Journal of Cereal Science 59 (2014) 25–32

Contents lists available at ScienceDirect

Journal of Cereal Science

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

Properties of starch-palmitic acid complexes prepared by high pressure homogenization

Shuang Meng [a,b], Ying Ma [a,*], Da-Wen Sun [a,c,**], Lifeng Wang [a], Tianyi Liu [a]

[a] School of Food Science and Engineering, Harbin Institute of Technology, 73 Huanghe Road, Harbin 150090, China
[b] Light Industry School, Harbin Commerce of University, 1 Xuehai Road, Harbin 150028, China
[c] Food Refrigeration and Computerised Food Technology, School of Biosystems Engineering, University College Dublin, National University of Ireland, Agriculture & Food Science Centre, Belfield, Dublin 4, Ireland

ARTICLE INFO

Article history:
Received 30 May 2013
Received in revised form
21 October 2013
Accepted 24 October 2013

Keywords:
Starch
Palmitic acid
Complex
High pressure homogenization

ABSTRACT

Aqueous mixtures of defatted corn starch and palmitic acid were heated and high pressure homogenized in order to form amylose inclusion complexes. The effects of homogenization pressure (0–120 MPa) and palmitic acid concentration (0.5–8% based on starch content) on starch-palmitic acid complex formation as well as on complex index, X-ray diffraction, thermal properties, viscosity and particle size were investigated. Complex index increased with an increase in the amount of palmitic acid and homogenization pressure, and reached a maximum value (about 60%) when the fatty acid content was 4% and the homogenization pressure was 100 MPa. X-ray diffraction patterns indicated the formation of V-helical complexes between starch and palmitic acid. This technology could prospectively be used in prepared starch-lipid complexes.

1. Introduction

Starch is a mixture of amylose and amylopectin which are the predominantly linear glucose polymer and the branched glucose polymer, respectively. In the presence of ligands such as fatty acid, iodine and alcohols, the leaked amylose from the destroyed granules due to gelatinization of starch undergoes conformation changes resulting in formation of helical inclusion complexes (Fanta et al., 1999; Hahn and Hood, 1987; Morrison et al., 1993). Inclusion complexes can modify the properties and functionality of starch, for example reducing solubility in water (Eliasson and Krog, 1985), retarding retrogradation (Eliasson and Krog, 1985; Tufvesson et al., 2001), decreasing viscosity of gelatinized starch (Gelders et al., 2006; Raphaelides, 1993; Raphaelides and Georgiadis, 2006) and effecting the progress of in-vitro digestibility (Crowe et al., 2000; Tang and Copeland, 2007; Tufvesson et al., 2001). The importance of complexes is reflected in numerous food applications. For example, starch-lipid complexes are used to retard bread staling (Riisom et al., 1984). In recent years, other fields of science, such as nanotechnology (Gelders et al., 2006; Lalush et al., 2005; Wulff et al., 2005) and biotechnology (Sivakama Sundari et al., 1999) begin to exploit the amylose-complexing abilities.

Since these changes in the functionality of starch are of interest to the food industry and for human nutrition, many different methods for the formation of amylose-lipid inclusion complexes have been researched. Heating of lipid and starch dispersion complexes are formed as soon as starch gelatinizes. Fanta and Eskins (1995); Fanta et al. (2010, 1999) and Byars et al. (2009) have extensively studied the formation of starch-fatty acid/sodium fatty acid complexes when these starch dispersions were jet cooked and then allowed to cool slowly. During twin/single-screw extrusion, cooking of starch in the presence of native lipids or added saturated and unsaturated fatty acids, glyceryl monostearate and sodium fatty acid formed V-amylose complexes (Bhatnagar and Hanna, 1994b, 1996; De Pilli et al., 2011, 2012, 2008; Galloway et al., 1989). More pure amylose–inclusion complexes can be formed when amylose, extracted from starch, is mixed with the desired lipid in DMSO or an alkaline solution (Godet et al., 1995a; Godet et al., 1995b; Lalush et al., 2005; Zabar et al., 2009). The major factors governing the formation of complexes are the solubility or dispersibility of the fatty acid in water and the amount of amylose released from the starch granule. Therefore, the development of an efficient process to improve the complexing probability of fatty acid and amylose is the key to prepare desirable starch-fatty acid

Abbreviations: CI, complex index; DMSO, dimethyl sulfoxide; DSC, differential scanning calorimeter; IBC, iodine binding capacity.

* Corresponding author. Tel./fax: +86 451 86282903.
** Corresponding author. Tel.: +353 1 7167342; fax: +353 1 7167493.
E-mail addresses: mengshuang1979@163.com (S. Meng), maying@hit.edu.cn (Y. Ma), dawen.sun@ucd.ie (D.-W. Sun).

0733-5210/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jcs.2013.10.012

complexes. High pressure homogenization, as one of the high pressure processing techniques (Angioloni, and Collar, 2013; Picon et al., 2013; Montiel et al., 2013; Falguera et al., 2013; Santos et al., 2013; Tao et al., 2012; Norton et al., 2009; Norton and Sun, 2008), is a promising alternative to achieve these complexes.

