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

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

[a] Plant Polymer and Functional Foods Research Units, USDA, Agricultural Research Service, National Center for Agricultural Utilization Research, 1815 N. University Street, Peoria, IL 61604, USA
[b] Functional Foods Research Units, USDA, Agricultural Research Service, National Center for Agricultural Utilization Research, 1815 N. University Street, Peoria, IL 61604, USA

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

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prepare 30–80 nm starch nanocrystals by the hydrolysis of pea starch in 3.16 M H_2SO_4 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.

2.4. Acidification of amylose–sodium palmitate inclusion complex, and isolation of precipitated amylose–palmitic acid complex

A solution of amylose–sodium palmitate complex was prepared by heating a 1% water dispersion of freeze-dried amylose complex to 80 °C and then cooling the solution to 25 °C. The solution (pH 7.2) was then titrated with 0.1 N HCl to a final pH of 4.5, and the acidified dispersion containing precipitated particles of amylose–palmitic acid inclusion complex was centrifuged for 2 h at 10,000 rpm, as described above. The clear supernatant was decanted, and the water-swollen settled solid was washed by dispersing in fresh water followed by centrifugation under the same conditions. Portions of the dispersion of water-washed solid and the supernatant were freeze-dried, and a 92% yield of water-insoluble solid, based on the starting weight of starch, was calculated from the weights of freeze-dried fractions.

2.5. PVOH composite films prepared with particles obtained from jet cooked dispersions of high amylose starch and palmitic acid (Procedure 1)

PVOH was dispersed in water at a concentration of 2%, and the dispersion was heated to 80 °C and then cooled to 25 °C to obtain a clear solution with a pH of 6.0. The un-centrifuged dispersion obtained by rapidly cooling a jet-cooked mixture of high amylose starch and palmitic acid was also diluted with water to a solids concentration of 2%. The two dispersions were then mixed to obtain 100 g quantities of dispersions with PVOH:starch ratios of 100:0, 80:20, 70:30, 60:40, and 50:50. Glycerol was added as a plasticizer (0.40 g, 20% based on total solids), and air bubbles in the dispersion were removed by briefly vacuum-evacuating the dispersion at room temperature. The dispersion was then poured into a 12.5 cm × 17.5 cm × 0.4 cm rubber frame on a Teflon-coated glass plate, and the dispersion was allowed to dry to a continuous film at ambient room temperature.

2.6. PVOH composite films prepared with particles of amylose–palmitic acid complex obtained by adding HCl to solutions of amylose–sodium palmitate complex before mixing with PVOH solution (Procedure 2)

Solutions of PVOH and amylose–sodium palmitate complex at solids concentrations of 2% were prepared separately by heating aqueous dispersions to 80 °C and then cooling to 25 °C. The solution of amylose–sodium palmitate complex was then titrated with 0.1 N HCl to pH 4.5 to precipitate the amylose–palmitic acid complex from solution. The acidified dispersion was then mixed with the PVOH solution to obtain 100 g quantities of dispersions with PVOH:starch particle ratios of 80:20, 70:30, 60:40, and 50:50. Glycerol was added as a plasticizer (0.40 g, 20% based on total solids), and films were cast as described above.

2.7. PVOH composite films prepared with amylose–palmitic acid complex particles obtained by adding HCl after combining solutions of amylose–sodium palmitate complex and PVOH (Procedure 3)

Solutions of PVOH and amylose–sodium palmitate complex in ratios of 80:20, 70:30, 60:40, and 50:50 (100 g of each solution at a total solids concentrations of 2%) were prepared by weighing the dry components into a beaker, heating in water to 80 °C, and then cooling the clear solutions to 25 °C. The solutions containing the two components were then titrated with 0.1 N HCl to pH 4.5 to convert complexed sodium palmitate to palmitic acid and thus precipitate the amylose complex from the PVOH solution. Glycerol plasticizer (0.40 g; 20% based on total solids) was added, and films were cast as described above.

