Carbohydrate Polymers 92 (2013) 905–920

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Review

Structure and physicochemical properties of octenyl succinic anhydride modified starches: A review

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ARTICLE INFO

Article history:
Received 7 July 2012
Received in revised form 4 September 2012
Accepted 21 September 2012
Available online 29 September 2012

Keywords:
Starch
Octenyl succinic anhydride (OSA)
Synthesis
Characterization
Structure–property relations

ABSTRACT

Starches modified with octenyl succinic anhydride (OSA) have been used in a range of industrial applications, particularly as a food additive, for more than half a century. Interest in these products has grown in recent years as a result of new methods and applications becoming available. Due to a combination of OSA's hydrophobic and steric contribution and starch's peculiar highly branched macromolecular structure, these starch derivatives display useful stabilizing, encapsulating, interfacial, thermal, nutritional and rheological properties. We review the synthesis procedures, structural characterization methods and physico-chemical properties, and the influences of the botanical origins and structural parameters of OSA starches on physico-chemical properties. A better understanding of these features has the potential to lead to products with targeted macromolecular structures and optimized properties for specific applications.

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http://dx.doi.org/10.1016/j.carbpol.2012.09.040

1. Introduction

Starch is a branched homopolymer of glucose, with α-(1 → 4) linear links and α-(1 → 6) branched links. As shown in Fig. 1, starch comprises two types of polymers, each of which has a broad distribution of molecular sizes and molecular weights: amylose, which is of moderate molecular weight ($\sim 10^6$) and with a few long-chain branches, and amylopectin, whose molecular weight is about two orders of magnitude higher and whose branches are much shorter. Starch is the bulk energy storage molecule in plants, and is widely available as a resource for industry. Starched-based products are usually safe for human consumption. In roles as food additives, modified starches present several benefits over alternative products, while also meeting the requirements of niche dietary requirements such as vegan-vegetarian, halal, kosher, non-fat and non-allergenic. Native starches generally have limited solubility in water and are limited in their industrial applications. Modification to bring about solubility can entail (i) structural changes that hydrolyze the starch into smaller molecules, and/or (ii) the addition of chemically substituted groups such as acetate or octenyl succinic anhydride (OSA), as shown in Fig. 2: the subject of the current review. These covalently linked substituents generally react with any available hydroxyl moiety of accessible glucose monomers to impart some desirable quality to the starch substrate.

The most commonly cited genesis of the technique using OSA is either one of two patents (Caldwell, 1952; Caldwell & Wurzburg, 1953), although these patents did not specifically use OSA as their substituent. When modified with OSA, the normally hydrophilic starch gains a hydrophobic element in the form of octenyl groups (see Fig. 2), resulting in whole molecules with an amphiphilic character. Amphiphilic polymers have a wide variety of applications, particularly in emulsification, encapsulation, films and coatings, and gel production. OSA starch (i.e. starch after chemical modification with OSA) has been used as a substitute for a variety of food substances including Gum Arabic, fats and proteins. Applications for OSA starch products are not limited to the food industry; indeed, there is an interest for any area where stable emulsions are required, to the extent that they are even showing promise as biodegradable, low-impact chemicals for use in crude oil extraction and mining (Crossman, Rosie, & Solarek, 2004; Eoff, Reddy, & Dalrymple, 2005). Applications will depend on functional requirements for a given application, which are dependent on the underlying substrate structure of the modified starch. This structure is very complex due to the heterogeneous branched structure of starch molecules, as well as the presence of variable amounts of different classes of starch molecules, particularly amylose and amylopectin.

Though the methods have been around for some time, there is increasing interest in OSA starches in recent years as evidenced by the increase in publication activity, as shown in Fig. 3. This review examines key aspects of OSA starch function as a product of underlying structures and production methods. This begins with an overview of the esterification and synthesis of OSA starches, including the choice of botanical origins and synthesis methods. The molecular structure of the starch substrate impacts several variables in the functionality of the end product. Indications are suggested on areas of research with potential for development, especially with regard to human health and nutrition.

2. Synthesis of OSA starches

2.1. Commonly used starch sources

2.1.1. Commercial OSA starches

Commercially produced OSA starches can be purchased from a range of producers. The majority of patents for OSA starch products belong to National Starch (now Corn Products International), which has pursued development of these products since securing the

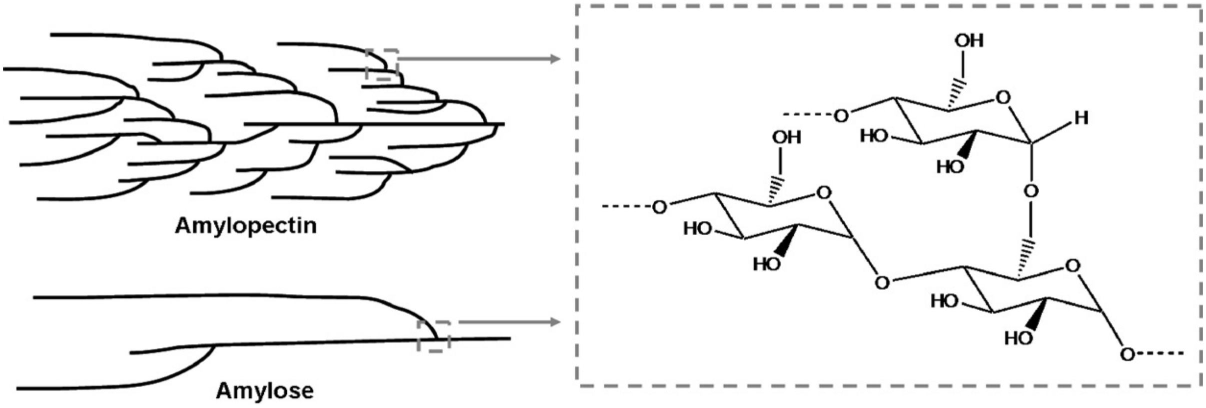

Fig. 1. Schematic of structural and chemical composition of amylose and amylopectin.

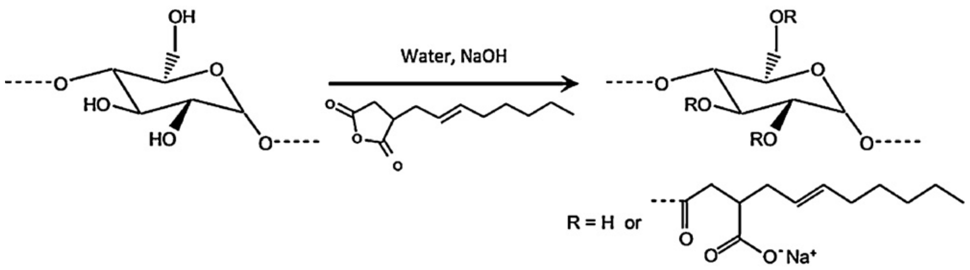

Fig. 2. Structure of OSA-modified starches.

original 1952-3 patents (Caldwell, 1952; Caldwell & Wurzburg, 1953). Botanical sources for commercial starch are subject to market considerations to a greater extent than those of scientific literature. For the most part, such starches are found to be waxy maize (e.g. N-Creamer^{TM}, Purity Gum^{TM}, CAPSUL^{TM}, Hi-CAP^{TM} [National Starch]; Mira-Cap^{TM} [Tate and Lyle]) or normal maize (DRYFLO^{TM} [National Starch]), as well as a few other sources (e.g. Tapioca – Clearam^{TM} [Roquette]). Some producers do not reveal the botanical origin. The narrow list of botanical origins in commercial products could indicate limited financial incentive towards alternative sources.

2.1.2. *Botanical origins: common sources of starch substrate*

About half the research literature is on maize or corn starch, the majority of which specify a waxy variety, as shown in Fig. 4. Of those publications that do not specify waxy varieties, only three specify high amylose (Shogren, 2003; Yusoff & Murray, 2011; Zhang et al., 2011), while several others report amylose contents of around 20 ± 5%. It is quite probable that several others where the reported starch is derived from corn are actually waxy varieties, as some commercial native corn starches are of waxy type, although not marketed as such (e.g. SIGMA S9679). Several comparisons between botanical sources have focused on the effect sources have on the modification with OSA itself (Bhosale & Singhal, 2006; He, Song, Ruan, & Chen, 2006). Others focus on functional properties, which tend to be affected by biological origins, but do not necessarily follow the relative patterns seen in the native forms of those starches (Han & BeMiller, 2007). Alternative sources have the potential to create benefits in various applications. Each biological origin will provide different amylose/amylopectin ratios, structural attributes and the presence of proteinaceous and other components endogenous to the source.

2.2. *Modification of starch with OSA in aqueous solutions*

2.2.1. *Commonly used synthesis procedure in aqueous media*

OSA starches are obtained from the esterification reaction between starch hydroxyl groups and octenyl succinic anhydride (Fig. 2). A commonly used parameter in this regard is the degree of substitution, *DS*, which is the average number of octenyl succinate, OS, derivatives per glucose unit.

The most widely described synthesis pathway is a reaction in aqueous medium under mild alkaline conditions with the starch in its granular form, although some authors have reported other procedures that will be discussed later. Slightly basic conditions help to reduce hydrogen bonding between starch chains by the formation of alkoxide functionalities with the starch OH groups, which consequently favours the swelling of starch grains and the diffusion of OSA molecules within the swollen starch granules. It is also possible to conduct the OSA reaction directly onto preformed starch films. After surface modification with OSA, Zhou, Ren, Tong, and Ma (2009) obtained corn starch films with decreased moisture sensitivity and increased surface hydrophobic character. Ren et al. (2010) observed that surface modification also significantly increased tensile strength and Young's modulus of starch films.

