packaging industry, cellulose has become one of the most abundant and extensively used polymers due to their unique characteristics, structure, and properties. Among countless applications, food packaging is the most attractive application of biopolymers and packaging plays an essential role in the food supply chain [25]. Cellulose and its derivatives are biodegradable, edible and they can be used to supplementation of the nutritional value of foods. It is also remarkable for its sensory and organoleptic properties, such as colour, appearance, aroma, flavour, and its taste [26]. Cellulose is considered as an inexpensive, non-toxic and lightweight material and it has a remarkable strength-to-weight ratio compelling to be used extensively in the packaging industry [27]. It is used for formation of multilayer packaging material along with other non-edible polymer films. Due to some unique characteristics of cellulose, they are affordable, cost effective, and fulfil the criteria for acceptable packaging materials. They allow slow release of bioactive compounds, provide selective gas barrier, water vapor barrier, regulate the ripening process, and extend shelf life by creating a modified atmosphere with respect to internal gas composition. Moreover, they are considered as a vehicle for incorporation of numerous food additives; thus, they help to prevent and reduce microbial spoilage during long-term storage of various foods. These are the main advantages of cellulose in food industry [26]. It helps to reduce the use of synthetic packaging material and volume of non-degradable waste.

One of the main functions of cellulose is to use them as carriers for antimicrobial agents and antioxidants, which are used for micro-capsulation and slow release of active compounds in the matrix [28].

2.3 Chitin / chitosan

Structure and properties of chitin

After cellulose, chitin is the most abundant polysaccharide which forms strong fibres. It is found in crustacean shells or in cell walls of fungi [29]. This molecule can perform as solid structures on its own as in insect wings, or they can combine with other components like calcium carbonate to make even stronger substances like the shell of a clam.

Chitin is a modified carbohydrate which contain nitrogen. It is made up with a linear polymer of N-acetyl-D-glucosamine monomers ($C_8H_{13}O_5N$) and those monomers are linked randomly to each other by β (1→4) glycosidic bond. This enables more opportunities of hydrogen bonding between polymers in chitin, and thereby renders increased structural strength. Removal of the acetyl $COCH_3$ groups from chitin results in the formation of chitosan, which unlike chitin, is soluble in water [30].

Chitin differs from cellulose because of the substitution that occurs on the glucose molecule. This will produce a dipole in the molecule, which can increase the hydrogen bonds that can form between these molecules and the molecules around them. When various compounds and other chitin molecules are combined in a matrix, the resulting structure can be very hard because of these interactions between nearby molecules.

Chitin is considered as a fibrous strengthening element in biological composite materials. Thus, it is nearly always associated with proteins and act as the matrix for enforcing reactions such as phenolic tanning in the exoskeleton of insects and mineralization in the shell of crustacea, some flies, and nacre [31].

Chitin is insoluble in aqueous solutions but chitosan is soluble in acidic conditions. Due to their natural origin, both chitin and chitosan cannot be defined as a unique chemical structure but as a family of biopolymers that exhibit high variability in their chemical and physical properties [30]. The waste generated from processing of shell-fish and fish scales around the worldwide production is a serious matter of growing magnitude. The easy deterioration of this abundant waste can lead to environmental hazards. The use of this waste for renewable products such as chitin as a biopolymer is a dual-purpose opportunity [32].

Extraction of chitin

Chitin exists within numerous taxonomic groups. Usually, commercial chitins are isolated from marine crustaceans, mainly because a large amount of waste is available as a by-product of food processing such as crab, shrimp, and krill shells as well as fish scales [30]. Annually around 1011 tons of chitin are produced in the aquatic biosphere alone [33]. Commonly, selected crustacean shell consists of 30-40% protein, 30-50% calcium carbonate and calcium phosphate, and 20-30 % chitin and also contain pigments of lipidic nature such as carotenoids [29].

Chitin can be extracted from fish scales and basically there are three main steps in chitin production. One is demineralization which includes removal of calcium carbonate ($CaCO_3$) and calcium phosphate ($Ca_3(PO_4)_2$). Demineralization is generally carried out by acid treatment using hydrochloric acid (HCl), nitric acid (HNO_3), sulphuric acid (H_2SO_4) and acetic acid (CH_3COOH). Among these acids, the most common reagent is dilute hydrochloric acid. Demineralization is easily achieved through the decomposition of calcium carbonate into the water-soluble calcium salts with the release of carbon dioxide. The second step is the deproteinization. It is the separation of protein and the last step is decolorization and deacetylation which is including removal of pigments and removal of acetyl groups respectively [29]. Both deproteinization and demineralization processes could be carried out using chemical or enzymatic treatments.

However, because chitin is a biodegradable molecule that dissolves over time, it is used in a number of industrial applications, such as surgical thread and binders for dyes and glues.

Applications of chitin and chitosan

As mentioned earlier, chitin is the most abundant biopolymer after cellulose. There is a wide range of applications due to their biocompatibility, biodegradation, scavenging of heavy metals and of cholesterol or other fats, antimicrobial and antioxidative behaviours. [34]. Chitin and chitosan are extensively used in biomedical applications such as tissue engineering, drug and gene delivery, wound healing, and stem cell technology [35]. Chitin, together with its variant with chitosan, has been shown to be useful as a wound dressing material, drug delivery vehicle and increasingly a candidate for tissue engineering. Chitin-based materials can be successfully applied in tissue engineering of nerves and blood vessels as a template for cells. Chitin-based scaffolding is a multi-purpose product that can be optimized for many renewable purposes. These biomaterials require of being prepared in porous forms and the porosity should be high to offer a channel for the migration of host cells into the matrix permitting growth into complete tissue analogues and be non-toxic to cells products once they have served their function in vivo [36].

