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# Optimisation of octinyl succinic anhydride starch stablised $w_1/o/w_2$ emulsions for oral destablisation of encapsulated salt and enhanced saltiness

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ABSTRACT

Sodium (salt) was encapsulated within the inner water phase of $w_1/o/w_2$ food emulsions externally stabilised by starch particles with the ultimate aim of enhancing saltiness perception. The physical properties of the starch particles were modified by octenyl succinic anhydride (OSA) treatment (0–3%) to vary the degree of hydrophobicity of the emulsifying starch. During oral processing native salivary amylase hydrolysed the starch and destabilised the o/w emulsion releasing the inner w/o phase and subsequently sodium into the oral cavity, resulting in a salty taste. Whilst increasing OSA treatment levels increased the stability of the emulsion, intermediate or low levels of starch modification resulted in enhanced saltiness. It is therefore proposed that 1.5% OSA modified starch is optimal for sodium delivery and 2% OSA modified starch is optimal for sodium delivery in systems that require greater process stability. It is also shown that sodium release was further enhanced by oral processing and was positively correlated with native amylase activity. The results demonstrate a promising new approach for the reduction of salt or sugar in emulsion based foods.



## 1. Introduction

Overconsumption of sodium remains an epidemic issue with salt as the main source of sodium in the human diet (Anderson et al., 2010). Although various salt reduction strategies have been explored for application in food products (He & MacGregor, 2008; Kilcast & Angus, 2007; Rama et al., 2013; Tian & Fisk, 2012), many are product or category specific and further efforts to reduce sodium consumption in food is needed, as the average global salt consumption remains above the recommended levels of 5 g/day (World Health Organization, 2012). The multifunctional role of salt increases the complexity of reducing sodium within the diet and furthermore reduction strategies must be delivered without compromising perception of the food product's acceptability.

Complex emulsions ($w_1/o/w_2$) are present in many foods, these may be formed either by design or as an artefact of processing or transiently formed during mastication/cooking. Through careful design, complex water-in-oil-in-water ($w_1/o/w_2$) emulsions may be able to encapsulate free sodium within their internal water phase and release it in a targeted fashion during the short time period of oral processing. This may allow lower salt levels without compromising on saltiness perception. We have recently reported on the use of $w_1/o/w_2$ emulsions to reduce sodium levels in liquid or semi-liquid systems by modulating salt perception through targeted delivery of encapsulated salt in the oral cavity (Chiu, Hewson, Fisk, & Wolf, 2015). Commercial octinyl succinic anhydride (OSA) starch was used as an external emulsifier with two key roles: (i) Emulsion stabilisation prior to consumption entrapping internalised sodium within the inner water phase and (ii) emulsion destabilisation during oral processing which releases the entrapped sodium for perception. In a previous study, fat crystals were used to stabilise $w_1/o/w_2$ emulsions and based on the osmotic pressure sodium either remained in the $w_1$ aqueous phase or moved to the $w_2$ phase (Frasch-Melnik, Spyropoulos, & Norton, 2010).

OSA treatment results in the formation of regions of

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hydrophobicity on the surface of the starch particle, ultimately resulting in an amphiphilic starch particle, this modified starch is surface active and can act as a particle stabiliser for o/w and $w_1/o/w_2$ emulsions (Matos, Timgren, Sjoo, Dejmek, & Rayner, 2013; Sweedman, Tizzotti, Schäfer, & Gilbert, 2013; Timgren, Rayner, Dejmek, Marku, & Sjöö, 2013; Yusoff & Murray, 2011). During oral processing, salivary amylase initiates starch digestion and during this initial process reduces the emulsification capability of OSA treated starch particles resulting in coalescence of the o/w emulsion and diffusion of the internal water phase into the saliva. This is in direct contrast to more stable complex emulsions, which do not destabilise in the oral cavity.

The present study furthers this concept, hypothesising that variation of the degree of OSA modification will modulate the rate of destabilisation (by coalescence) of the w/o/w emulsion during oral processing, and thus at lower levels of OSA treatment the inner salty water phase will be released more efficiently to elicit saltiness perception. Therefore, the aim of this study was to identify an optimum level of octinyl succinic anhydride (OSA) modification (within USA FDA permitted levels 0–3%) for waxy maize starch particles to maximise $w_1/o/w_2$ emulsion physical stability whilst still destabilising under oral processing conditions to release sodium for perception. Emulsion microstructure is monitored for 90 days to demonstrate shelf-life stability and sodium release was quantified *in-vitro* and *in-vivo* with accompanying sensory evaluation to determine saltiness perception.

