

Advances in bacterial exopolysaccharides: from production to biotechnological applications

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A vast number of bacterial extracellular polysaccharides (EPSs) have been reported over recent decades, and their composition, structure, biosynthesis and functional properties have been extensively studied. Despite the great diversity of molecular structures already described for bacterial EPSs, only a few have been industrially developed. The main constraints to full commercialization are their production costs, mostly related to substrate cost and downstream processing. In this article, we review EPS biosynthetic and fermentative processes, along with current downstream strategies. Limitations and constraints of bacterial EPS development are stressed and correlation of bacterial EPS properties with polymer applications is emphasized.

Bacterial exopolysaccharides (EPSs)

Only a few of the huge number of new bacterial EPSs reported over recent decades have emerged as industrially important biopolymers with significant commercial value, particularly with regard to their use as biomaterials (e.g. bacterial cellulose) [1,2] or as rheology modifiers of aqueous systems (e.g. xanthan gum) [3] (Box 1).

Some bacterial EPSs can directly replace polysaccharides extracted from plants (e.g. guar gum or pectin) or algae (e.g. carrageenan or alginate) in traditional applications, because of their improved physical properties (e.g. xanthan gum or gellan gum) (Table 1) [4,5]. Conversely, other bacterial EPSs possess unique properties that can launch a range of new commercial opportunities (e.g. bacterial cellulose or levan) [6,7]. Examples of two newly reported bacterial EPSs with great potential include GalactoPol, synthesized by *Pseudomonas oleovorans*, which is composed mainly of galactose [8], and FucosePol, a fucose-containing EPS that is synthesized by *Enterobacter A47* [9] (Table 1). Several microorganisms isolated from extreme environments, such as deep-sea hydrothermal vents, Antarctic ecosystems, saline lakes and geothermal springs have recently started to be studied as potential sources of valuable biopolymers, including EPSs [10,11].

The global market for hydrocolloids, which includes many polysaccharides, is still dominated by plant and algal polysaccharides (e.g. starch, galactomannans, pectin, carrageenan and alginate). This market valued at >4 million

US\$ in 2008, with xanthan gum being the only significant bacterial EPS, which accounted for 6% of the total market value [3].

For new polymers to arise as commodity products in large markets, such as the hydrocolloids, it is crucial to lower their production costs [12]. Approaches for the reduction of production costs might involve using cheaper substrates, improving product yield by optimizing fermentation conditions, or developing higher yielding strains (e.g. by mutagenesis or genetic manipulation), and optimizing downstream processing [2,13]. Nevertheless, the greatest potential of bacterial EPSs is related to their use in high-value market niches, such as cosmetics, pharmaceuticals and biomedicine, in which traditional polymers fail to comply with the required degree of purity or lack some specific functional properties. Such markets will provide opportunities for the development of up-and-coming bacterial EPSs; providing that they have unique desirable physicochemical properties. In such high-value applications, product quality wholly surpasses cost production and product yield issues. In particular, downstream processing requirements are highly demanding in these application fields. Separation processes become especially challenging when polymers are considered for medical applications because a high-purity product is envisaged.

This article reviews EPS production by bacteria, including recent advances in the elucidation of the biosynthetic pathways involved and the fermentative bioprocesses developed, as well as the main constraints to full commercialization of these biopolymers. The techniques used to study and characterize bacterial EPS physicochemical properties are described, followed by their correlation with actual and potential applications.

Processes for EPS biosynthesis

Biosynthetic pathways

Most bacterial EPSs are synthesized intracellularly and exported to the extracellular environment as macromolecules [2,6]. There are a few known exceptions (e.g. levans and dextrans) whose synthesis and polymerization occur outside the cells by the action of secreted enzymes that convert the substrate into the polymer in the extracellular environment [2].

Bacterial biosynthetic pathways comprise substrate uptake, central metabolite pathway and polysaccharide

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