زانكۆی سەلاحەدین - هەولێر
Salahaddin University-Erbil

Biopolymers; applications and properties

Research Project

Submitted to the Department of (Chemistry) in partial fulfillment of the requirements for the degree of **BSc**. in **chemistry**

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CERTIFICATE

This research project has been written under my supervision and has been submitted for the award of the **BSc**. degree in **chemistry** with my approval as a supervisor.

Signature

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DEDICATION

This effort I dedicate to **Allah** Almighty, my lord, my powerful foundation, my source of inspiration, wisdom, knowledge, and understanding throughout this project, he was the source of my energy, also my supervisor M. Darya jaleel who supported me.

ACKNOWLEDGMENTS

To begin, I thank (Allah) for His blessings, which enabled me to successfully complete and carry out this research. May Allah's blessings and peace be upon Muhammad (Allah's peace and prayers be upon him).

Finally, I'd want to express my gratitude to my supervisor, M. Darya, as well as everyone else I failed to include here, who helped me in some way, whether directly or indirectly, by providing even one helpful scientific word.

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Abstract

Biopolymers are polymeric compounds generated from biological sources and known as biopolymers. They've been studied because of their renewability, abundance, biodegradability, and other unique qualities like high adsorption capacities and ease of functionalization. For a variety of industrial uses, including sorption polysaccharides, in particular, Because of their large molecular weight, cellulose, chitin, and chitosan are important biopolymers. There's a lot of it, it's widely distributed, and it's cheap to make. This chapter provides an overview of material characterization, common processing methods, and a review of properties.

1- Introduction

An extensive sort of substances generally derived from organic reassets which include microorganisms, plants, or bushes may be defined the use of the term “biopolymer”. the term polymer has been repeatedly used in several industries for their immense characteristics in different applications. Polymers and their composites which were prepared from chemical monomer sources turned out to be potentially harmful to the environment due to their tedious degradation process. Biopolymers are natural substitutes for synthetic polymers which can be efficiently extricated from natural sources. They are predominantly available as polymeric units as well as monomeric units that are linked covalently. These environment-friendly biopolymers and their composites can be categorized based on their numerous sources, different methods of preparation and their potential form of usage. Materials produced via way of means of artificial chemistry from organic reassets which include vegetable oils, sugars, fats, resins, proteins, amino acids, and so forth also can be defined as biopolymer(Hernández et al., 2014). Most commercial biopolymers, such as polylactide (PLA), are not degraded under ordinary conditions even in presence of microorganisms. Furthermore, the disposal of biopolymer articles has the disadvantage. As compared to artificial polymers that have a less complicated and greater random shape, biopolymers are complicated molecular assemblies that undertake particular and described 3-D shapes and structures. This is one vital belongings which makes biopolymers energetic molecules in vivo. Their described form and shape are certainly keys to their function. For example, hemoglobin might now no longer be capable of deliver oxygen withinside the blood if it became now no longer folded in a quaternary shape. Biodegradable biopolymers from renewable sources had been synthesized to offer options to fossil-fuel-primarily based totally polymers. They are regularly synthesized from starch, sugar, herbal fibers, or different natural biodegradable additives in various compositions. The biopolymers are degraded via way of means of publicity to microorganism in soil, compost, or marine sediment. growing purchaser hobby in the use of “green” (or renewable sources) as the idea for purchaser products. The use of biopolymers from exceptional reassets has been investigated for decades for pharmaceutical and biomedical applications.

1.1- What is a Biopolymer?

