



Review

Enzymatic modification of polysaccharides: Mechanisms, properties, and potential applications: A review



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ABSTRACT

Polysaccharides are natural biopolymers found in almost all living organisms. They are used extensively in various industrial applications, such as food, adhesives, pharmaceuticals, and cosmetics. In many cases, their practical use is limited because of their weak solubility in neutral pH, their unsuitable hydrophilic/hydrophobic balance. In this context, chemical or enzymatic modification of their structure appears as a relevant way, to improve their properties, and thus to enlarge the field of their potential applications. Taking into account the reduction of the input energy and the environmental impact, and due to high specificity and selectivity properties, enzymatic bioprocesses have been investigated as attractive alternatives to toxic and non-specific chemical approaches. This review discusses the methods of enzymatic functionalization of four well-known polysaccharides, chitosan, cellulose, pectin and starch.

Particular emphasis was placed on the methods, the reaction types and the enzymes implicated in the modification such as laccases, peroxidases lipases, tyrosinases, and transglutaminases. The impact of functionalization on the properties and the applications of polysaccharide derivatives were described.

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Abbreviations: DS, degree of substitution; HRP, horseradish peroxidase; MT, mushroom tyrosinase; MTGase, microbial transglutaminase; BLG, beta-lactoglobuline; DMAC, *N,N*-dimethylacetamide; FA, ferulic acid; CA, caffeic acid; GA, gallic acid; CPO, chloroperoxidase; DDG, dodecyl gallate; TEMPO, 2,2,6,6-tetramethylpiperidine 1-oxyl; HEC, hydroxyethyl cellulose; CMC, carboxymethyl cellulose; SBP, sugar beet pectin; UV, ultraviolet; UV/Vis, ultraviolet-visible spectroscopy; ¹H NMR, proton nuclear magnetic resonance; FTIR, fourier transform infrared spectroscopy; H₂O₂, hydrogen peroxide; scCO₂, supercritical carbon dioxide; G-1-P, glucose-1-phosphate.

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1. Introduction

Polysaccharides are an important class of biological polymers joined by glycosidic bonds, universally found in almost all living organisms such as seaweeds (alginate, agar-agar and carrageenan), plants (cellulose, hemicelluloses, pectin and guar gum), microorganisms (dextran and xanthan gum), and animals (hyaluronan, chondroitin, chitin and heparin) [1]. The biological function of polysaccharides is usually either structural or storage-related. For example, starch is a storage polysaccharide in plants, whereas cellulose and chitin are structural polysaccharides found respectively in the plants cell walls and the exoskeletons of crustaceans [2,3]. Due to their diversity of structures and their properties, polysaccharides constitute interesting renewable sources that can be used as high-performance materials [4]. Most of them are biologically inert, safe for humans and abundantly available in the natural environment [5]. They have several other advantages such as low costs, biodegradability in the ecosystem, renewability [6], polyfunctionality, chemical reactivity, chelating and absorptive capacities in the treatment of wastewater [7]. However, in spite of these properties, the use of polysaccharides in their native forms is not always convenient (weak solubility and dispersion in various media, unsuitable hydrophilic/hydrophobic balance). For these reasons, various ways were explored to modify their structure and then to confer the required physical, chemical and mechanical properties.

Polysaccharides have many highly reactive groups (acetamido, amino, carboxyl and/or hydroxyl groups) that can be exploited in various functionalization pathways. In particular, they are characterized by a high hydrophilicity due to the presence of many hydroxyl groups on their structure [8]. Over the years, many chemical reactions such as oxidation, sulfation, esterification, amidation, have been performed involving the free carboxyl, amino or hydroxyl groups distributed along the polysaccharide backbone [9] aiming to create derivatives with determined/adapted properties [10,11]. These chemical processes usually lead to high conversion yields; however, their main drawbacks remain the toxicity of the chemical reagents used and the lack of selectivity. Faced with these limitations, an increased emphasis on eco-efficiency and green chemistry has driven a search for renewable and environmentally friendly processes.

In the past years, enzymatic bioprocesses have been increasingly explored as alternative methods to modify the structure and therefore the properties of polysaccharides. Their main advantages are the high selectivity and substrate specificity, enabling the synthesis of products with well-defined and/or stereospecific structures [12–15]. In addition, enzymatic reactions can be performed under mild conditions and are less likely to produce undesired by-products than chemical processes that require harsh conditions (e.g. strong acids for nitration and sulfonation) and highly reactive compounds (e.g. chloromethyl methyl ether, ethylene oxide, or acid chlorides) [15]. Such procedures have been successfully performed to graft molecules such as fatty acids, proteins, and phenols aiming to improve or create biopolymers with interesting mechanical and/or biofunctional properties.

This review article aims to present different strategies of enzymatic modification applied to four of the most abundant polysaccharides: the chitosan extracted from animal and microbial sources and the polysaccharides isolated from vegetal sources in the order of their natural abundance cellulose, pectin, and starch (Fig. 1). In order to facilitate the search for information according to the reader interest each polysaccharide was addressed according to the type of reaction it can undergo, the enzymes involved and the substrates grafted. The novelty of this paper is not only describing the main enzymatic pathways that were applied to produce polysaccharide derivatives, but also showing the impact of these transformations on the properties and then the applications of the polymers.

2. Chitosan

Chitosan is a natural cationic polysaccharide produced by alkaline *N*-deacetylation of chitin, the second most abundant natural polymer after cellulose [16]. Chitosan is essentially composed of β (1–4) *D*-glucosamine linked to *N*-acetyl-*D*-glucosamine residues. Commercial chitosan is extracted from industrial shellfish wastes [17] as well as from the mycelia of various fungi, containing mainly chitin [18]. The properties of chitosan such as its solubility, flexibility, conformation, and viscosity are greatly affected by its structure. This latter is correlated with the conditions under which chitosan is processed resulting in different deacetylation degree [19]. Chi-

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