



Preparation of starch derivatives using reactive extrusion and evaluation of modified starches as shell materials for encapsulation of flavoring agents by spray drying

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ABSTRACT

Acetylated, n-octenylsuccinylated (n-OSA) and phosphorylated waxy maize starches were prepared using reactive extrusion in a single-screw extruder. The starches were hydrolyzed with hydrochloric acid (3.4% dry basis, at 50 °C for 6 h) before they were esterified. n-OSA starch and acetylated starch were conventionally modified in a slurry and further hydrolyzed using a single-screw extruder. Starch phosphate was prepared by a conventional method in a slurry and by extrusion. Chemical modifications of n-OSA and acetylated starches were confirmed using Infrared Spectroscopy. The degree of substitution (DS), viscosity profile, water solubility index (WSI), and water absorption index (WAI) were measured to the modified starches. The viscosity of the modified starches was reduced after extrusion and the WSI and WAI increased. Microcapsules were produced by spray drying. n-OSA starch exhibited good emulsifying capabilities and a total oil retention (% w/w) of 94.75%, better than the control oil retention (commercial N-LOK) of 89.16%. Starch phosphates and acetates registered oil retentions of 55.75% and 61.31%, respectively. The modified starches prepared using reactive extrusion showed good characteristics as shell materials for encapsulation by spray drying.

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1. Introduction

Many flavors are volatile and can be retained in foods much more effectively when encapsulated. Microcapsule formulations can achieve controlled, sustained or delayed release and protect oxygen sensitive core materials during processing and storage (Brazel, 1999). Various carriers have been used to encapsulate food ingredients, including gums, carbohydrates, lipids and proteins (King, 1995). Spray-drying, a well known technology in the food industry is at the present the most commonly used microencapsulation method for food ingredients (Reineccius, 2006; Shefer and Shefer, 2003). The requirements for an ideal spray-drying carrier include a high degree of solubility, limited viscosity of solution at 35–45% solids content, good emulsifying properties, good drying properties, nonhygroscopic character, bland taste, nonreactivity, and low cost. Hydrolyzed starches, modified starches and gum Arabic make up the three classes of carriers in wide use today for flavor encapsulation (Reineccius, 2006). Starch-based food ingredients used for flavor encapsulation include maltodextrins, corn syrup solids, cyclodextrins and emulsifying starches (n-OSA starches), or some combinations thereof (Reineccius, 2006; Qi

and Xu, 1999; Gibbs et al., 1999; Shahidi and Han, 1993). Native starches and starch hydrolysis products are hydrophilic in nature, thus having little affinity for hydrophobic flavor oils. Their hydrophilic nature have been changed by esterifying them with hydrophobic groups or negatively charged groups. n-OSA treated starches contain hydrophobic octenyl side chains which impart an emulsifying capability to the starches. Un-depolymerized n-OSA starches are rarely used for spray drying because of their very high viscosity. Most n-OSA starches used for encapsulation are depolymerized to lower the viscosity in one of three ways: acid thinning or acid hydrolysis, pyrodextrinization, and enzyme hydrolysis (Qi and Xu, 1999).

Starch acetylation can be performed to improve significantly the physicochemical and functional properties of the starch, even with a low degree of substitution (Xu et al., 2004). Starch acetates with degree of substitution of 0.01–0.2 have been prepared for food use to improve film forming, binding, thickening, stability, and texturizing (de Graaf et al., 1998), although there is no information available about their use as encapsulating agents. Hydrophobicity of starch increases with increasing substituent carbon chain length and degree of substitution (Thiebaud et al., 1997; Zhang et al., 1997).

Phosphorylation is another technique used to improve the functional properties of starch. The resultant starch phosphate gives a clear paste with increased solubility, swelling power, and freeze-

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thaw stability (Lim and Seib, 1993; Solarek, 1989). Starch phosphates produced by conventional oven-heating methods and by extrusion have been reported for several food applications (Chang and Lii, 1992; Kim et al., 1999; Landerito and Wang, 2005; San Martín-Martínez et al., 2004; Salay and Ciacco, 1990; Seker et al., 2003), but there is no information about starch phosphates produced either by the oven-heating process or by extrusion used for microencapsulation purposes.

The conventional methods of starch modification require an excess amount of reagents and may cause environmental contamination from unreacted chemicals (Landerito and Wang, 2005). Extrusion technology is a high-temperature, short-time process with the advantage of high versatility and absence of effluents (Harper, 1992), that may overcome these problems using reduced amounts of reagents and moreover, a further hydrolysis of starch desirable for microencapsulation purposes can be achieved. During extrusion starch is heated, transported and compressed by the single screw or twin screw and pressed toward a die at high temperature and pressure resulting in molecular changes. Extrusion-cooking conditions can convert starch from a granular and semi-crystalline material into a highly viscous, plastic material (Brümmer et al., 2002). This conversion is accompanied by disruption of the crystalline structure of starch polymers and their reduction to smaller molecules (Vasanthan et al., 2001).

The aim of this work was to prepare starch-based novel microencapsulating agents using reactive extrusion in a first place as a mean of esterification (phosphorylated starches), or as a second step after conventional chemical modification (acetylated and n-octenylsuccinylated starches) for further hydrolysis of starch.