As the reaction is performed under heterogeneous conditions, one could expect (i) the substituent distribution to be unevenly distributed between granules and (ii) the OS groups to be preferentially connected at the surface of the granules. This was confirmed using Fourier transform infrared microspectroscopy and Raman confocal microscopic imaging (Bai, Shi, & Wetzel, 2009; Wetzel, Shi, & Schmidt, 2010a;Wetzel, Shi, & Reffner, 2010b). X-ray photoelectron spectroscopy analysis suggested that the OS groups are mainly located on the immediate surface of the modified starch granules with a concentration of about 3–4 times that of the bulk (Huang et al., 2010; Shogren, Viswanathan, Felker, & Gross, 2000). These results are in agreement with a recent study

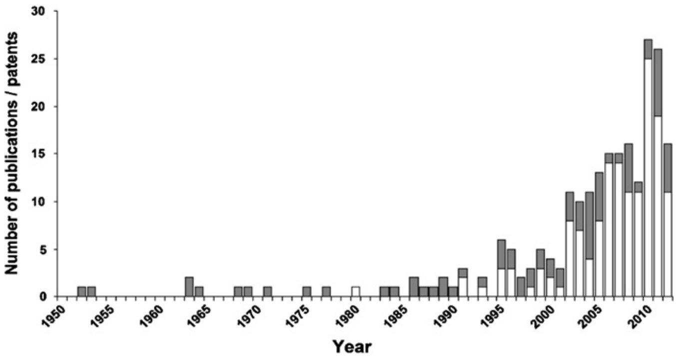

Fig. 3. Numbers of publications and patents on OSA starch (□: publications; ■: patents).

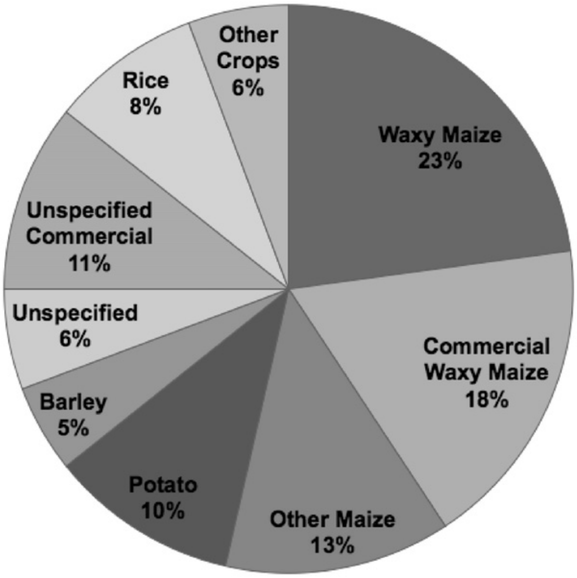

Fig. 4. The proportions of OSA starch in non-patent publications showing biological origin.

involving confocal laser scanning microscopy imaging on OSA starches (Zhang et al., 2011). By means of backscattered electron imaging on osmium-stained OSA starch grains and anion-exchange chromatography of OSA starches solubilized in water, Shogren et al. (Shogren et al., 2000) also found that more branches remained completely unmodified than predicted under statistically homogenous modification, meaning the reaction occurred across all branches heterogeneously.

2.2.2. Influence of experimental parameters

Jeon, Viswanathan, and Gross (1999) were the first to report a systematic study investigating the influence of various parameters on succinylation. They found that OSA reacts more efficiently with starch than do larger succinyl anhydrides: dodecanyl, hexadecanyl and octadecanyl. Their reaction was optimized for the dodecanyl succinic anhydride reaction with starch, in this case requiring an optimal temperature between 20 and 27 °C, whereas optimal conditions for OSA modification have been consistently found in the range of 30–40 °C, generally peaking at 35 °C. This applies across several botanical sources: Amaranth from *Amaranthus paniculatus* seeds (Bhosale & Singhal, 2006), *Indica* rice (Song, Chen, Ruan, He, & Xu, 2006a;Song, He, Ruan, & Chen, 2006b; Zhang, Zhao, & Xiong, 2010), maize (Abdollahzadeh, Mehranian, & Vahabzadeh, 2008), *Phaseolus lunatus* (Segura-Campos, Chel-Guerrero, & Betancur-Ancona, 2008), potato (Han, Zhu, & Zhang, 2011; Hui, Qi-he, Ming-liang, Qiong, & Guo-qing, 2009) and waxy corn (Liu et al., 2008; Xu et al., 2012; Zhu, Xie, Song, & Ren, 2011).

Song et al. (2006a) were the first to develop a quantitative model (by empirical fits to experimental data) for the reaction efficiency and *DS* as a function of several experimental parameters for the modification of *Indica* rice starch. A few alternative models have been reported subsequently (Abdollahzadeh et al., 2008; Liu et al., 2008; Segura-Campos et al., 2008; Song et al., 2006a). While all studies reviewed showed satisfactory correlation coefficients ($0.9440 \le R^2 \le 0.9905$) and good fit to experimental data, there is no clear indication that the results can be extended to other starch sources. He et al. (2006) have seen that the amylose content has a positive impact on the reaction efficiency, which corroborates with the hypothesis that the modification with OSA preferentially occurs within the amorphous part of the starch granules, in which amylose chains predominantly reside.

2.3. Alternative synthesis procedures

2.3.1. In aqueous media

There are various alternative methods for reaction efficiency optimization in aqueous media. Xu et al. (2012) performed chemical modification in presence of enzymes, while other OSA starches were prepared from a waxy corn starch through lipase-coupling esterification. These authors found that for given experimental conditions and targeted degrees of substitution, reaction times were drastically declined from hours to 30 min when using only 0.6 wt% of lipase (relative to starch), making the lipase-coupling esterification technically feasible for industrial scale-up production. However, for optimum results, the starch needs to be pre-activated in alkaline solution (pH 8) at 65 °C, 15 min before addition of the lipase and the OSA reagent.

The use of mechanically activated starches was also found to increase the reaction efficiency (Zhang et al., 2010). Zhang et al. used ball milling for up to 50 h to activate an *Indica* rice starch at room temperature before performing subsequent chemical modification with OSA (35 °C, pH 8.5, 3 h, 15 wt% of starch relative to water and 3 wt% of OSA relative to starch). This significantly disrupted the crystalline structure of the granules from 17.18% down to 1.05% crystallinity. The reaction efficiency was found to increase from 54.6% for the native starch to 90.4% for a milling time of 25 h. The decreased size of the damaged starch granules increased the reactive surface area and therefore the reaction efficiency; however, the vigorous pre-treatment induced a significant degradation of the starch chains.

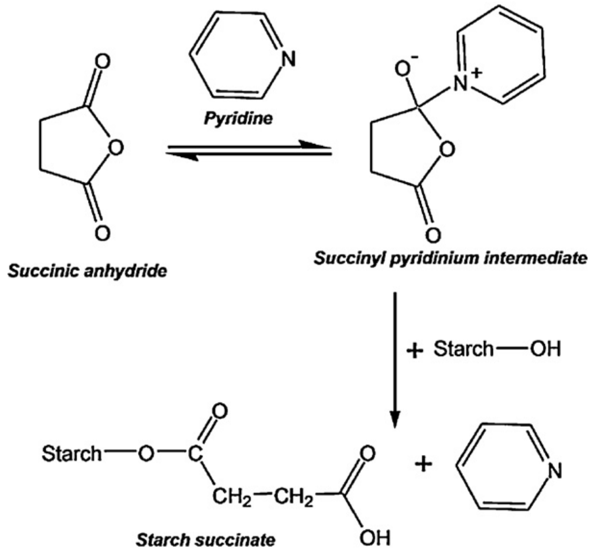

Fig. 5. Esterfication reaction of succinic moieties onto starch chains in presence of pyridine.

Redrawn from Bhandari 2002 (Bhandari & Singhal, 2002b).

Another promising way to increase the surface area of the starch particles and make it easier for the chemical reagent to infiltrate into the inner parts of the starch has been proposed by Huang et al. (2010). An enzymatic pre-treatment with α-amylase was used to produce micro-porous corn starch, when OS groups were found not only at the surface of the granules, but also in the inner and crystalline regions, as shown by X-ray photoelectron spectroscopy. Unexpectedly, the reaction efficiency was found to decrease with the level of pre-hydrolysis by α-amylase, and the authors postulated that the process had selectively removed highly accessible amorphous regions, causing the relatively more crystalline pre-treated starch granules to be less reactive with the OSA reagent. Following the same strategy, Bai et al. (Bai & Shi, 2011) used a mixture of α-amylase and glucoamylase in order to prepare micro-porous granules of waxy maize starch. Supporting Zhang's study and contrary to the results obtained by Huang et al., Bai's research resulted in higher reaction efficiencies, attributed to micro-pores which increased the surface area of starch granules.

2.3.2. Other synthesis procedures

Viswanathan (1999b) was the first to report synthesis conditions in non-aqueous media, using pyridine instead of water. This solvent serves to increase the initial reactivity of the starch grains and also works as a catalyst for the OSA starch reaction, as it forms a succinyl-pyridinium intermediate much more prone to react with the starch hydroxyl groups than the non-activated OSA molecules (Fig. 5). A more detailed synthesis procedure was later reported by Bhandari and Singhal (2002a). The reaction was carried out using a corn starch by refluxing in pyridine at 115 °C. This reaction requires a 2:1 weight ratio (pyridine/starch) in order to avoid charring of the starch. Viscosity measurements suggested that starch chains were nevertheless degraded during this process. Despite having a positive effect on the reaction efficiency, this method cannot be used on an industrial scale because of pyridine toxicity. Notwithstanding this, Wang et al. (2011) recently used the method to prepare delivery carriers for bioactive food components where very high degrees of substitution were targeted. *DS* from 0.2 to 1.3 were obtained using OSA/starch weight ratios up to 5/1. The resulting products were then turned into matrix tablets, which could deliver bioactive food components to the colon, providing protection from enzyme degradation during the earlier stages of digestion.

