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
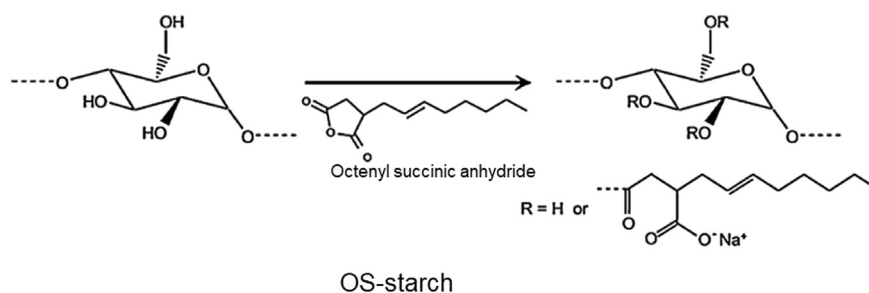
Fig. 1. Structure of starch modified with 2-Octen-1-yl succinic anhydride (OS-starch) (Adapted from Sweedman, Tizzotti, et al. (2013)).

pathway, and some applications of OS-starch in the food industry are all described.

2. Synthesis of OS-starch

2.1. Conventional methodology: aqueous slurry under mild alkaline conditions

The esterification of starch with the aim of introducing hydrophobic groups to produce derivatives with emulsifying properties was originally patented by Caldwell and Wurzburg (1953). The authors described the reaction of a polysaccharide (such as starch, dextrins and cellulose) to be esterified with a substituted cyclic dicarboxylic acid anhydride. Three possible routes were described, i.e. the aqueous method, consisting of the reaction in aqueous slurry with pH between 7 and 11; the dry method, which consists of the reaction without water between the acid and the starch previously alkali-treated; and the organic suspension method, which uses an organic liquid instead of water as the dispersion medium. Since this invention dating from 1953 was published, many authors have investigated the synthesis of OS-starches.

Currently, the most widely used route for synthesizing OS-starch consists of suspending the starch in its granular form in distilled water and adding OSA dropwise while stirring and maintaining the pH around 8 with NaOH. The reaction is usually carried out at temperature between 25 and 35 °C, and it is continued until the pH of the slurry stabilizes, or it might be ended by lowering the pH with HCl. This pathway for starch esterification with OSA has been investigated extensively and reaction conditions have been optimized. Reaction conditions values typically used for starch modification with OSA in aqueous slurry under mild alkaline conditions are exemplified in Table 1. After the reaction is ended, the mixture is filtrated or centrifuged and the product is washed with water and acetone or ethanol, and finally dried and ground. The extent of the modification is expressed by the degree of substitution (DS), defined as the average number of substituents per anhydroglucose unit. This value is mostly determined by titration (Bello-Flores, Nuñez-Santiago, Martín-Gonzalez, BeMiller, & Bello-Pérez, 2014; Sharma, Singh, Yadav, Arora, & Vishwakarma, 2016; Wang, Tang, Fu, Huang, & Zhang, 2016; Zhang, Mei, Chen, & Chen, 2017; Zheng et al., 2017); although, some authors have employed ^{1}H nuclear magnetic resonance (NMR) spectroscopy to that end (Simsek, Ovando-Martinez, Marefati, Sjöö, & Rayner, 2015; Sweedman, Hasjim, Tizzotti, Schäfer, & Gilbert, 2013; Whitney, Reuhs, Ovando Martinez, & Simsek, 2016).

Starch modified with OSA (maximum 3% w/w starch basis) is allowed by the FDA as a food ingredient. When starch is modified with 3% of OSA, the theoretical degree of substitution is 0.0231, provided all the OSA reacts with the starch. However, this theoretical DS is not easily reached; and most authors have reported lower values. The proportion of the substitution achieved is expressed as the reaction efficiency (RE), which is the result of dividing the DS obtained by the theoretical DS.

As shown in Table 1, the DS achieved by esterification of starch with OSA using the conventional aqueous slurry method depends on the botanical source of the starch used and the reaction conditions chosen; as illustrated by different authors which in the last few years have assayed the effects of starch source, reaction time and OSA percentage (Simsek et al., 2015; Sharma et al., 2016; Sweedman, Hasjim, et al., 2013; Zhang et al., 2017). Regarding the effect of OSA concentration on the DS, the degree of substitution of starch generally increases with the percentage of OSA added,

Table 1
Reaction conditions values most used in the recent literature for starch esterification with OSA in aqueous slurry under mild alkaline conditions. DS values reported corresponding to starches of different botanical origin (examples from the last five years).

Botanical origin of starch	Starch (% w/w)	pH	T (°C)	OSA (%w/w, starch basis)	Time (h)	DS	Reference
Cassava	30	8.5	35	1.5	3	0.008	(B. Zhang et al., 2017)
				3		0.018	
				6		0.029	
				9		0.035	
	30	8.5	25	3	6	0.018	(Simsek et al., 2015)
Corn	30	8.5	25	3	6	0.022	
Wheat						0.018	
Potato	35	8.5	35	3	2	0.017	(Wang, Tang, et al., 2016)
Unripe plantain	30	8.5	25	3	6	0.011	(Bello-Flores et al., 2014)
				15		0.038	
Pearl millet	35	8	35	3	2	0.018	(Sharma et al., 2016)
					3	0.021	
					4	0.021	
					5	0.022	
Ginkgo	30	8.5	35	1.5	8	0.006	(Zheng et al., 2017)
				3		0.017	

probably due to a greater availability of the OSA molecules near the starch molecules during the reaction. However, the increase in the DS is not usually proportional to the increment in the reagent concentration, leading to reduced RE.

2.2. Variations introduced to the traditional synthesis methodology

Given the low solubility of OSA in water in the conventional synthesis method, the reaction medium contains OSA droplets which have limited access to the interior of semi-crystalline starch granules. Therefore, the reaction of OSA and starch by the conventional aqueous phase methodology is believed to occur mainly on the granules' surface, which has often resulted in poor reaction efficiency and uneven distribution of OS groups. In fact, much higher octenyl succinate groups concentration on the granules surface has been reported compared to the corresponding bulk values (Chen, He, et al., 2014; Chen, Huang, et al., 2014; Huang et al., 2010; Shogren, Viswanathan, Felker, Gross, & a, 2000). In this context, in the last few years, much effort has been dedicated to improve the traditional method of synthesis of OS-starch, mainly focusing on reaching higher DS and RE values, reducing reaction time, altering the distribution of ester groups, and/or producing OS-starch with enhanced or specific properties. Several contributions have focused their objectives on reaching the inner parts of the starch granules with the substitution, since a better distribution of the OS groups within the granules is believed to yield better emulsifying properties (Wang, He, Fu, Huang, & Zhang, 2016). Modifications to the traditional synthesis methodology proposed within the last five years have mainly included in situ mechanical and ultrasonic treatments, and hydrothermal, chemical and enzymatic pretreatments (Table 2).

Mechanical treatment (e.g. ball milling) of starch granules prior to OSA modification has been previously reported as a mean to make starch more amenable to modification by decreasing the granules crystallinity (Zhang, Zhao, & Xiong, 2010). By increasing mechanical activation time up to 10 h, the crystallinity of the starch was progressively and significantly reduced, and DS and RE values were concomitantly increased (57% increase in DS and RE incremented from 54.22 to 85.16%). The behavior was associated with an easier dispersion of starch in water and a higher number of hydroxyl groups available for nucleophilic attack of the anhydride moieties.

In recent years, in situ mechanical treatment was proposed. Keeping all reaction conditions constant, Wang et al. (2015) reported an 11% increment of DS and RE increasing from 78.45 to 86.86% when high-speed shear treatment (10,000 rpm) -instead of mechanical stirring (500 rpm) -, was used during the reaction. Authors claimed that the cavitation effect of the treatment increased the area of starch by destroying the granular surface, and also reduced the drop size of the OSA, facilitating its penetration inside the granules. The high speed shear treatment resulted in the rupture of the starch granules as seen by scanning electron microscopy (SEM) (Wang et al., 2015). A more homogenous distribution of OS groups was also observed (see section 3.2. for details).