Drug delivery has become a very active area, especially chitosan is used as a carrier for various active agents including drugs and biologics. When delivering drugs, selecting the perfect chitosan type with specific characteristics is beneficial in developing sustainable drug delivery systems, prolonging the duration of drug action, increasing therapeutic efficacy, and minimizing side effects [30].

Another major application of chitin and chitosan is wound healing. This application combines most outstanding properties of chitosan like antimicrobial behaviour and biocompatibility. N-acetylglucosamine, the monomeric unit of chitin, takes place in the extracellular macromolecule hyaluronic acid, which is important in wound repair. Therefore, chitin should have beneficial properties to promote faster skin regeneration and faster wound healing, suitable for applications ranging from simple wound masks to modern artificial skin models.

Similarly, chitin and chitosan have new potential applications in hair care. With an organic diacid anhydride, chitin and acylated chitosan can be used for skin care. As well as chitosan can be used in shampoos, hair colorants, styling lotions, hair sprays and hair tonics [37]. Chitin and chitosan have been found to be used in creams as moisturizers, nail enamel foundations, eye shadows and lipsticks, cleansers and baths [38]. Another application of chitin is, it is used as dental filler also. These are the cosmetic field applications of chitin and chitosan.

Chitosan provides a wide range of unique applications in the food industry including preservation of foods from microbial deterioration, formation of biodegradable films, and recovery of material from food processing discards [30]. Furthermore, they can act as a dietary fibre and as a functional food ingredient. Biofilms which made from chitosan can tolerate the long exposure capacity to food.

Chitosan act as an elicitor, in fact, several plants possess chitinolytic enzymes that help them to protect themselves against pathogen aggressors, such as fungi. The introduction of chitosan into the growth medium stimulates the production of chitinolytic enzymes in plants, making them more resistant to their natural aggressors [39].

2.4 Agar

Structure and properties of agar

Agar is an important biopolymer which is used in different commercial industries. Agar is a combination of a linear polysaccharide called as agarose and a heterogeneous mixture of smaller molecules called as agaropectin. The gelling agent in this agar is agarose which is considered as the main component in the agar mixture [40]. Agarose is a linear and neutral polymer which has the molar mass of about 120000. Agarose composed with agarobiose repeating disaccharide units with alternating 1,3-linked-b-D-galactopyranose and 1,4-linked-3,6-anhydro-a-L-galactopyranose [41]. Agarose is usually extracted from some seaweed species. Seaweeds can categorize into three main groups. Green algae (Chlorophyta), Brown algae (Phaeophyta) and the Red algae (Rhodophyta) [41]. Among them red algae are commonly used for this. The most commercially important polysaccharides obtain from red algae are Carrageenan and Agar. Agar was discovered in 1658 by Mino Tarozaemon in Japan. Earlier agar was used as foods like desserts, seaweed soup, ice creams etc. Then the beginning of 19th century agar began to use for solid medium for growing various microbes. In 1882 agar was first used in microbiology by German microbiologist Walther Hess [42]. From the mid-1970s the production of agar had started to increase dramatically to approximately 10 000 tons annually. Since the agar production increased the seaweed population is over utilized [42].

Extraction of Agar

Gracilaria is the most usual resource of agar production among the other agrophytes. The extraction process has been explained by Jhurry and co-workers. According to them, as pre-treatment to seaweeds when extracting the agarose, they are washed properly with fresh water and cleaned seaweeds are dried in sunlight followed by drying in an oven at 800 °C to destroy microorganisms. Then seaweed sample has treated with NaOH (10–30%) for one hour at varying temperatures of about 70–100 °C. The treated seaweeds have collected by using the nylon mesh and washed thoroughly till neutral [41]. Those seaweeds boiled in water at 100 °C for 1-4 hours. The hot liquor has to be filtered through the nylon mesh and allowed to settle as a gel at room temperature. The formed gel has been frozen overnight and melting agar separates as a fibrous material suspends in water solution [41]. The extracted samples can be analysed using the methods such as FT-IR spectroscopic analysis, NMR characterization, SEM analysis, Elemental analysis, Viscometrical analysis, etc.

Applications of agar

Agar is used often in food packaging industry. By producing continuous and transparent film from agar gum it can use as a renewable alternative material for the plastic-based food packaging. But the pure agar film cannot use directly, because of it suffers from brittleness, high moisture permeability and poor thermal stability [43]. Many researchers have tried to improve the properties of agar films through the reinforcements of nanomaterials, blending with different types of biopolymers, incorporation of plasticizers, hydrophobic components, antimicrobial agents into their structures etc. De lacey and Lopez-Caballero have produced an agar based bioactive film containing probiotic strains, green tea extract and applied on hake fillets [44]. Using these films, the count of beneficial lactic acid bacteria has increased in fish and the shelf life of hake fillets have extended from one week [44]. Agar films containing grape fruit seeds and silver nanoparticles have used as a packing material to extend the shelf life of fresh potatoes [45]. Those films showed strong antimicrobial activities and prevented from condensed water formation, greening potatoes [45]. Vejdan and Ojagh have studied about the effects of gelatine/agar bilayer films containing TiO_2 nanoparticles on oxidative stability of fish oil. When increasing the TiO_2 concentration, fish oil photo oxidation was hindered [46]. Agar is used to pack fresh spinach as blend films containing Closite 30B. The films capable of high moisture adsorption capacity suggested to be utilized as an antifogging packaging material for higher respiring agricultural products [47]. Jang and Lim were used agar/gelatine blended film containing Cloister and thymol as chicken breast packaging. The shelf life of the product was extended by using this film via reducing microbial growth during the storage [48]. Jungyeon Jang has done a review on applications of natural biopolymers on geotechnical engineering and their strengthening mechanism using common biopolymers agar, xanthan gum, gellant gum, polyacrylamide and guar gum [49]. Surface compaction, drainage methods, vibration methods, pre-compression and consolidation, grouting and injection, chemical addition, soil reinforcements are the common soil improvement techniques using in industry. With those techniques, causing many harmful effects to the environment like changing soil pH, CO_2 emission etc. When agar gel forms, it gives rigid textures and it has been used as a stabilizer for soil [50]. When considering serious environmental issues with using the plastic-based materials, productions of biodegradable materials like agar from renewable natural sources are very much healthy for the environment.