2.8. PVOH composite film prepared from 50:50 mixture of PVOH and jet cooked waxy corn starch

A mixture of 100 g of waxy corn starch in 2 L of water was jet cooked under conditions similar to those used for mixtures of high amylose starch and palmitic acid. The cooked dispersion was cooled to room temperature and freeze-dried to obtain a storage-stable product that could be re-dispersed in hot water when needed. Solutions of PVOH and waxy corn starch at concentrations of 2% were prepared by heating aqueous dispersions to 80 °C and then cooling to 25 °C, and a solution for film casting was prepared by combining of 50 g of each solution. Glycerol was added to the combined solution as a plasticizer (0.40 g, 20% based on total solids), and a film was cast as described above.

2.9. Tensile testing of film samples

Sample thicknesses of cast films were measured at three different locations using a micrometer (Model no. 49–63, Testing Machines Inc., Amityville, NY). The average thickness of the films tested was 0.076 mm (SD = 0.011). Films were stored at constant relative humidity (50% RH) and temperature (23 °C) for five days before testing physical properties. Tensile strength, Young's modulus, % elongation to break and toughness were obtained for each sample using an Instron Universal Testing Machine Model 4201 and an ASTM D638 Type V test. Crosshead speed was 10 mm/min, gauge length was 7.62 mm, and either a 1 kN load cell or a 100 N load cell was used depending on the strength of the samples. Tensile property data are presented as the means and standard error for a minimum of four samples. Significant differences, where noted, are based on Student's *t* test ($p < 0.05$).

2.10. X-ray diffraction

X-ray scattering patterns of freeze-dried samples were provided by Texray Laboratory Services, Argyle, TX. Samples were ground into fine powders using a mortar and pestle, and powdered samples were loaded into a zero-background sample holder for XRD analysis. Analyses were carried out with a Bruker D5000 X-ray diffractometer. The X-ray source was Cu $K_{\alpha 1}$ ($\lambda = 1.5405$ Å), and samples were scanned from 2 to 35° 2θ with step size 0.02°.

2.11. Microscopy

Aqueous samples were observed with a Zeiss Axioskop light microscope equipped with an Axiocam ICc 3 digital camera (Carl Zeiss, Inc., Thornwood, NY) using phase contrast optics. For scanning electron microscopy (SEM), samples were dehydrated by adding aqueous dispersions to ethanol and allowing the particles to settle. Ethanol dispersions of dehydrated particles were then dried onto aluminum SEM stubs in a Tousimis Samdri-PVT-3D critical point drier (Tousimis Research Corp., Rockville, MD), sputter coated with gold, and examined with a JSM-6010LA SEM (JEOL USA, Peabody, MD).

Starch distribution in starch:PVOH cast films was examined by embedding dry film pieces in paraffin and obtaining cross sections with a thickness of 10 μm with a paraffin microtome using a steel knife. Sections were collected onto a microscope slide in a drop of I_2KI solution and a cover glass was applied. The stained sections were observed and photographed using bright field optics.

