



Preparation and properties of films cast from mixtures of poly(vinyl alcohol) and submicron particles prepared from amylose–palmitic acid inclusion complexes[☆]



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ABSTRACT

The use of starch in polymer composites for film production has been studied for increasing biodegradability, improving film properties and reducing cost. In this study, submicron particles were prepared from amylose–sodium palmitate complexes both by rapidly cooling jet-cooked starch–palmitic acid mixtures and by acidifying solutions of starch–sodium palmitate complexes. Films were cast containing poly(vinyl alcohol) (PVOH) with up to 50% starch particles. Tensile strength decreased and Young's modulus increased with starch concentration, but percent elongations remained similar to controls regardless of preparation method or starch content. Microscopy showed particulate starch distribution in films made with rapidly cooled starch–palmitic acid particles but smooth, diffuse starch staining with acidified sodium palmitate complexes. The mild effects on tensile properties suggest that submicron starch particles prepared from amylose–palmitic acid complexes provide a useful, commercially viable approach for PVOH film modification.

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1. Introduction

Starch is a polysaccharide comprised of repeating α -1,4 glucose units, and is isolated from plant sources as granules that contain varying percentages of a linear component, amylose, and a branched, higher molecular weight component, amylopectin. Due to its availability, biodegradability, and low cost, starch has been studied as a component in biodegradable plastics such as poly(vinyl alcohol) (PVOH). PVOH films have excellent physical properties; however, PVOH is expensive and has a relatively low rate of biodegradation (Chiellini, Corti, D'Antone, & Solaro, 2003). PVOH solutions used for film casting have therefore been blended with water solutions of starch to reduce costs and to increase the rate of

biodegradation (Azahari, Othman, & Ismail, 2011). Inorganic fillers have also been added to these composites as reinforcing agents. Publications related to the preparation, properties, biodegradability, and end-use applications of PVOH–starch composites have been summarized and reviewed by Tang and Alavi (2011).

The interest in submicron particles prepared from renewable products such as starch has led to extensive research in this area, and the preparation, properties and end use applications of starch-based nanoparticles have been reviewed (Dufresne, 2008; Corre, Bras, & Dufresne, 2010; Lin, Chang, Anderson, & Yu, 2011). A major application for starch based nanoparticles has been their use as fillers and reinforcing agents in polymer composites. Although the starch nanoparticles used for these applications have been prepared by a number of different techniques, perhaps the most widely-used method has been the acid hydrolysis of waxy starch at low temperature for prolonged periods of time (Le Corre, Bras, & Dufresne, 2010; Le Corre, Bras, & Dufresne, 2011; Le Corre, Bras, & Dufresne, 2012; Le Corre, Vahanian, Dufresne, & Bras, 2012). The nanometer-size crystalline lamellae of amylopectin are resistant to acid hydrolysis and are isolated after selective hydrolysis of the amorphous regions of starch granules. This method was used by Chen and coworkers (Chen, Cao, Chang, & Huneault, 2008) to

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prepare 30–80 nm starch nanocrystals by the hydrolysis of pea starch in 3.16 M H₂SO₄ solution at 40 °C. This study showed that the properties of PVOH composite films prepared from these nanocrystals were superior to the properties of composite films prepared from granular native pea starch.

Steam jet-cooking is a widely used method for the large-scale production of starch dispersions for commercial applications. In the steam jet-cooking process, water dispersions of granular starch are continuously pumped through a hydroheater where they are instantly heated with high-pressure steam to dissolve starch under high-shear conditions (Klem & Brogly, 1981). We have found that when mixtures of high amylose starch (70% apparent amylose) and fatty acids, such as palmitic and oleic, are jet-cooked under the same conditions used for starch, amylose–fatty acid 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, Lamberts, & Delcour, 2010). These amylose–fatty acid complexes precipitate from the hot, jet-cooked dispersions when the dispersions are cooled; and we have observed that the size and morphology of the precipitated spherulites formed from these complexes depend upon the rate of cooling (Fanta, Felker, Shogren, & Salch, 2008). Whereas 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 formed when the dispersions were rapidly cooled in an ice-water bath. Since smaller spherical particles and particle aggregates were observed when dispersions were more rapidly cooled, cooling in ice with rapid stirring was used in this study to obtain the most rapid rate of cooling, and thus the submicron-size particles of amylose–palmitic acid complex needed for reinforcement of PVOH composites. This method was used by us previously to prepare nanoparticles from jet-cooked dispersions of high amylose starch and oleic acid (Fanta, Kenar, & Felker, 2014). Amylose–palmitic acid complexes can also be precipitated by acidifying amylose–sodium palmitate inclusion complexes in water solution (Fanta, Kenar, Byars, Felker, & Shogren, 2010). The composition, size, and morphology of the amylose–palmitic acid particles by these two methods are different than those of the nanocrystals prepared from pea starch by Chen et al. (2008). Also, in contrast to the slow, acid-hydrolysis method used by Chen et al., the steam jet-cooking method used in this study is a commercially viable production process that can be scaled-up to produce submicron particles comprised of amylose–fatty acid inclusion complexes in quantities sufficient to determine their properties and end-use applications.

