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A COMPREHENSIVE REVIEW ON BIOPOLYMERS

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ABSTRACT

The environmental impact of persistent plastic wastes is raising general global concern, and disposal methods are limited. The continuously growing public concern in the problem has stimulated research interest in biodegradable natural polymers. Biopolymers (polysaccharides) have various applications in medicine, food and petroleum industries. Microorganisms can produce and excrete good amount of polysaccharides in simple but costly production conditions. A number of polysaccharides produced by microorganisms have either been adopted as commercial products or have the potential for commercialization. The advent of modern biotechnology has fundamentally transformed the way scientists view organisms and the materials they produce. The main drawback limiting the development of these polysaccharides is the lack of efficient processes for their extraction and purification. However new applications in agronomy, foods, cosmetic and therapeutic could in a near future accentuate the effort of research for their development. So this review focuses on various useful polysaccharides isolated from microbes as well as its applications in various fields.

Key words: Biopolymer, Plastic wastes, Polysaccharides, Biological activities.

INTRODUCTION

Approximately 140 million tones of synthetic polymers are produced worldwide every year. Since polymers are extremely stable, their degradation cycles in the biosphere are unlimited. Environmental pollution by synthetic polymers, such as waste plastics and water soluble synthetic polymers in waste water has been recognized as a major problem. Plastics and polymers are an integrated part of our daily existence. However, because of stability and resistance to degradation, these are accumulated in the environment, at the rate of about 8% by weight and 20% by volume of the landfills[1]. Polymers are a class of "giant" molecules consisting of discrete building blocks linked together to form long chains. Simple building blocks are called monomers, while more complicated building blocks are sometimes referred to as ''repeat units'. Biopolymers are defined as polymers formed under natural conditions during the growth cycles of all organisms. Therefore, they are also named natural polymers. They are formed within cells by complex metabolic processes. For materials applications, cellulose and starch are most interesting. However, there is an increasing attention in more complex hydrocarbon polymers produced by bacteria and fungi, particularly polysaccharides such as xanthan, curdlan, pullulan, chitin, chitosan and hyaluronic acid[2]. Biodegradable polymers are growing in importance, day the day and current research is focused on producing newer biodegradable polymers. A vast number of biodegradable polymers have been synthesized or are formed in

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nature during the growth cycles of all organisms. Some microorganisms and enzymes capable of degrading them have been identified e.g. Depending on the evolution of the synthesis, different classifications of the biodegradable polymers have been proposed[3].

Functions and synthesis of biopolymers

Living matter is able to synthesize a wide range of different polymers and in most organisms, these biopolymers contribute the major fraction of cellular dry matter. The functions of biopolymers are in most cases, essential for the cells and are as manifold as their structures. These biopolymers fulfill a range of quite different essential functions for the organisms such as –

- Conservation and expression of genetic information.
- Catalysis of reactions, storage of carbon, energy or other nutrients.
- Defending and protecting against the attack of other cells, hazardous environmental factors, sensing of biotic and abiotic factors.
- Communication with the environment and other organisms.
- Mediation of the adhesion to surfaces of other organisms or of non-living matter and many more.

All the biopolymers are synthesized by enzymatic processes in the cytoplasm, in the various compartments or organelles of cells, at the cytoplasmic membrane or at cell wall components, at the surface of cells or even extracellularly, synthesis of a biopolymer may be initiated in one part of a cell and may be continued in another part as it occurs [4,5].

Production of biopolymers

There are different ways to produce biopolymers in order to make them available for different applications:

(i) Many biopolymers occur abundantly in nature and are isolated from plants and algae, which grow in natural environments. Agar and alginates are isolated from red algae belonging to the genus *Gelidium* or from various brown algae also referred to as seaweeds.

(ii) Few biopolymers are isolated from extremely natural sources. An example of such an exception is hyaluronic acid, which is extracted from the umbilical cords of new born children.

(iii) *In vitro* synthesis of biopolymers with isolated enzymes in cell-free systems offers another possibility to produce biopolymers. One example is the application of the heat stable DNA polymerases in the polymerase chain reaction (PCR) to produce monodisperse defined DNA molecules. Another example is dextran, which can be produced on a technical scale with isolated dextran sucrase.

(iv) Fermentative production of biopolymers are used in industry, e. g. is polysaccharides. The biotechnological production of biopolymers may occur intracellularly or extracellularly. This causes several severe consequences regarding the limitations of the production and downstream process to obtain the biopolymers in a purified state.