Another method of maximizing the reaction efficiency and reducing the reaction time is to perform the modification with OSA under high temperature/pressure conditions. Shogren (2003) dried a corn starch at 120 °C in a vacuum oven and then mixed it with glacial acetic acid and OSA. Reaction was carried out in a differential scanning calorimetry (DSC) pans, which were hermetically sealed. After only 20 min at 180 °C, *DS* of about 0.5 was achieved, corresponding to 65% reaction efficiency. It was claimed that fewer by-products were formed since no catalyst or neutralization were required, but starch chains were clearly degraded, as indicated by viscosity measurements and browning of the products after reaction. Also working with a process that completely evaporated the aqueous solvent, Kim, Sandhu, Lee, Lim, and Lim (2010) prepared OSA-modified waxy rice starches by heat drying aqueous mixtures of starch and OSA at high temperature and low pH. Compared to the traditional reaction in aqueous medium, the dry-heat treatment appeared simpler and more economical. It is once again important to mention that such severe experimental conditions induced a noticeable decrease of the molecular weight, implying significant degradation of the starch during the process.

Another way to quickly obtain OSA starches with high *DS* is to perform a microwave-assisted modification. Pioneers of this method were Biswas, Shogren, Kim, and Willett (2006) who found a *DS* of 0.3 in only 5 min. The same approach was used by Rivero, Balsamo, and Muller (2009). First, a cassava starch was activated by suspension in an alkaline solution at room temperature, then filtered and dried under vacuum. A mixture of this activated starch and OSA in distilled water was subjected to microwave radiation, which led to a *DS* of about 0.045 in 7 min. As a comparison, the same reaction performed in water as described in Section 2.1 gave a *DS* of 0.032 after 24 h. Nevertheless, (i) the time needed to produce the activated starch considerably lengthens the microwave-assisted synthesis procedure, (ii) long reaction times for the "traditional" modification in aqueous medium tend to favour the breaking the OSA starch bonds (Bhosale & Singhal, 2006) and (iii) the microwave radiation at higher powers has the potential to degrade the starch (Makuuchi, 2010).

3. Structural characterization of OSA starches

3.1. Determination of the degree of branching (DB)

The degree of branching, *DB*, is the average number of branching points as a percentage of the average total number of glycosidic linkages per starch molecule. It can be measured by NMR, a reliable characterization technique so long as it is performed under conditions in which there is a complete and homogeneous dissolution of the sample. Significant improvements allowing greater accuracy have been suggested from the original technique in D_2O (Gidley & Bociek, 1985). Indeed, it is now widely accepted that water is not able to fully dissolve all starch samples, particularly those with high amylose contents (McCleary et al., 2006). It has been demonstrated that DMSO-d_6 gives total dissolution of starch (Schmitz, Dona, Castignolles, Gilbert, & Gaborieau, 2009) and is generally preferred. However, labile protons from OH or any other group containing exchangeable protons exhibit broad signals that can hide other peaks of interest and complicate the calculation of *DB*. Several methods for removing these unwanted signals have been reported. Hernandez et al. (2008) used a 80/20 DMSO-d_6/D_2O mixture instead of pure DMSO-d_6, but solubility issues and insufficient spectrum clarification were seen if D_2O was not added in this exact ratio, resulting in a restricted method. Nilsson and Bergenståhl (2006) performed a pre-deuteration of the starch prior to solubilisation in DMSO-d_6, by dissolution in boiling D_2O followed by freeze-drying, which was efficient but time consuming, as it has to be repeated several times before sufficient level of starch deuteration. The present authors (Tizzotti, Sweedman, Tang, Schaefer, & Gilbert, 2011) developed a fast and straightforward procedure involving a small amount of deuterotrifluroacetic acid, TFA-d_1, that quickly gives rise to a shift to high frequency of the exchangeable protons of the starch hydroxyl groups leading to clear and well-defined ^{1}H NMR spectra.

3.2. Determination of the degree of substitution in OSA starches (DS)

3.2.1. Titration method

There are two types of titration methods for finding the *DS* of OSA starches. The first relies on the saponification of the product in an alkaline solution followed by titration of the excess alkali. As a general procedure, the OSA starch is suspended in a basic solution (commonly NaOH, e.g. (Bhosale & Singhal, 2006), or KOH, e.g. (Bao, Xing, Phillips, & Corke, 2003)), which results in the saponification of the OS groups. The excess of alkali present in the medium is then titrated with a hydrochloric acid solution with an indicator. As the starch backbone is likely to undergo some degradation during this treatment, it is necessary to treat the native unmodified starch in the same manner to obtain a blank value.

In the second titration method (Hui et al., 2009), the OSA starch is dispersed in a hydrochloric acid/isopropanol solution. After filtration, the solid residue is washed with isopropanol until no Cl^- is detected (using $AgNO_3$ solution) and redispersed in distilled water. This mixture is then boiled and the final solution is titrated using indicator and NaOH solution added until neutralization. For the same reason explained above, the native unmodified starch is also titrated as a blank. A simplified method has also been suggested by Jeon et al. (1999) in which the product was simply dissolved in DMSO and the solution was titrated against a 50 mM standard NaOH solution using phenolphthalein indicator.

Despite being widely used for their convenience, both titration methods require consideration of the materials available; (i) each *DS* calculation requires between 2 and 5 g of product for accuracy, and (ii) it is necessary to also characterize the native unmodified starch. Such material may not always be available, especially when working with commercial samples which are already modified and often used as received. It is also apparent that titration methods should not be used to quantify the *DS* of products made with techniques that degrade the starch chains, as differences observed in titration results between the native starch and its modified counterpart may be due to both the presence of OS groups and/or the chemical degradation of the starch. Indeed, a "virtual *DS*" can be detected even on native unmodified starch samples (Plate, Diekmann, Steinhäuser, & Drusch, 2012). Some authors have reported a lack of accuracy and reproducibility due to difficulties in end-point detection, for which one causative factor may be the huge molecular weight of the starch chains (Čížová, Koschella, Heinze, Ebringerová, & Sroková, 2007; Jeon et al., 1999; Viswanathan, 1999a). This could be avoided by analysing depolymerized samples.

3.2.2. Measurement by NMR

NMR is widely used to quantify chemical modification of polymers such as OSA starches. The *DS* can be calculated from the intensity of OS groups' signals as a ratio of the starch anomeric protons which are used as an internal reference (see Fig. 6) (Shih & Daigle, 2003). The signals of the OS groups and starch require quite controlled conditions to be visible in the same analysis, as seen in one such method (Tizzotti et al., 2011). Only small

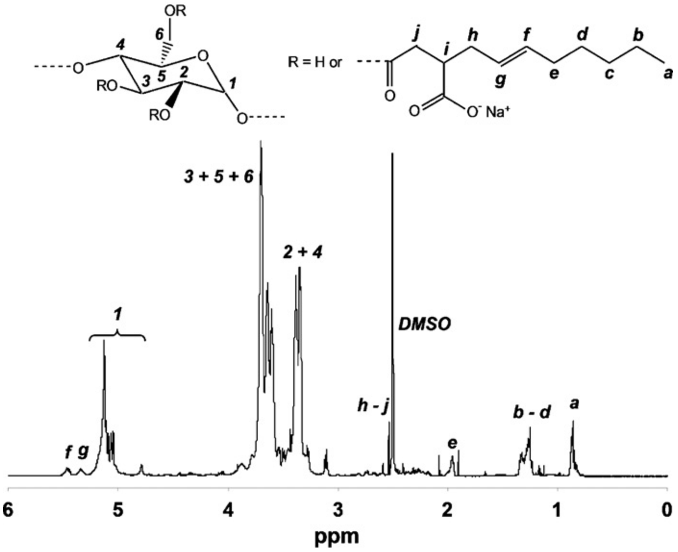

Fig. 6. ^{1}H NMR spectrum of a typical OSA starch in DMSO-d_6, from the authors' laboratory.

quantities of product (generally around 2–5 mg) and only minimal sample preparation are required per characterization, which constitutes a substantial advantage over titration methods. Moreover, NMR allows the determination of both *DS* and *DB* values of an OSA starch sample within the same experiment. However, NMR is not routinely available industrially.

Shih and Daigle (2003) performed NMR analysis in D_2O, which is known to dissolve starch samples only partially. Water solubility issues can be overcome by reducing the molecular weight of starch chains, either by basic hydrolysis at 70 °C using 0.5 M NaOD as analytical solvent (Shogren, 2003) or by means of α-amylase pre-digestion of the product (Bai, Shi, Herrera, & Prakash, 2011). Nevertheless, OSA starches are amphiphilic macromolecules (the starch backbone being the hydrophilic and the octenyl the hydrophobic component) able to form aggregates in aqueous media via the formation of hydrophobic interaction, which can lead to a significant signal reduction in NMR characterization (Tizzotti et al., 2010) and ultimately to an incorrect estimation of the *DS*.

Given that DMSO/LiBr solutions have been proven to fully dissolve any starch samples of concentrations appropriate for analysis, whatever their amylose content (Schmitz et al., 2009), and OSA is also soluble in DMSO, this appears to be the most suitable solvent system for the NMR characterization of OSA starches.

It is noteworthy that the OSA substitution was found to preferentially occur on the C-2 and C-3 hydroxyl groups of anhydroglucosyl units (Bai et al., 2011; Choi, Girek, Shin, & Lim, 2002). No substitution was detected from the C-6 OH groups, which appears surprising given that primary OH are usually more reactive than secondary ones.

