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Influence of ethanol-water solvent and ultra-high pressure on the stability of amylose-n-octanol complex

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ABSTRACT

B-type microcrystalline starch (BM) was allowed to react with n-octanol to produce amylose-n-octanol complex. The influences of ethanol concentration, processing time, and processing temperature on the stability of the complex were studied by processing the complex with ethanol-water solvent. Furthermore, the crystal structure of the complex before and after processing was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR). Results indicated that the ethanol concentration had great influence on the stability of the complex. The higher the ethanol concentration, the stronger the force between amylose and ligand, and some of the ethanol may act as a ligand to form a complex with amylose. The relative crystallinity increased with temperature. The higher the temperature, the more vigorously the molecules moved, strengthening the force between starch and ligand more effectively. However, when the temperature reached 60 °C, the crystallinity of the complex began to decrease due to the dissolution effect. The crystallinity of the complex increased with processing time. Ultra-high pressure treatment affected the shape and size distribution of starch complex in 40% ethanol solvent and converted starch complex (V-type) to the amorphous structure.

1. Introduction

Starch is the main form in which green plants store carbohydrates. It coalesces into granules, which are present mainly in seeds, roots, and tubers but are also found as in stems, leaves, and fruits, or even pollen grains. The differences in size (0.1–200 μm) and shape (globular, elliptic, polygonal, thrombocytic, and irregular tubule) of starch granules mainly depend on the type of plants (Witczak, Ziobro, Juszczak, & Korus, 2016). Starch is a polymeric amylose. It is natural, cheap, biodegradable, and capable of being fully used, and the process by which it is produced is easily reproducible (Ashogbon & Akintayo, 2014). XRD analysis showed that the crystal structure of starch can be divided into 4 types: A-type, B-type, C-type, and V-type (Gernat, Radosta, Anger, & Damaschun, 1993; Morrison, Law, & Snape, 1993; Zobel, 1988). A-type is mainly present in cereal starch and B-type in amylose-rich starch and tuber starch (Paris, Bizot, Emery, Buzare, & Buleon, 1999). A-type, B-type, and C-type polymorphisms are present in the starch of leguminous plants (Gernat, Radosta, Damaschun, & Schierbaum, 1990; Sarko & Wu, 1978), and V-type structure is rarely found in natural starch (Bogracheva, Morris, Ring, & Hedley, 1998). Under experimental conditions, amylose can form complexes (V-type single helix composite structure) with some ligands, such as C18 fatty acid (Seo, Kim, & Lim, 2015), ascorbyl palmitate (Kong & Ziegler, 2014), lecithin (Cheng, Luo, Li, & Fu, 2015), and aroma compound (Zhang et al., 2017).

Most existing reports about starch complexes have focused mainly on the preparation, characterization, and properties of the starch complex (Arijaje & Wang, 2016; Putseys, Lamberts, & Delcour, 2010; Tufvesson, Wahlgren, & Eliasson, 2003). However, the reports about the crystal structure stability of V-type starch are limited. Ethanol plays an important role in the preparation of starch complex by serving as a solvent. Chang, Lin, and Lii (2004) used ethanol solution at concentrations of 50%, 70% and 90% to process waxy corn starch containing 0.36% and 1.39% HCl at 65 °C. Their results showed the average granule size, maximum wavelength of the spectrum of iodine coloration (λ_{max}), pasting viscosity,

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gelatinization onset temperature (T_o), average molecular weight and average chain length of starch decreased after treated, while no obvious change on X-ray diffraction pattern and increase in solubility of treated starch was also found. The changes on pasting viscosity, T_o, average molecular weight and solubility of treated starch increased with increasing ethanol and acid concentrations. Liu, Xie, and Shi (2016) used an ethanol-water solution to process B-type microcrystalline starch and produced A + V type starch. Through univariate analysis, the influences of ethanol concentration, holding time, and holding temperature on the crystal structure of starch were explored. Comparison of primary starches, acidified starch, and B-type starch, showed that A + V type starch was more difficult to gelatinize than other starches. FT-IR analysis indicated that the absorption peak intensity of A + V type to be the most pronounced, and SEM figures showed that the A + V type starch was composed of flat structures and spherical granules.

