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Effect of pulsed electric fields treatment on the nanostructure of esterified potato starch and their potential glycemic digestibility

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ABSTRACT

Esterified starch macromolecules were studied in relation to the effects of pulsed electric fields (PEF) on *in vitro* digestibility and emulsion stability. The results show that starch acetates with higher electric intensity yielded emulsion with lower oil layer separation over a 30 days shelf life trial. The *in vitro* digestion suggests the quantity of slowly digestible starch (SDS) fractions increased from 6.63% in the control sample to 17.53% at 3.75 kV/cm. Scanning electron microscopy, X-ray diffraction, small-angle X-ray scattering and atomic force microscopy were used to determine the crystalline and nanostructure. The surface of native starch (as observed in the nanosheet images) exhibited a low roughness value (Ra = 0.639 nm), while starch acetates displayed an increase in surface roughness ((Ra = 0.766 nm (non-PEF) and 1.176 nm (PEF-combined)). The results illustrate that PEF has an important impact on the emulsification and SDS contents of potato starch granules.

Industrial relevance: Pulsed electric fields (PEF) are a technique widely used to improve the sterilization efficiency and help modify macromolecules. The present paper evaluates the potential applications of chemically modified potato starch molecules assisted by PEF process. Based on the investigation of the nanostructure and crystalline texture, the effect of PEF acted on esterificated starch macromolecules is proposed to explain these changes occurred to properties. The results have also demonstrated that the PEF treatment applied on esterification did promote the digestibility and emulsification stability of the product. Through the PEF treatment shows high potentials to be applied with esterification at an industrial level to enhance the reaction efficiency and to obtain novel products with better glycemic digestibility and emulsion stability.

1. Introduction

Starch is widely used as a functional component in prepared foods and is one of the most important sources of energy for humans and also the major glycaemic carbohydrate (Dhital, Bhattarai, Gorham, & Gidley, 2016; Zheng, Stanley, Gidley, & Dhital, 2016). Starch can be characterized from a nutritional viewpoint as rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) depending on the rate and extent of its digestion (Englyst, Kingman, & Cummings, 1992). Potato starch is one of the most common crops and staple food in the world, and it is highly easy to manage and cultivate (Apinan et al., 2007). Also, potato starch and other starch cultivars with high amylose contents can induce higher RS content in native starch granules during enzymatic reaction. RS is benefit for people with metabolic disorders and has potential to be transformed as SDS (Ozturk, Koksel, Kahraman, & Ng, 2009; Pongjanta, Utaipattanaceep, Naivikul, & Piyachomkwan, 2009). The important feature of SDS is that it is digested slowly throughout the entire small intestine, which leads to a slow and prolonged release of glucose with a low glycemic index (Carlos-Amaya, Osorio-Diaz, Agama-Acevedo, Yee-Madeira, & Bello-Perez, 2011). Food containing high amounts of SDS tend to sustain plasma glucose levels, this may help to control and prevent diabetes and may also be beneficial to satiety, physical performance, improved glucose tolerance, and reduced blood lipid levels in both healthy individuals and those with hyperlipidaemia (Huang, Zhou, Jin, Xu, & Chen, 2015; Jenkins, Kendall, Augustin, Franceschi, & Hamidi, 2002). Therefore, SDS is considered to be beneficial for the dietary management of metabolic disorders of common chronic diseases such as obesity, diabetes, and cardiovascular diseases. Besides that, it has been proved that more RS content can be yielded during acetylation (Juansang, Puttanlek, Rungsardthong, Puncha-arnon, & Uttapap, 2012). And in our previous study, it demonstrated that PEF can destroy the crystalline area of starch granules which made it easier to be attacked by enzyme (Han, Zeng, Yu, Zhang, & Chen, 2009). Therefore, the

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combination of acetylation and PEF could be a potential way to gain more SDS content in starch granules.

Recently, much research attention has focused on the modification of starch granule structure to improve starch digestibility and most starch esters being made commercially with low degree of substitution (DS) (< 0.1) are used in the form of aqueous solutions/suspensions for food applications, including esterification (Sweedman, Tizzotti, Schafer, & Gilbert, 2013; Zięba, Szumny, & Kapelko, 2011), hydroxypropylation (Karim, Sufha, & Zaidul, 2008; Liu et al., 2010) and cross-linking (Yousefi, Razavi, & Norouzy, 2015), where the substitution of hydroxyl groups were partially replaced by acetyl, octenylsuccinyl, hydroxypropyl, phosphate and so on. Starch modified by acetylation in an aqueous medium in the presence of an alkaline catalyst with a low degree of substitution is commonly used to improve the properties and functionalities of starch to satisfy industry requirements in food grade by introduction of hydrophobic acetyl group into the macromolecules of starch (Wang & Wang, 2002). Starch is also considered as a valuable stabilizer for food-grade emulsions. The size of particles used for emulsions varies from nano to micron sized and is consistent with the natural variations which exist in starch granule size from 0.5 to100 μm (Jane, Technician, Consultant, & Robyt, 1994). The hydrophobic nature of starch granules may limit the use in starch-based products in food applications due to its behavior in water and oil systems, and thus weaken its ability to form stabilized emulsions. However, the modification of starches, and manipulation of the degree of hydrophilicity, can be achieved by treatment with different acetic anhydrides, this will affect the emulsion properties of these products (Timgren, Rayner, Dejmek, Marku, & Sjöö, 2013).

