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Nanoparticle formation from amylose-fatty acid inclusion complexes prepared by steam jet cooking☆

George F. Fanta[a], James A. Kenar[b], Frederick C. Felker[b,*]

[a] Plant Polymer Research Unit, USDA, Agricultural Research Service, National Center for Agricultural Utilization Research, 1815 N. University Street, Peoria, IL 61604, USA

[b] Functional Foods Research Unit, USDA, Agricultural Research Service, National Center for Agricultural Utilization Research, 1815 N. University Street, Peoria, IL 61604, USA

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ABSTRACT

Starch-based nanoparticles are of increasing interest for use as biobased fillers in composites with rubber and other polymers. Different methods have been reported for producing them, many requiring lengthy or complicated procedures. The purpose of this study was to determine whether the previously reported formation of spherulites by slowly cooling jet cooked dispersions of amylose inclusion complexes could be modified for nanoparticle synthesis. High-amylose cornstarch combined with oleic acid was jet cooked and then cooled at different rates ranging from 110 min to 10 s. Dynamic light scattering and SEM analysis showed that nanoparticles with diameters from 63 to 375 nm were obtained. X-ray diffraction analysis confirmed that they were comprised of V_6 amylose complexes. Cooling rate and starch concentration affected yield of nanoparticles and their tendency to aggregate. Large quantities of starch-based nanoparticles can be prepared using this scalable method for further characterization and application development.

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1. Introduction

The interest in nanoparticles prepared from natural products such as starch has led to extensive research in this area, and the preparation, properties and potential end-use applications of starch-based nanoparticles has been the subject of several review articles (Dufresne, 2008; Le Corre et al., 2010; Lin et al., 2011). Examples of practical applications for starch-based nanoparticles are their use as fillers and reinforcing agents in polymer composites, carriers for drug delivery (Huang et al., 2013), barrier coating materials (Le Corre et al., 2014), and stabilizers in oil-in-water emulsions (Li et al., 2014).

Starch-based nanoparticles have been prepared by a number of different techniques. Extensive research has been carried out by Dufresne and coworkers on the preparation and properties of starch nanocrystals by acid hydrolysis of waxy starch at low temperature for prolonged periods of time (Le Corre et al., 2010, 2011, 2012a,b). The nanometer-size crystalline lamellae of amylopectin are resistant to acid hydrolysis, and were isolated after selective hydrolysis of the amorphous regions of starch granules. Kim et al. (2012) used this hydrolysis method to isolate and compare nanoparticles from different starch varieties with various percentages of amylose. Crosslinking with sodium hexametaphosphate was shown to reduce the tendency of starch nanocrystals to aggregate (Ren et al., 2012). Gamma irradiation was also investigated as a method for preparing nanoparticles by the degradation of starch (Lamanna et al., 2013). Nanoparticles of starch have also been prepared by precipitation of dissolved starch from solution. Tan et al. (2009) prepared starch acetate nanospheres by addition of water to acetone solutions of starch acetate; and nanoparticles were also obtained by addition of a solution of sago starch in aqueous NaOH/urea to ethanol (Chin et al., 2011), and by addition of a water solution of starch maleate monoester to ethanol (Tay et al., 2012). Juna et al. (2014a,b) prepared starch nanoparticles by dissolving pea starch and waxy corn starch in alkaline solutions and then precipitating the dissolved starch by addition to methanol or ethanol. High-intensity, high-shear mechanical treatments have also been used to prepare nanoparticulate starch. Liu et al. (2009) used high-pressure homogenization in water to reduce granules of high amylose cornstarch to nanometer-size particles, and starch-based nanoparticles

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* Corresponding author. Tel.: +1 309 681 6663; fax: +1 309 681 6685.
E-mail addresses: george.fanta@ars.usda.gov (G.F. Fanta), jim.kenar@ars.usda.gov (J.A. Kenar), frederick.felker@ars.usda.gov (F.C. Felker).

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were prepared by high-pressure homogenization and crosslinking with sodium trimetaphosphate in a water-in-oil emulsion (Shi et al., 2011). Szymońska et al. (2009) suspended dry potato starch and cassava starch in ethanol and used a vibration mill to reduce the particle size. Nanometer-sized starch particles were also prepared from starch granules by ultrasonication (Haaj et al., 2013) and by combining ultrasonication with acid hydrolysis (Kim et al., 2013a,b) and oxidation (Sun et al., 2014). Nanoparticles were also obtained by extruding corn starch in the presence of glyoxal as a crosslinking agent and then subjecting the extrudate to high-shear mixing in water (Song et al., 2011).

Steam jet cooking is a processing method that is widely used by the starch industry to prepare aqueous solutions of starch for commercial applications (Klem and Brogly, 1981). In the steam jet cooking process, water dispersions of granular starch are continuously pumped through a hydroheater where they are instantly heated with steam under high-temperature, high-shear conditions. We have found that when mixtures of high amylose starch and fatty acids are jet cooked under conditions similar to those used for starch, amylose inclusion complexes are formed, in which the hydrocarbon chain of the fatty acid is complexed within the hydrophobic central cavity formed by the amylose helix (Putseys et al., 2010). Spherulite particles with varying sizes and morphologies are formed from these inclusion complexes when the hot dispersions are cooled (Fanta et al., 2008). Whereas spherical and toroidal-shaped spherulites about 5–20 μm in diameter were formed when the dispersions were allowed to slowly cool over a period of 22 h, smaller particles were obtained when the dispersions were cooled more rapidly. The morphology of these particles implies that they could have been formed by aggregation of particles in the nanometer size range. These observations suggested that nanometer-size particles of amylose inclusion complexes could be prepared from these hot, jet cooked dispersions if the dispersions were rapidly stirred while maximizing the rate of cooling.