With the same aim, Chen, Huang, et al. (2014) prepared OS-starch with ultrasonic-assisted treatment during reaction. Authors found that 600 W was the optimum ultrasonic power to be used to maximize DS, with DS values 15% higher than the control, and RE increasing from 75.78 to 87.63%. Besides, when reaction was assisted by ultrasonic power, reaction time was drastically reduced from 6.5 to 1.5 h. Again, results were attributed to reduction and homogenization of OSA droplets size by the generated forces, and to cavitation effects, which might have increased the surface area by destruction of the granules surface and creation of pores and grooves. Ultrasound assistance was also reported to moderately reduce the uneven distribution of OS groups, as a consequence of smaller OSA droplets which may have reached the inner regions of the starch granules via the generated grooves.

With a different approach devoted to enhancing granules accessibility, Chen, He, et al. (2014) performed a hydrothermal pretreatment on cornstarch before esterifying it with OSA. The pretreatment implied contacting the starch with water at different temperatures (48–62 °C) with stirring during 3 h. The authors reported increased DS and RE values which reached a maximum when the pretreatment temperature was set at 60 °C (16% increase in DS, and RE increased from 72.20 to 81.76%); and a more even distribution of OS groups. Authors associated the observed improvements with the increased swelling power and porosity of the pretreated granules whose increased accessibility must have made migration of OSA droplets inside the starch granules easier.

Jiranuntakul et al. (2014) also performed a hydrothermal treatment to enhance octenyl succinylation of starch. The results obtained indicated that octenyl succinylated heat–moisture treated starch (moisture content of 25%, 100 °C, 1–5 h) showed higher DS

Table 2
Variations introduced to conventional synthesis methodology of OS-starches (data from starch of different botanical sources). Relative increase in DS values (at optimum conditions) with respect to control (traditional method).

Variation introduced to the traditional method	DS (3% OSA)			RE (%)[a]		Other advantages/disadvantages	Reference
	Control	Modified method	Increment	Control	Modified method		
High-speed shear (corn)	0.0182	0.0202	11%	78.45	86.86	Better OSA penetration/Plausible granule rupture	(Wang et al., 2015)
Ultrasonic Power (corn)	0.0176	0.0203	15%	75.78	87.63	Lower time of reaction, better OSA penetration	(Chen, Huang, et al., 2014)
Hydrothermal pretreatment (35% starch suspension, 60 °C, 3 h) (corn)	0.0164	0.0190	16%	72.20	81.76	Better OSA penetration	(Chen, He, et al., 2014)
Heat-moisture pretreatment (25% moisture, 100 °C, 5 h) (cassava)	0.0154	0.0181	18%	66.49	78.09	Strengthened granules	(Jiranuntakul et al., 2014)
Debranching (pullulanase) pretreatment (waxy rice)	0.0130	0.0202	55%	56.1	87.4	/Lower recovery yield	(Klaochanpong et al., 2017)
Chemical pretreatment (hydrolysis with HCl)[b] (high amylose maize)	0.0131	0.0152	16%	56.5	65.5	Better emulsifying properties[b]	Sweedman et al. (2014a,b)

[a] RE values correspond to data reported by authors.
[b] Results varying with the botanical source of the starch.

and RE than the non-pretreated counterpart (18% increase in DS, and RE increased from 66.49 to 78.09% for the optimum condition which implied a 5 h-heat–moisture pretreatment of starch granules). The results were attributed to reduction/alteration of starch crystallinity and generation of channels, voids and hollows inside the granules, all facilitating the entry and reaction of OSA inside the granules.

Generation of channels inside the granules by use of enzymatic pretreatment has also been proposed. Huang et al. (2010) studied the effects of pretreating granular cornstarch with an α-amylase prior to OSA modification. α-amylase treatment is known to induce pore formation in the starch granules, thus increasing their surface area and promoting chemical reagent access to their inner region. However, reported DS values of pretreated starch were significantly lower than non-pretreated controls. Results were explained in terms of a more ready access of α-amylases to the amorphous regions of starch, whose preponderant removal resulted in granules less prone to reaction with OSA. On the other hand, although the DS values reached were lower upon α-amylase pretreatment, an increased distribution of OSA groups in the interior of enzyme pretreated starch granules was observed (conclusions derived from X-ray photoelectron spectroscopy (XPS) data), suggesting improved access of OSA droplets to the inner part of starch granules through the produced pores.

With the same approach, in the contribution of Bai and Shi (2011) authors pretreated waxy maize starch granules with α-amylases and glucoamylases, aiming to increase the granules surface area by creating numerous pinholes from the surface to the interior. Increased DS values were only observed at OSA concentrations ≥9%, as a result of a higher surface area and more OSA diffusion inside the granules (Bai & Shi, 2011). However, the corresponding RE was relatively low. Authors concluded that only a limited substitution is attainable from OSA modification of granular starch via the aqueous slurry reaction methodology, and highlighted the high DS and RE attained when water-soluble maltodextrin was used and all the hydroxyls along the oligomers were available for reaction.

In this context, higher accessibility of OSA to hydroxyl groups of starch by allowing the acylant to react directly with dispersed/hydrolyzed starch molecules has been recently proposed. With this aim, Klaochanpong et al. (2017) compared the efficiency of OSA esterification of waxy starches in granular and debranched forms, with the latter implying complete gelatinization of starch followed by pullulanase treatment. Authors observed an increase in the DS attained when debranching the starch by hydrolysis with pullulanase before OSA modification, which they attributed to reaction occurring more efficiently on dispersed starch chains compared to chains packed in the starch granules, due to the difficulty of OSA in reaching the crystalline regions of the granules. However, recovery of dispersed OS-starch molecules by complexation with ethanol for precipitation was not complete, and an important portion of the debranched starch could not be recovered after OSA modification resulting in lower yields when compared with granular starch.

In reference to acid hydrolysis pretreatment of starch, Sweedman et al. (2014a,b) hydrolyzed different starch sources with HCl prior to esterification with OSA to study how the structure of the OS-starch (i.e. molecular size, degree of branching and amylose content) affects its properties, mainly those related to emulsification (See details in section 5.1). The acid hydrolysis negatively affected the OSA substitution of waxy and normal starches. Conversely, for starch with high amylose content, the DS attained was increased upon acid hydrolysis pretreatment.

2.3. Alternative methods of synthesis of OS-starch

Apart from the traditional pathway for the synthesis of OS-starches in aqueous slurry under mild alkaline conditions, and the corresponding modifications reported in the last years described in section 2.2, alternative methods for OS-starch production have been proposed. Some examples are: esterification of starch with OSA without using water in the presence of acetic acid under high temperature and pressure (Shogren, 2003); esterification in pyridine at 110 °C (Viswanathan, 1999), and microwave assisted esterification of starch pre-activated at pH 8.5 (Biswas et al., 2006; Rivero et al., 2009). For more details on these alternative methods readers can refer to the previous review of Sweedman, Tizzotti, et al. (2013). More recently, other alternative methods have been proposed and some examples are shown in Table 3.

Sandhu, Sharma, and Kaur (2015) esterified potato starch with OSA in aqueous slurry using a starch concentration higher than usual (100 g starch per 120 mL of OSA-water solution). Also different from the conventional method, authors assayed the effect of pH (not only conventional alkaline pH 8 medium, but also pH 6 and pH 4 were assayed) on DS and RE. After 1 h of reaction, the starch was dried without washing to a moisture content ≤5%, and finally heated in an electric oven at 130 °C for 2 h. The authors reported maximum DS for the reaction performed at acidic pH. However, at this condition, extensive changes on granules surfaces and loss of definition of their edges were observed by SEM, especially in small granules.