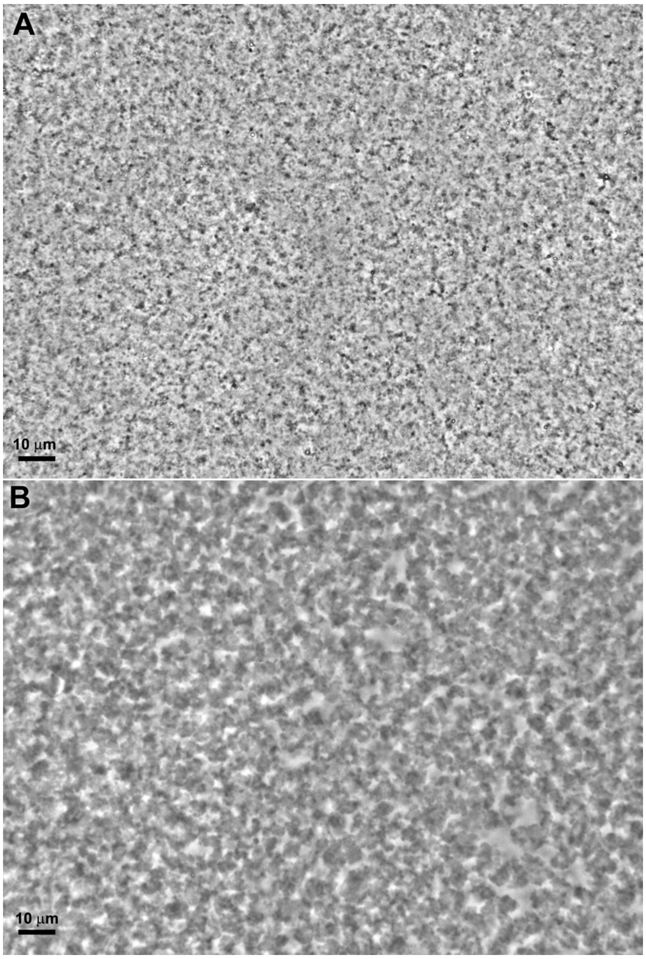

Fig. 1. Phase contrast light micrographs of particle dispersions prepared by (A) rapid cooling of high amylose starch jet-cooked with palmitic acid and (B) acidification of a solution of amylose–sodium palmitate complexes prepared by steam jet cooking.

3. Results and discussion

An aqueous dispersion of submicron-size particles of amylose–palmitic acid inclusion complex was prepared by steam jet-cooking a mixture of high amylose corn starch and palmitic acid, and then rapidly cooling the hot, rapidly-stirred dispersion in ice to 25 °C to precipitate the particles from solution. A phase contrast micrograph of the cooled dispersion (Fig. 1A) shows a range of particles and aggregates up to several microns in diameter. A portion of the dispersion was centrifuged to separate insoluble particles from dissolved starch, and a particle yield of 82% was calculated, based on the starting weight of high amylose starch. A particle yield greater than the 70% apparent amylose content of high amylose starch could be due to entrapment of amylopectin within the precipitating particles of amylose complex, or to the formation of palmitic acid complexes with the longer branches of amylopectin. Identification of the particles as amylose–palmitic acid inclusion complex was confirmed by the 6_1V X-ray diffraction pattern observed for a freeze-dried sample (Fig. 2A). Scanning electron micrographs of the precipitated particles (Fig. 3A) revealed primary particles up to about 200 nm with aggregates of various sizes including some larger than one micron.

Submicron particles were also prepared by acidifying dispersions of amylose–sodium palmitate complexes resulting in a suspension of small gelatinous fragments (Fig. 1B). As observed for the particle dispersion prepared with palmitic acid, the yield of precipitated solid (92%) was greater than the 70% apparent amylose content of starch used. The X-ray diffraction pattern of a freeze dried sample of the precipitated complex is shown in Fig. 2B. As observed for the particles prepared by jet cooking high amylose corn starch with palmitic acid, a 6_1V X-ray diffraction pattern was

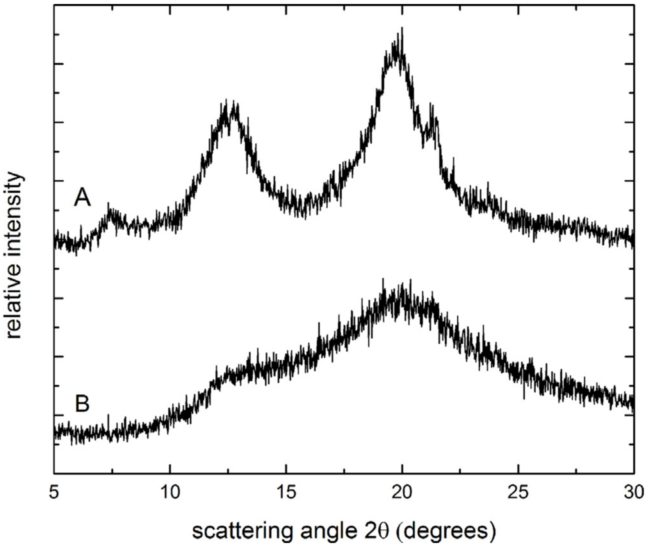

Fig. 2. X-ray diffraction patterns of freeze-dried samples of particle dispersions prepared by (A) rapid cooling of high amylose starch jet-cooked with palmitic acid and (B) acidification of a solution of amylose–sodium palmitate complexes prepared by steam jet cooking.