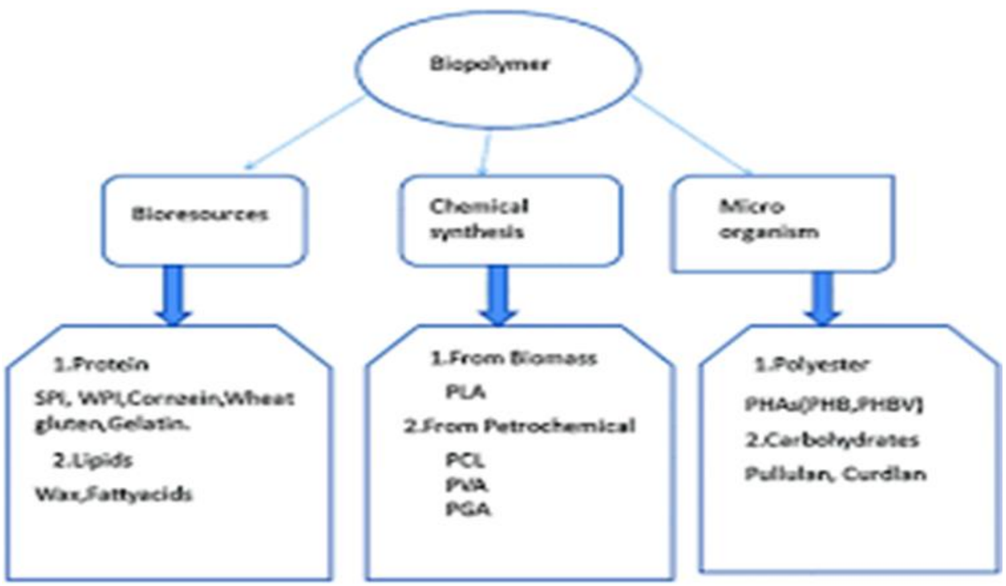
The prefix 'bio' way they're biodegradable substances produced via way of means of dwelling organisms. As the name suggests, biopolymers are polymers synthesized by living organisms. Therefore, they are polymeric biomolecules i.e. long chain biomolecules comprised of covalently linked repeating monomeric units. Living organisms (plants, animals, bacteria, fungi and yeast) synthesize a wide range of biopolymers such as deoxyribonucleic acid (DNA), ribonucleic acid (RNA), proteins, cellulose, chitin, starch, etc(M.E. Ojewumi, et al., 2018). Biopolymers carry out countless number of vital functions, such as storage of energy, preservation and transmittance of genetic information, and cellular construction, in vivo. DNA and RNA are the hereditary materials for the storage and passage of the genetic information in all living organisms, and thus making perpetuation of life possible in the planet. Proteins not only catalyze reactions (e.g. enzymes) and take part in cell signaling (e.g. hemoglobin) but also provide structural support (e.g. collagen). Cellulose is the major structural component of the plant cell walls.(Numata, 2015)

Fig.1. biopolymer in nature

2- Classification of Biopolymers

2.1- Biopolymers can beclassified differently based on a different scale, Based on their origin:

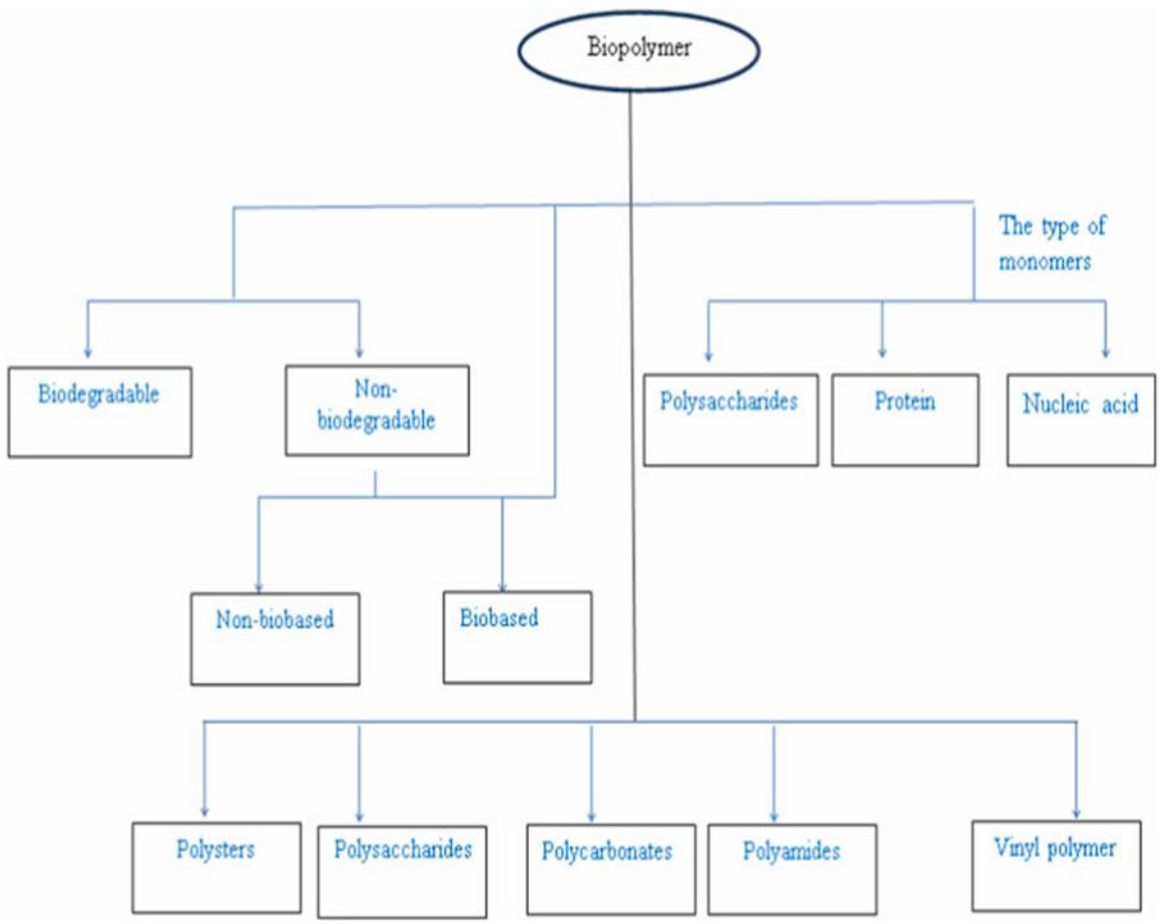
three types of biopolymers can be traditionally distinguished into natural, synthetic and microbial biopolymers as shown in Fig.3.



