Industrial Crops and Products 51 (2013) 220–223

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Short communication

Changes in crystalline structure of microspheres of corn starch and amylose under isothermal and temperature cycling treatments

Xia Bai [a], Zhao Dong [a], Xiuli Wu [a,b], Jin Tong [a], Jiang Zhou [a,*]

[a] Key Laboratory of Bionic Engineering (Ministry of Education), College of Biological and Agricultural Engineering, Jilin University, 5988 Renmin Street, Changchun 130022, China
[b] College of Biological Science and Technology, Changchun University, 6543 Weixing Road, Changchun 130012, China

ARTICLE INFO

Article history:
Received 14 May 2013
Received in revised form 4 September 2013
Accepted 5 September 2013

Keywords:
Starch microsphere
Crystalline structure
Temperature treatments

ABSTRACT

Microspheres of corn starch and amylose were prepared by precipitating starch paste solution with absolute ethanol. The V-type crystalline structure was observed in the obtained microspheres. By storing the microspheres at three temperature conditions under 95% RH, constant temperatures at 8 °C and 30 °C as well as temperature cycles at 8 °C for 1 day and at 30 °C for 1 day, for different periods of time, changes in crystalline structure of the microspheres were investigated by X-ray diffraction (XRD) analysis. The results showed that the diffraction peaks of V-type crystalline structure vanished after the temperature treatments. Retrogradation yielding A-type crystalline structure took place in all the corn starch microspheres and only the amylose microspheres with 8 °C/30 °C treatment. Comparing with the isothermal treatments, the temperature cycling accelerated retrogradation of the microspheres.

1. Introduction

As one of the most abundant biopolymers in nature, starch is found in the tissues of many plants and has been considered as an alternative material for industrial applications because of its availability from renewable resources, biodegradability, derivability, non-toxicity and low cost. Starch microspheres, as one of starch products, have found applications in pharmaceutical industry (Fang et al., 2008), food industry (Glenn et al., 2010), material industry (Ma et al., 2008) and environmental engineering (Miao et al., 2010; Yang et al., 2010). The microstructure of starch microspheres has deep effects on these applications because it will determine performance of the microspheres, such as loading and release characteristics, mechanical properties and adsorption performance.

Although there are several approaches to prepare starch microspheres, such as spray drying (Glenn et al., 2010), emulsion-crosslinking technique (Atyabi et al., 2006; Miao et al., 2010) and emulsion-gelation process followed by supercritical drying (García-González et al., 2012), the precipitation is a commonly used method (Ma et al., 2008; Tan et al., 2009; Chin et al., 2011). The precipitation process involves a successive addition of a dilute starch solution which is prepared by using solvent or gelatinizing starch in water to a nonsolvent or inversely. Therefore, the microstructure of the starch microspheres is dependant upon the preparation conditions and compositions.

It is known that retrogradation will take place in gelatinized starch. Starch retrogradation is a non-equilibrium thermoreversible recrystallization process, its rate and extent depend on ratio and structures of amylose and amylopectin, storage temperature and time as well as water content. The retrogradation can be accelerated by treating gelatinized starch with temperature cycles between a temperature near the glass transition temperature and a higher temperature up to the melting temperature (Jacobson and BeMiller, 1998). Retrogradation of starch has been the subject of considerable investigation, but most research was carried out with high-moisture and intermediate-moisture starch materials such as pastes and gels (Jacobson and BeMiller, 1998; Park et al., 2009; Zhou et al., 2010). No detailed information is available about the retrogradation of starch microspheres with low moisture content. Understanding the changes of crystalline structure and crystallinity in starch microspheres is necessary for applications of starch microspheres.

In this paper, starch microspheres were prepared by precipitation using corn starch and amylose. Then, the microspheres were stored under isothermal (8 °C and 30 °C) as well as temperature cycles of 8 °C and 30 °C for different periods to investigate changes in crystalline structures aiming at getting deeper insights of the influence of storage conditions on microstructure of starch microspheres.

* Corresponding author. Tel.: +86 431 85095760x414; fax: +86 431 85095760x888.
E-mail address: jiang.zhou@jlu.edu.cn (J. Zhou).

0926-6690/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.indcrop.2013.09.007

2. Experimental

2.1. Materials

The corn starch (with about 25% amylose) was purchased from Changchun Jincheng Corn Development Co. Ltd. (Changchun, China). The amylose was purchased from Shaanxi Tianwei Biological Production Co. Ltd. (Xi'an, China). Absolute ethanol was purchased from Beijing Beihua Fine Chemicals Co. Ltd. (Beijing, China). All the materials were used as received.

2.2. Preparation of corn starch microspheres and amylose microspheres

Ten grams of starch (corn starch or amylose) was mixed with 200 mL of deionized water, and the mixture was heated to 95 °C and kept at this temperature for 1 h in water bath with constant stirring. After the temperature of the gelatinized starch solution was reduced to 50 °C, 200 mL of absolute ethanol was dropwise added at the speed of 3 mL/min under constant stirring of 400 rpm. When the obtained microsphere suspension was cooled to room temperature, another 200 mL of absolute ethanol was dropwise added with constant stirring. The precipitate was collected by centrifugation with 6000 rpm, washed two times by using absolute ethanol to remove water, then air-dried at room temperature overnight (12 h).