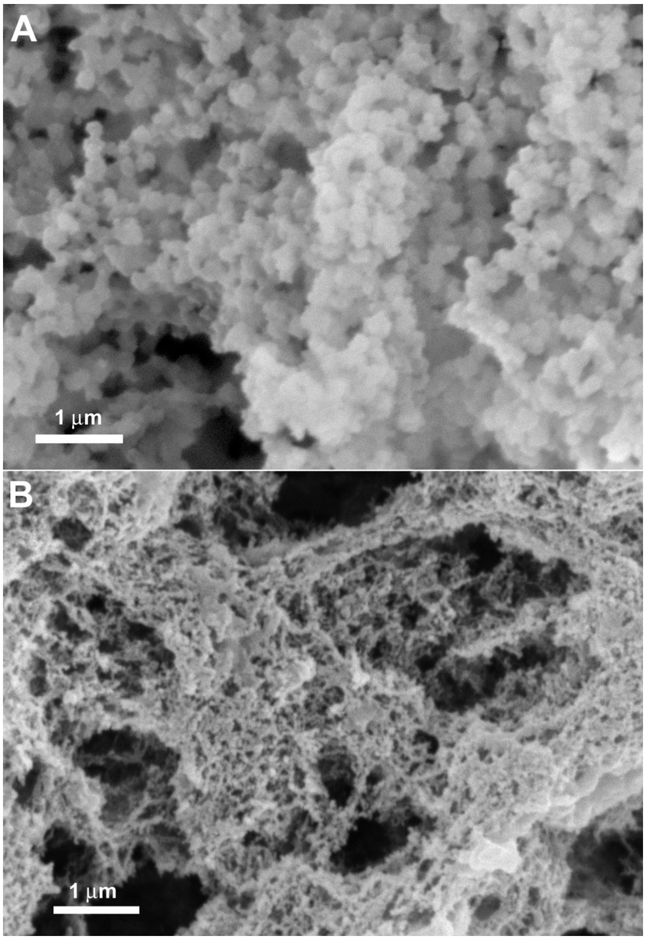

Fig. 3. Scanning electron micrographs (SEM) of particles prepared by (A) rapid cooling of high amylose starch jet-cooked with palmitic acid and (B) acidification of a solution of amylose–sodium palmitate complexes prepared by steam jet cooking.

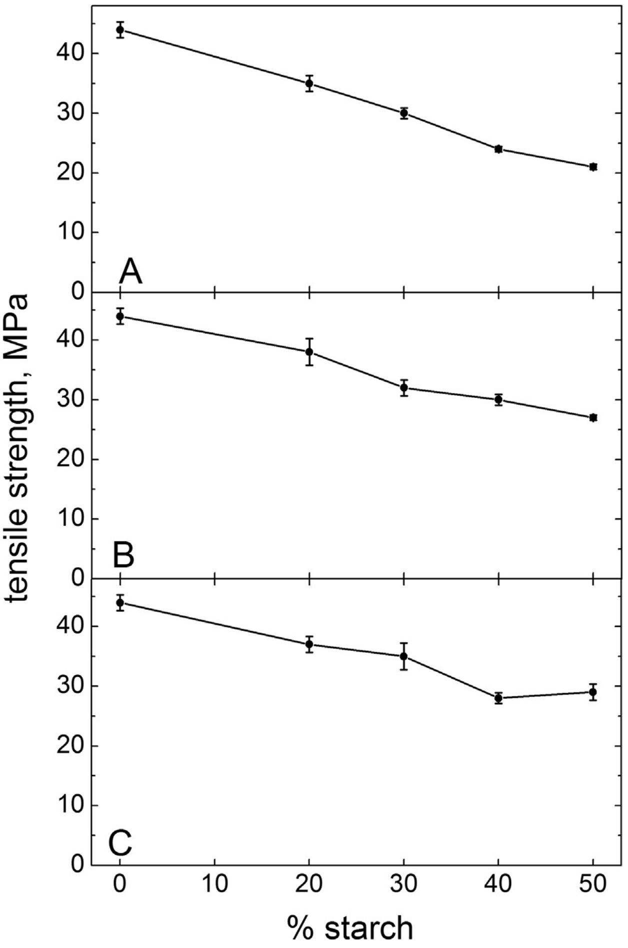

Fig. 4. Tensile strength of films prepared by (A) Procedure 1, (B) Procedure 2, and (C) Procedure 3 (see Sections 2.5–2.7).