- Fig.2. Classification of biopolymers according to their oregion.

2.2- Degradability can be used to classify biopolymers;

in fact, we define two families ,principally ,biodegradable and non-biodegradable and alternatively,into bio-based and non-bio-based biopolymers .Also ,they can be classified into polymer backbone, sowe find thesegroups:polyesters,polysaccharides,polycarbonates,polyamides,andvinylpolymers.De pending on the type of monomer ,we can find three groups: polysaccharide, protein and nucleic acid .Another way to classify Biopolymers based on their response to heat is sowe find elastomers, thermoplastics, and thermosets. There are different Categories to classify biopolymers, we note that each group can be classified into several subgroups(Balkus, 1996). Fig.4. shows all these classes.



- Fig.3. Classifications of biopolymer based on biodegradability, polymer back bone and type of monomers.

2.3-Biopolymers can also be classified based on then ways in which they respond to heat:

as thermoplastics, thermosets. Nowadays, the volume of bio-based thermoset biopolymers exceeds the volume of bio-based thermoplastic biopolymers.

2.3.1-Thermoplastics

Thermoplastic polymers are polymers that can be repeatedly heated and molded without effecting any change in their chemical or physical properties

examples of thermoplastics include acrylic, polyester, polypropylene, polystyrene, nylon and Teflon.

2.3.2-Thermosets

Thermoset polymers are polymers that once molded and hardened, cannot be reshaped or recycled. Examples of Thermosetting Plastic Examples: Vulcanized Rubber, Bakelite, Duroplast, Urea-Formaldehyde Resins Melamine-Formaldehyde Resins, Epoxy Resins, Polyimides, Silicon Resins, Polyurethane, Polyester Resins. Examples: Vulcanized Rubber, Bakelite, Duroplast, Urea-Formaldehyde Resins Melamine-Formaldehyde Resins, Epoxy Resins, Polyimides, Silicon Resins, Polyurethane, Polyester Resins.

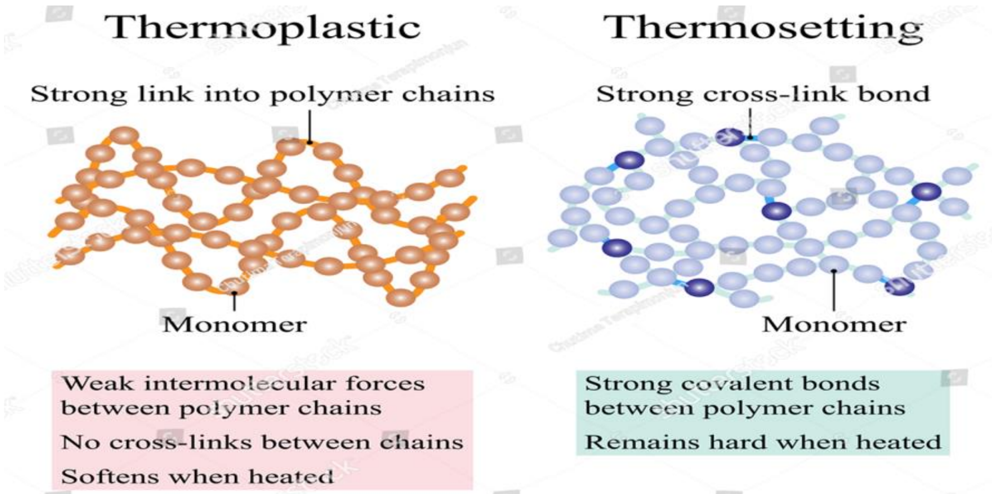


Fig.4. structure of thermoplastic and thermosetting biopolymers.

