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Starch nanoparticle formation via reactive extrusion and related mechanism study

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ABSTRACT

In this study, starch nanoparticles were prepared by a reactive extrusion method. The mechanism of starch nanoparticle formation during extrusion was investigated. The effects of extrusion conditions, including temperature (50–100 °C), screw speed, torque, starch water content and crosslinker addition, on particle size were studied. The results indicate that, with the addition of appropriate crosslinkers, the starch particles with an average size about 160 nm could be obtained. The morphology, crystalline property, and rheological properties of starch nanoparticles were also characterized.

1. Introduction

Starch is polysaccharide existing as energy reserve in various plants. Starch is composed of two different components, linear amylose and branched amylopectin. Normally, there are 20–30% amylose and 70–80% amylopectin in starch, depending on the species of source. The size and shape of starch granules vary in different plant species. Starch granules have a semi-crystalline structure with a typical crystallinity around 15–45% (Zobel, 1988). As an abundant natural polymer, starch has many attractive properties such as biodegradability and biocompatibility. Since starch is a low-cost versatile biopolymer, it has been widely used in food and many industrial applications (Jobling, 2004; Song, Zhao, Dong, & Deng, 2009).

In recent years, preparation and application of biodegradable nanocrystals/nanoparticles have been attracting more research interests. As a typical biodegradable natural polymer, starch is a good candidate for nanocrystals/nanoparticles. Recently, Le Corre, Bras, & Dufresne (2010) published a comprehensive review on starch nanoparticle preparation, characterization, and applications. Starch nanoparticles or nanocrystals have many potential applications in various aspects, such as plastic fillers (Angellier, Molina-Boisseau, & Dufresne, 2005; Angellier, Putaux, Molina-Boisseau, Dupeyre, & Dufresne, 2005; Kristo & Biliaderis, 2007), food additives, drug carriers (Simi & Emilia Abraham, 2007), implant materials (Thielemans, Belgacem, & Dufresne, 2006), biodegradable composites (Chen et al., 2008), coating binders (Bloembergen, McLennan, Lee, & Leeuwen, 2008), adhesives (Bloembergen et al., 2005), and so on. Starch nanoparticles also have a great potential for use in papermaking wet end, surface sizing, coating and paperboard as a biodegradable adhesive for substitution of petroleum based adhesives. In addition, starch nanoparticles have many advantages over traditional cooked starch, due to its unique properties such as low viscosity of the suspension even at very high solid concentration (up to 30 wt%), and higher bonding strength (Bloembergen et al., 2005, 2008).

Starch nanocrystals/nanoparticles can be prepared by three different ways, including acid or enzymatic hydrolysis, regeneration, and mechanical treatment (Le Corre et al., 2010). Acid hydrolysis is a typical way to generate starch nanocrystals (Dufresne, 2008; García, Ribba, Dufresne, Aranguren, & Goyanes, 2011; Namazi & Dadkhah, 2010; Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003). With acid hydrolysis, platelet-like starch nanocrystals with a length of 20–40 nm and a thickness of 4–7 nm were obtained (Dufresne, 2008; Putaux et al., 2003). The method of acid hydrolysis is difficult for practical application due to its low yield, long treatment period, and use of acid. Nanosized starch particles can be generated by precipitating starch solution with some organic solvents (Ma, Jian, Chang, & Yu, 2008; Valodkar & Thakore,

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2010). Ma et al. (2008) used ethanol as a precipitant to precipitate pre-cooked native starch, and starch nanoparticles at 50–100 nm were obtained. By using a combination of complex formation with *n*-butanol and enzymatic hydrolysis, Kim & Lim (2009) prepared starch nanoparticles with a size of 10–20 nm. Bastioli et al. (2009) filed a patent for producing starch nanoparticles by complexing modified starch with complexing agents followed by mixing with a hydrophobic polymer. Starch nanoparticles can also be prepared by processing starch granules with mechanical and thermal treatment. Liu, Wu, Chen, & Chang (2009) proposed a simple and environmental friendly mean using high pressure homogenization method for preparing starch nanoparticles. Experimentally, 5% starch slurry was passed through a specially designed microfluidizer several times under high shear pressure. They found the starch particle size could be reduced from 3–6 μm to 10–20 nm after 20 passes. By combining high-pressure homogenization technique with miniemulsion cross-linking, Shi, Li, Wang, Li, & Adhikari (2011) prepared sodium trimetaphosphate (STMP)-cross-linked starch nanoparticles. As a pure mechanical treatment process within a water system, the higher pressure homogenization method is environmentally friendly. However, as only low concentration starch slurry could be processed for homogenization, the yield is still not high. Another environmental friendly mechanical method is extrusion. Giezen, Jongboom, Gotlieb, & Boersma (2000) filed a patent of preparing starch nanoparticles via reaction extrusion. Basically, the premixed starch and plasticizer were loaded into a twin screw extruder, and reversible crosslinkers, such as glyoxal, was added. The extruded starch particles with a size less than 400 nm were obtained, and the starch nanoparticle dispersion at 10% solid content demonstrated a low viscosity of 26 MPa at a shear rate of 55 s^{-1} at room temperature. As the extrusion is conducted under semi-dry conditions (around 65% solid content), therefore the yield is high. The starch nanoparticles prepared by reactive extrusion were also considered as “regenerated starch” nanoparticles because of the crosslinking step (Le Corre et al., 2010). Based on this technology, commercial product, Eco-Sphere is produced by Ecosynthetix. However, the mechanism of starch nanoparticle formation during extrusion was not reported.

