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A two-tier modified starch-oxidation followed by *n*-octenyl succinylation as gum Arabic substitute: Process details and characterization

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ABSTRACT

Corn starch was oxidised using sodium hypochlorite to enhance its film forming property and reduce viscosity. This oxidised starch (OS) was further modified by *n*-octenyl succinic anhydride (OSA) to introduce hydrophobicity. This dual modified starch (OS-OSA) was characterized for crystalline and thermal attributes. The emulsion stability, viscosity and particle size of OS-OSA based emulsion with 60% soybean oil loading was compared with OS and gum Arabic (GA). The spray dried microcapsules using OS-OSA and GA as wall materials at 20% (w/v) containing emulsions demonstrated similar surface morphology (smooth surface devoid of cracks) and particle size. Microencapsulation with OS showed lower encapsulation efficiency (13%) than those with OS-OSA and GA (similar at 58%). The half-life of OS-OSA (39 weeks) microcapsules was lower than GA (44 weeks) but the final encapsulation efficiency after 18 weeks was similar in both cases. Thus OS-OSA corn starch can potentially replace gum Arabic for microencapsulation applications.

1. Introduction

Starch has been the biopolymer of choice for physical and/or chemical modifications to fulfil the needs of the continuously developing consumer goods industries. Starch modification by pregelatinization, annealing, cross-linking, esterification, etherification, oxidation, among many others have been widely studied (Murphy, 2000). The primary objectives of these modifications are to either alter physicochemical properties such as retrogradation, solubility, flowability, viscosity, mechanical strength (of solutions, films), or emulsifying properties for targeted applications. Starch oxidation leads to reduction in gelatinized starch viscosity, improved clarity, and film forming property (Chattopadhyay et al., 1997; Kuakpetoon and Wang, 2006). Esterification of starch with *n*-octenyl succinic anhyride (OSA) imparts partial hydrophobic character to starch and resistance to enzymatic hydrolysis (Sweedman et al., 2013).

Combination modifications of starch have been engineered to develop novel molecules with desired properties such as improved emulsifying ability, drug delivery and reduced digestibility (Zia-ud-Din et al., 2017). Octenyl succinylation of hydroxypropylated potato starch (Baranauskienė et al., 2016) and cross-linked nanocrystalline starch has been studied for widening their respective applications (Ren et al., 2016). Dual modification of potato and glutinous corn starches by response surface methodology have been reported (Liu et al., 2011; Ren et al., 2009), and so is its use for flocculation in kaolin suspensions (Järnström et al., 1995). In another study, the oxidised-OSA modified waxy maize starch was synthesized, minimally characterized, and used for microencapsulation with no details on storage study (Kong et al., 2010).

Microencapsulation is a technique of covering tiny droplets or particles by a shell/wall of appropriate properties to form small capsules. This technique confers protection, controlled release, and improves handling of the core material (Bakry et al., 2016). Amongst the various techniques of microencapsulation, spray

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drying is the most common. The wall material used for encapsulation of any hydrophobic core is required to possess properties such as good film forming, emulsifying, rheological (low viscosity at high concentration), chemical non-reactivity, solubility in acceptable solvents, food grade status and low cost (Desai and Park, 2005). A partial hydrophobicity is desirable in wall materials used for microencapsulation of lipophilic core material as it aids in making stable emulsions that ensures efficient and effective encapsulation (Cheuk et al., 2015; Tesch et al., 2002). Edible oils such as flaxseed, fish and soybean have been microencapsulated using a wide range of wall materials such as whey protein, soy protein, OSA-starches, pectin and cellulose for designing functional foods, protection against oxidation, and masking of unpleasant flavour (Carneiro et al., 2013; Encina et al., 2016; Tolve et al., 2017). This has propelled scientists all over the world to look for economical and effective wall materials that can also be readily available for use at industrial level.

Gum Arabic, a tree exudate harvested in Asia, Egypt and sub-Saharan region has been the biopolymer of choice for microencapsulation purpose (Williams and Phillips, 2009) and is also considered to be the industry standard. Structurally, the side chains are composed of two or five 1,3-linked β-D-galactopyranosyl units, joined to the main chain by 1,6-linkages and conjugated with proteins (Sanchez et al., 2017). The seasonal variation, high costs and limited availability have promoted research in the field of developing substitutes (Kshirsagar and Singhal, 2007; Sarkar et al., 2012).

The primary aim of this study was to develop a commercially feasible gum Arabic substitute as a wall material for microencapsulation. The approach proposed for this purpose was dual modification comprising of oxidation of starch to reduce its viscosity and impart film forming property, followed by *n*-octenyl succinylation of the resulting oxidized starch for imparting hydrophobicity. The native starch, oxidized starch and the dual modified starch so obtained were characterized for structural and thermal attributes. The reaction conditions for both the modifications were tailored such that the properties matched that of gum Arabic. Soybean oil was used as a model oil system for emulsification. Its high content of long chain triglycerides makes many bioactives more bioaccesible (Salvia-Trujillo et al., 2013). The emulsions were studied for their stability and then spray dried. The microcapsules were then characterized for particle size, surface morphology and kinetics of retention of oil on storage.

