LWT - Food Science and Technology 91 (2018) 258–264

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

Effect of acid hydrolysis and OSA esterification of waxy cassava starch on emulsifying properties in Pickering-type emulsions

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ARTICLE INFO

Keywords:
Waxy cassava starch
Pickering emulsions
Chemical modification
Stabilizer agent
Rheology

ABSTRACT

The emulsifying properties of waxy cassava starch modified by acid hydrolysis and esterification with octenyl succinic groups in Pickering-type emulsions were evaluated using zeta potential, emulsification index, light microscopy and rheology behavior. The optimal conditions of acid hydrolysis to achieve the highest emulsification index were determined to be a hydrochloric acid concentration of 4 mol/L for 5.20 h. After that, the starch was esterified to obtain a double modification. The emulsification index values were acid treated/succinated starch > optimal acid treated starch > native starch. The acid treated/succinated starch emulsion presented higher storage modulus (G′) values, without G' and loss modulus (G") crossing point in the evaluated frequency range. Acid hydrolysis modified the emulsifying properties of waxy cassava starch improving its interaction at the oil/water interface. According to observations by light microscopy and rheology behavior, the double modification formed a more uniform and stable network over time through granule-granule and granule-interface interactions.

1. Introduction

Solid stabilized emulsions or "Pickering" type emulsions comprise a continuous phase, a dispersed phase and a solid particle (emulsifying stabilizer) such as nanoparticles, modified starches, native starches, hydrocolloids, or proteins (Binks, 2002; Shah et al., 2016). Pickering emulsions have certain advantages, such as high stability and properties to reduce Ostwald ripening explained by the creation of a kinetic barrier (due to the accumulation of particles at the interface) against droplet coalescence by volume exclusion and steric hindrance. This phenomenon produces a strong irreversible adsorption at the interface (even at large droplet sizes) over extended periods of time favored by the size, shape and partial dual wettability of the adsorbed particles (Dickinson, 2012; Marku, Wahlgren, Rayner, Sjöö, & Timgren, 2012; Rayner et al., 2014).

Starch granules have been used in Pickering-type emulsions due to their availability, relatively low costs and their acceptation as food ingredient and pharmaceutical excipient (Rayner et al., 2014; Saari, Heravifar, Rayner, Wahlgren, & Sjöö, 2016; Ye et al., 2017). Studies carried out by Li, Li, Sun, and Yang (2013) and Timgren, Rayner, Dejmek, Marku, and Sjöö (2013), showed that waxy maize, rice, wheat, potato, quinoa and waxy rice native starches have been shown to have good emulsifying properties in O/W (oil/water) emulsions.

A few native starches lack the characteristics required for use as emulsifying stabilizers and must be modified (Bello-Pérez et al., 2015; Timgren et al., 2013) to increase and improve their functionality in Pickering-type emulsions. One method, acid hydrolysis, causes starch depolymerization modifying the surface charge and generating a greater number of functionalizing points for ester groups (Wang & Copeland, 2015). The optimal conditions of acid hydrolysis to achieve these functionalities without dramatically altering the granular structure are unknown.

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https://doi.org/10.1016/j.lwt.2018.01.057
Received 17 July 2017; Received in revised form 17 January 2018; Accepted 19 January 2018

Another widely used starch chemical modification to enhance the emulsification properties is the incorporation of octenyl succinic anhydride (OSA) groups to confer hydrophobicity to the intact granule (Bello-Pérez, Bello-Flores, Del Carmen Nuñez-Santiago, Coronel-Aguilera, & Alvarez-Ramirez, 2015; Rayner, Sjöö, Timgren, & Dejmek, 2012; Simsek, Ovando-Martinez, Marefati, Sj, & Rayner, 2015; Timgren, Rayner, Sjöö, & Dejmek, 2011). OSA groups are an alternative of the surfactants and emulsifiers in products as dairy products, mayonnaise, sausages, among others.

In the CIAT (International Center for Tropical Agriculture) in Colombia, a waxy cassava starch has been developed (Ceballos et al., 2007). Studies have focused on the physicochemical and functional properties (Sánchez, Dufour, Moreno, & Ceballos, 2010) and structural characteristics of the waxy cassava starch (Rolland-Sabaté et al., 2012). However, the uses for this starch have not been evaluated; as such, advantages offered by chemical modifications could include its application as a solid particle-stabilizer of Pickering emulsions. Thus, in this study, the acid hydrolysis of waxy cassava starch was optimized to make it more available for subsequent esterification with octenyl succinic groups. The effects of these modifications on the emulsifying properties of waxy cassava starch granules in solid stabilized emulsions were subsequently evaluated.

2. Materials and methods

2.1. Materials

Waxy cassava starch (WCS) was acquired from the International Center for Tropical Agriculture (CIAT) in Colombia. 2-Octen-1-yl succinic anhydride (OSA, 97% purity) was obtained from Sigma-Aldrich Co. (St. Louis, MO, USA). Hydrochloric acid was purchased from J.T. Baker (37%, purity). All reagents were analytic grade.