3.2.3. *Measurement by Fourier transform infrared spectroscopy (FTIR)*

Despite the many papers using FTIR to investigate the presence of grated OSA groups in starches after chemical modification, only a few studies have quantified the *DS* with this technique. Compared with spectra from native starches, two new absorption bands at 1726 and 1572 cm^{-1} appear after OSA esterification corresponding to the C=O stretching vibration of an ester group and the asymmetric stretching vibration of a carboxyl group, respectively (Zhang et al., 2011). The intensities of these two absorption bands increase with the *DS* and a linear relationship between *DS* and the intensity at 1726 cm^{-1} and the *DS* has been highlighted (Čížová, Sroková, Sasinková, Malovíková, & Ebringerová, 2008). Unfortunately, FTIR has only been found reliable for high *DS* (≥0.3) (Biswas et al., 2006; Čížová et al., 2008), which makes it unsuitable for most of the industrial applications where only lower *DS* are allowed (e.g. ~0.02 for food-grade products).

3.3. *Measures of size structural parameters*

Size structural parameters of OSA starches are rarely reported. Evaluating the structural characteristics of complex polydisperse branched polymers requires several different parameters to communicate meaningful information about size of the molecules in the population. Two studies (Chung, Lee, Han, & Lim, 2010; Thirathumthavorn & Charoenrein, 2006) have used the average degree of polymerization to estimate the number-average molecular weight $\overline{M_n}$ of macromolecules in samples of tapioca, rice and waxy corn starches before chemical modification with OSA. $\overline{M_n}$ was quantified by measuring the reducing sugar content before and after complete hydrolysis with a strong alkali. While this method is quite common and easy to perform, it is possible that either connected OS groups or free OSA can interfere with the reducing sugar test used. Moreover, the technique is only accurate for low molecular weight species such as amylose. More complex methods are available that can provide more meaningful insights into the structure of OSA starches.

3.3.1. *Size exclusion chromatography (SEC)*

This technique can be used to quantify both the hydrodynamic size distribution of the fully branched starch (including OSA-modified varieties), and also that of individual branches following enzymatic debranching.

To quantify size parameters effectively, molecules must be completely dissolved in the eluent. As discussed previously, water is known not to be the best solvent for whole, unmodified starch; however, some authors have reported results obtained with aqueous eluent phases. Starch may be made soluble in aqueous media by pH changes to the solvent or by hydrolysis, breaking it into smaller parts, as has been performed by Shogren et al. (2000) who debranched OSA-modified waxy maize starches with pullulanase and subjected them to SEC. In this case the eluent phase was 0.1 M NaCl, 1 mM potassium phosphate buffer, 0.02% NaN_3 at pH 6. Kim et al. (2010) also used an aqueous eluent phase (50 mM $NaNO_3$) to characterize fully branched samples made from waxy rice starch. Their samples were strongly degraded during the synthesis, which obviously had increased their water solubility. Pérez-Gallardo et al. (2012) used DMSO to pre-dissolve their modified acid-hydrolyzed waxy maize starches, and then used an aqueous mobile phase ($NaNO_3$ buffer + 0.02% NaN_3 at 40 °C) for the SEC characterization. It has not been rigorously demonstrated that any SEC characterization of whole starch molecules in an aqueous eluent, irrespective of any pre-treatment, gives a true molecular dissolution with aggregation or degradation (Gidley et al., 2010).

To date, the most advanced and reliable methods for SEC characterization of starch require an eluent phase containing DMSO/LiBr solutions at a temperature of ~80 °C (Vilaplana & Gilbert, 2010). The group of the present authors seems to be the only one to have used such experimental conditions for the characterization of OSA starches.

This technique separates by hydrodynamic size, not molecular weight—branched polymers have a range of branching structures, and hence molecular sizes, for a given molecular weight. With differential refractive index detection, this gives the SEC weight distribution, which is essentially the weight of molecules as a function of molecular size (see, for example, (Gilbert, 2011; Vilaplana & Gilbert, 2010) for details).

It is interesting to question the possibility that OSA modification may affect the physical arrangement of starch molecules in solution, and thus affect their size in solution. We have used this technique to study changes in molecular size distribution with OSA modification under mild, aqueous conditions based on those in (Song et al., 2006b) (see Section 2.2.2 for more details). The data shown in Fig. 7 show the initial and final size distributions after modification with different amounts of OSA.

As can be seen, the presence of OSA has no effect on the size distribution of starch molecules. This is of course understandable, since starch is expected to be fully soluble at all *DS* used in the given solvent system (DMSO 99.5%, LiBr 0.5%, 80 °C); however these findings discount any possible effects of steric factors of OS groups on dissolved starch arrangement, or any damage incurred by the modification process. The latter point means that preformed substrates may now be used in the study of structures relationship with function in modified starches, without those structures being compromised by the modification process.

3.3.2. *Asymmetric flow field-flow fractionation (AF^4)*

SEC is known to cause shear degradation of very high molar mass branched macromolecules such as amylopectin (Cave, Seabrook, Gidley, & Gilbert, 2009), and AF^4 has been considered as an alternative. However, it has been shown that it cannot be used for whole native starch, because of signal to noise problems with differential refractive index detection in DMSO (Gilbert, 2011). Nilsson and colleagues (Nilsson & Bergenståhl, 2007b; Nilsson, Leeman, Wahlund, & Bergenståhl, 2007) have used AF^4 to determine the size of large OSA starches; these studies are reliable because the starch was sufficiently degraded as to be soluble in an aqueous eluent, thereby avoiding the DMSO signal:noise problem. They also performed characterization in aqueous $NaNO_3$ solutions against ferritin standards. Their data from AF^4 analysis were used to indicate that high-pressure homogenization strongly damages the starch chains and that the extent of molar mass reduction was related to the turbulent flow conditions during homogenization (Modig, Nilsson, Bergenståhl, & Wahlund, 2006; Nilsson, Leeman, Wahlund, & Bergenståhl, 2006).

4. Physicochemical properties of OSA starches

4.1. *Surface-active properties*

4.1.1. *Aggregate formation in aqueous media*

Modification with hydrophobic groups gives the starch amphiphilic properties. When dissolved in water, such macromolecules preferentially migrate to the air/water interface forming a boundary layer whereby hydrophobic groups are oriented toward the air and starch extending into the water. Two studies have shown that OSA starches have excellent capability of lowering surface and interfacial tension at the air/water interface and were found to be better candidates for this purpose than other popular starch derivatives (e.g. starch acetates, phosphate derivatives or oxidised starches) (Prochaska, Kędziora, Le Thanh, & Lewandowicz, 2007a; Shogren & Biresaw, 2007). When the interface is saturated, amphiphilic macromolecules start to aggregate. Krstonosic, Dokic, and Milanovic (2011) have referred to the critical micelle concentration, CMC, in their paper, however this terminology may be misleading given the polydispersity and large size of starch molecules, leading to unstructured and large aggregates rather than micelles according to the IUPAC definition (IUPAC, 1997). As such, we prefer to use the term critical aggregation concentration, CAC. Krstonosic's study used two commercial modified waxy corn samples with four different techniques: viscometry, conductimetry, surface tension and dye solubilization. The CACs obtained ranged between 0.41 and 0.88 g L^{-1} depending on the sample and the technique. These values were much lower than the ones previously reported by (i) Varona, Martín, and Cocero (2009), between 4.5 and 6.6 g L^{-1} for four commercial samples derived from waxy maize and tapioca; and (ii) Järnström, Lason, Rigdahl, and Eriksson (1995), 1.8 g L^{-1} for a OSA-modified potato starch (*DS* = 0.018). Values from this method are highly dependent on the ratio between the total volume and the area of the hydrophobic interface, so comparisons between values from slightly different method parameters must account for this; furthermore, studies in this field would benefit from greater emphasis on the reporting of structural properties.

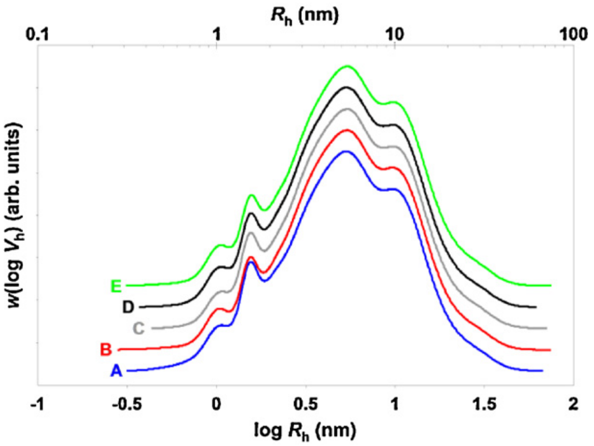

Fig. 7. SEC molecular size distributions of a waxy maize starch before (A) and after modification with OSA (B, *DS* = 0.005; C, *DS* = 0.017; D, *DS* = 0.037; E, *DS* = 0.058). The *X* axis is the hydrodynamic radius R_h, which is the effective size of the molecule; the *Y* axis is the weight of molecules with that size, with arbitrary vertical displacement for visual clarity.

Unpublished data from our laboratory.