The objective of the present study was to investigate the role of acetylation and PEF intensity on the enzyme susceptibility, SDS content and emulsification of potato starch. Its crystalline structure and nanostructure of macromolecules were explored to understand the relationship between starch structure and its functionality. Furthermore, the crystalline structure and selected physicochemical properties of obtained starch acetates will be investigated by spectroscopic, microscopic, thermal, and physical techniques and potential applications of emulsification, digestibility were also discussed clearly.

2. Materials and methods

2.1. Materials

Potato starch was obtained from Ningxia Huajing Industrial Co., Ltd. (Guyuan, China). Acetic anhydride and anhydrous ethanol were purchased from Beihua Fine Chemicals Co., Ltd. (Beijing, China). Porcine pancreatin (catalogue no.P7545) and amyloglucosidase (catalogue no. A7255) were obtained from Sigma-Aldrich, Inc. (St. Louis, MO). All chemicals used in the study were of analytical grade.

2.2. Preparation of acetylated (AC) starch

Preparation of acetylated starch was achieved by the conventional method as described by Sodhi and Singh (2005) with minor modification. A slurry of 35% starch (in distilled water) was placed in a 250 mL three-neck flask and stirred for 5 min. Firstly, 6% cooled acetic anhydride was added drop-wise to the mixture within 30 min. The acetylation was conducted in a 30 °C water bath. The slurry was stirred at 300 rpm maintaining the pH at 8.0–8.5 with 3% (w/w) NaOH for 60 min after which the reaction was terminated by adding absolute ethanol. The slurry was washed with excess absolute ethanol three times and then oven-dried at 45 °C for 12 h (Linpin Isotemp 202-00 A, Linpin Scientific, Shanghai, China).

Acetylated starches were PEF treated by adjusting the electrical conductivity of the suspensions to 11.00 mS/cm by adding 2.0 mol/L sodium chloride solution after first step of acetic anhydride addition. Then samples were pumped through PEF chamber with a peristaltic pump (Yz1515x, Longer Precision Pump Co., Ltd. Baoding, China) for the following reaction. Native and acetylated starch samples were treated in a bench-scale, continuous PEF system (SCUT PEF Team, the South China University of Technology, China). The schematic system was seen in Fig. 1.The PEF treatment time is 60 min for the continuous esterification and the efficient PEF treatment time is 51.0 ms as calculated according to our previous study (Hong, Zeng, Buckow, Han, & Wang, 2016). The temperature of the slurry before pumped into the chamber is 30 °C controlled by a heat exchanger (SYSTEM II, Thermo Scientific Co., USA). The parameters of PEF system were as follows: square-wave form, bipolar pulses; pulse frequency, 1000 Hz; field intensity of 1.25, 2.50, 3.75, and 5.00 kV/cm; pulse duration time, 40 μs; the shape of chamber is cylinder with diameter, 0.30 cm and electrode gap, 0.30 cm; and sample flow rate, 60 mL/min.

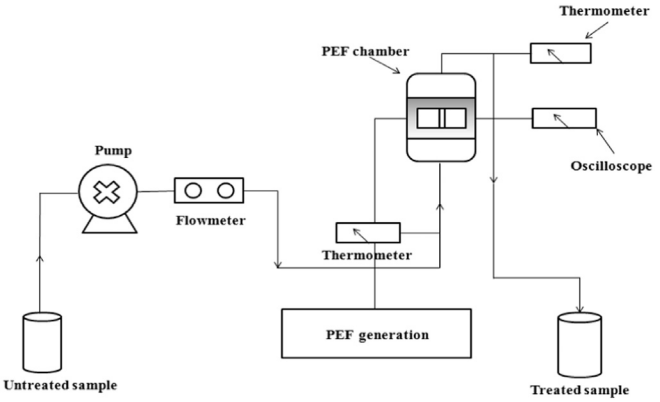

Fig. 1. Schematic diagram of the continuous PEF system used in this study.

2.3. Determination of the degree of substitution (DS)

The value for the degree of substitution for the starch samples were determined titrimetrically, following the method outlined by Singh, Chawla, and Singh (2004). AC starch (1.0 g, db) was placed in a 250 mL flask and 50 mL of 75% ethanol in distilled water was added. The stoppered flask was agitated, heated to 50 °C for 30 min, naturally cooled to room temperature (25 °C), then 40 mL of 0.5 M NaOH was added. The excess alkali was back titrated with 0.5 M HCl using phenolphthalein as indicator. The solution was rested for 2 h, and then any additional alkali, which may have leached from the sample, was titrated. The original unmodified starch was also used as the blank sample. Titration volumes of blank and treated samples were in mL. The unit of sample weight was g. The content of acetyl was calculated by Eq. (1) and the DS value was calculated by Eq. (2).

$$\text{Acetyl\%} = \frac{(V_b\text{-}V_s) \times M \times 0.043 \times 100}{W(db)} \quad (1)$$

where V_b and V_s are the volume of HCl required for blank titration and sample titration, W(db) is the dry weight (g) of AC starch sample, and M is the molarity of HCl solution.

$$DS = \frac{162 \times \text{Acetyl\%}}{4300 - 42 \times \text{Acetyl\%}} \quad (2)$$

where 162 is the Mw of glucose unit, 4300 is 100 × Mw of acetyl group, and 42 is the Mw of acetyl group minus the Mw of hydrogen atom.

2.4. Scanning electron micrographs (SEM)

Scanning electron micrographs (SEM) were taken by a scanning electron microscope (S-3700N, HITACHI, Japan). A small quantity of each sample was spread directly on the surface of the stub. All samples were subsequently coated with thin gold layer before investigation then