There have been few studies on the structural stability of V-type starches. Many factors influence the stability of starch-alcohol complexes, which depend mainly on the properties and types of ligand as well as on the types of starch. The reaction solution and water activity also exerted important influences on V-type starch complexes. Because ethanol solution could prevent starch granules from swelling and high temperatures could destroy the crystalline structure of starch, the V-type starch complex dispersed in ethanol solution was processed at high temperatures. Results showed that the crystal structure of granules and starch granules could not be destroyed at the same time. This study was a preliminary exploration of the influence of ethanol-water solvent and ultra-high pressure (UHP) on V-type starch crystal structure. Amylose-n-octanol complex was used as the main ingredient in the study of the influences of ethanol-water solvent, processing temperature, and processing time on the crystal structure stability of short-chain amylose-n-octanol complex and further explored the rules for changes in the crystallization of V-type starch. These results may provide a theoretical basis and reference for the stability research of starch complexes.

2. Materials and methods

2.1. Materials

Native potato starch was purchased from Hengyang Import & Export Co. Ltd., Henan, China. The native potato starch has 25.3% amylose, 19.48% moisture, 0.36% ash, 0.10% protein, and a little fat. The reagents used here were of analytical grade (hydrochloric acid, isopropanol, ethanol, octanol).

2.2. Methods

2.2.1. Preparation of BM

Native potato starch (150 g) was added to aqueous hydrochloric acid (500 mL, 2.2 mol/L) at 35 °C. After 7 days, the suspension was washed several times with deionized water until the pH was 7. After filtration, the precipitate was washed with ethanol three times. Finally, the solid was collected and dried in air to get the acid modified starch for further applications.

The above prepared acidified starch (5 g) was added to deionized water (100 mL) to prepare a suspension (5% w/w), which was heated at 80 °C in order to fully dissolve the starch. The resulting solution was cooled to room temperature and centrifuged to remove insoluble substances. The supernatant was refrigerated at 18 °C for 12 h, then allowed to thaw slowly at room temperature. When only a small amount of ice remained after thawing, the residue was immediately filtered, washed with cold water, and aired at room temperature to give the B-type amylose (Liu et al., 2015).

2.2.2. Preparation of amylose-n-octanol complex

Preparation of V-type amylose-n-octanol complex (Liu, Liu, & Li, 2013): B-type microcrystal starch 1.0 g was dissolved in 20.0 mL water. The starch solution was heated to boiling in a three-necked flask equipped with a reflux condensation system. Octanol was dissolved in ethanol, and the solution was added to the heated starch solution. This mixed solution was heated and refluxed for 10 min and then cooled to room temperature. The solution was allowed to stand for crystallization and then centrifuged, separated, and washed with ethanol. The white precipitate was lyophilized to obtain the V-type amylose-n-octanol complex.

2.2.3. Influence of ethanol-water solvent on V-type short chain amylose-n-octanol complex

Then 0.5 g of the V-type complex described above was added to the ethanol solution at specific concentrations. The complex was processed at different stirring times and temperatures. It was then rapidly centrifuged, separated, lyophilized, and stored for further testing.

2.2.4. XRD analysis

Starch sample (0.5 g) was placed in a rectangular opening on an aluminum plate (opening size: 15–20 mm; thickness: 1.5 mm) and pressed. XRD (BurkerD8, Germany) was used to characterize the measurement of the starch samples, and the wavelength of the monochromatic Cu–Ka rays used was 0.1542 nm. Other test conditions included a tube voltage of 3 kV, the pipe flow of 20 mA, the scanning speed of 4°/min, a scan area of 5–35°, a sampling step width of 0.02°, and 1 repetition (Lebail, Buleon, Shiftan, & Marchessault, 2000).

The calculation method devised by Nara and Komiya (1983) was applied to process the crystallinity of the XRD curve. The separation methods of the crystalline and amorphous portions in the X-ray diffractograms of potato starch were shown in Fig. 1. The upper area (a_c) which was separated with the smooth curve connecting each point of the minimum intensity corresponded to the crystalline portion and the lower area was background containing the amorphous portion (a_a). a_a was assumed to be the upper area separated with the straight line joining the two points of intensity at 37° and 4° (8°) in the background.

$$RC = \frac{a_c}{a_c + a_a}$$

The ratio of the each value of a_c, a_a, and a_c/a_t ($a_t = a_c + a_a$) of the moistened sample to that of the air-dried one was calculated to give the relative crystallinity.

2.2.5. FT-IR analysis

Starch sample (2 mg) and dry KBr (150 mg) were fully mixed in a high speed mill, and put into the pressure medium voltage to prepare tablets approximately 1 mm thick. Then, the sample was analyzed in FT-IR (S3000, BIO-RAO, America). Test conditions: the range of scanning wave number was 4000–400 cm^{-1} and resolution was 4 cm^{-1}. The DTGS detector was used and air was used as blank. An average of 32 scans provided the infrared spectrum of the sample.

2.2.6. SEM analysis

Samples were mounted on metallic stubs, and then coated with gold (50 s) with a sputter coater (Polaron Sputter Coat System,