

The Preparation of B-type Starch Spherocrystals by Freezing Crystallization

Yan Qi LIU, Jiu Gao YU*, Xiu Ping SUN

College of Science, Tianjin University, Tianjin 300072

Abstract: The B-typed starch spherocrystals were prepared by the dissolution and freezing crystallization of acid-hydrolyzed starch obtained by the mild hydrolysis of maize starch. The spherocrystals were characterized with scanning electron microscope (SEM), X-ray diffraction, thermogravimetry (TG) and gel pervasion chromatogram (GPC). The results show that the preparation was a B-type spherocrystal with the average degree of polymerization of 14 glucose units, and the average diameter of crystal particles was about 7 μ m.

Keywords: Starch spherocrystal, freezing crystallization, crystallinity, acid-hydrolyzed maize starch, X-ray diffraction.

Starches are semi-crystalline polymers of amylose and amylopectin¹. The starch granules consist of alternate layers or shells containing crystalline and amorphous regions. The generally accepted description of amylopectin structure is that the short branches are arranged in clusters. It is believed that these short branches form double helices, which to a great extent are organized into crystallites²⁻⁵. Amylopectin is usually thought to be the dominating component in the crystalline regions of starch granules, while amylose can be recrystallized from solution in A, B or V form³. This ability was used to determine the three-dimensional (3D) structure of these different polymorphs, and to investigate the structure of crystalline domains in natural starches.

In earlier papers⁵⁻⁷, A-type and B-type starch spherocrystals were prepared by adjusting the content of solvent (water) and slowly decreasing the temperature of solution. The present study developed a new preparation method of B-type starch spherocrystals.

Experimental

The hydrolysis of starch was performed by adding 5.0 g starch to 100 mL of 2.2 mol/L hydrochloric acid at 35 °C. At the end of the reaction, the remained solid was obtained by filtration with a G4 sand core filter, and then washed to neutrality with distilled water. Thereafter the solid was sequentially washed with ethanol and acetone, finally dried at room temperature.

The aforementioned solid was dissolved in boiling water at the concentration of

* E-mail: gaojiuy@eyou.com

0.5-10%. The solution was cooled to room temperature and the insoluble substance was removed by centrifugation. The supernatant was frozen at -5°C for 12 h, and then slowly thawed at room temperature. The B-type spherocrystals was obtained by filtration of the thawed preparation washing with cool water, and finally drying in vacuum.

Results and Discussion

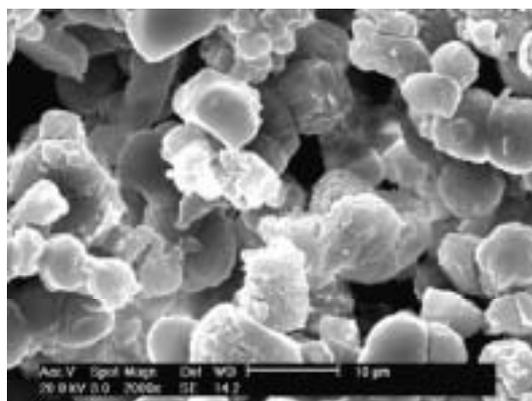
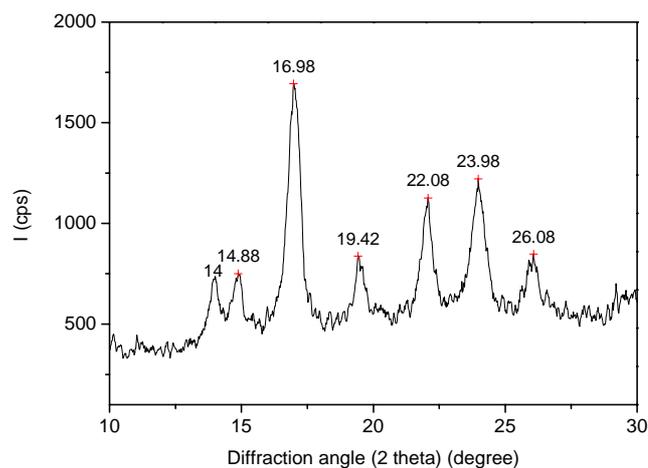
As described above, crystalline residues of starch (lintners) were obtained by lintnerization of maize starch granules, which was thought to be composed of short chains of α -1,4-D-glucan ($\text{dp}_n \sim 15$)². According to the report by Wang L. F. *et al.*⁸, the amorphous regions within the natural starch, which have an incompact structure, were decomposed first as it suffered from mild hydrolysis (HCl 2.2 mol/L, 35°C). Alternatively in crystal regions the double helix, which packs in A-type crystalline, is compact and integral. It strongly resists to acid hydrolysis. The longer of the hydrolysis time, the higher the ratio of crystalline part. The crystallinity increased with the increase in hydrolysis time. This indicated that the crystalline parts of natural starches remained in the residues. The longer chains of starches, which are insoluble in hot water, must be removed before the solution was frozen. The concentration of the solution was increased during the process of freezing, so this method allows a larger range of concentration.

Inspection of the SEM photograph of starch spherocrystals (**Figure 1**) revealed that a large percentage of the specimen consists of spherocrystals, and the size of the particles with the average diameter of about $7\ \mu\text{m}$ was well-balanced. Slight conglutination between the particles can be observed, which might be ascribed to the occurrence of deformities of the surfaces of spherocrystals when thawed from frozen solution, as well as the fusion between the particles when the surfaces of the crystal regions were partially melted.

Figure 2 presented the X-ray diffraction curves of starch spherocrystals. The characteristic diffraction peaks of B-type starch at 15° , 17° , 22° and 24° can be observed. Two peaks at 14° and 14.8° identified the occurrence of peak 15° . The peaks at 19.5° and 26° can also be viewed as the characteristic diffraction peaks of B-type crystals. The observation was in accordance with the report by Gidley⁹. The crystallinity of the B-type starch spherocrystals was calculated to be 81.3% according to the method of Komiya and Nara¹⁰.

The chain length distribution of spherocrystals was determined by gel permeation chromatography (GPC) (data not shown). There are two adjacent peaks in the curves, and the molecular weights of them are 1718 and 2488 respectively. The average molecular weight (M_w) of the B-type spherocrystals is 2339, and dp_n was concluded to be about 14.

The results of thermogravimetry showed that the initial decomposition temperature of B-type spherocrystals was lower than natural maize starch and acid-hydrolyzed maize starch. The weight lost of B-type spherocrystals at 350°C was less than natural starch but larger than the acid-hydrolyzed residues.

Figure 1 SEM photograph of B-type starch spherocrystals. Magnification: 2000 × .**Figure 2** X-ray diffraction curve of B-type starch spherocrystals

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