Intracellular versus extracellular production of biopolymers

Polyhydroxyalkanoates, cyanophycin, glycogen, starch, and polyphosphate are example of biopolymers, which are accumulated in the cytoplasm of cells. The availability of space in the cytoplasm therefore limits the amount of polymer that can be produced by a cell. This is particularly relevant for fermentative production processes mostly employing microorganisms. Therefore, the yield per volume is limited/determined by the cell density and the fraction of the biopolymer in the biomass. Poly (β-D-glutamate) and many polysaccharides, such as alginates, dextran, xanthan, curdlan, pullulan, chitosan and microbial cellulose are examples of biopolymers, which occur outside the cells, either as a result of extracellular synthesis or of excretion by the cells. For these biopolymers, the volume of the bioreactor would be available to deposit the desired biopolymer. Furthermore, breakage of cells is not required and separation of the biopolymer from the other biomass is not very complex. Other strategies and the use of cell-free production processes, may take advantage of the features of extracellular processes. One strategy is to apply *in vitro* synthesis of biopolymers employing isolated enzymes. Another strategy is to produce the constituents of polymers as monomers by fermentative processes and to polymerize these components subsequently by solely chemical processes. Both these strategies have already entered reality and many different examples of scale have been demonstrated (i.e., not only at the laboratory scale but also at the large scale). Polylactic acid, for example has been produced on a large scale by such a combined biotechnological and chemical approach[6].

Genetic engineering and biopolymer technology

Modern biotechnology has given scientists revolutionary tools to probe and manipulate living systems. Genetic engineering permits extraordinary control over the time, place, level, and type of 'gene expression'. The simplest case applies to protein polymers. Having access to the genetic blueprint (gene) of a particular protein polymer allows one to change both the system that produces the polymer and the composition of the polymer itself. Recombinant DNA techniques permit the creation of polymer chains that are virtually uniform in length, composition, and stereochemistry or spatial orientation[7].

Genetically engineered biopolymer production systems

Genetically engineered products are regulated on the basis of their intended use, rather than the method or process by which they are made. For example, under current Food and Drug Administration (FDA) rules, genetically engineered foods are treated the same way as conventional products. The FDA does not require that new products be approved or labeled, as long as such products are essentially similar in composition, structure, and function to food items already available on the market. However, U.S. Department of Agriculture, and Environmental Protection Agency (EPA) do regulate field tests of genetically modified plants. As of now, more than 700 permits have been granted for the field testing of genetically altered plants and other organisms[8].

Bacterial cellulose

Cellulose is the most abundant component of biomass and the basic feedstock of the paper and pulp industries. Traditionally extracted from plant tissue (trees, cotton, etc.), cellulose can also be produced by certain bacterial species by fermentation, yielding a very pure cellulose product with unique properties. The most prevalent applications of bacterial cellulose exploit its very large surface area and its ability to absorb liquids. Consequently, very low concentrations of bacterial cellulose can be used to create excellent binding, thickening, and coating agents. Because of its thickening properties, many applications in the food industry are possible[9-11].

Xanthan

Xanthan gum, a complex copolymer produced by a bacterium, was one of the first commercially successful bacterial polysaccharides to be produced by fermentation. The xanthan polymer building blocks or "repeat units" contain five different sugar groups produced by the bacterium *Xanthomonas campestris*. It is used extensively in both the food and the non-food sectors. Examples of industrial applications include oil recovery (provides viscosity control in drilling mud fluids), mineral ore processing (used as a biocide), paper manufacturing (used as a modifier), agriculture (acts as plant growth stimulator), pharmaceuticals (being evaluated for sustained drug release), and cosmetics (controls dust release). Food applications include gelling agents for cheese spreads, ice creams, puddings, and other deserts[12-14].

Dextrans

Dextran is the generic name of a large family of microbial polysaccharides that are assembled or polymerized outside the cell by enzymes called dextran sucrases. This class of polysaccharides is composed of building blocks (monomers) of the simple sugar glucose and is stored as fuel in yeasts and bacteria. Dextran polymers have a number of medical applications. Dextrans have been used for wound coverings, in surgical sutures, as blood volume expanders, to improve blood flow in capillaries in the treatment of vascular occlusion, and in the treatment of iron deficiency anemia in both humans and animals. Dextran-hemoglobin compounds may be used as blood substitutes that have oxygen delivery potential and can also function as plasma expanders[15-17].