2.3. Morphology observation

Morphologies of corn starch microspheres and amylose microspheres were observed using a Philips XL30 FEG-ESEM (FEI Philips Electroscan, Mass., USA). Samples were mounted on specimen stubs with carbon black tape and then sputter-coated with gold before observation.

2.4. Temperature treating conditions

The obtained starch microspheres were weighed into glass petri-dishes and stored under 95% RH at three different temperature conditions: constant temperatures at 8 °C and 30 °C, and temperature cycles at 8 °C for 1 day and at 30 °C for 1 day (8/30 °C).

2.5. X-ray diffraction (XRD) analysis

The crystalline structures of the starch microspheres were characterized using a Rigaku D/max-2500 X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu-Kα radiation (λ = 1.542 Å) at 40 kV and 250 mA. The XRD patterns were recorded over the 2θ range of 4–40° at a speed of 2°/min. Relative crystallinity was evaluated from the ratio of the areas of the diffraction peaks to the area of the whole diffraction pattern subtracted amorphous background patterns (Nara and Komiya, 1983).

2.6. Moisture content

Samples were dried in a vacuum oven at 105 °C until constant weight. The moisture content (MC) of the starch microspheres was calculated using the measured wet weight, W_W, and the dry weight, W_D, by

$$MC = \frac{W_W - W_D}{W_D} \times 100\% \quad (1)$$

3. Results and discussion

3.1. Corn starch microspheres (CSM)

The obtained CSM consisted of particles ranging in size from approximately 15 μm to 100 μm with a mean size of 37.40 μm measured by using a laser particle size analyzer (BT-9300H, Bettersize Instruments Ltd., Dandong, China). Fig. 1(a) showed the SEM image of the CSM, which revealed that the CSM were basically spherical shape with some concavities and small irregular fragments on surface, though some particles were irregularly shaped. X-ray diffraction patterns of the CSM stored at three temperature conditions for 0, 2, 6, 10 and 20 days were given in Fig. 2(a). The fresh CSM possess a typical V-type crystalline structure with diffraction peaks at 7.7°, 13.3° and 20.4° of 2θ. This result is different from that in the starch microspheres prepared using an aqueous two-phase system consisting of two structurally different polymers (poly(ethylene glycol) and starch), which gave A-type diffraction patterns (Elfstrand et al., 2006). However, after 2 days storage under the selected conditions, the diffraction peaks of V-type crystalline structure disappeared and the A-type crystalline structure with diffraction peaks at 15.3°, 17.2°, 19.8° and 22.8° of 2θ was formed in the sample stored at 8 °C for 20 days, and the ones at 30 °C for 10 and 20 days, as well as the ones at 8/30 °C for 6, 10 and 20 days. These observations suggest that, for the CSM, the temperature cycling treatment at 8/30 °C is more helpful to formation of the A-type structure than the isothermal treatments at 8 °C or 30 °C.

The relative crystallinity and moisture content of the CSM stored under the three conditions were presented in Table 1. Compared to the crystallinity of 6.41% in the crosslinked starch microspheres prepared from soluble starch and *N*,*N*′-methylenebisacrylamide (Miao et al., 2010), the crystallinity (16.58%) of the fresh CSM in this study was much higher. The data in Table 1 indicated that storing the CSM at 8/30 °C gave rise to higher rate and extent of retrogradation compared with storing isothermally at 8 °C and 30 °C. This may be because the temperature cycling induces a stepwise nucleation

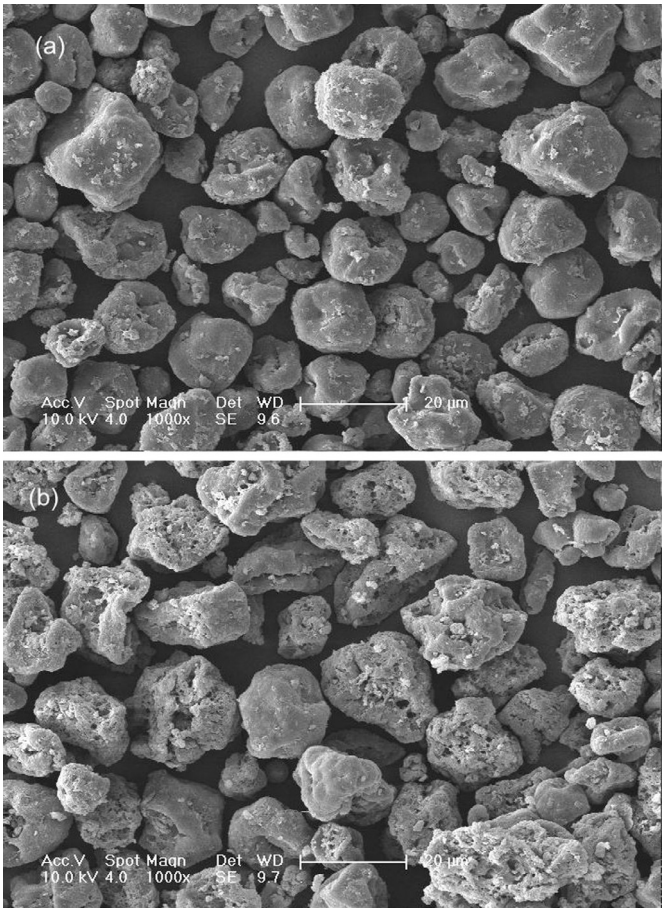

Fig. 1. SEM images of corn starch microspheres (a) and amylose microspheres (b).