In recent years, dry milling methods have also received much attention. Following this approach, Chen, Yin, et al. (2014) modified waxy rice starch with OSA using a dry media mill in which NaOH (0–1.1%), OSA (0–9%) and starch were mixed without water (except for the water present in the NaOH solution (4%)). The mixture was mechanically activated in the dry media mill at room temperature and 450 rpm during different time intervals varying from 0 to 70 h. The authors reported optimum NaOH and OSA concentration values (0.9% and 4%, respectively), and DS and RE values increasing with the reaction time. Results were associated with mechanical

Table 3
Alternative pathways for the modification of starch with OSA found in the recent literature.

	Advantages	Other outcomes	Reference
Aqueous medium, at pH 4 + dry heating	Higher DS	Granule damage	(Sandhu et al., 2015)
Dry media milling, NaOH	Simple technology, low cost, and environmental protection	Granule damage Loss of crystallinity	(Chen, Yin, Chen, Xiong, & Zhao, 2014)
Dry media milling, Na$_2$CO$_3$	Simple technology, low cost, and environmental protection Short time	Granule damage Loss of crystallinity	(Hu et al., 2016)
Ionic liquids (IL) media and lipase as catalyst	IL are lowly toxic, nonflammable and recyclable. Green catalyst.	Destruction of granule structure, loss of crystallinity, thermal stability reduced, lipase inactivation possible	(Li et al., 2016)

forces generated by dry media milling which diminished the granule size and thus increased their surface area. Besides, destruction of the crystalline structure of starch resulted in the exposure of reactive sites imbedded in the crystalline region of starch granules, thus offering more sites for esterification (Chen, Yin, et al., 2014).

OS-starch synthesis by dry milling was also reported recently by Hu et al. (2016). In this case, cassava starch, OSA (8%) and sodium carbonate were reacted in a customized ball mill at 60 °C for time intervals varying from 30 to 120 min. The authors achieved high DS (0.0295) in only 30 min and a maximum DS (0.0397) after 90 min of reaction. Again, granule damage/fracture was observed and the crystallinity of the starch was reduced with milling time due to the progressive destruction of stable hydrogen bonds between the starch molecules by intense ball milling (Huang, Lu, Li, & Tong, 2007; Zhang et al., 2013). These changes induced by mechanical activation during reaction can increase the accessibility and reactivity of starch, while contact between starch and reagents in solid-state condition is also improved. The advantages of the dry milling method reported in both contributions (Chen, Yin, et al., 2014; Hu et al., 2016) are low cost, simple technology and environmental protection due to operation in absence of added solvents.

Another method reported in recent years for the synthesis of OS-starch involves the use of enzymatic catalysts in ionic liquids media. For example, in the contribution of Li, Zhang, and Tian (2016), authors reported a two-step method in which waxy maize starch was initially dissolved in 1-butyl-3-methylimidazolium chlorine to destroy the semi-crystalline structure and increase granules surface area, and then esterified with OSA in 1-octyl-3-methylimidazolium nitrate using Novozyme 435 (immobilized lipase from *Candida antarctica*) as catalyst. The concentration of starch, lipase load, reaction time and temperature were all optimized, and the optimum values reported were 5%, 1%, 3 h and 50 °C, respectively. As expected, the starch granules were disrupted by the pretreatment with [BMIm]Cl, they appeared as clusters in the images obtained by scanning electron microscopy (SEM), and they showed a completely amorphous X-ray diffraction patterns. However, the maximum DS achieved was 0.0130, much lower than the DS achieved by the conventional octenyl succinylation protocole, probably due to the low activity of the lipase even if the ionic liquid used as reaction medium was designed to be more favorable to enzymatic activity.

3. Characterization of OS-starch

3.1. Confirmation of OSA substitution and determination of its extent

After OSA modification starches are usually analyzed with the aim of confirming that the substitution actually took place and determining its extent. The variable generally employed to this end is the degree of substitution (DS), defined as the average number of OS groups introduced per anhydroglucose unit of starch. Three techniques are mainly employed in the literature to confirm and quantify the modification of starches with OSA. These are titration, Fourier transform infrared spectroscopy (FT-IR) and NMR spectroscopy.

Titration is the method most employed to determine the DS of OS-starches (Bello-Flores et al., 2014; Sharma et al., 2016; Zhang et al., 2017; Zheng et al., 2017), since it is simple, reliable and does not require special equipment. Two different procedures have been reported in the literature. The first of them relays on the saponification of the OS groups with a NaOH solution, and the subsequent neutralization of the excess alkali with HCl. However, in recent years this method has seldom been applied to determine de

DS of OS-starch. More frequently, titration to assert DS implies dispersion of OS-starch in a hydrochloric acid/isopropanol solution, and the subsequent filtration and washing of the sample to remove the Cl^- groups. The starch is then re-dispersed in distilled water, cooked in a boiling water bath for 20 min and finally neutralized with NaOH solution. In both titration methods a sample of native starch is also titrated and used as blank, which together with the big quantity of sample usually required (1 g or more), are the two main disadvantages of titration methods.

On the other hand, FT-IR is considered an ideal technique for determining the functional groups and chemical structure of polymers. Comparison of the FT-IR spectra of native and OS-starches, generally evidences the presence of a new absorption band at $1725\ cm^{-1}$ in OS-starches which is attributed to the stretching vibration of ester carbonyl group introduced (C=O). Another absorption band at $1570\ cm^{-1}$ is also generally detected and ascribed to the asymmetric stretching vibration of carboxylate $RCOO^-$ (Fig. 2a). The presence of these two peaks confirms the introduction of the OS groups. Besides, some authors have observed the increase of their intensity with DS (Chen, Huang, et al., 2014; Hu et al., 2016; Li et al., 2016; Simsek et al., 2015; Zhang et al., 2017; Zheng et al., 2017).

Although less frequently, ^1H NMR has also been used to confirm OSA modification and determine DS (Bai, Kaufman, Wilson, & Shi, 2014; Simsek et al., 2015; Sweedman, Hasjim, et al., 2013; Whitney et al., 2016). With this purpose OS-starch samples have been dissolved in D_2O (Simsek et al., 2015; Whitney et al., 2016) or in DMSO-d_6 containing LiBr (Sweedman, Hasjim, et al., 2013; Wang, He, et al., 2016). Bai and Shi (2011) performed ^1H NMR to calculate the DS of α-amylase hydrolyzed OS-starch samples and they compared the results with the values obtained by titration, validating the method. The ^1H NMR spectra of OS-starches usually show new peaks between 0.8 and 2.7 ppm, resulting from the groups introduced (see Fig. 2b). The peak at 0.8–0.9 ppm corresponds to the methyl protons of OS groups, and its integral has been often used to quantify DS (Bai & Shi, 2011; Simsek et al., 2015; Tizzotti, Sweedman, Tang, Schaefer, & Gilbert, 2011; Whitney et al., 2016).

3.2. Determination of OS groups distribution within the starch granules

Besides the extent of the modification achieved, in the last years much attention has been paid to determine where the OSA esterification reaction occurs within the starch granules. The techniques mainly used to asses this issue have been XRD, acid hydrolysis, X-ray photoelectron spectroscopy (XPS), and confocal laser scanning microscopy (CLSM) using Methylene Blue (MB^+) as a fluorescence dye to highlight the $-COO^-$ of OS groups.