2.5 Starch

Structure and properties of starch

Starch is a carbohydrate which stored in various locations in plants such as in cereal grains, roots, tubers, stem – piths, leaves, seeds, fruits, pollen etc. Starch is occurring as discrete granules. The botanical source decides the size and shape [51]. Starch is semi-crystalline, water insoluble, and dense in granule form. Since starch hydrates only to small degree, a large amount of carbohydrate can store in a small volume. Glucose is the main building block of starch and it commonly containing 2 parts; a linear fraction amylose and the branched counterpart, amylopectin. There are many sources that collecting starch for industrial uses. Potato, wheat, Maize, Waxy maize are those sources [52]. Potato starch is the only commercial starch that containing appreciable amount of covalently bonded phosphate monoester groups can calculated as phosphorus.

Extraction of starch

Starch can be extracted by using various methods in commercial industries. Conditions which can increase the production of starch have analysed and reported in literature.

Farming and agricultural processing generate million tons of wastes annually which are containing various amounts of polymeric components like starch, lignin, sugar, cellulose, hemicellulose etc. Starch composition is varying from one plant species to the other. Extracting starch from plantain peel is one way to add a value to a waste [53].

There are two main methods, dry extraction and wet extraction use to extract starch from plants according to the research paper [53]. In one research, green plantain peels have used as raw material and wet extraction method has selected. Plantain peels were washed in order to remove the impurities. Then peels were disinfected after 25 minutes in the 1% (v/v) Sodium hypochlorite (NaClO) solution. To avoid the effects of starch degradation because of the actions of endogenous enzymes, the peels were then sliced into 4 mm pieces prior to immersion in antioxidant solution [54]. Immersion times of the test were 5, 15, 30, and 60 minutes and the antioxidant solution varied between 1, 2, 3, and 5% (w/v). The material was mashed with a grinder to get a paste. The paste was filtered and washed in 4-5 times [54]. The paste was kept for decanting about 24 hours in the glass separating funnels. To reduce the water percentage, the vacuum filtration was applied. Finally, the filtered material was dried about 10 hours at 40 ºC and sieved [55]. At the end the mass of starch yield varied from 3.25 to 9.49 g from a 150 g wet plantain peel samples. This extraction of starch from plantain peel wastes has contributed for waste recycling within agricultural activities and the food processing industries while producing value added products in paper, textile, pharmaceutical, adhesives, food, water treatment, and biopolymer industries [54].

Applications of starch

These natural polymeric materials can use in environmentally friendly industrial applications after some modifications [56]. Most of the time starch has to modify to increase its good properties by physically or chemically to use in practical applications. The modification can be described as altering the structure and affecting the hydrogen bonding in a controllable way to increase the starch applications [57]. Physical modification and chemical modification are the two starch modification methods. In general, physical modification is done by annealing, heat moisture treatment, and dry heating of the starch. While the chemical modification is done by acid hydrolysing, oxidizing, etc [58]. Starch can be used in the paper, textile, pharmaceutical, adhesives, food, water treatment, and polymer industries.

Use of starch biopolymer as an alternative to synthetic plastic materials has been tested for several times. Researchers have developed thermoplastic applications based on starch. Thermoplastic starch has produced with native starch using a swelling or a plastifying agent with the dry starch in compound extruders without adding water [59]. Bioplastics developed from starch can be disposed in an environmentally sound and inexpensive manner within the natural cycle without doing any harm or disturbances to the environment. These bio plastics are fully biodegradable at the end of their life [60]. Starch also showing some interesting optical properties too. Starch can be fabricated as a form of anisotropic transparent gels as well as possible to fabricate starch-based nanostructures as granules [59].

Formation of Ag nanoparticles during gel assisted laser ablation can take as starch assisting in formation of nanoparticles [61]. As in previous research articles, in biological matters-based systems like dye-dope biopolymeric matrices can observed the random lasing [61]. In the article “Starch: Application of biopolymer in random lasing” proved that starch-based systems can observe improvement of photostability with respect to DNA based materials due to low oxygen permeability [61]. The starch biopolymeric matrix has been prepared from starch doped with Rhodamine 6G laser dye. In the methodology, the generation of lasing action happened due to formation of higher spontaneous roughness. Starch shows higher stimulated laser emission stability than the DNA based systems. Because of the experimental results starch consider as a fully functional material in photonics applications and simultaneously using to make biological photonic devices [62]. So as mentioned in these research papers above, starch can applicable in various industries by with or without modifications, instead of using harmful and non-biodegradable synthetic materials.