Pullulan

Pullulan is a water-soluble polysaccharide produced outside the cell by several species of yeast, most notably *Aureobasidium pullulans*. Pullulan is a linear polymer made up of monomers that contain three glucose sugars linked together. Pullulan compounds are biodegradable in biologically active environments, have high heat resistance and display a wide range of elasticities and solubilities. This versatility allows them to be utilized in many different ways. It can be used as a food additive, providing bulk and texture. It is tasteless, odorless and nontoxic. It does not break down in the presence of naturally occurring digestive enzymes and therefore, has no caloric content. Consequently, it can be used as a food additive in low-calorie foods and drinks, in place of starch or other fillers. Pullulan can be used as a binding agent for solid fertilizers. The biopolymer can be used as a flocculating agent for the precipitation of potash clays, uranium clays, and ferric hydroxide from slurries used in the beneficiation of mineral ores. In the medical area, pullulan acts as a plasma expander without undesired side effects. After metabolic turnover, it is completely excreted. Pullulan compounds can also serve as drug carriers, and can be used as medical adhesives. Although markets for many of the applications listed here are still relatively small, with some applications only in the exploratory stage, pullulan appears to have long-term commercial potential. In sum, pullulan's many disparate uses may entitle it to become known as a biopolymer "wonder material"[18-20].

Glucans

Glucans are homopolymer of the simple sugar glucose. Glucan is commonly used to describe the glucan component of the yeast cell wall. A common source for this glucan is *Saccharomyces cerevisiae*, although it is also found in other sources. Glucans are the most abundant polymers in yeast, making up approximately 12 to 14 percent of the total dry cell weight. Glucan is readily purified from yeast cells by using hot alkali treatment to remove all other cellular materials, thereby allowing recovery of the insoluble glucan material. Because of its action as an immunomodulator, a number of studies have been performed exploring the use of glucan as an anti-infectious agent. Glucan is also effective as an antiviral agent in plants. Several studies using different tumor models in mice and rats have revealed that glucans can inhibit tumor growth. Another interesting property of glucans is that they are radio protective. This enhances the survival of test animals after otherwise lethal doses of radiation.

β-glucans consist of a backbone of glucose residues linked by β-(1,3)- glycosidic bonds, often with attached side-chain glucose residues joined by β-(1,6) linkages. These β-glucans appear to possess potential for treating several diseases. About half the mass of the fungal cell wall consists of β-glucans[21-23]. Individual fungal β-glucans differ in their effectiveness as immunomodulators. Even β-glucans with similar reported structures, molecular weights and solution conformations can differ markedly. This may reflect our inability to acquire sufficient detail from their structural analyses to allow us to recognize possible subtle structural differences between them, using the present methodologies of nuclear magnetic resonance (NMR) and methylation analyses to determine branching patterns. Yet these response differences are much more noticeable when structurally quite different glucans are compared. The most popular β-glucans, lentinan, schizophyllan and, grifolan from *Lentinus edodes*, *Schizophyllum commune*, and *Grifola frondosa* are all β-(1,3) (1,6)-glucans, but with different reported branching frequencies (Table 1). All are effective against the same tumour model, but at quite different doses[21-27].

Table 1: Fungal β-glucans and their chemical diversity

Glucan	Abbreviation	Fungal source
Curdlan	-	*Alcaligenes faecalis*
Grifolan	GRN	*Grifola frondosa*
Lentinan	-	*Lentinula edodes*
Schizophyllan	SPG	*Schizophyllum commune*
Scleroglucan	SSG	*Sclerotina sclerotiorum*
Zymosan	-	*Saccharomyces cerevisiae*
Betfectin	PGG	*Saccharomyces cerevisiae*
Krestin	PSK	*Trametes versicolor*
Yeast whole β-glucan particules	WPG	*Saccharomyces cerevisiae*
Pestolotan		*Pestalotia sp. 815*
Epiglucan	-	*Epicoccum nigrum*

Chitin and chitosan

Chitin is a skeletal polysaccharide making up a basic shell constituent of crabs, lobsters, shrimps, and insects. Chitin is widely available from a variety of sources among, which the principal sources are shellfish and crustacean waste materials. It is insoluble in its native form, although chitosan, a partly deacetylated form of chitin, is water-soluble. They are widely used in the cosmetics industry, due to their water-retaining and moisturizing capacities. Used as carriers, chitin and chitosan (Fig. 1) allow the synthesis of water-soluble prodrugs[28-30].

