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Synthesis and characterization of octenyl succinic anhydride modified starches for food applications. A review of recent literature

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ABSTRACT

Starch is esterified with octenyl succinic anhydride (OSA) to yield a hydrocolloid with amphiphilic properties, octenyl succinylated starch (OS-starch). OS-starch finds wide application in the food industry mainly as emulsifier, encapsulating agent and fat replacer. As a result of the new hydrophobic groups introduced and concomitant changes produced in the granules structure, OSA modified starches typically show reduced gelatinization temperature and enthalpy, lower digestibility, higher swelling power, and increased paste viscosity and paste clarity.

Traditionally, OS-starches have been synthesized in aqueous slurry under mild alkaline conditions, resulting in reaction taking place mainly on the surface and amorphous regions of starch granules. However, in the last years, alternative methodologies and modifications to the conventional method (e.g. *in situ* mechanical and ultrasonic assistance, and hydrothermal, mechanical, enzymatic and chemical pretreatments of starch) have received much attention; aiming to increase reaction efficiency, reduce reaction time, attain a more even distribution of ester groups within the granules, and/or produce OS-starches with enhanced or specific properties.

Considering the importance of octenyl succinylation methodology on the resulting OS-starch structure, functional properties, and uses derived from them, in the current review OS-starch production routes, products properties and main food applications described in the literature within the last five years have been summarized.

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1. Introduction

Starch is a natural polysaccharide that serves as energy storage in plants. It is one of the most abundant bio renewable materials on earth along with cellulose, as it is found in leaves, seeds, roots, stems, fruits, grains and tubers of most vegetal species. Many crops that are extensively grown for human consumption all over the world such as wheat, rice, maize, barley, rye, beans, sorghum, cassava, potatoes, bananas, are sources of starch; hence this polymer provides an important part of the calories consumed by humans. Starch is used in the food industry for thickening, texturizing, gelling, stabilizing and replacing more costly ingredients. Besides food uses, starch also finds applications in other sectors, being a raw material for the paper and textile industries and for plastics or polymer compositions, among others.

Starch is stored in plants in the form of water-insoluble particles or granules with semi-crystalline properties. Within the granules amylose and amylopectin molecules, the two polymers of D-glucose that are the main components of starch, are both inter and intra molecularly linked by hydrogen bonds and hydrophobic bonds which hold the molecules together, giving a water-insoluble granule. The arrangement of the molecules in the granules results in different physical and morphological properties found in starches from different sources (Robyt, 2008). The internal order of the starch granules is partially lost when the material is heated in the presence of water, producing swelling and gelatinization which occurs at different temperatures depending on the type of starch (Thomas & Atwell, 1999).

Unfortunately, native starch is unsuitable for most industrial applications in foods due to inadequate process tolerance and little shelf stability. Therefore, the industry has developed techniques to improve the properties of starch allowing it to maintain appearance and texture during food processing, and expanding its range of utility. Among them, chemical modification of starch mostly involves esterification, etherification or oxidation of the available hydroxyl groups on the glucose monomers.

Starch esterification with octenyl succinic anhydride (OSA) involves the partial substitution of hydroxyl groups with hydrophobic substituents, thus giving the starch an amphiphilic character and interfacial properties. The product obtained from OSA modification is the octenyl succinylated starch (OS-starch) (Fig. 1) which is mainly used as emulsifier and encapsulating agent (Mason, 2009). The physicochemical properties of OS-starches depend on the properties of the starch used as raw material, the processing conditions used during the modification (and also the processing conditions used before and after modification in case pretreatments/post-treatments are applied), the extent of derivatization, and the distribution of the introduced groups within the starch granules. Therefore, a variety of OS-starches can be synthesized with different properties and useful for a wide range of applications. When OS-starches are produced for the purpose of application in foods, the amount of OSA is limited to 3% (w/w starch basis) since this is the maximum allowed by the Food and Drug Administration of the United States (FDA, 2016).

Generally, OS-starches are synthesized by esterification with OSA in aqueous slurry in slightly basic conditions. Using this methodology, several works have been published in the last years; in some of which the reaction conditions set were optimized to maximize reaction efficiency (Bhosale & Singhal, 2006; Jeon, Viswanathan, & Gross, 1999; Liu et al., 2008; Song, He, Ruan, & Chen, 2006; Xu et al., 2012). The influence of the experimental parameters using this methodology have been previously reviewed by Sweedman and collaborators, and also by Ačkar and collaborators (Sweedman, Tizzotti, Schäfer, & Gilbert, 2013; Ačkar et al., 2015). However, the low solubility of OSA in water has often resulted in poor reaction efficiency and uneven distribution of OS groups (Chen, He, & Huang, 2014; Chen, Huang, Fu, & Luo, 2014; Huang et al., 2010; Shogren, Viswanathan, Felker, & Gross, 2000). In this context, a variety of modifications to the conventional method have been investigated in the last years, searching for shorter times of reaction, higher degree of substitution, higher reaction efficiency, a more homogeneous distribution of the OS groups within the starch granules, and/or enhanced functional properties. The modifications proposed have mainly included *in situ* mechanical and ultrasonic assistance, and hydrothermal, mechanical, enzymatic and chemical pretreatments of starch (Chen, He, et al., 2014; Chen, Huang, et al., 2014; Jiranuntakul, Puncha-arnon, & Uttapap, 2014; Klaochanpong, Puncha-arnon, Uttapap, Puttanlek, & Rungsardthong, 2017; Sweedman, Hasjim, Schäfer, & Gilbert, 2014; Wang, He, Fu, Luo, & Huang, 2015). Enzymatic and chemical post-treatments of conventionally obtained OS-starch have been studied as well (Xu, Huang, Fu, & Jane, 2015; Sweedman, Schäfer, & Gilbert, 2014; Hong, Li, Gu, Wang, & Pang, 2017). On the other hand, methods for OS-starch production with a different chemical basis have also been developed, such as esterification of starch with OSA in the presence of acetic acid (Shogren, 2003), esterification in pyridine (Viswanathan, 1999), and microwave assisted esterification (Biswas, Shogren, Kim, & Willett, 2006; Rivero, Balsamo, & Müller, 2009). Irrespectively of the synthesis methodology selected, a number of characterization techniques have been frequently used to describe physicochemical, morphological and functional properties of the OS-starches synthesized, thus allowing the evaluation and prediction of their behavior in different applications.

The present review is focused on the synthesis pathways, characterization techniques and applications of OS-starches in the food industry that have been reported in the literature of the last five years. The traditional synthesis pathway, variations introduced to it (with their advantages and disadvantages), alternative synthesis methods, characterization techniques usually used to assert OS-starch properties obtained from all synthesis pathways, variation of OS-starches properties associated with their synthesis