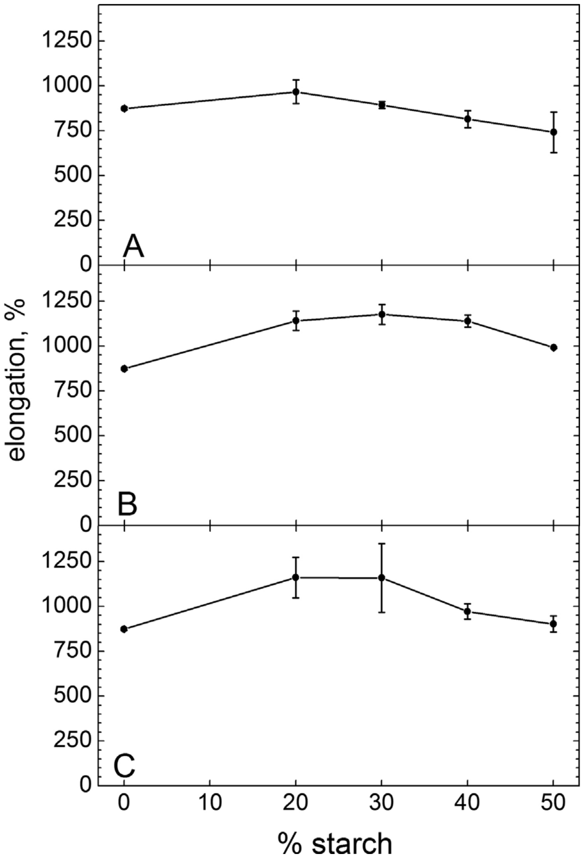

Fig. 5. Percent elongation at break of films prepared by (A) Procedure 1, (B) Procedure 2, and (C) Procedure 3 (see Sections 2.5–2.7).

observed, consistent with the formation of an amylose–palmitic acid inclusion complex. The broader diffraction peaks observed for the acid-precipitated material could be due to the formation of smaller crystallites by acid precipitation, and also to the larger amount of co-precipitated amylopectin, as indicated by the 92% yield of precipitated solid. Scanning electron microscopy (Fig. 3B) revealed a fine network of material in which individual nanoparticles approximately 50–100 nm in diameter were visible. These particles appeared to form a continuous network possibly bound together by soluble amylopectin. These particles were too small to be resolved by light microscopy within the microgel fragments shown in Fig. 1B.

To determine the effects of amylose–palmitic acid particles on the properties of PVOH cast films, the aqueous dispersions of starch particles prepared by the two methods described above were blended with water solutions of PVOH to give mixtures with total solids concentrations of 2% and PVOH:starch ratios of 100:0, 80:20, 70:30. 60:40 and 50:50. These submicron particles were not separated from soluble starch prior to film preparation, since this step would not be practical in commercial production. For each ratio of PVOH:starch, the dispersions of submicron particles were prepared and combined with PVOH by three different procedures. For Procedure 1, dispersions for film casting were prepared by mixing PVOH solutions with the rapidly-cooled, particle-containing dispersion prepared from jet-cooked high amylose starch–palmitic acid. For Procedure 2, solutions of PVOH and amylose–sodium palmitate complex were prepared separately, the amylose–sodium palmitate solution was acidified to pH 4.5, and the acidified dispersion containing precipitated particles of amylose–palmitic acid complex was mixed with the solution of PVOH. In Procedure 3, PVOH and amylose–sodium palmitate complex were dissolved together in water; and solutions containing both components were acidified to pH 4.5 to convert complexed sodium palmitate to palmitic acid and precipitate the amylose complex in the presence of dissolved PVOH. Whereas Procedures 2 and 3 are of similar convenience and yield the same composition, they were investigated in order to determine whether submicron particles formed in the presence of PVOH would give films with different tensile properties than those obtained when the particles were precipitated before blending with PVOH.

