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Pilot scale production and *in vitro* gastro-small intestinal digestion of self-assembled recrystallised starch (SARS) structures

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ABSTRACT

Two commercial maize starches (Hylon VII, HA7; and normal maize starch, MS) and a potato starch were processed in the presence of palmitic acid (C16:0, Palm) at 140 °C followed by retrogradation in order to produce self-assembled recrystallised starches (SARS). The new starch structures prepared from HA7 exhibited a stronger birefringence pattern under polarised light and greater relative crystallinity (%) than those prepared from potato and normal MS. Also, the SARS from HA7 showed a typical Vh pattern (2Θ: 8.5°, 15°, 23°) confirming a strong inclusion complexation between amylose and fatty acid. Effect of other fatty acids (stearic, C18:0 and oleic, C18:1) on SARS formation was also studied using HA7. The degree of relative crystallinity (%) of these samples showed an order of palmitic > oleic > stearic, with the former also showing greater yield (Y_{SARS}). The transition temperatures and enthalpies of melting or dissolution for SARS prepared from HA7 and three fatty acids (further referred to as HA7-SARS) ranged between 101 and 131 °C and 11–18jg^{-1}, respectively. The scanning electron micrographs of the freeze-dried HA7-SARS showed the presence of aggregated round and disc/torus shaped morphologies in varying amounts. An *in vitro* starch digestion model was used to study the kinetics of glucose release during digestion of ground and cooked HA7-SARS for 120 min. All the HA7-SARS samples exhibited slower and significantly lower overall starch hydrolysis than the native HA7 starch (70%), with the SARS prepared using palmitic acid showing the lowest hydrolysis (44%). Digesta from the latter also showed the presence of intact microparticles resistant to gastro-small intestinal digestion.

1. Introduction

Starch is a storage carbohydrate found in the form of granules in all higher plants. The starch granules are birefringent and semi crystalline (20–45% crystallized) having a size distribution ranging between 1 and 100 μm (Keetels et al., 1996). Native starch is composed of amylose and amylopectin, which are comprised of glucose chains linked through α 1–4 and/α 1–6 bonds. The native starch granules are organized into alternating crystalline and amorphous lamellae with a periodicity of 9 nm[2]. When starch suspension is heated above its gelatinisation temperature, the granules swell; their bi-refringence and crystallinity is lost; and amylose component becomes soluble. When solution is cooled down, amylose gelation occurs and forms a gel. A retrogradation phenomenon is commonly observed within a short time (less than a day) through the development of gel and crystallinity in amylose matrix whereas the crystallisation involving amylopectin occurs during longer term (over several weeks) storage at refrigeration temperatures (Zhou et al., 2002). Birefringence is not observed afterwards because of the loss of ordered structure (supra helical structure) (Miles et al., 1985; Morris, 1990). Starch heated above 130°C–150 °C provides the comprehensive native granule disruption and melting of starch components which allows the formation of new arrangements or structures with guest molecules through inclusion complexation. Self-assembled and recrystallised starch structures are formed from chain-folded, crystalline lamellae that grow (or stack) in a radial direction from the central nucleus (Smith et al., 1997). Individual chains of complexed amylose are oriented perpendicular to the plane of each lamella (Yamashita and Hirai, 1966). It may provide a specific crystallisation through self-assembly which shows birefringence under a polarised light. Birefringence of recrystallised material comes from a preferential orientation of molecules resulting from inclusion complexes to form either amorphous or semi-crystalline structures (Ring et al.,

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1987).

The extent of crystal order within the granule, the length of amylopectin chain involved in the crystalline domain, or the amorphous phase behaviour have a strong influence on starch gelatinisation (Whittam et al., 1990). Indeed, the parameters of the melting process of starch depend on several factors such as heating regime and the particular character of supermolecular structure of the native granules, which in turn depends on the biological origin of starch and the water content in gelatinisation systems (Donovan, 1979). The self-assembled spherulitic starch materials formed *de novo* are mainly composed of recrystallised amylose and sometimes also termed 'reformed amylose particles (Davies et al., 1980). The recrystallisation or reformation of amylose is caused or enhanced by a combination reaction between amylose and many organic compounds, which may be termed as high temperature retrogradation (Davies et al., 1980). Several authors have termed these reformed particles as spherulites (Foucault et al., 2010; Singh et al., 2010a; Conde-Petit et al., 2007; Fanta et al., 2006; Ziegler et al., 2003). The same term has traditionally been used in polymer science for spherical semicrystalline polymers. However, this may term may not be applicable when the reformed or self-assembled starch has a non-spherical morphology.

The morphology of the recrystallised melt depends on their processing method (temperature and time), starch source and complexing legends (Singh et al., 2010a). Differential Scanning Calorimetery (DSC) has been used to produce recrystallised starch structures because of its high sensitivity and ease of use (Singh et al., 2010a; Ziegler et al., 2003). Ziegler et al. (2003) and Shogren et al. (2006) have used DSC and a steam jet cooker, respectively, to produce recrystallised starchy material from different starch sources and have reported their physico-chemical and morphological characteristics.