OSA starches also interact with other macromolecules. Interactions with xanthan were first suspected by Ntawukulilyayo, de Smedt, Demeester, and Remon (1996a), then confirmed later by Krstonosic et al. (2011). Magnusson and Nilsson (2011) studied the interactions with α-β-livetin, the water-soluble fraction of egg yolk. As expected, interactions between these two biomacromolecules were observed to be highly pH-dependent, as pH 4 led to the strongest interactions. The formation of α-β-livetin/OSA–starch complexes was also dependent on the corresponding mass ratio. Light transmission experiments showed that complexes were preferentially formed at a 2:1 mass ratio. Interactions between proteins and polysaccharides have gained a growing interest over the recent years (Dickinson, 2009) and further research involving interaction with OSA starches can be anticipated, which could potentially lead to progress in the formulation of food emulsions. For example, Scheffler, Wang, Huang, San-Martin Gonzalez, and Yao (2010b) have shown that a combination of OS-phytoglycogen and ε-polylysine effectively block the permeation of pro-active compounds, resulting in high lipid oxidative stability of emulsions.

4.1.2. *Uses as an emulsion stabilizer*

Emulsification agents are colloidal stabilizers, containing both hydrophilic and hydrophobic moieties. The hydrophilic moiety can either be ionic (for example, as in the common electrostatic stabilizer sodium dodecyl sulfate), non-ionic (as in poly(ethylene oxide) nonyl phenyl ether), or both (e.g. some proteinaceous stabilizers). The stabilization can be entirely electrostatic, entirely steric (which is the mechanism whereby non-ionic water-soluble moieties stabilize because it is entropically unfavourable to compress these chains, as would occur if two sterically stabilized colloids were to come together), or both; the term for this last is electrosteric stabilization. OSA starches can function as electrosteric stabilizers, though due to the size of the molecules relative to the number of charged groups, their function is primarily steric, which affects their uses.

OSA starches are used in many food, cosmetics and pharmaceutical products as emulsifiers and stabilizers (Baydoun, Furrer, Gurny, & Müller-Goymann, 2004; Baydoun & Müller-Goymann, 2003; BeMiller, 2009; Dokić, Dokić, Dapčević, & Krstonošić, 2008; Mattea, Martín, Matías-Gago, & Cocero, 2009; Ntawukulilyayo et al., 1996a; Rayner, Timgren, Sjöö, & Dejmek, 2012; Reiner, Reineccius, & Peppard, 2010; Rodríguez-Rojo, Varona, Núñez, & Cocero, 2012; Taherian, Fustier, & Ramaswamy, 2007). Oils from various origins are generally selected as model systems to evaluate the emulsion stabilization properties, but some organic hydrophobic solvents (dichloromethane, ethyl acetate and hydrocarbons) have also been used (Chanamai & McClements, 2001; de Paz et al., 2012; Mattea et al., 2009; Nilsson et al., 2007; Viswanathan, 1999b). High surface loads have been reported (adsorption to cationic oil droplets, up to 40 mg m^{-2} (Nilsson & Bergenståhl, 2007a); emulsions of lavandin essential oil, up to 370 mg m^{-2} (Varona et al., 2009)), which suggests that a very thick layer of macromolecules was adsorbed at the oil/water interface. A special advantage is that OSA starches are almost colourless and tasteless in solution and that, unlike proteins, their capacities as stabilizers are essentially independent of pH and ionic strength of the medium (Tesch, Gerhards, & Schubert, 2002). This is because the steric stabilization is the dominant type in OSA starches (Erni et al., 2007; Taherian, Fustier, & Ramaswamy, 2006), although it is noted that because changes in pH and ionic strength can change chain conformations in solution, one does expect some slight depenedence on these parameters. When comparing the oil-in-water emulsions obtained with a whey protein and an OSA starch, Charoen et al. (2011) concluded that particles formed with the modified starch were more stable to external conditions (pH, salt and temperature). Mao and colleagues (Mao et al., 2009; Mao, Yang, Xu, Yuan, & Gao, 2010) also reported better stability against time for emulsions made using a commercial OSA starch rather than with whey protein isolate, although protein initially led to smaller particles immediately after homogenization. However, protein was found to offer β-carotene a better protection against oxidation than OSA starch stabilized emulsions. No data concerning the structural parameters of both the starch derivatives and the proteins were reported. OSA starch has also been reported to give more stable emulsions when used alone rather than in combination with sodium dodecyl sulfate, which is an effective surfactant (Krstonosic, Dokic, Nikolic, Dapcevic, & Hadnađev, 2012).

Emulsion capacity (the mass of oil dispersed per gram of sample) and colloidal stability of the particles over time have been reported to increase with *DS* (Segura-Campos et al., 2008; Segura-Campos, Chel-Guerrero, & Betancur-Ancona, 2010). Surprisingly, Bhosale and Singhal (2006) did not observe any significant differences in comparisons between native amaranth and waxy corn starches and their OS derivatives. Moreover, among three OSA-modified corn starches with different *DS* values (0.03, 0.07 and 0.11), Viswanathan (1999b) reported that the sample at *DS* 0.07 was able to form the best emulsions. A possible explanation is that at high *DS*, octenyl succinate groups are predominantly located at the midsections of starch chains, thus being unavailable for interaction with the hydrophobic phase. However, as some of the products used in Viswanathan's study were synthesized using the pyridine procedure, which appears to degrade starch chains, it is probable that the *DS*, the molecular weight and the *DB* were not kept constant, which may also have an influence on the stabilizing properties.

Dokić et al. (2008) compared the stabilities of corn oil-in-water emulsions obtained using two commercial OSA starches of unknown *DS* and *DB* (*DS* were probably close to 0.02 as these were food-grade modified starches), but different molecular weights. The oil droplets were more stable when using the surfactant of highest molar mass. By dispersing cyclohexane-in-water emulsions with an OSA-modified barley starch (weight-average molecular weight $\overline{M_W} = 8.6 \times 10^6$ g mol^{-1}, *DS* = 0.021, *DB* = 0.0502), Nilsson et al. (2007) showed that the high molar mass chains adsorbed preferentially over those of low molar mass at the cyclohexane/water interface. This selective adsorption was assumed to be due to convective mass transport in the turbulent flow fields during formation of the emulsion, which seems to favour the transport of the largest macromolecules to the interface. Existing data tend to show that the emulsifying capacity of OSA starches increases with the molecular weight of the macromolecules; however, this is contradicted by results reported by Liu et al. (2008) where the authors tested the emulsion capacity of an OSA-modified waxy corn starch after being subjected to enzymatic treatment with α-amylase to decrease its molecular weight. It was found that the product showed better emulsion capacity and stability properties after enzyme treatment, i.e. after its molar mass was reduced. Note that the *DB* and the size dispersity of the starch chains can also be affected by α-amylase, which can affect the CAC. Liu et al. did not characterize the structural parameters of the samples either before or after α-amylase treatment.

Nilsson and Bergenståhl (2006, 2007b) suspected the amount of dispersed oil to be connected to the surface substituent density (i.e. the density of OS groups on the surface of the macromolecules assuming (i) spherical geometry and (ii) that all OS groups are situated close to the surface). This latter assumption is increasingly uncertain with higher *DS* and molar mass, but more likely to be valid as the flexibility of the macromolecule increases; a flexible molecule is able to adapt its confirmation in order to optimize the interaction with the surface (Nilsson & Bergenståhl, 2007a). By comparing oil-in-water emulsions obtained with OSA-modified waxy corn starches and phytoglycogens, Yao and colleagues (Bi, Yang, Bhunia, & Yao, 2011; Scheffler, Huang, Bi, & Yao, 2010a; Scheffler et al., 2010b) concluded that with treatments with equivalent percentages of OSA, modified phytoglycogen and starch derivatives showed similar *DS*, though no studies were reported on the distribution of OS groups. More importantly, OSA-modified phytoglycogen displayed even greater emulsion capacity than the equivalent starch. While there are several differences between phytoglycogen and amylopectin, the key structural difference lies in the *DB* and branch structure, leading to the suggestion that increasing the *DB* or having a more random branch structure tends to give better emulsion stabilizing properties (*DB* values were not reported, but one expects the *DB* of phytoglycogen chains to be higher than that of pure amylopectin (Cuevas, Gilbert, & Fitzgerald, 2010)). Also, droplets in emulsions stabilized by OSA-modified phytoglycogen were smaller and more stable in time than those with OSA starch. This highlighted that the branched structure of the starch backbone plays a key role on the physical stability of the emulsion: more branched implies more rigid macromolecules, which implies thicker adsorbed layer around the droplet, which would normally suggest that the droplets would be more stable. Because of the influence of *DB* on the flexibility of the OSA-modified macromolecules, the coverage on the surface of an oil droplet also depends on this parameter. These implications are yet to be tested empirically and would benefit from further research. Scheffler et al. have observed that it is possible to reduce the susceptibility of lipids to lipid-degrading compounds, and thus to improve lipid oxidative stability of emulsions by increasing the *DB* (Scheffler et al., 2010a).

Some attention had also been given recently to the emulsifying capacity of starch particles, including intact granules, after surface modification with OSA. Yusoff and Murray (2011) were the first to mention the use of such products as particle stabilizers of oil-in-water emulsions: so-called Pickering emulsions for which droplets are stabilized by amphiphilic solid particles rather than surface-active molecules. While Yusoff and Murray used physically degraded particles by freeze-milling, Timgren et al. have used more intact granules in Pickering emulsion systems. This resulted in large droplets relative to classic surfactants; however, it was observed that such emulsions are very stable in time and exhibit excellent barrier properties that can be controlled well by formulation (Timgren, Rayner, Sjöö, & Dejmek, 2011). The properties of Pickering emulsions containing OSA starches make them suitable for applications such as encapsulation of sensitive, bioactive and/or valuable ingredients in food and pharmaceutical products.

