Available online at www.sciencedirect.com
ScienceDirect
Food Hydrocolloids 22 (2008) 1467–1474
FOOD HYDROCOLLOIDS
www.elsevier.com/locate/foodhyd

Synthesis and partial characterization of octenylsuccinic starch from *Phaseolus lunatus*

M. Segura-Campos, L. Chel-Guerrero, D. Betancur-Ancona*

Facultad de Ingeniería Química, Universidad Autónoma de Yucatán, Av. Juárez No. 421, Cd. Industrial, C.P. 97288, Apdo. Postal 26, Suc. Las Fuentes, Mérida, Yucatan, Mexico

Received 9 March 2007; accepted 20 September 2007

Abstract

Phaseolus lunatus starch was modified by esterification with octenyl succinic anhydride (OSA) and reaction effect evaluated in terms of chemical composition, gelatinization, pasting and emulsification properties. Succinylation was done using a 2^3 factorial design with four replicates of the central treatment. Evaluated factors and levels were OSA concentration (1% and 3%), pH (7 and 9) and reaction time (30 and 60 min). Succinyl group percentage was the response variable. The optimum treatment was a reaction with 3% OSA at pH 7 for 30 min, which produced 0.5083% succinyl groups and 0.0083° of substitution. No significant changes were observed in proximate composition between the native and derivative starches. Apparent amylose level decreased notably from 32.4% to 23.6% due to OSA inclusion. Succinylation decreased starch gelatinization temperature (75.3–64.6 °C), decreased enthalpy (10.7–9.7 J/g), increased viscosity (700–1000 BU), increased emulsifying capacity (0.47–0.53 ml oil/ml sample), and made emulsions more stable over time. Starch modification did not, however, improve stability in heating–cooling processes.

Keywords: *Phaseolus lunatus*; Starch; Succinylation; Octenylsuccinic anhydride; Functional properties

1. Introduction

Industrial use of native starches is limited due to the instability of pastes and gels produced with them (Jyothi, Rajasekharan, Moorthy, & Sreekumar, 2005). Efforts to improve the properties of native starches have focused on their low shear stress resistance, easy thermal decomposition, high retrogradation and syneresis (Singh, Kaur, & Singh, 2004). Native starches contain free hydroxyl groups in the 2, 3 and 6 carbons of the glucose molecule, making them highly reactive. This allows them to be modified by different chemical treatments and thus regulate their properties (Bao, Xing, Phillips, & Corke, 2003). Stabilization reactions, for example, diminish molecule reassociation, thus increasing starch stability, through the reaction of hydroxyl groups for esterification or etherification (Van Hung & Morita, 2005).

Succinylated starch is a stabilization-modified starch produced by esterification of native starch with succinic anhydride. When modified in this way the starch tends to swell in cold water and gelatinize at lower temperatures. Succinylation can be done using octenyl succinic anhydride (OSA) as a substitution agent. This makes it possible to introduce a chemical group with a long hydrophobic chain into the starch molecule, giving the derivative surface activity and colloid protector properties that make it suitable for emulsion preparation (Bao et al., 2003; Wurzburg, 1995). Succinylated starches have more stable pasting and gelatinization properties because the OSA groups interrupt the linearity of the amylose and the ramified portion of the amylopectin, which is reflected in increased paste viscosity and decreased gelatinization temperature (Trubiano, 1986). OSA starch acquires the ability to stabilize oil/water emulsions by combining the hydrophobicity of the octenyl group with the hydrophilic carboxyl or sodium carboxylate groups. The amphiphilic nature of these derivatives broadens their

*Corresponding author. Tel.: +52 999 9460989; fax: +52 999 9460994.
E-mail address: bancona@uady.mx (D. Betancur-Ancona).

0268-005X/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodhyd.2007.09.009

potential uses in the food industry (Shogren, Viswanathan, Felker, & Gross, 2000).

As in all chemical reactions, succinylation depends on factors such as reactant concentration, pH and reaction time. Successful starch modification depends on the control of reaction conditions to favour the substitution reaction and minimize the effect of anhydride and derivative hydrolysis that can occur parallel to the main reaction (Betancur, García, Cañizares, & Chel, 2002).