3- Methods of preparation

Biopolymers can be produced either by fermentation or by polymerization of monomers. Biopolymers that are produced using microorganisms with specific carbon, nitrogen, minerals and salts as sources by the process of fermentation are termed as microbial biopolymers. The mechanism behind the production of these microbial biopolymers are mainly due to their defense mechanism or storage material. Another method of preparation is by chemical polymerization of monomeric units that can be degraded by microorganisms, enzymes or by natural resources(Mohan et al., 2016). Some of the common methods available for the preparation of biopolymers from natural and synthetic sources would be discussed as follows.

3.1- Polymerization of monomers

For the synthesis of any microstructure, the monomer which is at fluid state is allowed to flow through a tubular channel at standardized flow rates. During the flow of the stream, illumination is projected on the flow and the reflected pulse shape is used to determine the microstructure of at least one unit in the monomeric fluid. Polymerization step follows a series of different reactions corresponding to the functionalities of the reactants and their steric effects. For instance, alkene units require simpler steps compared to carbonyl groups which require complex steps, while the alkanes react only in the presence of strong acids (Doyle et al., 2010). One of the common natural polymers, Polycaprolactone (PCL) is mainly produced for its high miscibility with other polymers, disposability and improved properties. The production of PCL was achieved using two methods namely, poly condensation of a hydroxyl carboxylic acid and ring-opening polymerization of ε-caprolactone. Different conditions such as, time, miscibility, percentage and different catalysts were studied before the initiation of the process. On comparison, the Ring Opening Polymerization (ROP) pathway using lactone provided a suitable and desired polymer.

3.2- Solvent based extraction

A thermochemical conversion process of biomass called liquefaction was performed with organic solvents to produce biopolymers. Varying solvent systems are utilized for the pretreatment and extraction of biopolymers from different biomass (Mahmood & Moniruzzaman, 2019). The alternative green solvents used for the extraction include ionic liquids, deep eutectic, bio-derived, non-halogenated and accelerated solvent systems. Due to their unique properties like low vapor pressure, non-toxicity, reusability and thermal stability, they are used for biopolymer extraction. The ionic liquids like 1-allyl-3-methylimidazolium bromide (AMIMBr), 1-Butyl-3-methylimidazolium chloride (BMIMCl), 1-Ethyl-3-methylimidazolium acetate (EMIM Ac), N, N-Diisopropylethylamine (DIPEAAc and DIPEA P) are used for the extraction of chitin, keratin and collagen.

3.3- Fermentation

Biopolymers were conventionally produced using microbes like bacteria, fungi, and other algae by the process of fermentation (Chang et al., 2015). For instance, Xanthomonas campestris was inoculated to produce Xanthan biopolymer. The formation of cell mass was constantly measured using optical density to measure the relative growth. The viscosity of the culture depicted the formation of the biopolymer product. Industrial wastes can be efficiently exploited as fermentation feedstocks for the synthesis of biopolymers, by converting those toxic pollutants into useful biopolymers such as polyhydroxyalkanoates (PHAs) and bacterial cellulose.

3.4- Exo-biopolymer production

Submerged cultures involving liquid media are usually recommended for the production of biopolymers from fungi. The carbon, nitrogen and the inorganic salt sources and the pH, temperature and agitation conditions were optimized in the bioreactor for the growth of exo-biopolymer and mycelia. The time dependent mycelial growth from Paecilomyces japonica was allowed by optimizing the sources with respect to the dry weight of biomass ("Optimazation of Submerged Culture Conditions for Exo-Biopolymer Production by Paecilomyces Japonica," 2000). The carbon sources include a wide range of sugars like, fructose, sucrose, glucose, maltose, lactose and xylose, while the nitrogen sources include yeast extract, tryptone, types of peptone and salts of ammonium and nitrate. Mineral sources include the potassium nitrate, magnesium sulphate and bivalent salt of potassium.