2. Material and methods

2.1. Raw materials

Waxy maize starch (Corn Products, donated by CPI, Mexico) was used as a raw material for starch modification. Sodium tripolyphosphate (Sigma–Aldrich), acetic anhydride and n-octenyl succinic anhydride (Sigma–Aldrich) were used to prepare the modified starches. Orange peel oil (donated by Food Specialities, Mexico) was used as internal phase of microcapsules. A commercial modified starch, (N-LOK from National Starch and Chemical Co., donated by Aranal Mexico, based on waxy maize starch), was used as a control.

2.2. Sample preparation

Starches were hydrolyzed with hydrochloric acid before they were esterified according to the methodology described by Zambrano and Camargo (2001) with some modifications. A slurry of 40 g of starch (d.b.)/100 mL of distilled water was prepared and an aqueous HCl solution at a final concentration of 3.4 g of pure HCl/100 g of starch (d.b.) was added; hydrolysis was carried out in a water bath at 50 °C with constant stirring for 6 h. After hydrolysis, the pH was adjusted to 5.0 ± 5.20 by slow addition of aqueous sodium hydroxide (5 g/100 mL); hydrolyzed starch was centrifuged for 10 min at 6000 rpm in a centrifuge Hermle Z200 A, washed three times with distilled water and dried in a convection oven at 45 °C during 48 h. The dried powder was milled and sieved in a mesh of 250 μm opening size.

2.3. Starch chemical modifications

2.3.1. Starch phosphorylation

It was achieved by a conventional method and by extrusion.

Conventional phosphorylation of starch was achieved according to the method proposed by Paschall (1964) with some modifications. About 12.6 g of sodium tripolyphosphate (STP)/100 g of starch (d.b.) were added to a slurry of starch (100 g (d.b.) of starch/167 mL of distilled water) with constant stirring. The slurry was centrifuged for 10 min at 6000 rpm in a centrifuge Hermle Z200 A. The solid product was dried in a convection oven at 40–45 °C for 24 h, milled using a hammer mill (model 200 Pulvex, Mexico) and sieved in a mesh of 250 μm . The dried powder was heated to 65 °C for 90 min and to 155 °C for 20 min. The powder was washed twice with distilled water, centrifuged, dried and milled in the same conditions described above for the slurry, for viscosity determinations.

Starch phosphorylation was performed according to Chang and Lii (1992) with some modifications, using a laboratory single-screw extruder designed and manufactured by CINVESTAV-IPN, Mexico, with an internal barrel diameter of 20 mm ($L/D = 20$). Barrel temperatures were 70–80, 150 and 180 °C at the feeding, transition and high pressure extrusion zones, respectively. Screw speed was 80 rpm and feed rate was 70 g/min. The compression ratio of screw was 3:1 and a 4.0 mm diameter die nozzle was used. Sodium tripolyphosphate (4 g/100 g of starch) was dissolved in an aqueous solution of HCl (5% v/v), added to the dried powder of hydrolyzed starch and mixed. pH was adjusted at 5.0–5.2 and the moisture content of starch before extrusion was 15–16%. Samples were stored in polyethylene bags at 4 °C for subsequent extrusion processing. Extruded samples were dried in a convection oven (45 °C) for 2 h, milled using a hammer mill (model 200 Pulvex, Mexico) and sieved in a mesh of 149 μm opening size. Powders were packed in polyethylene bags for characterization analysis and microcapsules preparation.

2.3.2. Starch succinylation

It was conducted using the method proposed by Jeon et al. (1999) with some modifications. A slurry of 45 g of hydrolyzed starch (d.b.)/100 mL was prepared with vigorous stirring. The pH was maintained between 8.5 and 9.0 using an aqueous NaOH solution (5 g/100 mL). About 2 mL of n-octenyl succinic anhydride/50 g of starch (d.b.) were added drop wise over 2 h and the reaction was allowed to proceed for a total of 6 h. The pH was then brought to 5.0 ± 0.20 using 5% (v/v) aqueous HCl solution and the slurry was centrifuged for 10 min at 6000 rpm; the solid product was washed and dried for 24 h in a convection oven at 45 °C. The dried powder was milled and sieved in a mesh of 149 μm opening size.

2.3.3. Starch acetylation

It was performed as described by Phillips et al. (1999). 100 g of starch (d.b.) were dispersed in 225 mL of distilled water and stirred for 60 min at 25 °C. The suspension was adjusted to pH 8.0 with an aqueous NaOH solution (3 g/100 mL). Acetic anhydride (2.5 g) was added drop wise to the stirred slurry while maintaining the pH range within 8.0–8.4. The reaction was allowed to proceed for 10 min after completion of acetic anhydride addition. The slurry was then adjusted to pH 5.0 with 0.5 N HCl and centrifuged for 10 min at 6000 rpm. It was washed free of acid twice with distilled water and dried in a convection oven at 45 °C for 24 h and milled in the same conditions as succinylated starch. After esterification n-OSA and acetylated starches were further hydrolyzed in a single-screw extruder in the same conditions used for starch phosphorylation.

2.4. Water solubility index (WSI) and water absorption index (WAI)

Both indexes were determined for the extruded starches following the method described by Anderson et al. (1969). Three repeti-

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