The crystalline structure of native starch is usually studied by XRD, exhibiting three types of pattern: A-type for cereal grains, B-type for tubers and C-type for legume starches, which is actually a mixture of both A and B patterns. The degree of crystallinity of starch as measured by XRD is generally between 25 and 48%, depending on the plant source of the starch (Buléon, Colonna, Planchot, & Ball, 1998). In general, when starch is modified in aqueous medium in alkaline conditions, the crystalline pattern is maintained and little or no change is observed in the percentage of crystallinity of starch granules after OSA modification. Therefore, it is generally accepted that by this route the OSA substitution takes place mainly in the amorphous regions of the starch (Shogren et al., 2000; Zhang et al., 2017; Zheng et al., 2017). Fig. 3 shows the X-ray diffraction pattern and degree of crystallinity of starches before and after esterification with OSA by traditional methodology (a, c), and by alternative methods (b, dry milling; d, ionic liquids) in which
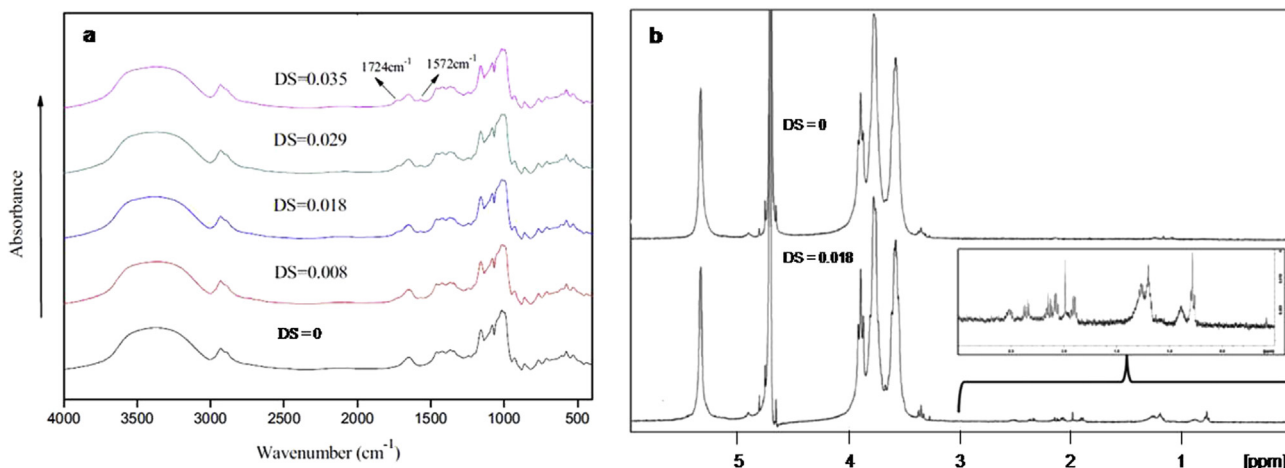
Fig. 2. a: FT-IR spectra of native and OS cassava starch samples with various DS (Adapted from B. Zhang et al. (2017)). b: ¹H nuclear magnetic resonance spectroscopy of native and OSA esterified tapioca starches (Adapted from Simsek et al. (2015)).
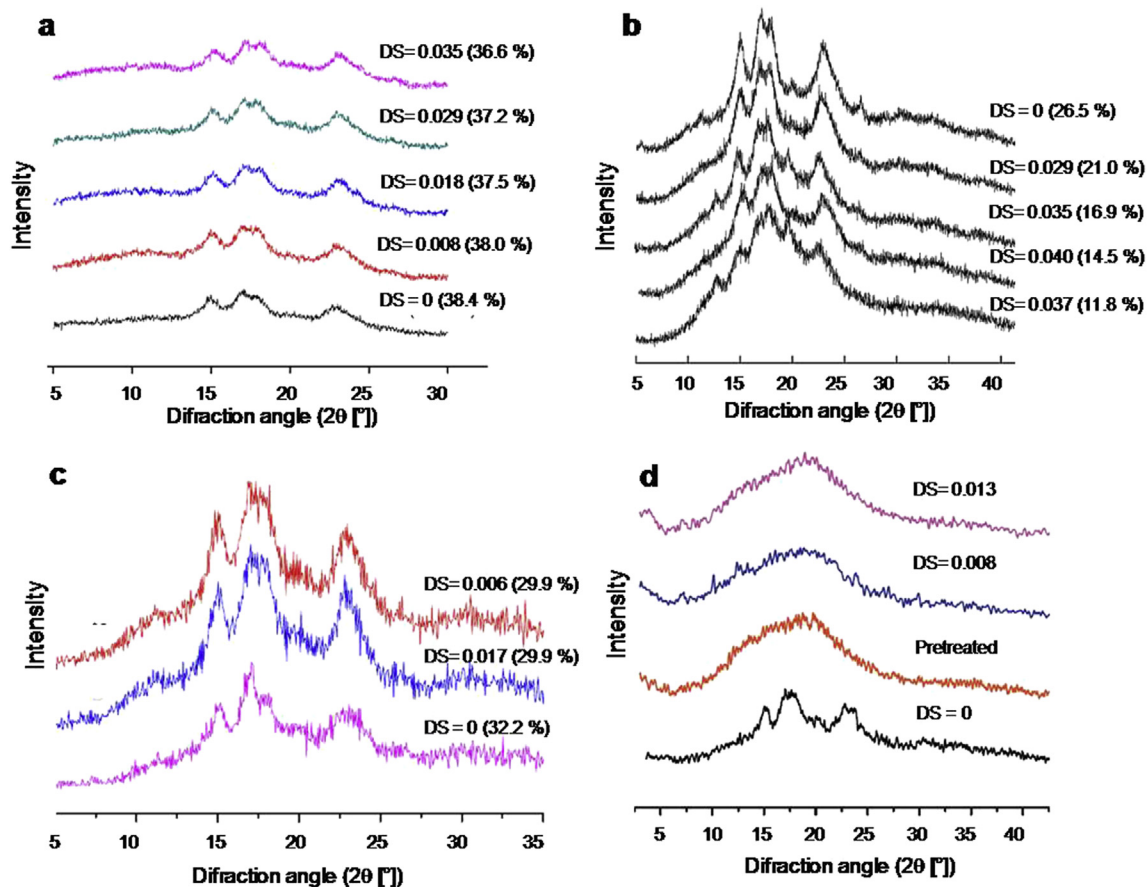

Fig. 3. XRD diffraction patterns and % of crystallinity obtained for, a: cassava starch modified with OSA (1.5–9%) in aqueous medium and alkaline conditions (adapted from B. Zhang et al., 2017); b: Cassava starch modified with 8% OSA by dry milling for times between 30 and 120 min (adapted from Hu et al., 2016 Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission); c: Ginkgo starch modified with OSA (1.5–3%) in aqueous medium and alkaline conditions (adapted from Zheng et al., 2017); d: waxy maize starch esterified with OSA using ionic liquids as solvents (adapted from Li et al., 2016). Patterns identified as DS = 0 correspond to native starches.

concomitant milling or previous dissolution of starch in ionic liquids resulted in less crystalline or amorphous structures.

To investigate the distribution of OS groups among amorphous and semicrystalline regions, Chen, Huang, et al. (2014) performed the acid hydrolysis of OS-starch with HCl (5%, 1.0 g starch/1.27 mL acid) at 55 °C for time intervals varying between 0 and 12 h, and

measured the resulting DS. Authors reported that the DS decreased with hydrolysis time, suggesting that the OS groups were placed in the amorphous region of the starch. A similar approach was employed by Huang et al. (2010) who hydrolyzed OS-starches with HCl 2.2 M (1.0 g starch/10 mL acid) at 35 °C for periods ranging from 1 to 4 days. Authors observed that DS decreased with hydrolysis

time up to 3 days and slightly increased after that; and concluded that the OSA substitution occurred mainly in the amorphous regions of the granules that were hydrolyzed first.

On the other hand, modifications to the conventional aqueous slurry method have generally resulted in a more even distribution of OS groups as a consequence of mechanical, ultrasonic, hydrothermal or enzymatic methods which have succeeded in creating channels/cracks/pores in the granules and thus enhanced OSA droplets access to the granules' interior (section 2.2). Using the acid hydrolysis protocol described aimed at removing amorphous regions, Chen, Huang, et al. (2014) concluded that for OS-starches obtained with the ultrasonic assisted reaction, the DS of hydrolyzed starch was higher than the control, indicating that ultrasonic power helped OSA penetration in the granules, even into the crystalline regions. Similarly, Huang et al. (2010) reported that for α-amylase-pretreated OS-starch the DS kept decreasing until the end of the assay, indicating that some OS groups were placed at the crystalline domains of α-amylase pretreated OS-starch.