4.1.3. Uses as an encapsulating agent

As a result of their excellent stabilizing properties in aqueous emulsions, OSA starches have been extensively used to make solid microcapsules that contain hydrophobic compounds: essential oils (Baranauskiene, Bylaite, Zukauskaite, & Venskutonis, 2007; Paramita, Furuta, & Yoshii, 2012), fish oils (Drusch, Serfert, & Schwarz, 2006a;Drusch, Serfert, Van Den Heuvel, & Schwarz, 2006b; Serfert, Drusch, & Schwarz, 2010), fruit oils (Partanen, Hakala, Sjövall, Kallio, & Forssell, 2005; Partanen, Yoshii, Kallio, Yang, & Forssell, 2002) and dietary oil (Tuomasjukka, Kallio, & Forssell, 2006). As a general procedure, the OSA starch is dissolved in an aqueous medium also containing the hydrophobic product to be encapsulated. The mixture is then spray-dried and capsules are obtained. The operating conditions can be adjusted to control the size and morphology of capsules, as well as the percentage of chemical encapsulated (Santos, Martín, Meireles, & Cocero, 2012; Varona, Kareth, Martín, & Cocero, 2010). Interestingly, Li et al. (2009) reported the synthesis of cross-linked OSA starch microcapsules made from the reaction between starch hydroxyl groups and trisodium trimetaphosphate. Microcapsules were obtained simply by air-drying after the crosslinking reaction, which constitutes an alternative to spray-drying. Deterioration of sensitive ingredients has been reported (Hogan, O'Riordan, & O'Sullivan, 2003) at the high drying temperature used in spray-drying (often more than 200 °C). These last authors did not compare the physico-chemical properties between cross-linked microcapsules and those obtained by spray-drying. However, a recent study found that microcapsules of lycopene obtained by spray-drying were relatively stable to extrusion temperatures up to 187 °C (Choudhari, Bajaj, Singhal, & Karwe, 2012).

The choice of an encapsulating agent has a direct influence on the functional properties of the resulting microcapsules. After encapsulation of orange-peel oil, an OSA starch ($DS = 0.042$) showed better oil retention capability after spray-drying than phosphate and acetate derivatives made from the same waxy maize starch ($DS = 0.046$ and 0.033, respectively) (Murúa-Pagola, Beristain-Guevara, & Martínez-Bustos, 2009). Microcapsules made from OSA derivatives also exhibited better retention performances than β-cyclodextrin (Jeon, Vasanthan, Temelli, & Song, 2003), maltodextrin and whey protein (Brückner, Bade, & Kunz, 2007). Schwarz and colleagues (Drusch & Schwarz, 2006; Serfert, Drusch, Schmidt-Hansberg, Kind, & Schwarz, 2009) showed that starches of high molecular weight can lead to viscous solutions that are difficult to spray-dry, decreasing the efficiency of the microencapsulation process. Increasing the viscosity of the emulsion before spray-drying increases the amount of dissolved oxygen and the droplet size, resulting in microcapsules with low oxidative stability and low oil retention. Thus low molecular weight products such as glucose syrup (Drusch, Serfert, Scampicchio, Schmidt-Hansberg, & Schwarz, 2007) or enzymatically hydrolyzed starches (Zasypkin & Porzio, 2004) can be used in combination with OSA starches in order to decrease the viscosity of the medium prior to spray-drying. It is noteworthy that these products also act as plasticizers, affecting the microcapsules' glass transition temperature T_g. For each formulation, an optimal compromise must be found between (i) a sufficiently high T_g that ensures good stability against humidity and temperature, promoting flavour retention, and (ii) emulsions that are easy to spray-dry, thus optimizing the encapsulation rate.

OSA starches have also been used for microencapsulation in combination with other polysaccharides, e.g. konjac glucomannan (Yang, Xiao, & Ding, 2009) and soybean soluble polysaccharide (Anwar & Kunz, 2011). Shen, Augustin, Sanguansri, and Cheng (2010) also used a cationic polysaccharide, chitosan, for encapsulation. The chitosan formed electrostatically bound complexes with anionic OSA starch, resulting in very stable microcapsules.

4.1.4. Surface and interface properties

As a result of the chemical modification with OSA, the hydrophobicity of modified starch macromolecules is greatly increased. Prochaska, Kędziora, Le Thanh, and Lewandowicz (2007b) reported that OSA starches ($DS = 0.01$) stand out from acetylated starch derivatives for their excellent capability to lower surface and interfacial tension at the air/water and toluene/water interfaces, even at lower *DS* (acetylated distarch phosphate, acetylated starch and acetylated distarch adipate with *DS* by acetyl groups of 0.03, 0.06 and 0.07, respectively). The hydrophobicity increases directly with *DS*, demonstrated by cassava derivatives in which the modification with OSA causes the water sorption capacities to decrease significantly.

Other researchers have evaluated some potential applications of OSA starches in material science, for which interfaces often play a key role in end-use properties. Järnström et al. (1995) used modified potato starches as efficient dispersing agents for kaolin particles in aqueous media. Films made with OSA starches were found to exhibit better water barrier properties than those made with oxidized and acetylated cross-linked starches (Pérez-Gallardo et al., 2012). Barrier properties of the films were found to depend on the ability of starch macromolecules to reorganize. The interactions between those chemical substituents tested were observed to hinder or promote reorganization. One can conclude that octenyl groups can effectively interact with each other, leading to films with compact microporosity through which water can barely diffuse. However, another study pointed out that hydroxypropylated starches gave films with better water barrier properties than OSA starches (Jansson & Järnström, 2005). The hydroxypropyl group values of *DS* used in this study (0.11–0.13) were much higher than those for OS (0.02–0.04), which limits comparison between the two starch derivatives. Ben Arfa, Preziosi-Belloy, Chalier, and Gontard (2007) used OSA starch as paper coatings and inclusion matrices of two antimicrobial compounds: cinnamaldehyde and carvacrol. The starch chains allow a good adhesion to the paper surface (i.e. cellulose) and the octenyl groups give the hydrophobicity needed to retain and progressively release the hydrophobic chemicals, although soy protein isolates were shown to be better candidates for this application.

As quite cheap and sustainable resources, polysaccharides are increasingly used in combination with synthetic polymers to try to make partially degradable plastics. The main challenge is to increase the fraction of bio-sourced products in the blend while keeping satisfactory physico-chemical properties. Lawton, Doane, and Willett (2006) made starch derivative/polyhydroxyester composites, but observed that using OSA starches instead of unmodified starches did not lead to significant improvements in mechanical properties: tensile strength, Young's modulus and elongation at break. The authors did not test the properties of pure polyhydroxyester, making it impossible to evaluate any potential gain from such a combination. Evangelista, Nikolov, Wei, Jane, and Gelina (1991) studied the effect of compounding and starch modification with OSA on properties of starch-filled LLDPE (linear low-density polyethylene). It was found that the addition of either modified or native starch to LLDPE decreased both the tensile strength and the elongation of the resulting films; however this drop in mechanical properties was less marked when using the OSA starch rather than the unmodified one. Rivero et al. (2009) successfully used an OSA starch as compatibilizer in a LLDPE/starch blend to enhance interactions between these two polymers. The mechanical properties of the composite were significantly improved by adding 10 wt% of compatibilizer ($DS = 0.045$). Some formulations even exhibited similar yield stress to pure LLDPE.

4.2. Pasting properties

4.2.1. Gelatinization process

The gelatinization of starch and starch derivatives in water corresponds to the melting of granules to form a gel, and is generally characterized by DSC. Gelatinization properties are defined by the three following temperatures: T_0 (the onset temperature at which the gelatinization starts), T_p (the peak temperature which represents the endothermic peak on the DSC thermogram) and T_c (the conclusion temperature at which the sample is fully gelatinized). OSA starches exhibit significantly lower T_0, T_p and T_c than their native counterparts, a feature emphasized as the *DS* increases. This is attributed to the disruption of the crystalline structure of the starch grains after modification with OSA (Bhosale & Singhal, 2007). OS groups tend to weaken the interactions between starch macromolecules, allowing the granules to swell and to melt at lower temperatures. This assumption is strongly supported by the fact that the gelatinization enthalpy ΔH_g also decreases as the *DS* increases, indicating that modified starch granules require less energy to melt. For example, Bao et al. (2003) observed a significant drop in gelatinization temperatures from 75.2 to 52.5 °C for a rice starch with *DS* ranging from 0 to 0.0452, respectively. At the same time, ΔH_g was found to decrease from 11.4 to $6.4\,\mathrm{J\,g^{-1}}$. Many authors have since studied the gelatinization properties of OSA starches from other botanical origins and drawn similar conclusions: corn (Bhosale & Singhal, 2007; Chung et al., 2010; Han & BeMiller, 2007; Zhu et al., 2011), wheat (Bao et al., 2003), tapioca (Thirathumthavorn & Charoenrein, 2006), rice (Thirathumthavorn & Charoenrein, 2006), amaranth (Bhosale & Singhal, 2007), *P. lunatus* (Segura-Campos et al., 2008, 2010), banana (*Musa paradisiaca* L.) (Carlos-Amaya, Osorio-Diaz, Agama-Acevedo, Yee-Madeira, & Bello-Peĭrez, 2011) and high amylose maize (Zhang et al., 2011).

Contrasting with the results above were those of OSA-modified potato starches for which T_0, T_p and T_c were higher than for the native starch, despite quite high *DS* being used (up to 0.0397) (Bao et al., 2003). This was also seen in another study with waxy potato (Ortega-Ojeda, Larsson, & Eliasson, 2005). The authors gave no explanations as to why potato starch derivatives behave so differently, though one might assume that this is related to the presence of phosphate groups in potato starches, which could prevent the formation of strong interactions between the chains. This hypothesis is not supported by other experimental data, as the ΔH_g of native potato starch ($17.2\,\mathrm{J\,g^{-1}}$) has been reported to be much higher than for native rice and wheat starches (11.4 and $10.8\,\mathrm{J\,g^{-1}}$, respectively) (Bao et al., 2003). Another possible explanation would be that potato starch chains are disproportionately affected during the chemical modification with OSA, compared to starches from other botanical sources. This could be linked again to the presence of phosphate groups.

