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Review

Structure, functionality and applications of debranched starch: A review

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ABSTRACT

Background: Starchy products have been widely used in the food, paper, textile, plastic, cosmetics, adhesives, and pharmaceutical industries. To meet specific requirements of their applications, different modification techniques, such as physical, chemical, and enzymatic methods, have been employed to enhance or inhibit their inherent properties or to endow specific properties of starch.
Scope and approach: Debranched starch (DBS), modified by pullulanase or isoamylase, acquires remarkable new properties and functionality, as a result of the generation of linear short chains released from amylopectin. In this review, the structure, functionality, and applications of DBS are discussed. The effects of debranching on the granule morphology, molecular composition, crystalline and helical structures are considered. Functionality, like gelatinization, hydrogel formation, and *in vitro* digestibility, is discussed. This paper also highlights promising applications of DBS, e.g., as tableting excipients, fat replacer, and as coating materials for ready-to-eat cereals.
Key findings and conclusions: DBS is an excellent functional material, with promising applications attributed to its gel forming and recrystallization properties. Linear short chains released from amylopectin during debranching endow DBS with increased mobility and facilitate molecule alignment and aggregation, leading to the formation of gel networks and crystalline structures. A combination of gel network and crystalline structure controls the formation of SDS/RS. The applications of DBS as tableting excipients, fat replacer, and coating materials for ready-to-eat cereals are mainly attributed to its gelling properties. Molecular inclusion drives the formation of inclusion complexes, self-assembling spheroids, and DBS-based nanoparticles.

1. Introduction

Starch, the second largest biomass on earth, is a natural, abundant, cheap, available, renewable, and biodegradable polymer (Fig. 1) (Doi, Clark, Macquarrie, & Milkowski, 2002; Le Corre, Bras, & Dufresne, 2010). Starch products have been widely used in many industries, such as food, paper, textile, plastic, cosmetics, adhesives, and pharmaceutical industries (Du, Zang, & Du, 2011; Meshram, Patil, Mhaske, & Thorat, 2009; Ochubiojo & Rodrigues, 2012). It was described as a wholesome food as far back as the first century A.D. by Celsus, a Greek physician (Mason, 2009). Starch is a major component of foods as well as a raw material in industrial production (Oates, 1997). Starchy foods are the major source of carbohydrates in the human diet and constitute ~80% of the global average calorie intake (Barsby, Donald, & Frazier, 2001).

Native starch, extracted from plants, cannot always withstand the extreme processing conditions, e.g., high temperature, freeze-thaw cycles, strong acid and alkali treatments, and high shear rates (Hermansson & Svegmark, 1996; Wang & Copeland, 2015). Therefore, its use is limited and it unacceptable in many industrial applications. Thus, different techniques are used to modify the native starch to enhance or inhibit its inherent properties or to endue its specific properties to meet the requirements of industrial applications. Common modification modes include physical (e.g., high pressure autoclave, osmotic pressure treatment, extrusion), chemical (e.g., oxidation, esterification, etherification, hydroxypropylation), and enzymatic modifications (e.g., dextrin) (da Rosa

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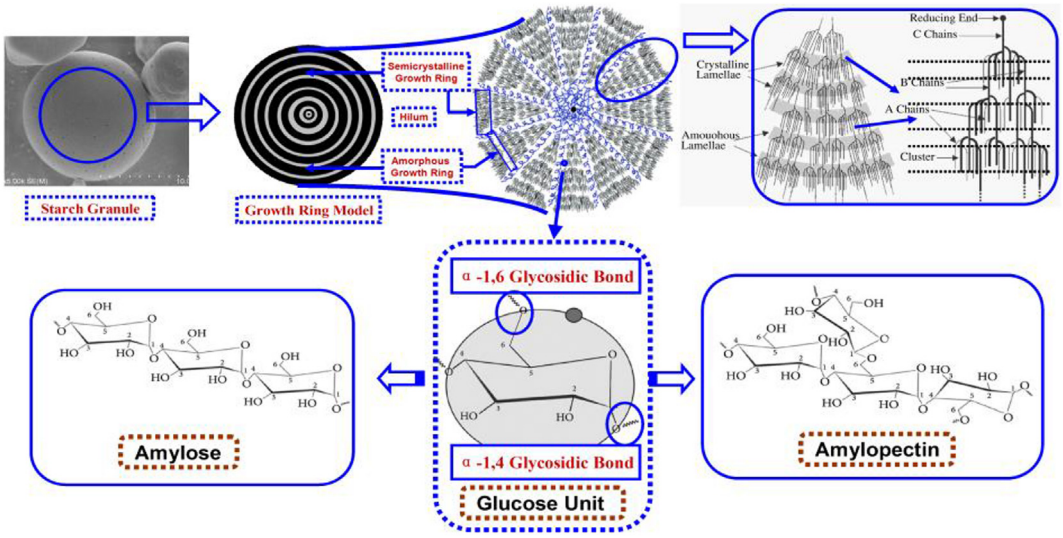

Fig. 1. Schematic diagram of starch structure.