With a different approach to assert OS groups distribution throughout the starch granule, Shogren et al. (2000) employed XPS to determine the surface element composition of OSA modified waxy maize starch granules. Results indicated that the DS at the granule surface was 3–4 times that of the bulk. Authors attributed the results to the low solubility of OSA in water, which results in a fraction of dissolved OSA that can react with both the granular surface and the granules interior, and remaining OSA droplets that can only reach the granules surface. XPS was also used by Huang et al. (2010) who for the conventional esterification protocol reported surface DS values 2 times the bulk DS. On the other hand, α-amylase-pretreated starch granules resulted in a surface DS lower than the bulk DS, from which authors concluded that the pinholes generated during the pretreatment allowed more OSA penetration and promoted reaction of OSA with the inner part of starch granules.

The preferential presence of OS groups in the surface of OS-starch granules resulting from the traditional aqueous slurry method (with no mechanical/enzymatic/hydrothermal/chemical pretreatment or in situ mechanical/ultrasonic assistance) was also observed by confocal laser scanning microscopy (CLSM) (Chen, He, et al., 2014; Whitney et al., 2016), which confirmed that the OSA modification by the traditional method is mainly a surface phenomenon. On the other hand, as a result of esterifying starch in aqueous medium aided by high speed shear and ultrasonic power, Chen, Huang, et al. (2014), Wang, He, et al. (2016) and Wang et al. (2015) found by CLSM that the OS groups were better distributed inside the granules (Fig. 4). Authors ascribed the result to the formation of smaller OSA droplets. Additionally, Chen, He, et al. (2014)

observed that OSA penetrated more inside hydrothermally pretreated starch granules, as a consequence of the swelling produced by heating the starch in the presence of water. Lu et al. (2016) also observed by CLSM more OS groups in the interior region of soluble starch nanoparticles when dual-enzyme pretreatment was used, which authors attributed to a reduction of density on the surface region as a result of enzymatic modification.

3.3. Inspection of changes in the molecular structure of starch upon modification with OSA

High performance size exclusion chromatography (HPSEC) with multi angle light scattering (MALS) and refractive index (RI) detector has been extensively employed to identify changes in the molecular weight of starch upon esterification with OSA. The M_w of corn, tapioca, rice, potato, wheat (Simsek et al., 2015), ginkgo (Zheng et al., 2017) and plantain (Bello-Flores et al., 2014) starches, has been reported to decrease upon OSA modification, with the effect being more pronounced as higher DS values were attained. Although M_w might be expected to increase upon introduction of OS groups, the decrease in M_w has been attributed to starch degradation due to the reaction conditions employed in the traditional methodology. This is in agreement with Sweedman, Hasjim, et al. (2013) who stated that OSA modification seemed to cause mild degradation of waxy maize and waxy sorghum starch molecules. On the other hand, working with debranched starch, Klaochanpong et al. (2017) reported a significant increase in the M_w after OSA modification. Since the mass increase resulting from the introduction of OS groups at the measured DS was not enough to explain the increase registered in M_w, the result was attributed to the possible association of OS-debranched-starches by H-bonding between hydroxyl groups, ester bonding between hydroxyl groups of starch chains and carboxyl groups of OS starch, and/or hydrophobic interactions between hydrophobic parts of OS-starch (Klaochanpong et al., 2017).

Finally, in terms of OS groups distribution within amylose and amylopectin molecules, octenyl succylation occurs preferentially in the amorphous regions of starch granules, which are commonly associated with amylopectin branching regions, and in some cases also with amylose (He, Song, Ruan, & Chen, 2006; Van Der Burgt et al., 1999). In reference to the distribution of OS groups along amylopectin, Bai et al. (2014) hydrolyzed OSA modified waxy maize starches with high and low DS to investigate the position of the OS groups within amylopectin molecules. Authors found that for low DS the OS groups were mostly near the branching points of the amylopectin, whereas for high DS the OS groups could also be found near the non-reducing ends. As a result of this work, they
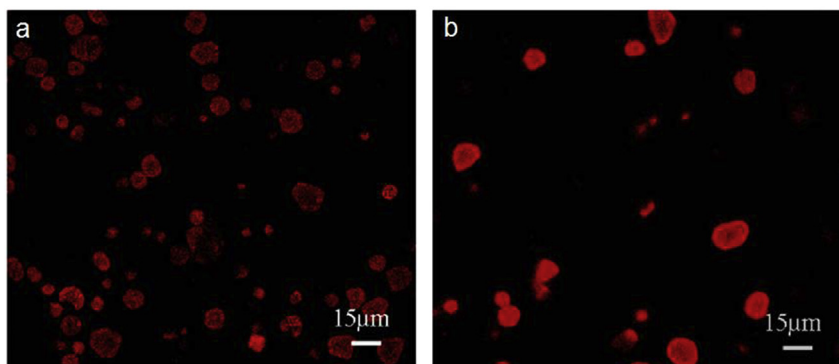

Fig. 4. CLSM image of OS-starch granules; a: waxy maize starch modified with OSA in aqueous slurry with typical mechanical stirring (500 rpm) DS = 0.038; b: waxy maize starch modified with OSA in aqueous slurry with aid of a high-speed homogenizer (10,000 rpm) DS = 0.041 (Reprinted from Wang, He, et al. (2016)).

proposed model structures of OS waxy starches with high and low DS (Fig. 5). This is in agreement with Wang, He, et al. (2016) who also hydrolyzed waxy maize starch with β-amylase and found that the amount of OS groups near the non-reducing ends of the amylopectin molecules increased with DS. Besides, the authors reported that high speed shear assisted reaction yielded OS-starch with more OS groups near the non-reducing ends compared with the control OS-starch with the same DS, which also resulted in better emulsifying properties.

4. Functional characterization

Swelling, gelatinization, pasting and retrogradation are important aspects of starch performance in most applications. When starch is mixed with water, as the temperature increases the granules swell until they are ruptured and the crystalline structure is destroyed, which is known as gelatinization. Gelatinization implies the braking of the hydrogen bonds that hold the molecules together within the granules and results in irreversible changes in properties such as water uptake, solubility and viscosity development (Biliaderis, 2009). However, after some time, gelatinized starch partially recrystallizes, which is known as retrogradation. This is undesirable in many applications, especially in foods since the properties of the product are changed resulting in reduced quality, short shelf life, and poor stability.

4.1. Thermal properties

Gelatinization of starch is usually assessed by differential scanning calorimetry (DSC). As samples of starch are heated in the presence of water (percentage of moisture is usually around 70%), heat flow is measured and an endothermic peak is registered in the DSC curve which corresponds to the gelatinization of the starch. The parameters obtained from the assay are: onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and gelatinization enthalpy (ΔH_g). Some values of thermal parameters usually obtained in DSC data from native and OS-starches compiled from the literature are shown in Table 4. Native starch gelatinization generally starts at around 60 °C and ends at 85 °C, depending on the type of starch. OS-starches have been reported to gelatinize at lower temperatures and with lower ΔH_g compared to their native counterparts. Besides, lower values are found as DS increases (Bello-Flores et al., 2014; Sharma et al., 2016; Zhang et al., 2017; Zheng et al., 2017). Upon esterification with OSA, peak temperature is generally reduced between 1 and 5 °C, depending on the DS and on the botanical source of the starch, while the enthalpy reduction is usually between 1 and 5 J/g (Table 4). ΔH_g is the energy required to disrupt the double helices in the crystalline and amorphous regions of starch, hence lower gelatinization temperatures and lower ΔH_g have been attributed to a weakening of the hydrogen bonds caused by the presence of hydrophobic groups, and also to the structural flexibility resulting from the introduction of bulky groups which allows granules swelling at lower temperature (Sharma et al., 2016; Zheng et al., 2017). Wang, He, et al. (2016) observed that this effect was enhanced when OS-starch was synthesized using high-speed shear.