4.2.2. Rheological properties of OSA starch pastes

Once dissolved in water at the appropriate concentration, OSA starches form pastes with pseudoplastic properties. Bhandari, Singhal, and Kale (2002) observed a strong shear thinning behaviour in pastes obtained from corn and amaranth starch derivatives. These authors also found higher viscosities with an increase of *DS*. Later work of Park, Chung, and Yoo (2004) led to similar conclusions, i.e. dynamic frequency sweep tests on OSA starch pastes showed that both elastic and loss moduli, G' and G'', increase with increasing the *DS*. This could be due to any or all of the three following reasons:

(i) Attached hydrophobic groups along starch chains act as hydrogen bonding disrupters making the starch chains more readily water-soluble, which results in more viscous solutions than that of native starches. Indeed, the clarity of pastes increases with *DS*, testifying to the positive impact of attached hydrophobic groups on the solubility in aqueous media (Bhosale & Singhal, 2007; Song et al., 2006b; Song, Zhu, Li, & Zhu, 2010). Note that improved paste clarity is an important parameter for the manufacture of many food products that require transparency (Jyothi, Rajasekharan, Moorthy, & Sreekumar, 2005).
(ii) Attached hydrophobic groups can aggregate in aqueous media, which gives rise to weak intra- and intermolecular hydrophobic interactions in aqueous solutions, leading to physical polymer networks at concentrations above the critical overlap concentration (Creuzet, Kadi, Rinaudo, & Auzély-Velty, 2006; Tizzotti et al., 2010).
(iii) Amylose is suspected to form complexes with hydrophobic groups, leading to the formation of a physical network (Ortega-Ojeda et al., 2005). Amylose is known to form inclusion complexes with certain hydrophobic ligands such as iodine, alcohols, fatty acids or surfactants (Egermayer, Karlberg, & Piculell, 2004). This cannot be ruled out in the Park et al. study, as the maize starch used was not explicitly of a waxy variety, i.e. not one with no amylose.

Pasting properties of OSA starches are of great importance for the food industry and have been extensively studied by rapid viscoanalyser (RVA) measurements. Samples are generally prepared by mixing the OSA starch and water. The solution is then transferred into the RVA and undergoes a heating–cooling cycle under stirring. Peak viscosity (PV), cool paste viscosity (CPV) and hot paste viscosity (HPV) are the most important parameters obtained from these measurements. It has been widely reported that OSA starches have significantly higher PV, CPV and HPV than the corresponding unmodified native starches, regardless of botanical source: rice (Bao et al., 2003; He et al., 2006; Shih & Daigle, 2003; Song et al., 2006a; Thirathumthavorn & Charoenrein, 2006; Tukomane & Varavinit, 2008), *P. lunatus* (Segura-Campos et al., 2008, 2010), corn (Chung et al., 2010; Han & BeMiller, 2007; Song et al., 2010; Zhu et al., 2011), tapioca (Han & BeMiller, 2007; Thirathumthavorn & Charoenrein, 2006), banana (*M. paradisiaca* L.) (Carlos-Amaya et al., 2011), wheat (Bao et al., 2003) or potato (Han & BeMiller, 2007; Hui et al., 2009).

Contrary to all of the other botanical sources listed above, it has been reported that increasing the *DS* does not necessarily lead to higher viscosities when using potato starches. Bao et al. (2003) noted that the HPV of OSA-modified potato starches decreases as the *DS* increases, despite modified products being more viscous than the unmodified starch. This was also seen by Wang, Su, and Wang (2010) who also observed a noticeable drop of the paste viscosity at *DS* greater than 0.016 for OS-potato starch samples. By performing small deformation oscillatory rheometry measurements on pastes made from OSA-modified potato starches, Ortega-Ojeda et al. (2005) noticed that high levels of OS substitution resulted in lower G' and G'' values. As with the properties mentioned in Section 4.2.1, a possible explanation is again the high phosphorus content. The presence of phosphate moieties along chains may reduce hydrogen bonding, possibly making native potato starches more readily soluble in water and therefore leading to more viscous pastes than starches from other botanical sources (Noda et al., 2006).

For obvious reasons, the viscosity is expected to increase with molecular weight, all other things being equal. Song et al. (2010) performed acid hydrolysis on a waxy corn starch followed by modification with OSA, which led to three samples with equivalent *DS* but different molecular weights. The RVA pasting curves of these three samples indicated that PV, CPV and HPV strongly decrease with the degree of acid hydrolysis of the starch backbone, i.e. its molecular weight. The same conclusions were drawn for tapioca and rice starches and their OSA-modified derivatives (Thirathumthavorn & Charoenrein, 2006). It is noteworthy that even when acid treatment reduced the degree of polymerization of starch chains by half, the HPV of OSA starches was still higher than for native starches. This emphasizes the dominant impact of the *DS* over the molecular weight on the viscosity of the pastes. Also, He et al. (2006) observed a negative correlation between amylose content and RVA parameters (PV, CPV and HPV), which is directly related to the low water solubility of amylose chains.

4.2.3. *Freeze-thaw stability of OSA starch pastes*

OSA starches have long been identified as having desirable qualities in frozen food products, particularly as a fat substitute in maintaining texture through multiple freeze-thaw cycles. The utility of this feature has been recognized in patents since 1968 (Ganz & Harris, 1968). Generally, the stability is measured by a straightforward method involving the free water development (syneresis) after each freeze-thaw cycle. The expelling of water from starch gels after having been stored at low temperatures is through the amylose and amylopectin chains realigning, forming a gel matrix throughout the liquid. Other authors have measured the freeze-thaw stability by noting the number of cycles the starch gel can withstand before expelling water or becoming spongy. Huang et al. (2010) used corn starch, subjected to enzyme hydrolysis to varying degrees and modified counterparts to *DS* between 0.015 and 0.022, with the results indicating some retrogradation in all samples after just two cycles of freeze-thaw stress. This metric is not quantitative, (i) because the gelation is binary, syneresis or no syneresis and (ii) because a great deal of syneresis can happen in the forthcoming cycles. The majority of freeze-thaw studies used quantitative methods, which determine the percentage of water developed over multiple freeze-thaw cycles. By this method, modification with OSA has been demonstrated to impart excellent freeze-thaw stability to rice starch with *DS* as low as 0.012 (Song et al., 2006a). The positive effect is likely to increase with *DS*, as noted by Song et al., though their range of *DS* was limited to a maximum of 0.019. In this case, four freeze-thaw cycles caused native starch gels to exhibit syneresis of 54%, compared to 4.2% at the highest *DS*. OSA-modified waxy corn starches also showed good freeze-thaw stability (Abdollahzadeh et al., 2008; Song et al., 2010), with nil syneresis after up to four cycles at *DS* above 0.0163 (Zhu et al., 2011).

Amaranth starches also showed noticeable improvement in freeze-thaw stability when modified with OSA, the effect improving with increased *DS* up to and above 0.02 (Bhosale & Singhal, 2007). With both amaranth and waxy maize starches, Bhosale and Singhal included a pre-treatment of storage at 4 °C and saw nil syneresis for up to six freeze-thaw cycles at the highest *DS*, while the same research group found similar starches resisted syneresis for up to seven cycles without the pre-storage at 4 °C (Bhandari & Singhal, 2002a). A more recent study agreed that increasing the *DS* of potato starch (∼20% amylose) also resulted in better freeze-thaw stability. In this case the syneresis rate was improved only for a single cycle, from 88.3% in native starch to as low as 39.0% for *DS* 0.021 (Wang et al., 2010). In all the examples listed above, reduction in the extent of retrogradation of OSA starches is attributed to the steric effect imposed by OS groups, which prevents the alignment of starch chains when the sample is stored at low temperatures.

While the general consensus indicates significant improvement to freeze-thaw stability resulting from modification with OSA, one exception has been noticed when using starch from the legume *P. lunatus* (Segura-Campos et al., 2010). In this case, chemical modification seems to have a negligible or deleterious effect on the freeze-thaw stability. It also seems in Segura-Campos' study that almost all of the damage done by freeze-thaw stress occurs in the first cycle. While it is accepted that syneresis is generally inhibited by OS substitution, it is apparently increased according to the degree of hydrolysis (Song et al., 2010). This should indicate that where freeze-thaw stability is a priority, the best OSA starches are those of high *DS* and high molecular weight.

4.3. *Human health*

4.3.1. *Nutritional/digestive properties*

OSA starches appear as ingredients in many food products under the International Numbering System codex E1450. Starch modified with OSA has different digestive properties to the native substrate. This is especially apparent by the increase in starch components that are either slower to be digested or completely resistant to digestion. One can divide starch samples into three families of molecules: rapidly digested starch (RDS), slowly digested starch (SDS) and resistant starch (RS), representing their relative susceptibilities to digestion.

Modification with OSA is known to increase levels of SDS and RS more than other modifications such as hydroxypropylation, acetylation or crosslinking in various combinations (Han & BeMiller, 2007), resulting in high SDS functional fibre which is considered beneficial to human nutrition (Wolf, Bauer, & Fahey, 1999). One of the earliest publications on the enzymatic digestion of OSA-modified waxy maize starch showed a considerable inhibitory effect that continued to increase with *DS* (Viswanathan, 1999a). The *DS* used in Viswanathan's study were all higher than the 3% equivalent limit for food products; however, the implications at this higher level of *DS* offer good insights into the behaviour of the product. Han and BeMiller also noted that heat treatment of OS-waxy maize starch lowered the RS and increased the SDS to even greater nutritional advantage. More recently, similar modifications have been investigated with canna starch, where products modified with OSA showed higher RS than any other modification; however crosslinking produced slightly more SDS at the highest cooking times (Juansang, Puttanlek, Rungsardthong, Puncha-arnon, & Uttapap, 2012).