In this study, we will show that nanoparticles of amylose-oleic acid complexes can be prepared in high yield by this jet-cooking procedure. In contrast to the methods previously used to prepare starch-based nanoparticles, steam jet cooking is a practical, scalable processing method that can be used to prepare nanoparticles in quantities large enough to evaluate their end-use applications and thus lead to their use in consumer products. High amylose cornstarch was used in this study because it is the least expensive source of amylose and the most practical for producing large quantities of material composed of amylose inclusion complexes. However, any amylose-bearing starch source, such as other cereal grains or root crops, could also be used. Oleic acid was used as the complexing ligand for this study because it is a non-toxic liquid that can be blended with dry starch to provide a homogeneous mixture that can be easily dispersed in water prior to steam jet cooking. Although nanoparticles of amylose inclusion complexes were previously prepared in small amounts by allowing aqueous DMSO solutions of starch and dextrins to migrate into *n*-butanol through a membrane filter to form amylose-butanol complexes (Kim and Lim, 2009; Kim et al., 2009), this method would not be practical for large-scale production.

2. Materials and methods

2.1. Materials

High-amylose corn starch (AmyloGel 3,003) with an apparent amylose content of 70%, provided by the manufacturer, was a product of Cargill, Minneapolis, MN. Percent moisture in starch products was calculated from the loss in weight after drying at 100 °C under vacuum, and all starch weights are given on a dry weight basis. Oleic acid (NF/FCC) was purchased from Fisher Scientific, Pittsburgh, PA.

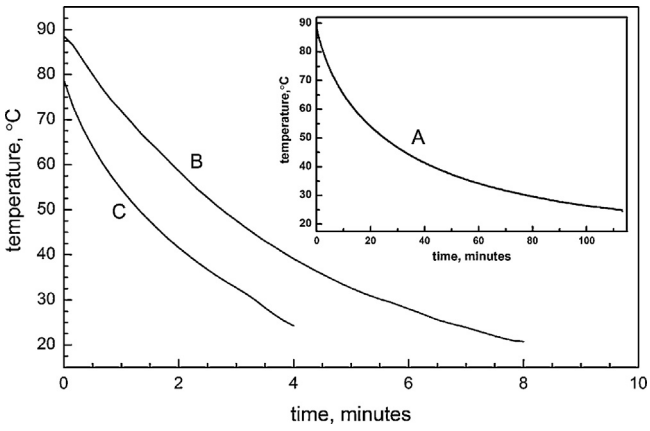

Fig. 1. Time-temperature cooling curves for procedures: (A) cooling rate = 110 min, (B) cooling rate = 8 min, and (C) cooling rate = 4 min.

2.2. Preparation of amylose-oleic acid complexes by steam jet cooking

Oleic acid was blended with high-amylose corn starch to give a mixtures containing 10% oleic acid, by weight, based on the apparent amylose content of 70%. The mixtures were then dispersed in 1000 mL of water at starch concentrations of 12.5–100 g/L, and the dispersions were passed through a Penick & Ford (Penford Corp., Englewood, CO) laboratory model steam jet cooker operating under excess steam conditions (Klem and Brogly, 1981). Temperature in the hydroheater was 140 °C, the steam back pressure was 380 kPa (40 psig) and the steam line pressure from the boiler was 550 kPa (65 psig). Pumping rate through the jet cooker was 1 L/min. After allowing the jet cooker to run for 15–20 s to flush excess water from the cooker and thus achieve a constant concentration of starch-oleic acid in the jet cooked dispersion, 500 mL of starch-oleic acid dispersion was collected in a 500 mL Dewar flask that was preheated with 100 °C water from the jet cooker. The hot dispersions in the Dewar flask (94–98 °C) were then cooled under the following conditions to determine the effects of starch concentration and cooling rate (shown in Fig. 1) on the size and yield of nanoparticles in the cooled dispersions:

Procedure A: Cool to 22 °C in 110 min – the 500 mL of hot dispersion was poured into a 1000 mL open-top, resin reaction flask (Sigma–Aldrich No. Z508446-1EA) equipped with a 1.9 × 4.8 cm Teflon paddle stirrer rotating at 450 rpm. A thermocouple probe was positioned in the stirred flask to record the rate of cooling, and plots of temperature vs. time were recorded with an OMB TempBook/66 thermocouple data acquisition system purchased from Omega, Stamford, CT. The stirred dispersion was allowed to slowly cool to 22 °C without external cooling.

Procedure B: Cool to 22 °C in 8 min – the reaction flask, stirred as in Procedure A, was cooled in an ice bath prior to addition of 500 mL of hot, jet cooked dispersion, and remained in the ice bath throughout the cooling period.

Procedure C: Cool to 22 °C in 4 min – similar to Procedure B, except only 145 g of jet cooked dispersion was cooled in the resin flask to give a faster cooling rate due to the reduced amount of jet-cooked dispersion.

Procedure D: Cool to 10 °C in 10 s – the 500 mL of jet cooked dispersion collected in the Dewar flask was poured into 1500 g of crushed ice prepared from deionized water. The cold dispersion was separated from un-melted ice by vacuum-filtering through a porcelain Buchner filter funnel with no filter paper.

Weight percent solids in the cooled dispersions were calculated from the weights of dry solids obtained by freeze-drying weighed portions of the dispersions. As observed in all jet