4.2. Pasting properties

Pasting properties are measured by applying a heating-cooling cycle to a suspension of starch in water with constant stirring while viscosity is measured as the resistance to mixing. The most important parameters obtained are peak viscosity (PV) and pasting temperature (PT, the temperature at which the viscosity starts to rise). The viscosity rise is a consequence of starch granule swelling, which is caused by the weakening of the internal structure of the granules. In agreement with results obtained by DSC, many authors have observed a decrease in the PT of starch after OSA modification and an increase in PV (Fig. 6), which is attributed to the incorporation of OS groups that destroy the ordered structure of starch and disrupt the hydrogen bonds allowing more water penetration and swelling at lower temperature (Bello-Flores et al., 2014; Chen, He, et al., 2014; Chen, Huang, et al., 2014; Sharma et al., 2016; Wang et al., 2015).

In terms of changes in these values induced by modifications to the conventional synthesis methodology, in the octenyl succinylation of starch with high-speed shear condition Wang et al. (2015) reported slightly lower PT and PV values than the control OS-starch (equal DS). Changes in PT were attributed to fissures and fractured particles resulting from the high-speed shear force used which makes starch more prone to be destroyed by heat. PV reduction was attributed to the degradation of starch molecules and a more even OS group distribution.

In reference to the effects of hydrothermal pretreatment on the pasting properties of OS-starches, Chen, He, et al. (2014) reported PV values significantly higher than the corresponding controls. PV values increased with the pretreatment temperature and showed a positive correlation with the samples' DS. Jiranuntakul et al. (2014) studied the pasting properties of starch after heat-moisture pretreatment (25% moisture, 100 °C, 1–5 h) and observed that PT was increased and PV was reduced with increasing pretreatment time. The changes suggested that starch granules were strengthened by the heat-moisture treatment as a consequence of structural rearrangement. However, after esterification with OSA, heat-moisture pretreated starches showed higher peak viscosity than control OS-starch (without pretreatment), probably due to the higher DS obtained. On the other hand, PT of heat-moisture pretreated OS-starches were higher than the control, and even higher than the native counterpart for long times of pretreatment, indicating that this method allowed to obtain OS-starches more resistant to heat.

Conversely, OS-starches with PV lower than their native counterparts have been synthesized by alternative methods different from the traditional aqueous slurry pathway. A decrease in PV and increase in PT were observed when OSA substitution was carried out at low pH (Sandhu et al., 2015). The decrease in PV was attributed to the hydrolysis of starch resulting in the reduction of the molecular size. Also, some molecular degradation was also observed by Chen, Huang, et al. (2014), who reported lower PV and
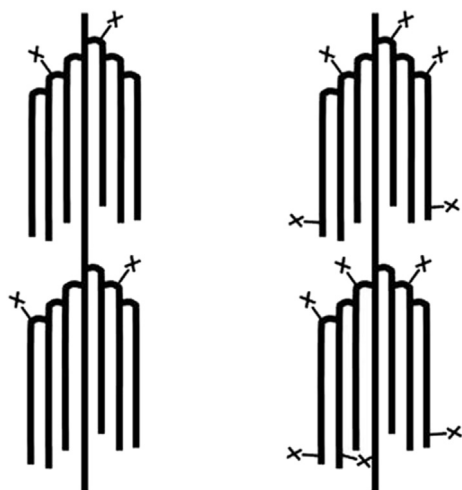

Fig. 5. Proposed model structures for octenyl succinylated starches with DS of 0.018 (left) and 0.092 (right) (Reprinted from Bai et al. (2014)).

Table 4
Thermal parameters obtained by Differential Scanning Calorimetry of OS-starches of different botanical origins with varying DS.

| Botanical source (% moist)	OSA %	DS	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_g (J/g)	ΔT_o (°C)	ΔT_p (°C)	ΔT_c (°C)	$\Delta(\Delta H_g)$ (J/g)	Reference
Unripe plantain	0	0	70.4	75.4	84.0	11.9					(Bello-Flores et al., 2014)
(78%)	3	0.011	68.8	73.7	79.2	9.5	−1.6	−1.7	−4.9	−2.4	
	15	0.038	66.9	70.7	76.9	9.2	−3.5	−4.7	−7.1	−2.7	
Ginkgo	0	0	70.2	75.7	83.7	13.4					(Zheng et al., 2017)
(67%)	1.5	0.006	68.1	74.6	82.3	12.9	−2.1	−1.1	−1.4	−0.5	
	3	0.017	67.1	73.2	82.0	12.4	−3.1	−2.5	−1.7	−1.0	
Pearl millet	0	0	59.9	62.6	73.6	11.9					(Sharma et al., 2016)
(80%)	3	0.018	56.2	60.0	69.4	10.8	−3.7	−2.6	−4.2	−1.1	
	3	0.022	53.4	57.7	64.0	8.2	−6.5	−4.9	−9.6	−3.7	
Cassava	0	0	57.8	67.1	77.3	10.5					(Zhang et al., 2017)
(67%)	1.5	0.008	55.4	65.4	74.4	8.7	−2.4	−1.7	−2.9	−1.9	
	3	0.018	52.9	62.2	70.5	6.2	−4.9	−4.9	−6.7	−4.3	
Waxy maize	0	0	69.2	74.3	85.8	19.2					(Wang, He, et al., 2016)
(70%)	Control	0.018	63.9	73.9	81.5	15.1	−5.2	−0.4	−4.3	−4.2	
	HSS	0.019	59.1	72.2	82.9	14.7	−10.1	−2.1	−2.9	−4.6	
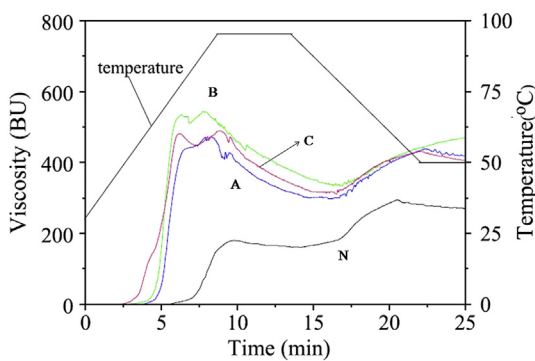
Fig. 6. Pasting characteristics of OS-starches. N: native corn starch; A, B: OS-starch synthesized with typical mechanical stirring (500 rpm), DS = 0.018, 0.0267, respectively; C: OS-starch synthesized with aid of a high-speed homogenizer at 10,000 rpm, DS = 0.0267. Adapted from Wang et al. (2015).

slightly higher PT for OS-starch obtained with ultrasonic power assistance compared to control OS-starch. Regarding OS-starch obtained by dry milling, Hu et al. (2016) found that the damaged granules showed lower PV compared to native starch, and they stated that this was due to the intense impact of mechanical milling, which changed the structure and physicochemical properties of starch to the point of rupturing macromolecular chains.

4.3. Swelling and paste clarity

Swelling power of OS-starches obtained in aqueous alkaline media has been reported to increase with temperature and DS, due to the introduction of bulky OS groups that cause a weakening of the intramolecular hydrogen bonds allowing more water molecules to interact with OH groups of the starch molecules (Bello-Flores et al., 2014; Sharma et al., 2016). In this context, Lawal (2004) stated that following introduction of bulky groups on starch molecules, structural reorganization occurs as a result of steric hindrance and this results in repulsion, thus facilitating an increase in water percolation within the granules and subsequent increase in swelling capacity. This is in agreement with results obtained in DSC and pasting properties assays, where the reduction in the gelatinization temperature and PT, and the increase in PV generally observed have been attributed to a higher swelling capacity of OS-starches compared to their native counterparts. Also, Chen, He, et al. (2014) observed an increase in the swelling power of starches hydrothermally treated before OSA modification, and they

highlighted the importance of this property in starch application as a thickener. Paste clarity of OS-starches has been reported to improve with DS as a consequence of more water retention, in agreement with the increase observed in swelling power. The introduction of OS groups causes the inhibition of an ordered structure also retarding retrogradation of starch and improving freeze thaw stability, i.e. retarding water release, again related to the increase in water retention (Hu et al., 2016; Wang, He, et al., 2016; Wang et al., 2015).

