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Preparation and characterization of modified starch granules with high hydrophobicity and flowability

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ABSTRACT

Normal cornstarch (NC) was chemically modified by octenylsuccinic anhydride (OSA) and $Al_2(SO_4)_3$. The effects of the concentration of NaOH, OSA, and $Al_2(SO_4)_3$ on the properties of modified starch(OS-starch-Al) were investigated. The OS-starch-Al was characterized by repose angle, activation index, inductively coupled plasma-atomic emission spectrometry (ICP-OES), light microscopy, SEM, FT-IR, and ^{27}Al NMR. The results showed that pH 4 was the optimum condition for Al^{3+} cross-linking with OS-starch and for obtaining high flowability and hydrophobicity. When the concentration of OSA and $Al_2(SO_4)_3$ was 2%, the OS-starch-Al was characterized by high flowability. A concentration of 4% OSA and $Al_2(SO_4)_3$ yielded the highest activation index. The moisture content affected the flowability of native NC, but had a minor effect on OS-starch-Al. SEM and polarized microscopy revealed that the modification had slight effects on the crystalline structure and morphology of NC. During the preparation, some dust particles functioning as flow additives were produced on the surface of starch granules. The results of FT-IR, ICP-OES, and ^{27}Al NMR confirmed the formation of ester group and the cross-link with Al^{3+}.

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1. Introduction

Flow difficulties and caking are common problems in industries producing or utilizing food powders (Peleg, Mannheim, & Passy, 1973). Several powders, such as powered fruits and vegetables are known for their tendency to cause flow problems while other powders such as starch under normal storage conditions are known to be relatively free flowing. Various ways can be used to overcome these problems, such as drying to low moisture content and addition of anticaking agents. Modified starch with high flowability and hydrophobicity are usually used as a disperse carrier mixed with small amount of enzymes, food additives and are added to food systems (flour, fruit and vegetable powders).

Various physical or chemical modifications have been adopted to improve the flowability and hydrophobicity of starch granules. Starches are, generally, chemically modified by treatment with reagents, such as anhydride (Bai & Shi, 2011; Bai, Shi, Herrera, & Prakash, 2011; Sui, Huber, & Bemiller, 2013), and organic acid (Neumann, Wiege, & Warwel, 2002; Simi & Emilia Abraham, 2007), which introduces a substituent via reaction with the hydroxyl groups in the starch molecules (Bao, Xing, Phillips, & Corke, 2003). Octenylsuccinic anhydride (OSA) modified starch (OS-starch) was first synthesized by Caldwell & Wurzburg in 1953. OS-starch contains both hydrophilic and hydrophobic groups, resulting in an amphiphilic character (Sweedman, Tizzotti, Schafer, & Gilbert, 2013). Due to its amphiphilic character, the consumption of OS-starch has grown rapidly worldwide. Use of OS-starch in pharmaceutical, cosmetic and food industries has been limited due to starch's poor flowability (Tomas & Kleinschmidt, 2009). Therefore, investigations into the methods that enhance the hydrophobicity and flowability of starch granules have been a popular research topic.

When particle sizes are less than 100 μm, interparticle adhesion forces including van der Waals forces, exceed the gravitational forces by several orders of magnitude resulting in poor flowability (Tomas & Kleinschmidt, 2009). Small amounts of flow additives can be used to improve the surface roughness of particles to reduce the van der Waals forces, resulting in good flowability. The application of additives can promote the discharge of powders and then improve the flowability of the particles (Tomas & Kleinschmidt, 2009). The effects of different coating materials on the flowability of cohesive powders were examined by coating with both hydrophobic and hydrophilic silica (Yang, Sliva, Banerjee, Dave, & Pfeffer, 2005). The possible roles of the flow additives, partially coated on the particle surfaces, in the particle system (glass beads, polyester

Abbreviations: NC, normal cornstarch; NMR, nuclear magnetic resonance; ICP-OES, inductively coupled plasma-atomic emission spectrometry; OSA, octenylsuccinic anhydrate; OS-starch, octenylsuccinic starch ester; OS-starch-Al, starch samples modified by OSA and $Al_2(SO_4)_3$; SEM, scanning electron microscopy; FT-IR, Fourier transform infrared spectroscopy.

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resin and corn starch) have been elucidated (Xu, Zhang, & Zhu, 2009). Cai, Li, Shen, Ma, and Xing (2009) have previously investigated the addition of hydrophobic reagents on the surface of the starch granules in the preparation of hydrophobic starch with flow additives in order to improve starch flowability.

Caldwell and Hills (1952) used starch acid ester cross-linking with a compound containing a polyvalent metal to enhance the flowability of starch granules. However, to the best of our knowledge, little work has been done to elucidate the characterization and surface morphology of this modified starch. The objective of this study was to investigate the effects of the concentration of OSA, aluminum ion, and NaOH on the hydrophobicity and flowability of OS-starch-Al. Also, the mechanism of the chemical modification on improving the flowability and hydrophobicity of starch were investigated.