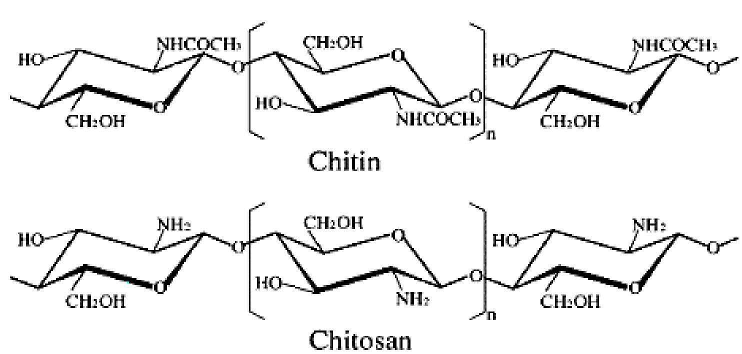

Fig. 1: Structure of chitin and chitosan

As seen above, both chitin and chitosan have similar chemical structure. Chitin is made up of a linear chain of acetylglucosamine groups while chitosan is obtained by removing enough acetyl groups (CH_3-CO) for the molecule to be soluble in most diluted acids. However, unlike plant fiber, chitosan possesses positive ionic charges, which gives it the ability to chemically bind with negatively charged fats, lipids, cholesterol, metal ions, proteins and macromolecules. Industrially, chitosan is derived from the chemical deacetylation of chitin. However, this process fails to produce chitosan of uniform quality. The process of deacetylation involves the removal of acetyl groups from the molecular chain of chitin, leaving behind a compound (chitosan) with a high degree chemical reactive amino group (-NH_2)[31-33]. Chitosan has attained increasing commercial interest as suitable resource material due to its excellent properties like biocompatibility, biodegradability, adsorption, ability to form films and to chelate metal ions[34].

The IR spectroscopy method, which was first proposed by Moore and Roberts, is commonly used for the estimation of degree of deacetylation. The following are some baselines proposed for the determination of the degree of deacetylation of chitosan.

Domszy and Roberts, DDA = 100 – [(A1655 / A3450) x 100/1.33]

Sabnis and Block, DDA = 97.67 – [26.486 x (A1655 / A3450)]

Baxter et al., DDA = 100 – [(A1655 / A3450) x 115]

Rout, DDA = 118.883 – [40.1647 x (A1655/A3450)]

RESULTS AND DISCUSSION

The biodegradable polymers are used in various fields and it has resulted in the development of many commercial products. Because of their high specialization and greater unit values, particularly medical applications have developed more rapidly than the others. An important group of biopolymer is represented by the homopolymers of β-glucans because of its very low-to-negligible toxicity. They have tremendous potential use in a variety of diseases. Modern medical research has reached a phase where the basic mechanisms of glucan effects are known and the relationship between structure and activity has been outlined clearly. For many years, the major focus of drug research has been on the synthesis or discovery of new drugs. The use of biopolymer materials for drug delivery can minimize tissue reaction and allow drugs to be administered in nonconventional ways. The use of biopolymers in these formulations has thus far been restricted to a narrow set of applications. Drug formulations incorporating polymer drug delivery systems are currently undergoing registration and are likely to make an impact on the market in near future. The major area of application for these novel sustained release systems is in the treatment of cancers and diseases of the elderly. In the treatment of hormone disorders and geriatric diseases, biopolymer delivery systems allow drugs to be administered occasionally.

CONCLUSION

As the research on the properties of newer microbial polysaccharides continues to grow, we need to streamline the commercialization of such compounds against traditional products, and somehow balance the improvement in original structures with the cost of production and development. Currently existing methods are not able to extract all microbial polysaccharides. The main drawback for the commercialization of new polysaccharides lies in the identification of new or superior properties compared to the one possessed by traditional products. The second obstacle for improvement of original structures is the cost of production and development that may be again a limiting factor. The polymers actually available as products in the market are very few compared to the large number of polysaccharides whose structures are either published or patented. Moreover, specific action as food additives could be approved and research with β-glucans.

Ultimately, the pharmaceutical industry may provide new markets for chemically□modified glucans, like the sulfated ones, and help develop new generations of polysaccharides with more beneficial biological activities.

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