2. Materials and methods

2.1. Materials

Corn starch (industrial grade) was procured from R. K. Enterprises (Masjid Bandar, Mumbai, India). Sodium hypochlorite solution (4%, w/v) was procured from Merck specialities Private Ltd. (New Delhi, India). OSA (Sigma-Aldrich, Chemical Co., MO, USA) was generously gifted by Roquette India Pvt. Ltd. Soybean oil of FORTUNE® brand was used. All other chemicals and reagents of analytical grade were used.

2.2. Methods

2.2.1. Oxidation of starch

Corn starch was dispersed in water (20, 30, 40 and 50%, w/w) and the pH (7, 7.5, 8, 8.5, 9, 9.5 and 10) of this dispersion was adjusted using 0.1 N NaOH. The reaction was carried out at room temperature (30 ± 2 °C). Sodium hypochlorite (0.004 g Chlorine/g of starch) was added over 1.5 h of the total reaction time (1.5, 2 and 2.5 h). At the end of the reaction, the pH was adjusted to 7 using 0.2 N sodium bisulfite solution. The starch was separated by vacuum filtration and washed with water till it was free of chlorine (tested using 0.1 N silver nitrate solution) (Chattopadhyay et al., 1997). The mass was dried in an oven at 50 °C.

2.2.2. Characterization of oxidised starch

The viscosity of the oxidised starch was determined by first gelatinization of the starch slurry (20%, w/w) followed by cooling to 27 ± 2 °C. The viscosity was determined at 60 rpm using LV spindle no. 61 and 62 (Brookefield Rheometer-III, Brookefield, UK). The carboxyl and carbonyl content of the oxidised starch sample closest to GA in terms of viscosity was determined as reported by Chattopadhyay et al. (1997). Films were prepared from the aforementioned oxidised starch and GA and evaluated for their tensile strength as per a reported method (Shah et al., 2016) using the tensile grips (A/TG) on texture analyser (TA.XT2i, Stable Microsystems, Surrey, UK) at a test speed of 1 mm/s.

2.2.3. OSA modification of oxidised starch

Oxidised starch (OS) giving the desired viscosity was esterified with OSA. The esterification was performed as reported by Bhosale and Singhal (2006). The OS was dispersed in water and the pH (7, 8, 9 and 10) adjusted as per the reaction using 0.1 N NaOH. OSA (1%, 1.5%, 2%, 2.5% and 3%, w/w of starch) was added to this slurry dropwise over 2 h every 30 min. The reaction pH was maintained using 0.1 N NaOH till its completion (3 h, 6 h, 12 h, 18 h and 24 h). The slurry was neutralized using 0.1 N HCl or NaOH. It was then centrifuged and washed thrice with distilled water followed by overnight drying in vacuum oven at 40 °C. A native starch batch at OS-OSA optimized reaction conditions was performed to assess the effect of oxidation on *n*-octenyl succinylation of starch.

2.2.4. Estimation of degree of substitution

The degree of substitution (DS) of the OSA modified oxidised starch was estimated by the alkali saponification method followed by back titration of the excess alkali (Bhosale and Singhal, 2006). The DS was calculated according to the equation:

$$W = \frac{(\mathrm{Blank} - \mathrm{sample}) \times \mathrm{N} \times \mathrm{M} \times 100}{\mathrm{Wt\ of\ sample\ in\ gm} \times 1000} \tag{1}$$

$$DS = \frac{\mathrm{R} \times \mathrm{W}}{100 \times \mathrm{M} - \{(\mathrm{M} - 1) \times \mathrm{W}\}} \tag{2}$$

Where Blank = volume of HCl required for blank titration; Sample = volume of HCl required for sample titration; N = normality of HCl solution; M = Molecular weight of OSA (210); R = Molecular weight of repeating unit (162).

2.2.5. Characterization of native corn, OS and OS-OSA starch

2.2.5.1. Fourier transform infrared spectroscopy (FTIR). The FTIR (IR-Prestige21, Shimadzu, Japan) analysis of native corn starch, OS and OS-OSA starch at optimized conditions was performed. The samples were mixed with KBr and analysed by dispersive method for the presence of the functional groups from 400 to 4000 cm^{-1}.

2.2.5.2. X-ray diffraction studies (XRD). The native starch, OS and OS-OSA were analysed for their percent crystalline content using an X-ray diffractometer (XRD-6100, Shimadzu, Japan) using $\mathrm{CuK}_\alpha = 1.54$ Å with scanning rate of 2° per min and a 2θ ranging from 5° to 35° with a current of 30 mA and voltage of 40 kV. The total mass crystallinity was determined as the ratio of the area of crystalline regions to the total area of crystalline and amorphous regions (Ribotta et al., 2004) using Origin software (version 9.1). For