2.6 Collagen

Structure and properties of collagen

Collagen is the most abundant protein in the human and animal tissues and it is containing 25% of the total protein content of the body. As a biopolymer collagen is one of the long fibrous structural proteins whose activity differs from that of global proteins such as enzymes. It is a naturally occurring matrix polymer and a type of biological macromolecule which forms a highly organized, three-dimensional architecture [63]. Collagen is the scaffold material that provides an optimal environment for physiologically highly active cells and cellular components in tissues. That means collagen forms a scaffold to provide strength and structure. Due to the high tensile strength of collagen, it has become the main component of cartilage, ligaments, tendons, bones and teeth. Collagen plays a versatile role due to its great properties such as biodegradability, biocompatibility and easy availability. Therefore, it is considered as a biomaterial because of its wide applicability in various fields

Collagen has the ability to form cross-linked solids or lattice-like gels. Therefore, it can carry any component due to the network-like structural nature. Collagen is the major extra-cellular component of most connective tissues in the body. Collagen is a trimeric molecule which means it is composed of three chains and consisting of three polypeptide α-chains. The three-helical domain structure of collagen consists of three different α-chains, which give collagen the name "tropocollagen". Each of these chains contains a sequence of polymer L-handed amino acids, often referred to as polypropylene type II helix [64]. Glycine residue is required at every third of the polypeptide chain to bend each of these chains properly. For example, each α-chain consists of a triple sequence of Gly-Y-Z where Y and Z can be any amino acid. Y is commonly found as proline and Z as hydroxyproline. The presence of hydroxyproline at site Y also contributes to the stability of the helical form. These repeating units allow the formation of a triple helix which is the characteristic structural feature of the collagen superfamily. Each member of the collagen family contains at least one triple-helix domain, which is secreted and deposited in the extracellular matrix.

Extraction of collagen

Collagen can be extracted from various types of animal species and usually, it is derived from animal skin, tendon, cartilage, and bone. The main sources of collagen are the bones and skin of bovine animals such as cows, ox, buffalo, and cattle. Recently some researchers are investigating different approaches to collagen extraction from different animal sources, such as fish and birds [65]. There are a few different methods of collagen extraction such as enzymatic extraction, acid extraction, etc. Collagen extraction primarily involves the removal of covalent intra- and inter-molecular cross-links, including the contaminants of lysine and hydroxy-lysine, ester bonds, and other bonds with saccharides.

The process of collagen extraction consists of mainly two steps. The first step is the removal of non-collagen proteins and other impurities such as lipids, calcium etc in order to increase the purity of the extracted collagen [66]. That is called as pre-treatment and it is performed using an acid or alkaline process, which varies according to the origin of the raw material. Before pre-treatment different raw materials from the products should be divided into different categories such as skin, bone, swimming bladder and scales. This helps in easy cleaning, removal of contaminants and reduction in volume. The second step is the acidic extraction.

Applications of collagen

Collagen has many applications in various fields and it is a common compound of many pharmaceutical, biomedical and cosmetic industries. Collagen is major product of cosmetics that is widely used as moisturizing and softening agents for the treatment of dry skin and maintenance of normal skin. It is mostly used in cosmetic field due to its high biocompatibility. Many collagen products, including creams and powders, claim to revitalize the skin by increasing collagen levels in the body. Collagen represents one of the key constituents of cosmetic compounds because of its moisturizing, regenerating and film-forming properties. Excellent water binding ability helps maintain proper water content in the skin during the day [67].

Collagen is a resorbable biopolymer which means it can be broken down then converted, and absorbed back into the body. As mentioned earlier collagen can also be formed into compacted solids or lattice-like gels. Therefore, it is clinically versatile and suitable for various medical applications such as skin fillers. wound dressing, tissue regeneration, vascular prothesis, cardiac applications, cosmetic surgeries, bone grafts, drug delivery, eye implants etc.

As a biopolymer collagen has the biodegradability and cross-linking property which improves the dissolving capacity of shield when placed under the eye for a maximum period of 72 hrs. In addition, it expands its biomedical utility as a drug delivery vehicle and as a safe and lubricating agent. When the collagen shield is placed under the retina, the retina is epithelialized and this property is especially useful for eye surgery. It also serves as a valuable therapeutic tool as it delivers drugs such as antivirals, anti-fungal and immunosuppressive agents [63].

Collagen membranes are used for periodic and replacement therapies to promote the growth of specific types of cells. During oral surgery, collagen barriers can prevent the rapidly growing cells around the gums from migrating to the tooth lesion. This protects the space where the tooth cells have a chance to regenerate. Collagen-based membranes help to heal in these cases and they do not need to be surgically removed after the main operation as they can be repaired.

Collagen is also useful for wound healing and burning wounds in the form of powder or collagen membranes and scaffolding. And also, there are many applications in the field of dermatology like augmentation of soft tissues, skin replacement, skin tissue engineering and artificial skin dermis, in cardiology for replacement of heart valves, in surgery for wound repairing and dressing, in orthopaedic for repair of tendon, ligament and bone, in ophthalmology for cornea grafting and contact lenses grafting and in vascular system for vessels replacement and grafting [68].