3.5- Endo-biopolymer production

Similar to the exo-biopolymers, endo-biopolymers (EBP) were produced using liquid submerged culture, where Pleurotus eryngii was supplemented with Potato Dextrose Agar (PDA) with optimized acidic pH conditions. The EBP produced after 10 days was subjected to purification from the mycelial pellet using hot water extraction with centrifugation to separate the supernatant containing the endo-biopolymer. Further, it was washed with ethanol, filtered, lyophilised and stored for their usage in anticancer and immunomodulatory properties (Ujang et al., 2007).

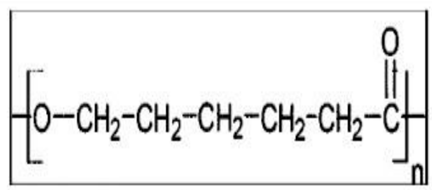
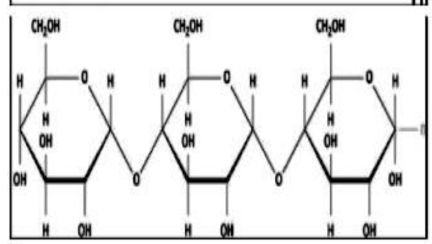
3.6- Bulk synthesis of biopolymers

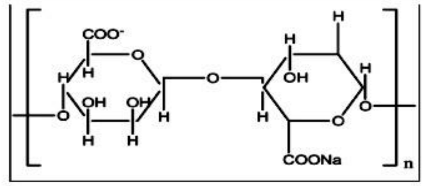
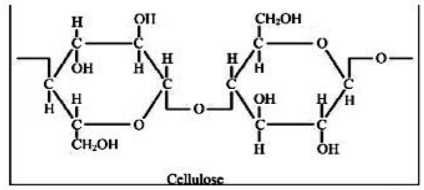
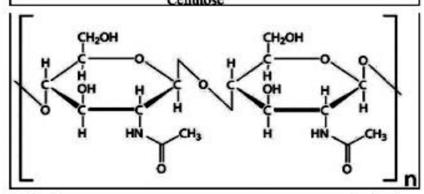
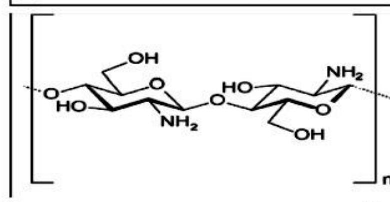
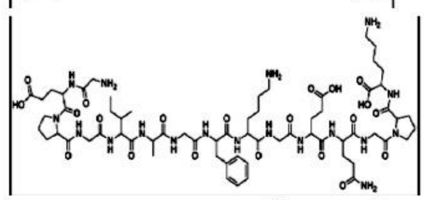
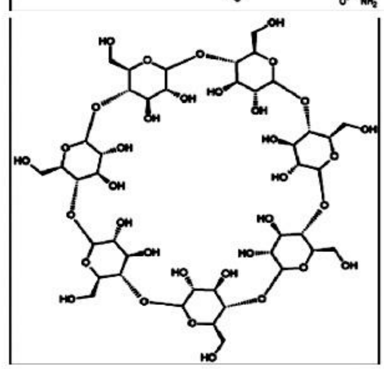
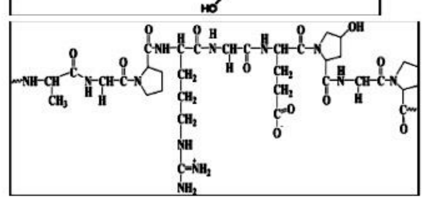
Optimizing the feed for any kind of bioreactor determines the cost efficiency of the product biopolymer. A reduced kinetic model was developed which contains a mixture of different cultures. It was studied that constant feeding rate of both carbon and nitrogen is required for the production of PHB in a fed-batch reactor fed with Ralstonia eutropha. But the cultivation of mixed culture showed the decrease of substrate inhibition and a doubling of the biopolymer production using dynamic feeding strategy. This signifies the highest production of biopolymer during the usage of multiple microbes and substrates. Some of the other parameters considered for the production include, pH, substrate concentration, Retention time and the feeding rate of biomass. Similarly, the designed mathematical model based on Genetic algorithm for batch cultivation can be successfully extrapolated to fed-batch cultivation by considering the nutrient feeding criteria and dilution rates for high PHB production from biomass (Khanna & Srivastava, 2005).