Tensile strengths of films as a function of starch content are shown in Fig. 4 for the three film preparation procedures. Using Procedure 1, the tensile strength decreased gradually from 44 MPa for pure PVOH films to 21 MPa for films containing 50% starch. However, using Procedures 2 and 3, which result in smaller particles, tensile strength declined to 27 and 29 MPa, respectively. This is consistent with the observations of Chen et al. (2008), who observed smaller tensile strength decreases with nanoparticles prepared by acid hydrolysis of pea starch versus native pea starch granules.

The percent elongation of films prepared with any of the three procedures did not significantly decrease at any level of starch content (Fig. 5). Procedure 1 films were unchanged at all PVOH:starch ratios (Fig. 5A), whereas films made with Procedure 2 with 20, 30, 40, and 50% starch showed significantly higher % elongation ($p < 0.05$) than the control PVOH films (Fig. 5B). For Procedure 3, the 20 and 30% starch films were significantly higher, while the 40 and 50% starch films were not significantly different from control PVOH films (Fig. 5C). These results contrast with those obtained for PVOH composite films prepared with pea starch nanocrystals.

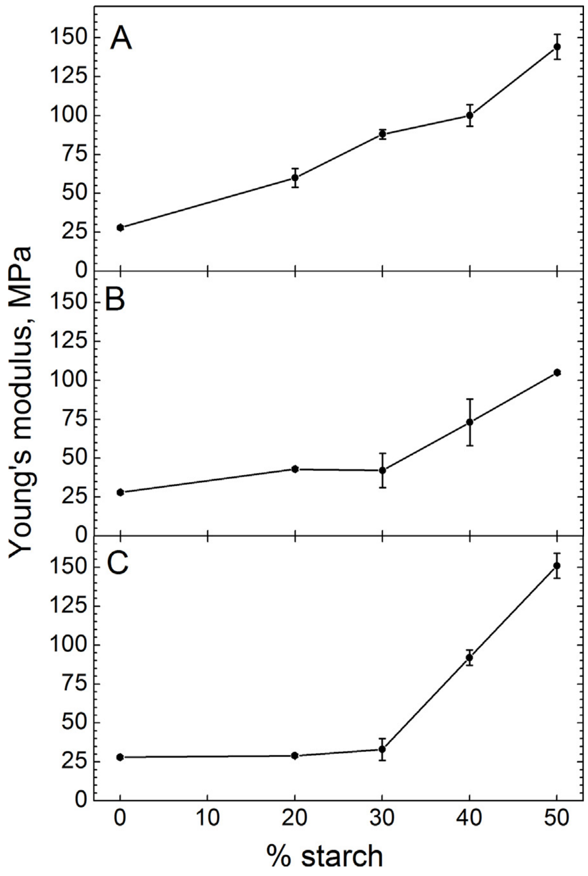

Fig. 6. Young's modulus of films prepared by (A) Procedure 1, (B) Procedure 2, and (C) Procedure 3 (see Sections 2.5–2.7).

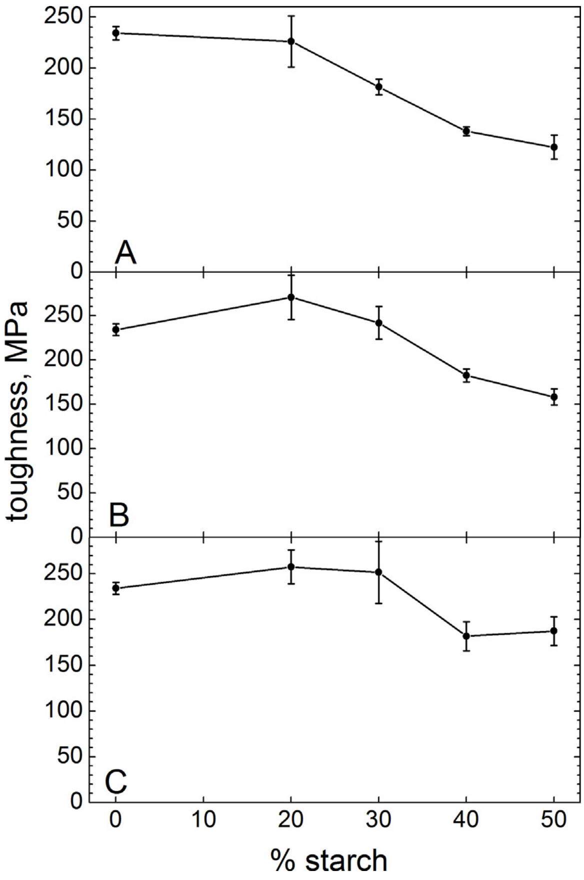

Fig. 7. Toughness of films prepared by (A) Procedure 1, (B) Procedure 2, and (C) Procedure 3 (see Sections 2.5–2.7).