The result of resistant components in OSA starch has also been tested in vivo in human subjects, where commercial OSA-modified waxy maize starch was tested against glucose for glycemic response and effects on other gastrointestinal functions. In this instance it was not compared directly in vivo with waxy maize starch of a similar structure, but in vitro results suggest OSA-modified waxy maize starch has a greater resistance to digestion compared to cooked and uncooked waxy maize starch in the later stages (Wolf et al., 2001). The knowledge of Han's heat-treated, high *DS* OSA-modified waxy maize starch and Wolf's in vivo methods contributed to a later study demonstrating a greatly decreased glycemic response in subjects who consumed heat-treated OSA-modified waxy maize starch (He, Liu, & Zhang, 2008).

Another study by Wolf's group also looked at glycemic response, finding that increases in breath hydrogen could indicate that OSA was being absorbed by the body as the starch was degraded in the small intestine (Heacock, Hertzler, & Wolf, 2004). This aspect was a confirmation of a much earlier study in infant feed formulas containing high levels of OSA starches, which showed signs of OSA in blood samples and metabolites in urine (Kelley, 1991).

These metabolites are highlighted as a potential false positive when performing various routine tests on the composition of urine in the diagnosis of disease.

The products of the digestion process have been presented in a study into the in vitro fermentation of 35 different carbohydrates, including commercially sourced OSA starch, by monitoring the amounts of short-chain fatty acids (SCFA) produced as a result of the application of human faecal inoculum. In their tests, various SCFAs were counted in proportion to raffinose as the standard (Ferguson & Jones, 2000). OSA starch resulted in higher overall SCFA than 21 of the 35 carbohydrates surveyed, but two specific varieties of SCFA stand out as important in the case of OSA starch: butyric acid was higher in 28 of these 35 and iso-valeric acid was higher in only 5 out of 35.

Attention more recently has turned to high amylose starches after modification with OSA (Zhang et al., 2011). One study looking at high amylose OSA-modified maize starch found the SDS and RS of cooked starch actually decrease with the initial low levels of chemical modification ($DS = 0.009$) but increase at higher DS, whereas the uncooked starch showed consistent increase in RS with DS, but a decrease in SDS. This may be attributed to the initial disruption of starch crystal structure by modification with OSA.

One paper has been published that rejects an undescribed OSA starch as a candidate from a list of possible replacements for traditional emulsifying salts in processed cheese (Černíková et al., 2010). Other papers find OSA starch to be a suitable partial substitute for fat in muffins (Chung et al., 2010), mayonnaises (Thaiudom & Khantarat, 2011), and as a texturizer in sausages (Song et al., 2010). In the case of muffins, Chung et al. synthesized their OSA starches from waxy maize starch under dry heating reaction conditions to find how the pH of the reaction affected textural changes, primarily stemming from differences in the degree of hydrolysis caused in parallel with the esterification.

4.4. *In vivo effects*

No adverse effects have been observed in rats given diets high in OSA starch (Buttolph & Newberne, 1980) and to date no major issues have been highlighted by international food safety authorities (EFSA, 2010). Furthermore, OSA starches, though normally seen as a sodium salt, have been investigated and found safe when combined with aluminium (Nair & Yamarik, 2002).

OSA starches have been assessed for ocular tolerance in topical applications such as eye drops (Baydoun et al., 2004). This study used rabbits for in vivo treatments and excised porcine cornea to evaluate the damage done by two commercial OSA starches. While a small amount of irritation ensued from the treatment, it was determined to be within the generally accepted limits. This built on their previous work to confirm the applicability of OSA starches to facilitate permeation of the cornea by bioactive emulsions.

In terms of bioavailability, positive effects have been noted with formulations that include OSA starch as an encapsulating agent, where the total effect of the formulation was to protect the bioactive compound from premature metabolism (Ge, Zhang, Gan, & Gan, 2008). This goes hand-in-hand with the increase of SDS and RS as described in the previous section, as it is these components that serve to protect some compounds in transit through the small intestine to the colon, where those bioactive compounds have more desirable effects (Wang et al., 2011). In human studies, Ntawukulilyayo, Vervaet, Remon, Görtz, and Berlo (1996b) found the combination of OSA starch with xanthan gum to be effective in limiting the release and uptake of bioactive components (in this case ibuprofen) so that the effect of such components could be attenuated and diffused over a longer time period. This was contrasted with xanthan gum alone, which released the active ingredients in a relatively smaller time period. All this is supported by other studies showing desirable qualities imparted by OSA starches, such as wettability, lack of unpleasant flavour and low chemical interference when delivering suspensions of pharmaceutical products (Kuentz, Egloff, & Röthlisberger, 2006; Ntawukulilyayo, Bouckaert, & Remon, 1993).

5. Concluding remarks and future directions

The number of publications in the field of OSA starch synthesis and characterization has significantly increased in the last decade. Although some new synthesis procedures have been reported, modification of starch with OSA in aqueous media remains the most widely used technique, as it does not require any hazardous organic solvents and allows acceptable reaction yields with mild experimental conditions (temperature about 30–35 °C and pH around 8.5), which preserve the integrity of the starch chains.

Whereas the optimization of synthesis conditions has been the topic of a reasonable number of studies, it is surprising that so few authors have investigated the structural characterization of the modified products. While the degree of substitution DS is often provided, this is not the case of other structural parameters such as the degree of branching DB, the average molecular weight, the size and the size polydispersity of the macromolecules. However, those parameters probably exert a significant influence on the end-use functional properties of OSA starches. Improved SEC and NMR techniques of starch characterization have recently been developed and proven to be easily transposable to starch derivatives.

A comprehensive characterization of OSA starch structural parameters would undoubtedly lead to a better understanding on their impact on physico-chemical properties. Profitable future directions include the correlation between the macromolecules' structure and their emulsion stabilizing, encapsulating, pasting or digestive properties. Specific attention should be paid to the influence of the intrinsic highly branched structure of starch chains, which makes starch such a unique polysaccharide when compared to other common bio-sourced polymers like cellulose. It is likely that starch chains' macromolecular parameters would be less critical when used in the form of intact granules rather than as individual surfactant macromolecule, but OSA starch Pickering emulsions also warrant more attention given the promising outcomes reported so far. Enzymatic digestion properties also deserve more attention, as these products are widely used as food additives.

Another field of research that could attract more interest is the botanical source of the starch substrate, as starches from different sources often have very different structures. Waxy maize varieties are very widely studied in the literature when compared to other starch varieties, because of industry limitations and resource availability. However, academic studies may yet find innovation in less explored sources, illustrated by the distinction between OSA-modified grain and potato starches. Little work has been reported on products made from high amylose starches. Such derivatives could potentially be of interest for food applications, as high amylose starches are known to result in firmer gels and exhibit better enzymatic resistance than waxy varieties rich in amylopectin, which is due to a higher initial content of resistant starch (RS) and a lower glycemic response. Another relevant example is potato starches; indeed, OSA-modified potato starches were reported to exhibit different pasting and gelatinization properties, possibly due to the presence of phosphate groups. As stressed in Section 4.2, the attachment of OS groups in alkaline conditions is suspected to affect these phosphorylated starches, which could result in different pasting behaviour. Variations in the amount of phosphate moieties in potato-based starch products before and after chemical modification with OSA may be investigated with a comprehensive ^{1}H and ^{31}P NMR analysis and/or elemental analysis. Finally, despite not being technically classified as starch, phytoglycogen derivatives were found to possess superior emulsion stabilization properties, which emphasize the impact that the branching density and distribution may have on this feature. Phytoglycogen is not usually found in healthy plants, but can be produced in small amounts, for example, by maize with mutant *sugary1* genes (James, Robertson, & Myers, 1995). For this reason it is unlikely to be available in the quantities required for any commercial use, but it should be seriously considered for some niche applications with high value-added products like in vivo biocompatible and biodegradable drug carriers.

The preparation of OSA starches is a well-established field of research. Nevertheless, the correlations between the structural parameters and the physico-chemical properties are still far from exhaustively investigated. Such progress will ultimately lead towards tailor-made structures and chemical compositions leading to products with optimized functional properties for targeted applications.

Abbreviations and terminology

OSA starch: any starch that has been modified with OSA, which results in the addition of an octenyl succinate group to the starch; AF^4: asymmetric flow field-flow fractionation; CAC; critical aggregation concentration; CMC: critical micelle concentration; CPV: cool paste viscosity; TFA-d_1: deuterated trifluoroacetic acid; DMSO-d_6: deuterated dimethyl sulfoxide; *DB*: degree of branching; *DS*: degree of substitution; DSC: differential scanning calorimetry; FTIR: Fourier transform infrared; G': storage modulus; G'': loss modulus; GI, glycemic index; HPV: hot paste viscosity; LLDPE: linear low-density polyethylene; $\overline{M_n}$: number-average molecular weight; $\overline{M_w}$: weight-average molecular weight: NMR: nuclear magnetic resonance; OS: octenyl succinate; OSA: octenyl succinic anhydride; PV: peak viscosity; RDS: rapidly digested starch; RS: resistant starch; RVA: rapid viscoanalyser; SCFA: short-chain fatty acids; SDS: slowly digested starch; SEC: size exclusion chromatography; SEM: scanning electron microscopy; T_g: glass transition temperature; ΔH_g: enthalpy of gelatinization.

Acknowledgements

We gratefully acknowledge funding from the Australian Research Council (LP100100225 and LP0990769) and from DSM Nutritional Products.

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