4- Types of biopolymers, sources, and structures

Biopolymers are derived from natural biological sources like plants, animals, microbes, and agricultural wastes. They can be chemically synthesized from monomeric units such as sugars, oils, and amino acids, from plant sources such as maize, rice, wheat, potatoes, sorghum, yams, cassava, banana, corn, tapioca, cotton, and barley. Animal sources mainly include cattle and marine sources include corals, sponges, fishes, lobster, shrimps, while the microbial sources include algae, fungi, and yeasts (Flaris & Singh, 2009).

Table.1. Some of the important biopolymers in use with their sources and diagrammatic representation of their chemical structure

Biopolymer	Sources	Structure
Poly (e-caprolactone)	Polycondensation of e-caprolactone.	
Starch	Maize, cassava, banana, rice, potatoes, sorghum, wheat, yams.	

Biopolymer	Sources	Structure
Alginate	**Brown seaweed** ***Laminaria digitata, Laminaria japonica, Laminaria hyperborea, Macrocystis pyrifera and Ascophyllum nodosum.***	
Cellulose	**Agricultural wastes like sugarcane bagasse and rice husk. Seaweed. Plant sources like wood, bamboo, sugarbeet, banana rachis, potato tubers, cotton, fique, kapok, agave, jute, kenaf, flax, hemp, vine, sisal, coconut, grass, wheat, rice and barley.**	 Cellulose
Chitin	**Aquatic species like corals, horseshoe worms, lamp shells, sponges, squid, cuttle fish and clams.** **Mushrooms, yeasts, algae like coraline and green algae, velvet worms, ladybug, wax worm, silk worm, protozoa, butterfly, insects, spiders, beetle, honey bees, scorpions, grasshopper, millipedes, centipedes, shrimps, lobster, krill, prawns, crayfish, isopoda and crabs.**	
Chitosan	**Insects, algae, fungi, mollusks and crustaceans.**	
Collagen	**Marine sponge, jellyfish, fishes, tobacco, barley, maize, porcine, bovine, rodent, mollusk, squid, catfish, insects and recombinant systems.**	
Cyclodextrin	**Starch sources like potato, corn, wheat, rice and tapioca.**	
Gelatin	**Pig skin, bovine hide, pork and cattle bones, fishes, salmon, catfish, squid, bigeye snapper, cuttlefish, lizardfish, grouper, hoki, melon and sorghum bugs.**	

5- Biopolymers properties

Biopolymers extracted from fruits and vegetables wastes show different characteristics and properties that make them more or less suitable for the production of eco-friendly materials.(Jha & Kumar, 2019) Table.2. Properties associated with the main biopolymers extracted from fruits and vegetable wastes for bioplastics production.

Biopolymer name	**Biopolymer type**	**Properties**	**Fruits and Vegetable Wastes used as Biopolymer Source**
Cellulose	Polysaccharide	Highly structured intermolecular Hydrogen bonding network; impossibility of melting or dissolution by standard processes such as thermoforming	Banana peels, carrots waste, cauliflower waste, cocoa pod husks, orange peels, parsley steams, radicchio waste, rice hulls, spinach steams, tea leaves waste
Starch	Polysaccharide	Strong inter- and intra-molecular hydrogen bonding; water sensitivity and poor fowability; brittleness	Banana peels, cassava peels, potato peels
Pectin	Polysaccharide	Gelling ability but poor tensile and barrier properties; water sensitivity	Apple pomace, banana peels, citrus waste, orange peels
Cetin	Polyester of hydroxy fatty acids	Amorphous and flexible three-dimensional polymer; hydrophobic, low water sensitivity.	Tomato waste