In this report, we will describe the preparation and properties of cast films prepared from mixtures of PVOH and starch-based submicron particles comprised of amylose–palmitic acid inclusion complexes. These complexes were prepared by steam jet cooking using two different methods: rapid cooling of jet cooked dispersions of amylose–palmitic acid inclusion complexes, and acidification of water solutions of inclusion complexes prepared from jet cooked dispersions of high amylose corn starch and sodium palmitate.

2. Experimental

2.1. Materials

High-amylose corn starch (AmyloGel 03003), with an apparent amylose content of 70%, provided by the manufacturer, was a product of Cargill, Minneapolis, MN. Waxy #1 corn starch was a product of Tate & Lyle, Decatur, IL. Palmitic acid, 99%, and sodium palmitate, 98.5% were purchased from Sigma, St Louis, MO. PVOH, 99 mol% hydrolyzed, MW approx. 133,000, was purchased from

Polysciences, Warrington, PA. The moisture contents of starch and PVOH were determined by weight-loss after drying at 100 °C under vacuum, and weights of starch and PVOH are on a dry weight basis.

2.2. Preparation of amylose–palmitic acid inclusion complex by steam jet-cooking, and rapidly cooling to obtain precipitated submicron particles

A homogeneous mixture of high amylose starch and palmitic acid was prepared by dissolving 1.75 g of palmitic acid in 20 mL of ethanol, mixing the ethanol solution with 25.0 g of high amylose corn starch, and then allowing the ethanol to evaporate from the mixture at room temperature. The starch–palmitic acid mixture was dispersed in 1000 mL of water, and the resulting dispersion was passed through a Penick & Ford (Penford Corp., Englewood, CO) laboratory model steam jet cooker operating under excess steam conditions (Klem & Brogly, 1981). The 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 obtain a “center cut” with a constant concentration of starch–palmitic acid in the jet-cooked dispersion, 500 g of starch–palmitic acid dispersion was collected in an insulated Dewar flask. The hot (97 °C) dispersion was rapidly stirred and cooled to 25 °C by pouring into a 1000 mL open-top, resin reaction flask (Sigma-Aldrich No. Z508446-1EA) equipped with a 1.9 cm × 4.8 cm Teflon paddle stirrer rotating at 450 rpm. The flask was cooled in an ice bath prior to addition of the hot dispersion and remained in the ice bath throughout the 8 min. cooling period required for cooling to 25 °C. Weight percent of solids in the cooled dispersion was determined by freeze-drying weighed portions of the dispersion. In subsequent sections of the manuscript, this dispersion will be referred to as the “uncentrifuged dispersion”.

To separate the precipitated particles of amylose–palmitic acid complex from soluble starch, 100 g of the cooled dispersion was centrifuged for 2 h at 10,000 rpm (15,317 × g) using a Sorvall Legend centrifuge equipped with a Fiber-lite F14-6X250 rotor (Thermo Fisher Scientific, Hanover Park, IL); and the settled solid was washed by dispersing in 100 mL of water followed by centrifugation under the same conditions. The water-washed particles were then dispersed in water, and the weight of these particles was calculated from the weight and weight% solids of the resulting dispersion. Supernatants from the centrifugations were freeze-dried to determine the weight of soluble starch; and an 82% yield of water-insoluble particles, based on the starting weight of starch, was calculated from the weights of freeze-dried fractions.

2.3. Preparation of amylose–sodium palmitate inclusion complex

A dispersion of 150.0 g of high amylose starch in 2700 mL of water was jet-cooked under the conditions described above, except that all of the starch-containing dispersion was collected as opposed to a just center cut. A hot (94 °C) solution of 7.88 g of sodium palmitate in 300 mL of water was then added to the jet-cooked starch dispersion. The dispersion was stirred for 2 min and then cooled to 25 °C. When the cooled dispersion was centrifuged for 1 h at 10,000 rpm as described above, less than 1% of the total dispersed solid was insoluble and was removed from the dispersion by centrifugation. The centrifuged dispersion was then freeze-dried to obtain a storage-stable solid that could be re-dispersed in hot water when needed.

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