The extent of changes in starch properties during modification depends on starch source (Phillips, Liu, Pan, & Corke, 1999; Singh & Singh, 2003). *Phaseolus lunatus*, or Lima bean, is a non-conventional starch source cultivated in southeast Mexico. Its starch has potential in food and feed applications due to its significant protein and carbohydrate content, and relatively high agricultural yields of 850 kg/ha in Yucatan, Mexico (Sullivan & Davenport, 1993). However, use of this starch in the food industry is limited because of its high gelatinization temperature (75–87 °C). This requires the use of temperatures higher than applied with other common starches for complete gelatinization and thickening during thermal processes. Limitations of this kind diminish the potential uses of starches as thickening and stabilizing agents in foods (Betancur, Chel, Camelo, & Dávila, 2001.). Succinylated starches have been used as emulsifiers and emulsion-stabilizing agents in products such as beverages, salad dressings, soups, creams and hams, as well as flavour-encapsulating agents and clouding agents (Wurzburg, 1995). Esterification of native *P. lunatus* starch with OSA provides an opportunity to regulate the hydrophobic characteristics of this starch by incorporating hydrophobic alkenyl groups.

Recent research on esterified starches has involved diverse sources and different reaction conditions (reagent type, pH, reaction time, agent concentration) to provide the resulting starches with new characteristics and improve their functional properties (Betancur et al., 2002; Jyothi et al., 2005; Shogren et al., 2000; Singh et al., 2004; Song, He, Ruan, & Chen, 2006). No research exists to date, however, on preparation conditions for *P. lunatus* starch by succinylation, or the chemical and thermal properties of the resulting starches. The aim of the present study was to evaluate the effect of OSA concentration, pH and reaction time on substitution of native *P. lunatus* starch to establish optimum conditions for obtaining OSA starches from this source, and to evaluate the effect of succinylation on chemical composition, gelatinization, pasting and emulsifying properties.

2. Materials and methods

2.1. Seeds and chemicals

P. lunatus seeds were obtained from the February 2005 harvest in the state of Yucatan, Mexico. The seeds were milled to produce flour from which the native starch was extracted. All chemicals were reagent grade and purchased from J.T. Baker (Phillipsburg, NJ).

2.2. Starch isolation

A single extraction was done with 6 kg of *P. lunatus* seed. Impurities and damaged seeds were removed and the sound seeds milled in a Mykros impact mill. The resulting flour was sifted through a 20-mesh screen and then processed using the wet fractionation method reported by Betancur-Ancona, Gallegos-Tintoré, and Chel-Guerrero (2004). Briefly, whole flour (20 mesh) was suspended in distilled water at a 1:6 (w/v) ratio. The pH was then adjusted to 11 with 1 M NaOH, and the dispersion stirred for 1 h at 400 rpm with a mechanical agitator (Caframo Rz-1, Heidolph Schwabach, Germany). The suspension was wet-milled with a Kitchen-Aid mill and the fibre solids separated from the starch and protein mix by straining through 80- and 150-mesh sieves. The residue was washed five times with distilled water. The protein–starch suspension was allowed to sediment for 30 min at room temperature to recover the starch fraction, after which the solubilized protein was removed. The starch fraction was then washed three times by resuspension in distilled water and centrifuged at 4250*g* for 10 min. The product was dried at 50 °C for 12 h in an air convection oven (Imperial 5), weighed and then milled in a Cyclotec mill (Tecator, Hoganas Sweden) until it passed through a 20-mesh screen.

2.3. Starch succinylation

A 2^3 factorial design was used for starch succinylation with four replicates of the central trial. Factors and their corresponding levels were OSA concentration (1% and 3% of starch weight), pH (7 and 9) and reaction time (30 and 60 min). The succinylation procedure was performed according to Báez (1996). Briefly, 100 g of a starch suspension (40%, w/v) in water was prepared in a flask placed in a thermostatic bath (Grant model JB-3, Cambridge, UK) at 30 °C. A uniform slurry was prepared using a mechanical stirrer (Caframo RZI, Wiarton, Ontario, Canada), with a stainless-steel propeller, operated at 800 rpm. The pH was then measured with a Cole-Parmer Digi-Sense potentiometer and adjusted to 7 or 9 by simultaneous dropwise addition of a 3% NaOH solution and an OSA solution. This was performed carefully to maintain pH within the ranges established in the experimental design. After the reaction time had elapsed, pH was adjusted to 6.5 with 0.5 N aqueous HCl and the slurry vacuum-filtered through a piece of sailcloth. The modified starch was recovered and washed with 150 ml distilled water, and the slurry was filtered again to remove water. Washing was repeated and the recovered modified starch dried at 50 °C in a Lab-Line oven (Illinois, USA) with mechanical convection. When dry, the product was milled