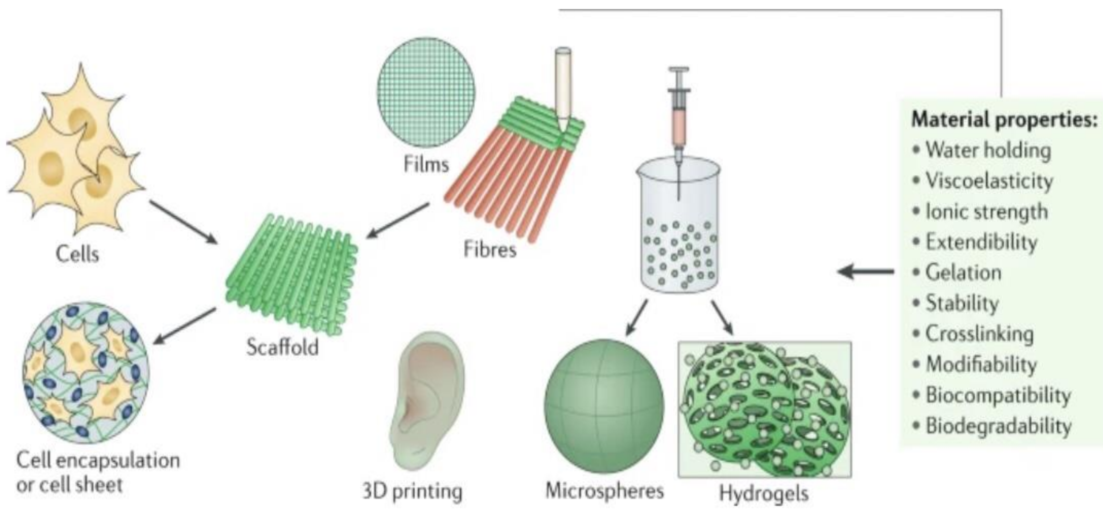


Fig.5. some properties of biopolymers

5- Advantages and disadvantages of biopolymers

5.1-Advantages:

- Localized delivery of drug
- Sustained delivery of drug
- Stabilization of drug
- Decrease in dosing frequcncy
- Reduce side effects
- Improved patient compliance
- Controllable degradation rate
- Readily & Abundantly Available.
- Comparatively Inexpensive.
- Nontoxic products.
- Can be modified to get semi synthetic forms.

5.2-Disadvantages:

- don't always readily decompose. Some need relatively high temperatures and can still take many years to break down. Even then, they may leave behind toxic residues.
- are made from plants such as corn and maize, so land that could be used to grow food for the world is being used to "grow plastic" instead.
- Some bioplastics, such as PLA, are made from genetically modified corn.
- cannot be easily recycled. To most people, PLA looks very similar to PET but, if the two are mixed up in a recycling bin, the whole collection becomes impossible to recycle.

6-Application of biopolymers

Applications and Parts The fields of application for biopolymers are increasing steadily. Biopolymer applications are characterized either by biodegradability or by sustainability or both(Niaounakis, 2013). Today, biopolymers can be found mainly within the following market segments:

6.1. **Service packaging**

(e.g., films, bags, containers, etc.).

Biopolymers have been used broadly in packaging. Starch-based biopolymers are the most commonly used biopolymers for biodegradable packaging. Starch accounts for a 50% share of biodegradable packaging globally in 2007. Starch based polymers are commonly used in biodegradable packaging such as compostable bags, consumer goods packaging, and fresh food packaging for fruits, vegetables, and bakery products. They are also used in disposable packaging for the food service industry. Starch is followed by PLA, which accounts for a 40% share by volume [108]. PLA dominates the fresh food packaging sector. The rapid capacity expansion of this polymer is set to boost the growth of its biodegradable packaging applications. Other polymers such as PHA and polyesters, account for the remaining 10% share.

6.2. Food services

(e.g., cups, trays, cutlery, bottles, etc.)

Food-related applications include beverage bottles, containers, cups, disposable tableware, and packaging. In 2007, 65% of bio-based biopolymers were used in packaging and food-related applications. In 2025 it is estimated that this share will shrink to just 40% because automotive and electronics applications, which have a higher profit potential than the packaging and food industries, are expected to profit and gain a higher market share, potentially reaching over 25%.

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6.3. Agriculture/forestry/horticulture

(e.g., mulch films, temporary replanting pots, delivery systems for fertilizers and pesticides, etc.). Biodegradable biopolymers are making rapid advances in the agriculture and horticulture sectors Mulch films and flowerpots made of decomposable biopolymers are the most successful products because of their adjustable lifespan and the fact that these materials do not leave residues in the soil. This helps reduce work and cost as these products can simply be left to decompose, after which they are plowed into the soil. Plant pots used for flowering and vegetable plants can be composted along with gardening and kitchen litter. Other applications of biopolymers in agriculture and horticulture include: yarns, tapes, and clips made of biodegradable biopolymers that are used to secure high-growing plantations. Compostable seed belts and active component capsulations made out of biopolymer have also proven to be beneficial. Additionally, biodegradable foils and nets are used for farming/growing mushrooms and the coating of tree and bushroots. Foils, yarns, and nets made out of biopolymers help to secure freshly created slopes and mounds and protect them from erosion until the roots of the plants have developed sufficiently.