2.7 Silk

Structure and properties of silk

Silk is a naturally generated protein fibre biopolymer. Mainly silk is producing by Silk worm called Bombyx mori. These silks are used in industrial purposes. As an industry, breeding silkworms for raw silk production has started in China about 5000 years ago, which spread to India, Korea, Nepal, Japan, Russia and western countries also [69]. There are some other manufactures of silk in living world. Caterpillars, web spinners, raspy cricketers, hymenopteran, silverfish, mayflies, thrips, leafhoppers, beetles, lacewings, flies are also producing silk in their life cycle but not commonly using in industrial purposes [70]. Silk is smooth and soft material which is not slippery unlike synthetic fibres [71]. Dry silk is a strongest natural fibre but not in wet. Silk is consisting with two major parts; sericin and fibroin. Fibroin is the structural centre while sericin is the sticky material surrounding the fibroin. Silk consists of about 75% of crystalline fibrous protein fibroin and about 25% of an amorphous matrix of a globular protein sericin [72].

Extraction of silk

Silk production is called as Sericulture. The first step of the silk production is cultivating silk worms on mulberry leaves. When worms start up pupating in their cocoons, they are dissolving in boiling water to extract fibres fed into spinning reel. To produce a kilogram of silk, about 104 kg of mulberry leaves should eat by about 3000 silkworms [69]. When considering physical properties of silk, Bombyx mori silk have a triangular cross section with 5-10 μm wide rounded corners. Fibroin-heavy chain is composed with generally beta-sheets due to the 59-mer amino acid repeat sequence with some variations.

Applications of silk

Silk is frequently used in various industries like textiles, furniture, parachutes, tyres, medicine and also in biomaterial industry. Since silk materials having high biocompatibility, silk and silk-based biomaterials have been used for wound closure by surgeons over 3000 years. Previous studies have confirmed that silk does not cause any severe inflammation or bad effects on other tissues in mammalian tissues [73]. And also, silk protein is effective to mammalian cell adhesion and proliferation as a substrate.

With the complete comprehension nature of silk, it is led to the many kinds of biomedical devices like wound dressings, tissue engineering scaffolds, nerve conduits, artificial ligaments etc [73].

Silk fibroin is a fibrous protein which is highly insoluble and produced by silkworms. They can form porous 3D structures such as foams, and sponges of scaffolds which can be used for biomedical applications. When considering the applications of silk fibroin, it is used widely in developing wound dressings because of its wound-healing effects and high biocompatibility. Silk dressing material can be fabricated using various methods and easily controlled the process. Silk fibroin films have good oxygen gas permeability than the other typical wound dressings produced from synthetic polymer films. Generally, lyophilization is used to make a porous structure in silk fibroin sponge dressings that provide gas permeability and exudation absorbability [73]. However, the cost of silk fabrication process is higher than using a synthetic polymer. That reduces the industrial usage of the silk fibroin as a raw material for wound dressings. If there is a way to decrease the fabrication cost of silk fibroin, it will highly be benefited the biomedical industry.

Silk is used in tissue engineering industry as an excellent substrate for mammalian cell cultures [73]. Many scientists have confirmed that silk has excellent cytocompatibility and capable of cell adhesion which make it a good scaffold. Silk is not affecting harmfully unlike other polymers like PLA, PCL, PLGA etc when biodegrading. The salt- leaching silk fibroin scaffolds are highly used in bone regeneration processes [74]. According to previous research reports, the regenerative silk fibroin materials provide cells participating in osteogenesis within a suitable environment [74]. These studies exhibit that the growth factor contained in the silk fibroin scaffold is effective for culturing stem cells and bone regeneration [73]. And the silk is also using as composite biodegradable polymer coatings which made out from silk fibroin for biomedical applications. Those biodegradable silk coatings were grown by performing matrix assisted pulsed laser evaporating on the titanium substrates [75]. They can apply in local tissue regeneration application by studying about physicochemical properties and the degradation behaviours in simulated body fluids at 37 °C.

Silk fibroins are capable in modifying as bioactive agents like drugs, growth factors etc. To test the silk fibroin as the composite biodegradable biopolymer coating, 2 μm granulation powder of degummed Bombyx mori silk fibroin were used as main raw material [75]. Another production of Silk fibroin is aerogels. Aerogel is a synthetic porous ultralight material in which the liquid gel component has been replaced with gas without any changes in gel structure. Aerogel is a solid with extremely low density and thermal conductivity [76].

These aerogels are used for insulation processes, chemical absorbencies, as a catalyst, thickening agent, in sport equipment production etc. Scientist are developing aerogels by improving mechanical properties, expanding their utility in high performance application for competitive industrial usages. Instead of using petroleum-based polymers, scientists and researchers are looking to use biopolymers for aerogel developments. Scientists have also used silk fibroin, extracted from silkworm cocoons with organically substituted alkoxysilanes in a aqueous solution through a sol-gel approach and produce homogeneous interpenetrated polymethylsilsesquioxane hybrid aerogel monoliths with high performances with improved mechanical properties [77]. Silk fibroin aqueous solution was extracted from silkworm cocoons by general extraction process.

First, silk cocoons of 5 g were cut into small pieces and boiled for 30 min in 2000 dm^3 of 0.02M aqueous Na_2CO_3 solution. After that the fibres were thoroughly rinsed with water and dried them overnight. Then the dry silk fibres were dissolved in 12-15 M aqueous LiBr solution at 60 °C for 4 hours and then dialyzed to reduce ultra-pure water for 48 hours. At last, this extracted silk fibroin solution was centrifuged and stored at 4 °C for experimental uses [78]. The composition of silk fibroin and PMSQ was observed with several techniques like EFTEM, EDX elemental mapping and EDX spectroscopy. The results have confirmed the homogeneous and fine dispersion of Silk fibroin in PMSQ at the molecular and nanoscale levels. Maleki et al. have successfully developed a mechanically robust, micro-macro porous, ultralight weight and super hydrophobic and hydrophilic PMSQ-SF hybrid aerogels via a simple, green and one pot strategy with excellent water and oil separation and thermal insulation performances [77]. These multifunctional gels are expected to further extend the practical applications because of their unique performances. They have mentioned that PMSQ – SF hybrid aerogels can be produced also to utilize textile industry's biomass or waste and that would beneficial to environment by mass reduction and greener environment with less carbon [77,78].