4.4. Digestibility

Starch as a food ingredient is a source of carbohydrates. However, some starches contain a portion that is not digestible and it reaches the colon where it is fermented releasing short chain fatty acids (SCFA). Regarding digestibility, starch is usually classified into three fractions: rapidly digestible starch (RDS, 0–20 min), slowly digestible starch (SDS, 20–120 min) and resistant starch (RS, > 120 min). SDS is interesting as a food additive since it does not produce hyperglycemia followed by hypoglycemia, and provides prolonged satiety, what makes it useful for treating diabetes and obesity (Han & BeMiller, 2007). RS can be used as a functional fiber that might release SCFA in the colon aiding prevention of colon cancer (Sajilata, Singhal, & Kulkarni, 2006). Besides, since it is not digested, foods containing RS have less calories and low glycemic index. Digestibility of OS-starch is generally determined *in vitro*, simulating the conditions inside the human digestive tract. A widely used method to do so is that reported by Englyst, Kingman, and Cummings (1992), in which enzymes α-amylase and amyloglucosidase digest the starch at 37 °C while the mixture is shaken. Aliquots are taken at 20 and 120 min and the glucose content of the samples is measured.

Native starches typically show levels of RDS around 80%, SDS around 15% and RS around 5%, which greatly vary with the plant source (Simsek et al., 2015). OS-starches have been reported to have less RDS and more SDS and RS than their native counterparts, and the reduction of the digestibility has been observed to increase with DS (Lu et al., 2016; Sharma et al., 2016; Simsek et al., 2015; Zhang et al., 2017; Zheng et al., 2017). OS-cassava-starch suitable for food applications (DS around 0.02) was reported to reach levels of SDS and RS around 20% leaving a portion of RDS of only 60% (Zhang et al., 2017). The OSA substitution with the introduction of ester groups and long carbon chains to the starch molecules restricts the enzymes activity retarding the glucose release. The shielding effect of the OS groups has been assigned to the physical

hindrance or the hydrophobic microenvironment they caused (Lu et al., 2016; Zhang et al., 2017).

5. Applications

OS-starch has been frequently used as emulsifier in foods (e.g. salad dressings, creams), pharmaceutical and industrial products; as clouding agent in drinks; encapsulating agent for enzymes, fatty acids, salt and flavors; and biodegradable plastics, among others. In the following sections two important uses of OS-starch, i.e. emulsifier and encapsulating agent are briefly reviewed.

5.1. OS-starch as emulsifier

An emulsion consists of two immiscible liquids, with one of the liquids dispersed as small spherical droplets in the other (McClements, 2005). Most food emulsions are oil-in-water (for example milk, cream, mayonnaise) or water-in-oil (for example butter and margarine). Flocculation and coalescence can occur in emulsions mostly during storage, resulting in the separation of the phases which causes the system to lose its functionality and acceptability. Hence, surfactant agents are necessary to maintain the stability of the emulsions (Agama-Acevedo & Bello-Perez, 2017). OS-starch is a hydrocolloid with both hydrophilic and hydrophobic moieties that can be applied as an emulsifier. Dickinson (2017) defined a hydrocolloid as a highly water-soluble (or water-dispersible) material that readily dissolves (or disperses) to form highly hydrated entities of colloidal dimensions. The polymer molecules of a hydrocolloid ingredient interact strongly via hydrogen bonding with the surrounding water molecules and with neighboring hydrocolloid molecules. However, to be effective as an emulsifying agent, the hydrocolloid ingredient should possess some surface activity, meaning that the predominantly hydrophilic macromolecules should contain some accessible hydrophobic groups to enable them to stick to and spread out at the interface, hence stabilizing the emulsion droplets. The emulsifying action of a colloidal stabilizer can be entirely electrostatic, entirely steric (based on the fact that it is entropically unfavorable to compress the molecules), or both (electrosteric). OS-starches act as electrosteric stabilizers; however, since the size of the molecules is very big relative to the number of charged groups, their function is mostly steric (Sweedman, Tizzotti, et al., 2013). An emulsion stabilized by particles, such as starch granules, is called a Pickering emulsion. These emulsions are known to show long-term stability. Hydrophobically modified starch is an accepted food ingredient and pharmaceutical excipient compared to other particles commonly used for Pickering emulsions such as latex, silica and clay (Timgren, Rayner, Sjöö, & Dejmek, 2011).

Many authors have investigated the application of OS-starch as an emulsion stabilizer. Changes in the homogeneity of the emulsions (separation of the phases), droplet size and microstructure are usually monitored during storage time.

Oil-in-water emulsions have been stabilized by rice, banana and maize (normal, waxy and high amylose) starches esterified with OSA in aqueous slurry under mild alkaline conditions as described in section 2.1 (Bello-Pérez, Bello-Flores, Nuñez-Santiago, Coronel-Aguilera, & Alvarez-Ramirez, 2015; Song et al., 2015; Song, Pei, Zhu, Fu, & Ren, 2014; Sweedman, Hasjim, et al., 2014; Xu et al., 2015; Ye et al., 2017). Emulsions containing OS-starches have usually showed uniform droplets size (Song et al., 2014) which were maintained or showed little variation with storage time (Sweedman, Hasjim, et al., 2014; Ye et al., 2017). When the microstructure of the emulsions was observed with an optical microscope, the starch particles appeared accumulated at the oil-water interface, forming a densely packed layer. Song et al. (2015, 2014)

stated that the stabilization was achieved since this layer prevented flocculation and coalescence by a steric mechanism. Regarding phase separation, Jiranuntakul et al. (2014) observed that oil-in-water emulsions stabilized with heat-moisture pretreated starches esterified with OSA presented less oil separation than native starch. Although the pretreated starches showed DS higher than control OS-starch, the emulsion stability was slightly improved by the pretreatment. Hu et al. (2016) observed that the emulsion stability of oil-in-water emulsions stabilized with starch determined by electric conductivity was improved by starch esterification with OSA and increased with DS.

Other changes in the emulsion characteristics such as viscosity and rheological properties have also been described by many authors since they are relevant in most food applications. Xu et al. (2015) explained that increased viscosity of the emulsion could retard free motion of the oil droplets delaying creaming, flocculation, and coalescence; providing another mechanism for emulsion stabilization. The authors reported viscosity increasing with OS-starch concentration, in agreement with Song et al. (2015). In general, emulsions stabilized by OS-starch have showed pseudoplastic behavior, i.e. viscosity decreasing with shear rate (shear thinning) (Dokić, Dokić, Dapčević, & Krstonošić, 2008; Song et al., 2015). Regarding dynamic rheological properties, oil-in-water emulsions stabilized by OS-starch generally showed gel like behavior, with G' higher than G" and almost constant with frequency (Bello-Pérez et al., 2015; Song et al., 2015; Ye et al., 2017).

5.1.1. Impact of the variations introduced to the synthesis method of OS-starches on their emulsifying properties

As explained in section 2.2, some variations to the traditional synthesis pathway of OS-starches have been investigated with the aim of producing OS-starches with enhanced emulsifying properties. These mainly include enzymatic and acid hydrolysis pretreatments and post-treatments. In this context, Xu et al. (2015) hydrolyzed OS-starch with β-amylase to different extents and used the products as emulsion stabilizers. When a high concentration (7%) of OS-starch was added to the emulsion, the best stability was observed for the less hydrolyzed OS-starches, and authors explained that the high viscosity obtained in the emulsion was the stabilization mechanism. Alternatively, when a low concentration (0.2%) of OS-starch was added, the most hydrolyzed OS-starches where the ones which showed best emulsifying properties, probably due to the fact that OS groups resulted more exposed in the molecules after the hydrolysis and the DS of these OS-starches was higher. On the other hand, with an enzymatic pretreatment, Wang, Fu, Tang, Huang, and Zhang (2017) completely debranched waxy maize and waxy potato starches with enzyme isoamylase, and allowed them to recrystallize forming spherulites prior to esterification with OSA. The OS-starch-spherulites produced emulsions that remained stable after two months of storage. With a similar approach, Lu et al. (2016) pretreated soluble starch particles with β-amylase and transglucosidase enzymes prior to esterification with OSA, and evaluated the emulsifying properties of the material obtained. The authors reported that the pretreatment led to higher DS and to a more homogeneous distribution of the OS groups within the starch particles. Moreover, authors reported that enzymatically pretreated starch produced OS-starch with better emulsifying activity, resulting in emulsions with lower droplet size and better stability.