The high pressure, intense mechanical shear, turbulence, and cavitation of the high-pressure homogenization process completely disintegrates starch granules to release amylose and also to reduce its molecular weight (Guraya and James, 2002; Le Thanh-Blicharz et al., 2012). Simultaneously, the high pressure homogenization processing improves the dispersibility of fatty acid in starch dispersion, and promotes the amylose to form inclusion complexes with the fatty acid. Lesmes et al. (2008) assessed a continuous production process with the dual feed homogenizer (operating pressure was 172 MPa) for the formation of starch-stearic acid complexes using three starches (waxy corn starch, corn starch and high amylopectin corn starch). The study demonstrates that the homogenization process causes significant size reduction in all three types of starches, with the temperature in which the starches are predissolved being of great technological importance, affecting the final particle sizes. Nevertheless, the paper studied the starch-fatty acid complexes formation through the homogenization process. In contrast, very little is known about the effect of homogenization pressure on the extent of complexes formation and the properties of the complexes.

In this context, the objective of the present study was to evaluate the starch-palmitic acid complexes prepared through heating combined with high pressure homogenization. This study also aimed at investigating the effect of homogenization pressure level and the fatty acid content on the degree of complex formation, molecular structure, thermal properties, particle size, and viscosity of starch-fatty acid dispersions.

2. Materials and methods

2.1. Materials

Corn starch (containing approximately 27.6% apparent amylose) was obtained from Dacheng Food Industry (Changchun province, China). The weight of starch is given on a dry weight basis. Defatted corn starch was prepared by soxhlet extraction with 75% aqueous n-propanol for 8 h (Perera and Hoover, 1999). The solvent was removed by vacuum evaporation and the starch was dried in an oven at 40 °C for 24 h to obtain dry starch samples. Palmitic acid (99%) was purchased from Aladdin Chemistry Co. Ltd (Shanghai, China).

2.2. Preparation of starch-palmitic acid complexes

Palmitic acid (0.5–8% weight based on defatted corn starch) was dissolved in 30 mL ethanol and then was intimately mixed with 40.0 g of defatted corn starch. The ethanol was then evaporated under ambient conditions. A mixture of a predetermined amount of palmitic acid, 40.0 g defatted corn starch, and 360 mL deionized water was placed in beakers and heated with constant stirring for 30 min in a water bath at approximately 95 °C and then cooled to 70 °C. The beakers were covered with preservative films to minimize moisture loss during heating and cooling. Then, starch paste mixtures were homogenized using a high-pressure homogenizer (NS1001L PANDA 2K, Niro Soavi S.p.A., Parma, Italy) at 0–120 MPa for three passes. The NS1001L PANDA 2K was a two-stage homogenizer with two high-pressure valves. In the first stage, the adjustable pressure levels were respectively 20, 40, 60, 80, 100, and 120 MPa, and in the second stage, the pressure was adjusted to about 1/10 of that of the first stage high-pressure. The homogenized dispersion was allowed to cool without stirring to ambient temperature. For chemical and physical analyses, the samples were dried at 40 °C in an oven for 24 h and were ground in a micro-mill (FW80-1, Tianjing Taisite Instruments Inc, China) to pass through a 100-mesh sieve. As a control, a sample without fatty acid (non-palmitic acid sample) was also prepared.

2.3. Complex index (CI)

CI was determined in order to understand the degree of starch–lipid complex formation (De Pilli et al., 2008; Guraya et al., 1997; Kawai et al., 2012; Tang and Copeland, 2007). This method involved the formation of a starch–iodine complex and measurement of starch which is not complexed with lipids. IBC is related to the portion of starch that is complexed to the iodine, and then the formation of complexes reduced IBC of the starches. The gelatinized starch-palmitic acid mixture (5 g) was mixed with 25 mL of distilled water in a 50 mL centrifuge tube for 2 min with vortexing. The dispersion was then centrifuged for 15 min at 3000*g* and 500 μL of the supernatant was mixed with 15 mL of deionized water and 2 mL of iodine solution [2.0% (w/w) KI and 1.3% (w/w) I_2 in deionized water] in a 25 mL test tube, and then the tube was turned over several times. IBC values of the sample and control (without palmitic acid sample) were measured at 690 nm with a UV-VIS spectrophotometer. The CI was evaluated using the following equation:

$$\mathrm{CI}(\%) = \frac{\left(\mathrm{IBC}_{\mathrm{reference}} - \mathrm{IBC}_{\mathrm{sample}}\right)}{\mathrm{IBC}_{\mathrm{reference}}} \times 100$$

All tests were performed in triplicate and the results averaged.

2.4. Microscopy of homogenized starch paste mixtures

The starch mixture pastes were observed using an optical microscope (CX21 Biological Microscope, Olympus Corporation, Japan) equipped with a CCD camera module.

2.5. Particle size analysis

Homogenized starch mixture suspensions were analyzed by laser scattering to monitor the particle size distribution of the resulting complexes after their production. The used equipment was a Mastersizer 2000 laser diffractometer (Malvern Instruments, UK) equipped with a He-Ne laser with a wavelength of 632.8 nm. The data obtained was then processed using the MS2000 software, with water as solvent, and distribution was expressed by volume.

2.6. Brookfield viscosity of aqueous dispersions of starch-palmitic acid complexes

A small portion of the dispersion was allowed to cool to 25 °C without stirring, and viscosity was measured with a Brookfield DV-E viscometer at a certain speed (30 rpm) (Fanta and Eskins, 1995).

2.7. X-ray diffraction

Samples were defatted in a Soxhlet extractor with petroleum ether to remove uncomplexed lipids before chemical analyses. Powdered samples were equilibrated at the same temperature and humidity (23 °C and 45% relative humidity) for 48 h prior to analysis so as to eliminate the error caused by moisture content. X-ray powder diffraction analyses were performed with a Rigaku D-max-2500V diffractometer (Rigaku Corporation, Japan) operated at 40 kV, 30 mA with graphite-filtered Cu Kα radiation and a θ compensating slit. The relative intensity was recorded in a