When considering about silk sericin it is also used in various industries as a bio product that recovered from the silk waste or effluent of silk industries by many extracting methods. Researchers have observed various great characteristics of sericin like, exemplary moisture absorption and dispensation properties, UV resistance, anticoagulant, antioxidant and anti-bacterial activities etc [72]. Sericin can extract only from the silkworms. Huge amount of sericin is attained from cocoon waste and silk waste in silk processing. Sericin can separate from the silk of silk fibroin with its solubility in hot aqueous solutions.

Among various separation methods, hot-water extraction method is widely used for sericin extraction. Silk is heated in a hot distilled water container, not adding any other chemical. The amount of sericin extracted is depended on time and temperature of the system. Researchers are preferring hot water extraction method because the easiness and it causes the degradation of sericin but degradation is to an extent that sericin retains their valuable characteristics and properties. After the extraction, sericin reformed to powder form [79]. The chemical structure and the molecular weight of sericin is depending on two major facts. First one is the method of separation of sericin and fibroin and the other fact is the method of recovering sericin from degumming liquor. Sericin is used in many industries because of the valuable properties of sericin such as gelling, moisture absorption, antioxidant, anti-bacterial, etc. Sericin is widely used as anti-frosting agents, as biomaterials by blending with resins, as a coating for art pigments to protection purposes, as a raw material in cosmetics industry and food industry.

Researchers also have considered about using sericin to make biofilms by replacing synthetic polymers, and making moisture absorbents as well [72]. According to those published research articles sericin also a valuable biomaterial but still not using efficiently in industries.

Hence, silk can be considered as a biopolymeric source that producing valuable raw materials for various commercial industries as renewable, regenerating and eco-friendly biomaterial.

3. Conclusion

There are a lot of bad effects of using synthetic materials on human health and the global environment such as increased fossil resource use, greenhouse gas emissions, environmental pollution, and human health impacts associated with plastics, etc. Man-made synthetic polymers can be replaced by biopolymers which are produced by cells of living organisms in nature such as trees, plants, animals, microorganisms, etc. Biopolymers reduce most of the environmental issues and the dependency of industries on non-renewable fossil fuels. The specific characteristics, extraction methods, applications were discussed in this review. Cellulose is the most abundant biopolymer in the world. It is derived from many bio-waste and residues from various foods. They are widely used in biomedical applications, food packaging, textile industry paper industry. After cellulose, chitin is the second most abundant polysaccharide made from smaller monomers of structural polymers form fibres. Commercial chitins are isolated from the waste of marine food processing. Chitin-based materials are applied in tissue engineering, wound healing, and hair care applications. Agar is often used in the food packaging industry as a substitution for plastics and polythene. Starch can be extracted from the waste of agricultural and farming processes and starch-based materials are used in biomedical applications, thermoplastics applications, pharmaceutical industry, etc. Collagen is another important biopolymer that has been discussed in this article. It is commonly used in the pharmaceutical, biomedical, and cosmetics industries. Then silk is a natural protein fibre biopolymer which produces valuable raw materials as renewable, regenerating, and eco-friendly biomaterial in many commercial industries. The physical and chemical properties and specific applications of different biopolymers are article and summarized in table 1.

Therefore, biopolymers can effectively replace the synthetic polymers in industrial applications. This will help to reduce a lot of environmental and health issues and subsequently leads to sustainable development in the world.

Table 1

Physical and chemical properties of bio polymers and their applications

Biopolymer	Physical and chemical properties	Applications
Cellulose	Insoluble in water	Food packaging industry
	High tensile strength	Textile industry
	High compressive strength	Paper production
	Low elasticity and resilience	Wound dressing
	Biodegradable	Tissue engineering
		Drug delivery
		As a primary scaffold material

Chitin/chitosan	Insoluble in water Soluble in aqueous acid solutions High viscosity Optical clarity	Tissue engineering Drug and gene delivery Wound healing Stem cell technology Hair care application Cosmetic industry Formation of biodegradable films
Agar	Insoluble in cold water but boiling water Low viscosity in solution High transparency High strength at low concentrations	Food packaging industry Formation of thin films Thickening agent Emulsifier Stabilizer
Starch	Insoluble in water White Order less	Paper industry Textile industry Pharmaceuticals Adhesives Water treatment
Collagen	High tensile strength Excellent biocompatibility and bio degradability Network like structure	Skin fillers Wound dressing Tissue regeneration Vascular prothesis Cardiac applications Cosmetic surgeries Bone grafts Drug delivery Eye implants
Silk	Moderate to poor elasticity Good moisture regaining Insoluble in water Good tensile strength	Tissue engineering Drug delivery Artificial ligaments As composite biodegradable polymer coatings

Conflicts of interest

There are no conflicts to declare.