Sweedman, Hasjim, et al. (2014) and Sweedman, Schäfer, et al. (2014) hydrolyzed maize starches (normal, waxy and high amylose) with HCl before esterifying them with OSA with the aim of studying the effect of OS-starches' structure on their emulsifying properties. Authors reported that acid modification of parent starches increased the stability of the droplet size in emulsions

stored at elevated temperature (55 °C), especially for normal and high amylose starches. Regarding chemical stability of emulsified β-carotene, the emulsions containing OS-starches from waxy and normal starches showed less protective effect when the molecular size of the starch had been reduced by acid hydrolysis pretreatment, since larger starch molecules produced higher paste viscosity and greater steric hindrance to stabilize the emulsion droplets. On the other hand, for high amylose starch, hydrolysis had a positive effect on the chemical stability of emulsified β-carotene. With a similar approach, Tizzotti, Sweedman, Schäfer, & Gilbert (2013) hydrolyzed waxy (maize), normal (rice) and high amylose (maize) starches with HCl before esterification with OSA to study the influence of the macromolecular architecture on the critical aggregation concentration of OS-starches. It was observed that OS-starches of larger molecular size aggregated at lower concentrations while the formation of aggregates was favored when decreasing degree of branching. In agreement with the results of Sweedman, Hasjim, et al. (2014) and Sweedman, Schäfer, et al. (2014), the opposite tendency was observed for high amylose maize starch, probably due to the strong physical interactions between the linear amylose chains.

HCl hydrolysis has also been assayed after esterification with OSA, with the aim of improving the emulsifying properties of OS-starch synthesized by the traditional method (Hong et al., 2017). Although the DS of the OS-starch was reduced with increasing HCl concentration and granule damage was observed after hydrolysis, the OS-starches most hydrolyzed showed better emulsifying properties such as smaller droplet size, uniform size of drops and better stability of emulsions compared to the normal OS-starch. Authors claimed that the hydrolysis produced smaller chains of starch molecules leaving the OS groups more dispersed in the emulsion.

With a different approach, Wang, He, et al. (2016) produced OS-starches under high-speed shear whose emulsions showed lower droplet size and better stability compared to those with control OS-starches. The enhanced emulsifying properties were related to the more homogeneous reaction achieved by high-speed shear that resulted in the OS groups better distributed inside the starch granules as observed by CLSM.

5.2. OS-starch as encapsulating agent

The amphiphilic character of OS-starch makes it an interesting wall material for encapsulating hydrophobic bioactive ingredients. The encapsulation technique allows the incorporation of bioactive compounds into foods while they remain protected from water, oxygen, heat, etc. In general, the OS-starch is dispersed in water and the hydrophobic compound is then added and mixed to form an emulsion. Finally, the OS-starch stabilized emulsion is spray dried (or freeze dried) and solid capsules containing the bioactive ingredient are produced. The material obtained is a powder that can be applied in food formulations and the encapsulated compound is expected to be released only when the OS-starch is digested by the enzyme α-amylase. Some examples of this application of OS-starch found in the literature describe the encapsulation of coenzyme Q10, propolis and conjugated linoleic acid (CLA) (Cheuk et al., 2015; Da Silva et al., 2013; He et al., 2016). The encapsulation performance is described by the size of the capsules, their stability, the protection of the bioactive ingredient against oxidation, and the compound release during digestion. In general, authors have concluded that OS-starch is an adequate encapsulating agent (Cheuk et al., 2015; Da Silva et al., 2013; He et al., 2016).

An interesting application of OS-starch as an encapsulating agent has been recently reported by Chiu et al. (2017) who encapsulated salt in the inner water phase of a water-in-oil-in-water emulsion stabilized by OSA modified waxy maize starch, aiming to enhance the saltiness perception. The authors reported emulsion stability increasing with DS. However, with increasing DS the saltiness perceived in the mouth was reduced due to decreased digestibility of the OS-starch by the native salivary amylase. Therefore they concluded that OS-starch containing between 1.5 and 2% of OS groups would be adequate for this application, that would allow reducing salt content in emulsion-based foods.

6. Foods formulated with OS-starch

OS-starch is an interesting ingredient for food applications due to its functional characteristics such as pasting properties and slow digestibility, and due to its emulsifying action as well (sections 4 and 5.1). In general, since OS-starch is a low-cost fat-free ingredient with some resistance to digestion, its application is advantageous in the formulation of functional foods that aim to attend the demand for healthier products towards the current world epidemic of obesity, diabetes and heart disease (WHO -, 2011).

Many authors have recently reported the application of OS-starch in food formulation as fat replacer or emulsifier. Chivero, Gohtani, Yoshii, and Nakamura (2016) formulated mayonnaise-like emulsions replacing egg yolk with commercial OS-starch and obtained a pseudoplastic system similar to mayonnaise. Ghazaei, Mizani, Piravi-Vanak, and Alimi (2015) also produced mayonnaise with egg yolk substitution with OS-starch. However, they concluded that an acceptable emulsion was obtained replacing up to 75% of egg yolk. Conversely, Ali, Waqar, Ali, Mehboob, and Hasnain (2015) prepared low fat mayonnaise replacing 75% of the oil in the formulation with a paste of OS-starch (20%) and they obtained a product with higher sensory scores and similar texture properties compared to full fat mayonnaise.

OS-starch also finds application in bread dough formulation where it can be used as a flour substitute or as a fat replacer. For example, Dapčević Hadnadev, Dokić, Hadnadev, Pojić, & Torbica (2014) replaced up to 10% of wheat flour with three types of commercial OS-starch: normal, pre-gelatinized and hydrolyzed. Even if the three OS-starches resulted in higher specific volume of the bread loaves, the best performance was obtained for pre-gelatinized OS-starch. However, the dough ability to retain moisture was reduced by flour substitution. On the other hand, Balic, Miljkovic, Ozsisli, and Simsek (2017) used OS-starch as a fat replacer in bread dough and obtained a product with similar characteristics compared to control bread. Dapčević Hadnadev, Hadnadev, Pojić, Rakita, & Krstonošić (2015) produced cookies replacing vegetable fat with oil in water (50%) emulsions using OS-starch as emulsifier and obtained a product with similar consumer acceptance compared to full fat cookies.

7. Conclusions

OS-starch is a food grade additive with amphiphilic properties. OS-starch is usually synthesized by esterification of starches of different botanical origin with OSA in aqueous slurry under mild alkaline conditions and at room temperature. As a consequence of the heterogeneous character of the system, the semicrystalline nature of the starch granules, and the low solubility of OSA in aqueous medium, characterization of OS-starches shows that the reaction is mainly a surface phenomenon, with esterification reaching mostly the amorphous region of the granules. Main changes in the starch properties due to OSA substitution include decrease in gelatinization temperature and enthalpy, increase in swelling power, paste viscosity and paste clarity; and reduced digestibility. However, in the last years a number of variations have been introduced to the conventional synthesis pathway searching

for higher reaction efficiency, a more even distribution of OS groups, and/or enhanced emulsifying properties. In general, the variations more often reported in the last five years are aimed at opening the compact structure of the starch granules, increasing its surface area, reducing its crystallinity, decreasing the OSA drops size, and/or dispersing starch molecules; thus allowing better OSA accessibility to hydroxyl groups and a more homogeneous distribution of the OS groups in the final product. As a result, reaction efficiency increments have often been reached, although some of the structural and functional properties of the starch may be changed.

In this context, the systematic introduction of modifications to the conventional aqueous slurry method appears as an opportunity to produce a wide variety of OS-starches with different functional properties. In this sense, further studies on the impact of the specific properties of these new OS-starches in definite applications as emulsifiers, encapsulating agents or fat replacers, are still needed. In the case of post-treatments, particularly enzymatic ones, seem to be a promising tool to yield tailored products with specific properties which will deserve much attention in the future.

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