2. Materials and methods

2.1. Materials

Normal cornstarch (NC) was purchased from COFOO Biochemical Energy Co. (Yushu, China). The 2-octen-1-ylsuccinic anhydride (OSA) was purchased from Vertellus Specialties Inc (Nanjing, China). Aluminum sulfate ($Al_2(SO_4)_3$) was purchased from Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). All other chemicals used in this study were of analytical grade.

2.2. Preparation of modified starch with hydrophobicity and flowability

2.2.1. Preparation of OS-starch

Normal cornstarch (NC) (100 g, dry starch base, dsb) was suspended in deionized water to prepare a (35%, w/w) slurry with vigorous agitation. The pH of the slurry was adjusted to 8.0 using NaOH solution (3%, w/w). A certain amount of octenylsuccinate anhydrate (1%, 2%, 3%, 4%, and 5%, dsb, respectively) was added slowly within 1 h while maintaining the pH at 8.0 with NaOH solution. The reaction was allowed to proceed at 35 °C in order to avoid the gelatinization of starch. After the pH was stable for 30 min, the reaction was ceased by adjusting the pH to 6.0 by HCl (5%, w/w). The mixture was recovered by filtration, and washed three times with ethanol (90%, v/v). The OS-starch was oven-dried at 45 °C for 24 h, and then ground to fine powder (Zhang et al., 2011).

2.2.2. Preparation of OS-starch-Al

A series of OS-starch slurries (35%, w/w, dsb) was heated in a water bath at 35 °C and their pH was adjusted to a certain value (pH = 2, 3, 4, 5, 6, and 7) by adding NaOH or HCl solution (3%, w/w). A certain amount of $Al_2(SO_4)_3$ (1%, 2%, 3%, 4%, 5%, dsb, respectively) was added to OS-starch slurry. After the pH was stable for 30 min, the mixture was recovered by filtration, and washed three times with deionized water to remove the free aluminum ion. The mixture was oven-dried at 45 °C for 24 h, and then ground to fine powder and passed through a 300 mesh nylon sieve.

2.3. Determination of activation index

The hydrophobicity of starch was quantified by the activation index. The hydrophobic starch would float on the water, but the hydrophilic starch precipitated. A higher fraction of starch that floated on the water indicated hydrophobicity in the starch (Cai et al., 2009).

A starch sample (5 g, dsb) was weighed and then placed into a 150 mL beaker, which was filled with 100 mL distilled water. The sample and the water were fully mixed by agitation for 5 min and the mixture was then kept static for deposition. After 1 h, the hydrophobic starch particles were separated. The floating starch was scratched off by a filter paper. Then, the deposited hydrophilic starch particles were filtered, dried, and weighted. The result was recorded as the weight of W_0, which is the weight of the hydrophilic starch. Then the activation index was calculated using the following formula:

$$H = \frac{W - W_0}{W} \times 100\% \quad (1)$$

where H is the activation index, W is the total weight of starch sample, and W_0 is the weight of the precipitated starch.

2.4. Determination of the repose angle

The repose angle is one of the measures of flowability of powders and it may be measured using a "self-made device" according to a previous report (El-Say, Refaey, Samy, & Badawy, 2010). The repose angle was calculated by a simple geometry from the base and height of the conical heap formed. The angle of repose was calculated using the following equation:

$$\theta = \arctan\left(\frac{2h}{d}\right) \quad (2)$$

where d is the diameter of base, and h is the height of the formed conical heap.

2.5. Moisture content

The moisture content was determined by using a moisture analyzer (MA35, Sartorius Stedim Biotech GmbH, Germany).

2.6. Metal ion content analysis

The metal ion (Al^{3+}) content was determined by inductively coupled plasma-atomic emission spectrometry (ICP-OES, Perkin Elmer, USA). Starch samples (500 mg, dry basis), deionized water (10 mL) and HNO_3 (5 mL) were added into 25 mL COD tubes. The tubes were capped and mixed by vortexing, and then placed in a boiling water bath for digestion until the color of the solution was light pink stably. After digestion, the solution was cooled to room temperature and filtered through a 0.45 μm filter membrane, and then transferred to a 100 mL volumetric flask. This solution was used for analysis of Al^{3+} by ICP-OES. Al^{3+} standard solutions were prepared by appropriate dilutions of 1000 mg/L stock solution immediately before use.

2.7. Light microscopy

Light microscopy was performed using an Olympus BX-51 light microscope (Tokyo, Japan) with normal and polarized light. A defined amount of starch powder was thinly spread onto a microscope glass slide and dispersed in a drop of a mixture of water: glycerol (1:1). The dispersed starch was gently covered with a cover slip. The images were recorded at 500× magnification.

2.8. Scanning electron microscopy (SEM)

Granular morphology was studied using an EVO18 SEM (ZEISS, Germany) operated at 10 kV accelerating voltage. Before examination, starch samples were mounted on aluminum stubs with sticky double-sided carbon tape and sputter-coated with a thin gold film.

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