6.4. Fishery (fishing lines and nets, fishing hooks, fishing gear, etc.).

6.5. Consumer electronics

(mobile phone casings, laptops, etc.).

Nowadays components and accessories of a large proportion of consumer electrical appliances are made of biopolymers or biocomposites. Biocomposites include materials containing a biopolymer in conjunction with structural reinforcement materials such as carbon, plant, or wood fiber.

6.6. Automotive industry

(e.g., interior trim, sparetire covers, etc.).

The automotive industry is a sector of bulk plastics users that has high-performance specifications. Automotive components that incorporate bio-based materials have been used by many automobile manufacturers around the world, including Audi, BMW, Chrysler, Fiat, Ford, General Motors, Honda, Mazda, Mercedes Benz, Opel, Peugeot, Renault, Toyota, Volkswagen, and Volvo.

6.7. Textiles/fibers

(carpets, clothing, upholstery, etc.).

In the sectors of fabrics and furnishings, the biopolymer products that are being heavily promoted are Ingeo (NatureWorks LLC) and Sorona (DuPont), both PLA-based fibers with a growing share of the fabric market; and soy-based foam for upholstery.

6.8. Medical/pharmaceutical sector

(e.g., medicines, sutures, implants, etc.).

Biopolymers have found very relevant and practical uses in the medical and pharmaceutical sectors, beginning with the biodegradable sutures first approved in the 1960s. Since that time, diverse products based on PLA and PGA and other materials, including PDS, PTT, and PCL, have been used as medical devices. Nowadays, the list of biopolymers used for medical and pharmaceutical purposes has been enriched with more “exotic” biopolymers, such as polyanhydrides, POEs, PPHOSs, and the like.

6.9. Cosmetics.

The continuing growth of biopolymers is driven by a variety of industries, including the cosmetics and health care sectors, which use a lot of fast-moving goods. The cosmetics industry is testing and perfecting packaging made from biopolymers. Cosmetics place very high demands on packaging materials, but there is still a call for more sustainability and an increased use of biopolymers. Here is an overview of some recent biopolymer-based products used in cosmetics:

- Body care packaging made from Earth First PLA (Sidaplax).
- Haircare packaging film made from Earth First PLA (Sidaplax).
- NatureWorks Cargo lipstick made from 100% Ingeo (Cargo Cosmetics).
- Cosmetic Bag made from Bio-flex.
- Cosmetic pen made from Biograde.
- Laundry olive oil soap "Ecolive" wrapped in fully compostable Bio-Flex.
- Impact Zero face & body lotion in PLA Bottle (Eudermic and NatureWorks).

6.10. Outdoors sports.

Outdoor sports and the environment are naturally intertwined, and the use of bio-based biopolymers in sporting goods has gotten a positive reception by the general public. In combination with the prerequisites of the sports market, such as high growth rates, high willingness to pay, and high material cost-insensitivity, the applications of bio-based biopolymers in sporting equipment and apparel are increasing.

Here is an overview of some recent biopolymer based sports products:

- The Hurricane ski boot from Scarpa and the Renu ski boot from Atomic use Arkema's biobased thermoplastic elastomer (TPE) Pebax Rnew, cotton, and bamboo.
- Wave Technology plates in four models of Mizuno's running shoes, and the FIFA soccer ball from Sony, contain Arkema's Pebax Rnew.
- Evolve snow goggles from Smith Optics use Merquinsa's Pearlthane ECO, a bio-based TPU that contains 20e90% Cerenol biopolyol from DuPont.
- Ghost ski boots made from Hytrel.
- Trekking poles made from APINAT.
- Green Silence running shoes and BioMoGo midsoles from Brooks Sports.

Fig.6. application of biopolymer

6- Conclusions

Researchers are considering natural and biodegradable polymers to replace synthetic polymers in a variety of applications as a result of growing awareness of sustainable development. Here comes the role of biopolymers, synthesized from completely natural monomers or from already existing sources in different forms. Biopolymers are created in a variety of ways. I presented the properties, processing, characterization and applications 9pf biopolymers. These environment-friendly biopolymers and their composites can be categorized based on their numerous sources, different methods of preparation and their potential form of usage.

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