## 2. Materials and methods

### 2.1. Materials

All materials used for starch modification and emulsion preparation were food grade. C*Gel 04201, a waxy maize starch containing approximately 95% amylopectin, was obtained from Cargill (Sas van Gent, Netherlands). Octenyl succinic anhydride (OSA) was donated by Vertellus (Pennsylvania, USA). Sodium hydroxide (NaOH) was obtained from VWR International Ltd. (Lutterworth, UK). Polyglycerol polyricinoleate (PGPR) used to stabilise the internal water phase ($w_1$) was donated by Danisco (Dorset, UK). Following protocol in our previous publication (Chiu et al., 2015), samples designed to not be susceptible to oral breakdown were stabilised with pea protein isolate (PPI, Myprotein, Manchester, UK). Sunflower oil and table salt was purchased from a local supermarket. Calcium chloride ($CaCl_2$), ethanol, hydrochloric acid (HCl), 4-morpholinepropanesulfonic acid sodium salt (MOPS sodium salt), phenolphthalein, porcine α-amylase, sodium azide and salivary amylase assay kit (MAK009) were obtained from Sigma-Aldrich (Gillingham, UK). Sodium azide was used as an antimicrobial agent and was only added to samples that were not intended for sensory analysis. Amyloglucosidase, D-glucose, standardised regular maize starch and thermostable α-amylase were provided as part of the Megazyme total starch assay kit (Megazyme, Co., Wicklow, Ireland). Deionised water, with a resistivity of 15 MΩ/cm was used for the preparation of all solutions.

### 2.2. Hydrophobic modification of waxy maize starch with octinyl succinic anhydride

C*Gel 04201 was hydrophobically modified by OSA treatment following Bhosale and Singhal (2006). C*Gel (125 g) was mixed with 475 mL deionised water using an overhead mixer with a four bladed propeller stirrer (EURO-ST D S2, IKA-WERKE, Staufen, Germany). The pH of the slurry was adjusted to pH 8.0 ± 0.2 by the addition of 2% NaOH solution. OSA up to 3% at 0.5% increments, based on the weight of starch, was added drop-wise to the slurry over a 2 h period at room temperature. During the addition of OSA, the pH was maintained at 8.0 ± 0.2 by the addition of 2% NaOH solution. The reaction was left to proceed for 24 h at 30 °C after which the pH was adjusted to 6.5 using 2% HCl. The slurry was then washed with water and centrifuged at 4193 g. This centrifugation process was repeated three times. The OSA starches were dried in an oven at 45 °C for 12 h and stored in a sealed container at room temperature until use. All steps of the modification procedure were repeated without the addition of OSA and the starch obtained from this process is considered as not hydrophobically modified. Albeit not corresponding to the original starch, C*Gel 04201 as obtained from the supplier, applied in this research, it is in the following referred to as unmodified starch.

### 2.3. Determination of the degree of substitution

The degree of substitution (DS) is the average number of hydroxyl groups substituted per glucose unit and was determined by alkali saponification and back titration of excess alkali with HCl according to Whistler and Paschall (1967). A suspension of the OSA starch (5 g of starch in 50 mL water) was mixed with 25 mL of a 0.5 M aqueous NaOH solution and stirred for 24 h. Excess alkali was titrated with 0.5 M HCl, using phenolphthalein as an indicator. A blank titration of a suspension of unmodified starch (5 g unmodified starch in 50 mL water) was performed and the difference in HCl added to the modified and unmodified starch suspension was assumed to be due to chemically bound OSA. OSA substitution (%) was then calculated with Equation (1).

$$\%\ OSA = \frac{\left[\left(V_{Blank} - V_{Sample}\right) \times 0.1 \times M \times 100\right]}{W} \quad (1)$$

where $V_{Blank}$ = volume of HCl required for back titration; $V_{Sample}$ = volume of HCl required for sample titration; $M$ = Molarity of HCl; $W$ = weight of sample taken (g).

DS was determined from % OSA substitution with Equation (2):

$$DS = \frac{Mw_g \times \%\ OSA}{Mw_{OSA} \times 100 - ((Mw_{OSA} - 1) \times \%\ substitution)} \quad (2)$$

where $Mw_g$ = molecular weight of glucose residue (162); $Mw_{OSA}$ = molecular weight of *OSA* (210).

### 2.4. Emulsion preparation

To prepare the water-in-oil-in-water ($w_1/o/w_2$) emulsions (1 L) initially a water-in-oil emulsion ($w_1/o$) containing 30 %w/w aqueous phase was formulated and then incorporated into the external water phase ($w_2$) at a ratio of 1:1 to create a $w_1/o/w_2$ emulsion. A high shear overhead mixer (Silverson L5M fitted with emulsor screen, Chesham, UK) was used for all steps of emulsion processing. The internal water phase ($w_1$) consisted of 141 mM aqueous NaCl solution and the oil phase contained 2.8% w/w PGPR 90 (premixed at 4000 rpm for 1 min and allowed to equilibrate). The aqueous phase was added to the oil phase and mixed for 2 min at 4000 rpm. The $w_1/o$ emulsion was subsequently mixed (at a ratio of 1:1) with $w_2$ at 4000 rpm for 2 min. The external water phase consisted of a 4% w/w aqueous suspension of unmodified or OSA modified starch.

### 2.5. Microscopy, image analysis and droplet size

The droplets of the $w_1/o/w_2$ emulsions were visualised using optical microscopy and image analysis was applied to quantify the droplet size distribution and the surface based mean droplet