The objectives of our study were to: 1) produce self-assembled recrystallised starch-fatty acid based structures (SARS) using a pilot scale batch process, 2) investigate their morphological, thermal characteristics and relative crystallinity, and 3) study their digestion using an *in vitro* gastric and small-intestinal starch digestion model.

2. Materials and methods

2.1. Materials

A high amylose maize starch (Hylon VII (HA7) and a normal maize starch (MS) were generously donated by Ingredion Ltd., Green Mount, Auckland (New Zealand), whereas fatty acids (palmitic acid, stearic acid, oleic acid, 99% purity) were purchased from Sigma-Aldrich. Potato starch (PS) was isolated from commercial supermarket potatoes as described by Singh et al. (2006). All the reagents used in the study were of analytical grade. Pepsin (porcine gastric mucosa; 800–2500 units/mg protein), pancreatin (hog pancreas; 4 x USP) and invertase (Invertase, Grade VII from baker's yeast, 401 U/mg solid) were purchased from Sigma-Aldrich Ltd., St Louis, USA. Amyloglucosidase (3260 U/mL) was supplied by Megazyme International Ireland Ltd., Ireland.

2.2. Methods

2.2.1. Moisture content

The moisture content of the starches and SARS in dry powder form was calculated from the weight loss upon overnight heating at 105 °C in an oven (AACC method 44-15 A, 1995).

2.2.2. SARS formation

SARS were produced using a process developed by Foucault et al. (2010) using a batch type pilot scale mixer- Limitech (Limitech, Denmark) (Fig. 1). In a typical process, each fatty acid (palmitic acid; stearic acid; oleic acid; 5% w/w based on amylose content of different starches) were dissolved (~10%, w/v) in 95% ethanol at 80 °C for 10 min. Different starch-fatty acid combinations (HA7-Palm, HA7-Ole, HA7-Ste), (MS-Palm, PS-Palm) were used to prepare SARS. About 250 g of starch was mixed with fatty acid-ethanol solution, and then transferred to the process tank containing 5 L of water. Several pilot scale trials were performed to produce SARS in bulk quantity. In a typical experiment for SARS production, the water/fatty acid/starch was heated (indirect heating mode, psig) at 140 °C (at a pressure of 2.8 bar), under continuous mixing for 45 min. The temperature is then lowered to 100 °C and heated slurry was transferred to metal cans and sealed. The sealed cans were immediately subjected to a 2-stage high temperature retrogradation, firstly at 110 °C for 2 h and after at 70 °C for 18 h in a hot air oven. After high temperature retrogradation, the cans were brought to room temperature and material was centrifuged at 3500g for 10 min with three washings with distilled water and then freeze-dried. The freeze-dried SARS materials were ground (Retsch® ZM200) and passed through 0.25 mm sieve to obtain fine powder.

2.2.3. Particle size distribution and amylose content

The native starch granule size distribution was determined with a laser diffraction particle size analyzer (Malvern Mastersizer, Malvern Instruments Limited, UK). The native starch sample

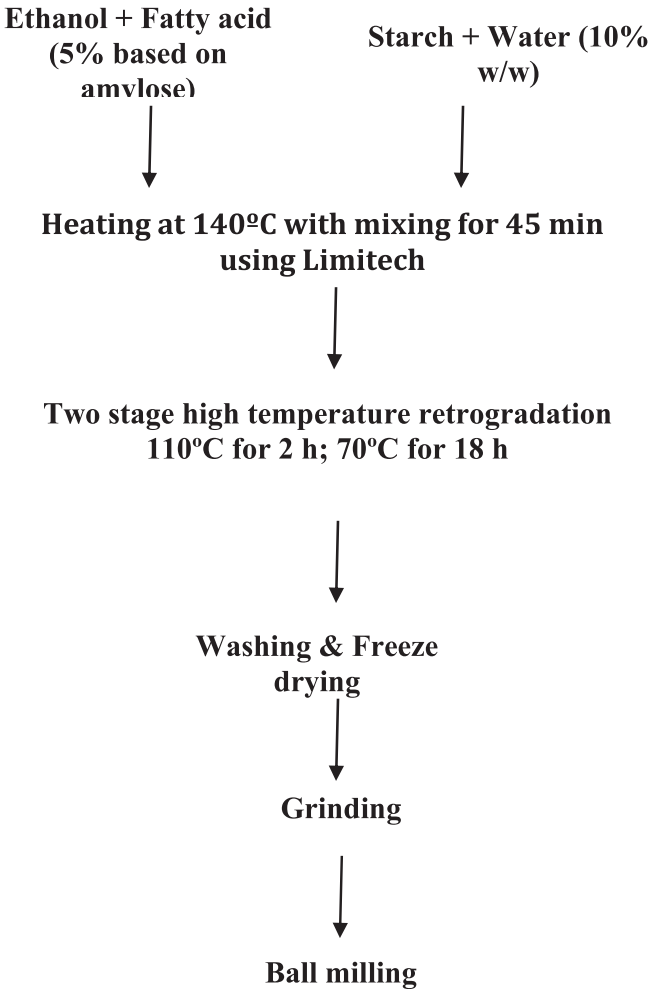

Fig. 1. Flow chart illustrating the SARS production at pilot scale.