References

[1] Namazi, H., 2017 Bioimpacts 7(2) 73-74

[2] Lizundia, E., and Kundu, D. 2020 Advanced Functional Materials 31(3) 1-29

[3] Adeyeye, O., Sadiku, E., Reddy, B., Makgatho, G., Ndamase, A., Agboola, O., Daramola, O., Machane, M., Sellemuthu, P., Perumal, A., Nambiar, R., and Fasiku, V., 2019 Green Biopolymers and their Nanocomposites 137 - 158.

[4] Jha, A., and Kumar, A., 2019 Bioprocess and Biosystems Engineering 42 1893-1901

[5] Hottle, T., Bilec, M., and Landis, A., 2017 Resources, Conservation and Recycling 122 295-306

[6] Puglia, D., Pezzolla, D., Gigliotti, G., Luigi, T., Bartucca, M. L., and Buono, D. D., 2021 Sustainability 13(5) 25-50

[7] Martins, J. A,, and Dias, M. S., 2009 Environmental Research Letters4(1) 21-28

[8] Gheorghita, R., Norocel, L. A., Filip, R., Dimian, M., and Covasa, M., 2021 polymers 13(6) 2729-2739

[9] Rebelo, R., Fernandes, M. and Fangueiro, R., 2017 Procedia Engineering 236-243

[10] Azeem, M., Batool, F., Iqbal, N. and Ikram-ul-Haq, 2017 Algae Based polymers,blends and composites 1-31

[11] Taylor, N. G., 2008 New phytologist 178(2) 239-252

[12] French, A. D., 2017 cellulose 24(11) 4605-4609

[13] Buselli1, R. A. F., Otoni, W. C., and Joshi, C. P., 2007 Brazilian Journal of Plant Physiology 19(1) 1–13

[14] Berglund, L., Noël, M., Aitomäki, Öman, Y. T., and Oksman K 2016 Industrial Crops and Products 92 84-92

[15] Seddiqi, H., Oliaei, E., Honarkar, H., Jin, J., Geonzon, L. C., Bacaba, R. G., and Nulend, J. K., 2021 Cellulose 28 1893–1931

[16] Ranganagowda, R. P. G., Kamath, S. S., and Bennehalli, B., 2019 Material Science research India 16(1)

[17] Johar, N., Ahmada, I., and Dufresne, A., 2012 Industrial Crops and Products 37(1) 93-99

[18] Seddiqi, H., Oliaei, E., Honarkar, H., Geonzon, L. C., Bacabac, R. G., Nulend. J. K., and Jin, J., 2021 Cellulose 28(1) 1893-1931

[19] Zhong, C., 2020 Frontiers in Bioengineering and Biotechnology 8(1) 1-19

[20] Moohan, J., Stewart, S. A., Espinosa, E., Rodríguez, A., Larrañeta, E., Donnelly, R. F., and Robles, J. D., 2019 Applied Sciences, 10(1) 1-25

[21] Farzamfar, S., Nosar, M. N., Vaez, A., Ehterami, A., Sahrapeyma, H., Samadian, H., Ghorbani, S., Goodarzi, A., Azimi, A., and Salehi, M., 2017 Cellulose 25(2) 1229-1238

[22] Suna, B., Zhangb, M., Shenc, J., He, Z., Fatehif, P., and Ni, Y., 2019 Current Medicinal Chemistry 26(14) 2485-2501

[23] Shanbhag, A., Barclay, B., Koziara, J., and Shivanand, P., 2006 Cellulose 14(1) 65-71

[24] Kavitha, A. A., Paul, K. T., and Anilkumar, P., 2020 Sustainable Nanocellulose and Nanohydrogels from Natural Sources 367-390

[25] Qasim, U., Osman, A. I., Al-Muhtaseb, A.H., Farrell, C., Al-Abri, M., Ali, M., Vo, D. V. N., Jamil, F., and Rooney, D. W., 2021 Environmental Chemistry Letters 19 613-641

[26] Liu, Y., Ahmed, S., Sameen, D. E., Wang, Y., Lu, R., Dai, J., Li, S., and Qin, W., 2021 Trends in Food Science & Technology 112 532-546

[27] Swain, S. K., and Mohanty, F., 2017 Bionanocomposites for packaging applications 191-208

[28] Becerril, R., Nerín, C., and Silva, F., 2020 Molecules 25(5) 1134

[29] Kumari, S., and Rathb, P. K., 2014 Procedia Materials Science 6 482-489

[30] Aranaz, I., Mengíbar, M., Harris, R., Paños, I., Miralles, B., Acosta, N., Galed, G., and Heras, A., 2009 Current Chemical Biology 3(2) 203-230

[31] Peter, M. G., 1995 Journal of Macromolecular Science 32(4) 629-640

[32] Mejía-Saulés, J. E.,, Waliszewski, K. N., Garcia, M. A., and Cruz-Camarillo, R., 2006 Food Technology and Biotechnology 44(1) 95-100

[33] Zaku, S.G., Emmanuel, S. A., Aguzue, O. C., and Thomas, S. A., 2011 African Journal of Food Science 5(8) 478-483

[34] Kumar, R., 2000 Reactive and Functional Polymers 46(1) 1-27

[35] Kazuo, A., Shinsuke, I., Tomohiro, O., Yoshiharu, O., and Saburo, M., 2014 Journal of Biomedical Nanotechnology 10(10) 2891-2920

[36] Khora, E., and Limb, L. Y., 2003 Biomaterials 24 2339-2349

[37] Rinaudo, M., 2006 Progress in Polymer Science31(7) 603-632

[38] Pokhrel, S., Yadav, P. N., and Adhikari, R. A., 2015 Nepal Journal of Science and Technology 6(1) 99-104

[39] Berezina, N., 2006 Physical Sciences Reviews 1(9) 1-8

[40] Edward, B., Madras: Printed at the Scottish Press, 1857.