Zavareze & Dias, 2011; Hong, Liu, & Gu, 2016; Miyazaki, Van Hung, Maeda, & Morita, 2006).

Debranched starch (DBS), a type of enzymatically modified starch, is modified by debranching enzymes (isoamylase or pullulanase) that selectively hydrolyze 1,6-α-D-glycosidic bonds, leading to the formation of linear short chain molecules of low molecular weights. The modification of starch molecules results in remarkable new properties and functionalities of these molecules, meeting the requirements of specific applications. Over the last several decades, DBS has been the focus of increasing research, aiming to reveal and establish the relationship between DBS structure, physicochemical properties, and functionality. The digestibility of DBS, e.g., generation of slowly digestible starch (SDS) or formation of resistant starch (RS), has been well studied (Miao, Jiang, & Zhang, 2009; Shi, Chen, Yu, & Gao, 2013; -Shi, Cui, Birkett, & Thatcher, 2005). Furthermore, DBS can be used as a fat/protein replacer in food products and control drug release as a tableting excipient in the pharmaceutical industry (Chiu & Mason, 1998; Chiu & N.J., 1990; Wai-Chiu & Kasica, 1995). Recently, other potential applications of DBS have been investigated. The inclusion complex, self-assembling spheroids, starch nanoparticles, and nanocrystals based on DBS have been prepared and studied. These studies can stimulate further research and expand the applications of DBS as an emulsion stabilizer, drug/nutraceutical carrier, and so on.

Based on the current knowledge, DBS is an important modified starch that possesses remarkable potential applications in functional foods. To the best of our knowledge, no review on this subject is currently available. We believe that it is worthwhile to review the recent advances in our knowledge of the structure, physicochemical properties, and functionality of DBS, and to discuss the potential applications of DBS.

2. Preparation and recrystallization of DBS

DBS are normally prepared by treatment of starch paste with pullulanase or isoamylase generating linear short chains and recrystallization under different storage conditions. The desired degree of debranching usually judged by the content of reducing sugar or the molecular weight distribution of starch components. The DBS properties were influenced by the processes during preparation and recrystallization, such as selection of debranching enzymes, storage temperature and time.

Debranching enzymes, including pullulanase (EC 3.2.1.41) and isoamylase (EC 3.2.1.68), can selectively hydrolyze the α-1,6-D-glucosidic bonds at branching points and prepare DBS (Kim, Nashiru, & Ko, 1996; Nakamura, Watanabe, & Horikoshi, 1975; Nigam & Singh, 1995). DBS components can be influenced by the selection of debranching enzyme. Generally, pullulanase can hydrolyze the α-1,6-D-glucosidic bonds in pullulan, limit dextrins and branched oligosaccharide leading to the formation of maltose, maltotriose and linear oligosaccharide (Chiu & Mason, 1998; Doman-Pytka & Bardowski, 2004; Kim et al., 1996; Ohba & Ueda, 1980; Saha & Zeikus, 1989). By contrast, isoamylase is unable to clave D-glusyl stubs in branched saccharides and requires a minimum of three D-glucose residues in the B- or C-chain of starch (Kainuma, Kobayashi, & Haraada, 1978). Thus, DBSs from pullulanase hydrolysis contain more linear oligosaccharide, and a more complete hydrolysis of α-1,6-D-glucosidic bonds in starch and a higher yield can be obtained compared to those from isoamylase.

After the debranching hydrolysis, the mixture was usually stored at a temperature to induce the recrystallization of DBS. Cai stored the completely debranched waxy maize starch at 4, 25, or 50 °C for 24 h (Cai & Shi, 2013). He found DBS samples recrystallized at a low temperature (4 or 25 °C) had a B-type crystalline structure, a large size (5–10 μm), a lower melting temperature (70–110 °C), and a higher digestibility. By contrast, samples stored at 50 °C had an A-type crystalline structure and a lower melting temperature (100–140 °C) (Cai & Shi, 2013). In some researches, DBS solution was stored at a cycled temperature rather than an isothermal temperature to promote the crystal formation. During temperature-cycled treatment (TCT), samples were stored at different temperatures for cycled interval between the nucleation and propagation temperature. TCT mainly affects the recrystallization process, providing a favorable environment for the nucleation and propagation of crystallites (Zeng et al., 2015). Temperature close to the glass transition temperature can induce the nucleation of crystallites, while a higher temperature up to the melting temperature favors the propagation of crystallites (Baik, Kim, Cheon, Ha, & Kim, 1997; Silverio, Fredriksson, Andersson, Eliasson, & Åman, 2000). Thus, TCT between the nucleation and propagation temperature can accelerate the rate of recrystallization and promote the growth of crystalline regions and the perfection of crystallites (Durrani & Donald, 1995; Silverio et al., 2000; Slade,