In these composite films, values for % elongation decreased with increased percentages of nanocrystals (Chen et al., 2008).

The Young's modulus of films increased steadily with increasing starch content for Procedure 1, but only at the 40% and 50% starch loadings for Procedures 2 and 3 (Fig. 6). For these films, the observation of a threshold at which the modulus increases above 30% loading suggests the possibility of a percolation threshold at which the concentration of particles is sufficient for significant interactions to occur, as was suggested for starch nanocrystal systems (Dufresne & Cavaille, 1998). The toughness values of films prepared by Procedure 1 were not significantly different at 20% loading, but decreased at higher loadings (Fig. 7). With Procedures 2 and 3, films up to 30% starch loading were not significantly different from control PVOH films in toughness, while 40% and 50% starch films were slightly lower. These results reflect the maintenance of percent elongation among all of the treatments (Fig. 5) along with the decreases of tensile strengths observed at higher starch loadings (Fig. 4).

Differences in tensile properties between our composite films and those prepared by Chen et al. (2008) may be due to the differences in morphology between our submicron particles and the nanocrystals prepared by Chen et al. by prolonged acid hydrolysis of pea starch. Whereas our particles formed from amylose–palmitic acid inclusion complexes are spherical in shape, the particles prepared by acid hydrolysis of pea starch are nanocrystals with the morphology of platelets (Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003). The large, flat surface areas of these nanocrystalline platelets enables them to form aggregates that are strongly hydrogen bonded when water dispersions are dried to form the films used for Instron testing, and these hydrogen bonded aggregates are not easily disrupted when the film samples are stretched during testing. Although our particles also form hydrogen bonded aggregates, the smaller areas of contact due to their spherical shape results in aggregates that are not as tightly hydrogen bonded and therefore separate more easily when the PVOH composites are tested. This difference in hydrogen bonding between our particles and those of Chen could be a factor responsible for the relative insensitivity of % elongation to the PVOH:starch ratio in the series of composites prepared with our spherical particles.

The distribution of starch in the cast films as indicated by iodine staining of thin (10 μm) sections is shown in Fig. 8. When placed in the aqueous iodine stain, the dry cross sections expanded from about 75 μm to about 200 μm in width (Fig. 8A and C), presumably due to swelling of the sample in water. Films produced by Procedure 1 revealed a network of discrete particles, with an accumulation of large particles on one side, suggesting that the largest particle aggregates settled before the film dried (Fig. 8A and B). In contrast, films produced with acidified sodium palmitate submicron particles revealed a homogeneous, diffuse network with uniformly distributed variations in staining intensity (Fig. 8C and D). Sections of films made with 20% starch are shown, as those with higher starch contents revealed the same distributions but with denser and more intense staining (not shown). There was no difference between the distribution patterns seen with Procedures 2 and 3. The diffuse staining pattern seen with the sodium palmitate-based submicron particle films is consistent with the size of the submicron particles being below the resolution of the light microscope. The appearance of the acidified precipitated amylose–sodium palmitate complexes (Fig. 1B) as a suspension of gelatinous fragments comprised of particles too small to be resolved by light microscopy suggests that these soft, flexible gel fragments fused together when the film dried, having been