[41] Jhurry, D., Bhaw-Luximon, A., Mardamootoo, T., and Ramanjooloo, A., 2006 Macromolecular Symposia 231(2) 16-27

[42] Hesse, W., 1992 Features 58(8) 425-428

[43] Mostafavi, F. S., and Zaeim, D., 2020 International Journal of Biological Macromolecules 159 1165-1176

[44] De Lacey, A. L., Lopez-Caballero, M., and Montero, P., 2014 LWT--Food Science and Technology 5(2) 559-564

[45] Kumar, S., 2019 Heliyon 5(6) 1867

[46] Vejdan, A., Ojah, S. M., and Abdollahi, M., 2017 International journal of food science & technology 52(8) 1862-1868

[47] Rhim, J., and Wang, L., 2013 Carbohydrate polymers 96(1) 71-81

[48] Jang, S. A,, Lim and Song, K. B., 2010 International journal of food science & technology 45(9) 1883-1888

[49] Jang, J., 2020 Advances in Materials Science and Engineering

[50] Prasidhi, A. K., Im, J., Chang I and Cho G 2015 Construction and Building Materials 77 430-438

[51] Smith, A. M., and Martin, C., 1993 Biosynthesis and Manipulation of Plant Products, Springer Netherlands

[52] Lineback, D. R., 1986 Journal of the Japanese Society of Starch Science 33(1) 80-88

[53] Hernandez-Carmona, F,, Morales-Matos, Y., Lambis-Miranda, H., and Pasqualino, J., 2017 Journal of Environmental Chemical Engineering 5(5) 4980-4985

[54] Agama-Acevedo, E., Nuñez-Santiago, M., Álvarez-Ramírez, J., and Bello-Pérez, J., 2015 Carbohydrate Polymers 124 17-24

[55] Rebello, L., Ramos, A. M., Pertuzatti, P. B., Barcia, M. T., Castillo-Muñoz, N., and Hermosin-Gutierrez, I., 2013 Food Research International 55 397-403

[56] Azubuike, C. P., and Okhamafe, A. O., 2012 International Journal of Recycling of Organic Waste in Agriculture 1(1)

[57] Shrestha, A. K., and Halley, P. J., 2014 Starch Polymers 105-143

[58] Wurzburg, O. B., 1995 Food polysaccharides and their applications 67-97

[59] Lorcks, J., 1997 Degradarion and Stability 59 245-249

[60] Mangaraj, S., Yadav, A., Bal, L. M., Dash, S. K., and Mahanthi, N. K., 2018 Journal of Packaging Technology and Research 3 77-96

[61] Cyprych, K., Sznitko, L., and Mysliwiec, J., 2014 Organic Electronics 15(10) 2218-2222

[62] Sznitko, L., Szukalski, A., Cyprych, K., Karpinski, P., Miniewicz, A. and Mysliwiec, J., 2013 Chemical Physics Letters 576 31-34

[63] Muthukumar, T., Sreekumar, G., Sastry, T. P., and Chamundeeswari, M., 2018 Advanced Material Scinece 53 29-39

[64] Shoulders, M. D., and Raines, R. T., 2009 Review of Biochemistry 78(1) 929-958,

[65] Kaewdang, O., Benjakul, S., Kaewmanee, T., and Kishimura, H., 2014 Food Chemistry 155 264-270

[66] Blanco, M., Vázquez, J. A., Pérez-Martín, R. I., and Sotelo, C. G., 2019 Marine Drugs 17(1) 1-13

[67] Sionkowska, A., Adamiak, K., Musiał, K., and Gadomska, M., 2020 Materials 13(19) 1-15

[68] Ahmed, M., Verma, A. K., and Patel, R., 2020 Sustainable Chemistry and Pharmacy 18 1-13

[69] Arunkumar, K. P., Metta, M., and Nagaraju, J., 2006 Molecular Phylogenetics and Evolution 40(2) 419-427

[70] Walker, A., Weisman, S., Church, J., Merritt, D., Mudie, S., and Sutherland, T., 2012 Plos one 7(2)

[71] Lewin, M., 1998 Handbook of Fiber Chemistry

[72] Rangi, A., and Jajpura, L., 2015 Journal of Textile Science & Engineering 5(1)

[73] Ki, C. S., and Park, Y. H., 2009 Macromolecular Research 17(12) 935-942

[74] Kim, H. J., Kim, U. J., Kim, H. S., Li, C., Wada, M., Leisk, G. G., and Kaplan, D. L., 2008 Bone 42 1226

[75] Miroiu, F. M., Stefan, N., Visan, A. I., Nita, C., Luculescu, C. R., Rasoga, O., Socol, M., Zgura, I., Cristescu, R., Cracium, D., and Socol, G., 2015 Applied Surface Science 355 1123-1131

[76] Pajonk, G. M., 1991 Applied Catalysis 72(2) 217-266

[77] Maleki, H., Whitmore, L., and Husing, N., 2018 Journal of Materials Chemistry (26) 18

[78] Daniella, N. R., Preda, R. C., Yucel, T., Wang, X., Lovett, M. L., and Kaplan, D. L., 2011 Nature Protocols 6 1612-1631

[79] Zang, Y. Q., Tao, M. L., Shen, W. D., Zhou, Y. Z., and Ding, Y., 2004 Biomaterials 25 3751-3759