Starch extrusion has been widely investigated by many researchers, particularly in food industry. During extrusion, starches are subjected to relatively high pressure, heat and mechanical shear. As a result, significant structural changes, including gelatinization, melting, and fragmentation might occur. The physicochemical change of starch during extrusion was reviewed by Lai & Kokini (1991). It was noted that, during extrusion, complete gelatinization would not occur because of the limited water content in starch. However, at high extrusion temperatures, starch granules soften and melt, and become more mobile. The softened and melted starch granules were physically torn apart by shear force so that faster transfer of water into the interior starch molecules can be achieved. Such mechanical disruption of the molecular bonds by the intense shear force may cause the loss of crystallinity during extrusion. It was found by X-ray diffraction that partial or complete destruction of the crystalline structure of the raw starch granule occurred. This is a good evidence of starch fragmentation during extrusion. During extrusion, hydrogen bonds between linear amylose and branched-chain amylopectin can be broken under high shear force and temperature (Lai & Kokini, 1991). It was found that the molecular weight (Mw) decreased exponentially when the specific mechanical energy input increased (Xie, Yu, Liu, & Chen, 2006). However, no starch particle size measurement was involved in these studies.

The objective of this study is to investigate the mechanism of starch nanoparticle formation via reactive extrusion. The effects of extrusion conditions, such as temperature, screw speed, crosslinker and water content on starch extrusion process and starch particle size were systematically studied. The transitional properties of starch particles, including morphology, crystallinty structure, and rheological properties, at different size levels were also characterized.

2. Materials and methods

2.1. Materials

Native corn starch (B200) was provided by Grain Process (Muscatine, IA, USA). Glycerol (99% pure) and glyoxal (40% aqueous solution) were purchased from Aldrich USA, and were used as plasticizer and crosslinker, respectively.

2.2. Process of nano starch preparation

The nanostarch was prepared using the method described in the patent (Giezen et al., 2000) with minor modification. Giezen used a continuous feeding extruder with 9 heat zones. In our study, a batch feeding extruder with one single heat zone was used. Native corn starch granules were premixed with water and glycerol using a lab blender at a ratio of 100:22:23 (starch:water:glycerol). The well mixed mixture was sealed into a plastic bag, and stored in a refrigerator at around 2 °C for 24 h. A co-rotating twin-screw extruder (HAAKE Minilab) was used to extrude the starch premix. The screw speed range is 100–360 rpm. Amount of starch used for each test is 5 g. 10% glyoxal aqueous solution was added in the starch premix or at the chemical addition point of the extruder (downstream hopper) at a dosage level of 0.5–3% pure glyoxal (based on dry starch amount). The extrusion was conducted within 55–110 °C. The starch samples could be directly flushed out through a die, or cycle inside for longer residence time. The torque was monitored and recorded by a reading screen, and the peak value was reported and used for comparison. In Giezen's patent, the extrudates were ground and sieved, followed by dispersing the starch particles in water. In our study, no grinding and sieving were conducted, and the starch extrudates were simply cut into small pieces (around 0.3 cm) and immersed in water for 1 h. The starch pieces were further broken by an Ultra Turrax homogenizer (IKA T18 BASIC) at a speed of 16,000 rpm for 30 min, producing starch particle suspension.

The prepared starch particle suspension was diluted, and used for particle size measurement and rheological tests. Part of suspension was freeze dried, and the dried powder was used for determining starch crystalline structure.

2.3. Characterization

The particle size and zeta potential of starch particles were measured using a Malvern Zetasizer 3000. The viscosity of prepared starch particle suspension was measured using a MCR 300 rheometer in rotating model with couette geometry. The morphology of starch particles was observed using a scanning electron microscopy (SEM LEO 1530). The crystalline structure of freeze dried starch powders was determined using a wide angle X-ray diffractometer (PANalytical X'Pert PRO) with Cu Kα radiation ($\lambda = 0.154$ nm). The scanning was conducted at 40 kV with a rate of 0.5° per minute. The diffraction data from 5 to 35° were collected.

3. Results and discussion

3.1. Characterization of extruded starch rods and particles

Premixed starch samples (starch with plasticizer) were loaded into the extruder and processed under different conditions, including temperature, screw speed, crosslinker dosage and starch water