2.2. Preparation and characterization of modified waxy cassava starch

2.2.1. Acid hydrolysis and optimization process

The acid hydrolysis of WCS was performed according to the methodology of Utrilla-Coello et al. (2014) with modifications. Briefly, 100 g starch dry basis were placed in a 500 mL Erlenmeyer flask, and 300 mL of an aqueous solution of hydrochloric acid were added at certain times fixed by a central composite design for the optimization process. During the hydrolysis, the solution was stirred and kept at room temperature (25 °C). The solution was neutralized dropwise with a 20 g/100 mL of sodium hydroxide solution. Then, the starch was washed three times with distilled water and centrifuged at 8000 g for 15 min in a Hermle Labortechnik centrifuge (Z300K model Wehingen, Germany). The sediment was dried in an air-circulating oven (Ambi-Hi- Low Chamber, Lab-Line, USA) at 40 °C for 24 h. Subsequently, the starch was ground in a mortar and sieved using a 250 μm mesh. The powdered starch was stored in plastic sheeting bags at approximately 25 °C until further analysis.

For the optimization process of the emulsions elaborated with acid treated WCS a central composite rotatable design with two factors and five levels (hydrolysis time and concentration of HCl; levels for each factor (-α) = 1.37, (-1) = 2, (0) = 3.5, (+1) = 5, (+α) = 5.62) was used to obtain acid treated starches and emulsification index (EI) response. The EI data obtained at 14 d was analyzed by multiple linear regressions and fitted to a second order polynomial model (Equation (1)). Statistical analysis was performed using the statistical package Design-Expert version 7.1.5. (Stat-Ease, Minneapolis, USA).

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} \times 1 \times {}_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 \tag{1}$$

The optimization of acid hydrolysis for WCS was performed using the EI response at 14 d. The method of maximum slope was used to optimize the EI which was proposed by Box and Wilson (1992). This method seeks the maximum increase in the evaluated response. At the end of the optimization process, an optimized acid treated waxy cassava starch (HWCS) was obtained.

2.2.2. Esterification with octenyl succinic anhydride

The esterification of optimal acid-treated starch (HWCS) with 2-octen-1-yl succinic anhydride (OSA 3% dry basis), and the determination of the degree substitution were carried out using the methodology described by Bhosale and Singhal (2006) to obtain acid treated-OSA waxy cassava starch (OHWCS). Briefly, 25 mL of a 0.5 mol/L aqueous NaOH solution was added to the suspension of the OHWCS (5 g of starch in 50 mL distilled water) and then shaken for 24 h. Excess of alkali was titrated with 0.5 mol/L HCl, using phenolphthalein as an indicator. A blank was simultaneously titrated with WCS. The test was performed in triplicate.

Degree substitution (DS) was determined from % OSA substitution using equations (2) and (3).

$$OSA\ substitution = \frac{(V_{blank} - V_{sample}) \times 0.1 \times N \times 100}{W} \tag{2}$$

where V_{blank}, volume of HCl required for blank titration; V_{sample}, volume of HCl required for sample titration; W, weight of sample taken (g); N, Normality of HCl solution.

$$DS = \frac{162 \times OSA\ substitution}{21.000 - (209 \times OSA\ substitution)} \tag{3}$$

where 162 = molecular mass of glucose unit minus water; 21.000 = 100 × molecular mass of octenyl succinyl group; 209 = molecular mass of octenyl succinyl group.

2.2.3. Scanning electron microscopy (SEM)

Granules of WCS, HWCS and OHWCS were analyzed using a scanning electron microscope (JSM-6300, JEOL, Japan). Completely dry samples were placed on a slide with two-sided carbon conductive tape and sputter-coated with gold. The running conditions were 15 A and 20 kV. Granule size was determined by measuring twenty different granules for each treatment using Jeol PC-SEM 7401 software.

2.2.4. Infrared spectroscopy

WCS, HWCS and OHWCS were analyzed using an infrared spectrophotometer (System 200 FT-IR, Perkin Elmer, USA) equipped with an attenuated total reflectance system (ATR-diamond crystal) at 25 °C to know the substitution of hydroxyl groups by carbonyl groups of OSA groups. For each sample, a region from 400 to 4000 1/cm was scanned at 4 1/cm resolution over 48 scans. Each sample was analyzed in triplicate. The baseline correction was performed automatically using Spectrum software.

2.2.5. ζ-potential

ζ- Potential measurements of WCS, HWCS and OHWCS were performed using a ZetaSizer (Nano ZS90, Malvern Instrument, England). Briefly, 250 μL of oil-in-water emulsion were dispersed in 25 mL of a 0.01 mol/L $NaNO_3$ electrolytic solution at 25 °C. The solution pH was adjusted with 0.1 mol/L HCl and 20 g/100 mL NaOH solutions. Each sample was tested in triplicate.

2.3. Preparation and characterization of emulsion stabilized by modified waxy cassava starch

2.3.1. Preparation of starch granule stabilized-emulsions

Emulsions stabilized by modified WCS were prepared according to Timgren et al. (2013) with modifications. Briefly, 6 mL of the continuous phase (5 mmol/L phosphate buffer at pH 7 and 0.2 mol/L NaCl), 4 mL of the dispersed phase (liquid paraffin), and 800 mg of starch (200 mg/mL oil) were put in glass test tubes. The samples were mixed with an Ultraturrax (T25 digital, IKA, USA) at 12,000 rpm for