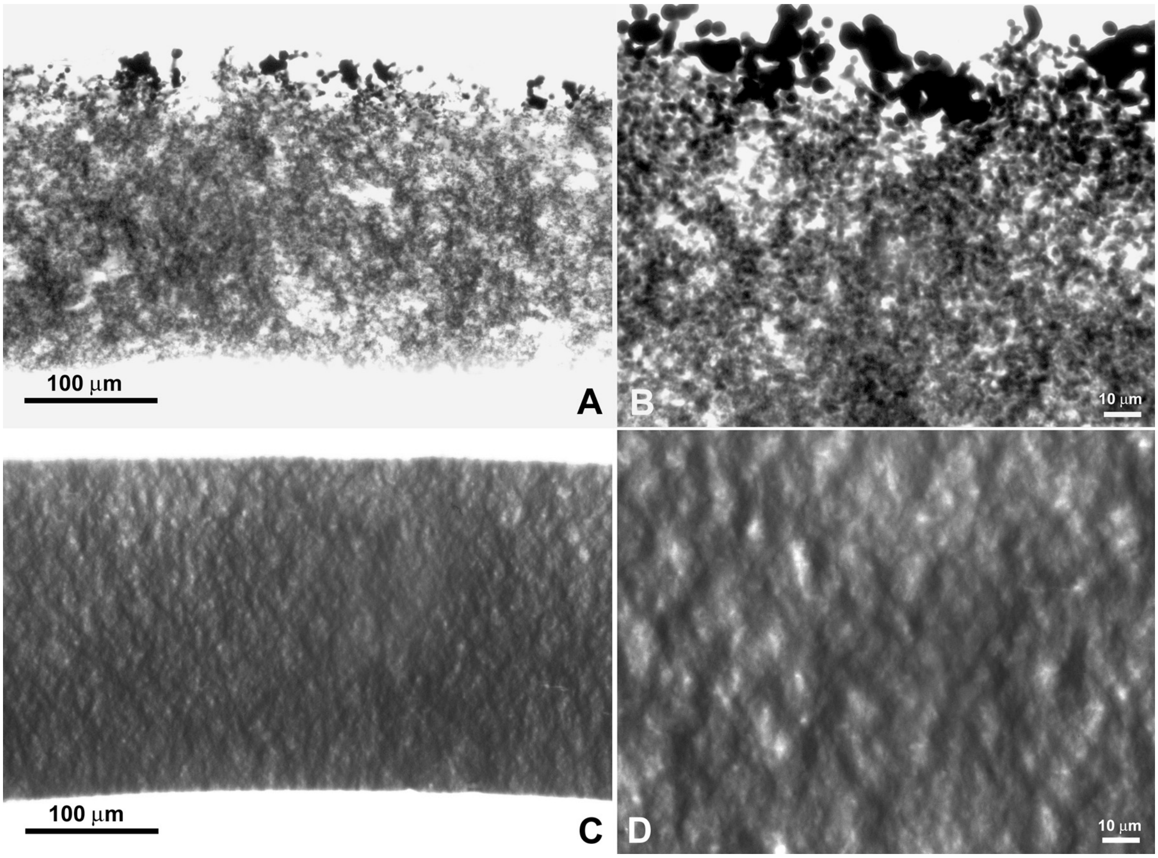

Fig. 8. Light micrographs of 10 µm cross sections of PVOH:starch films stained with iodine to reveal starch. Film prepared using Procedure 1 (rapidly cooled starch–palmitic acid dispersion) showing entire cross section (A), same at higher magnification (B), film prepared using Procedure 3 (acidified starch–sodium palmitate complexes) showing entire cross section (C), same at higher magnification (D). Both films contained 20% starch loading.

infiltrated with the dissolved PVOH. The swelling and dissolution of the PVOH in the aqueous iodine stain did not cause the starch component to disintegrate, which indicated that the starch formed a relatively stable interconnected network as the films dried. The loose, deformable organization of these clusters of spherical particles may contribute to the maintenance of high percent elongation of the films even up to 50% loading with starch.

4. Conclusions

Continuous films with good tensile properties can be prepared from mixtures of PVOH and the submicron particles obtained by rapidly cooling jet-cooked starch–palmitic acid mixtures (Procedure 1) and by acidification of starch–sodium palmitate complexes prepared from sodium palmitate and jet-cooked dispersions of high amylose starch, which yielded smaller particles. Acidification of sodium palmitate complexes was carried out both before (Procedure 2) and after (Procedure 3) combining with PVOH. Tensile strength decreased with increasing starch loadings, however the decrease was less with the smaller particles obtained with the acidified sodium palmitate complexes. At all starch concentrations and with any of the 3 procedures, percent elongation of films was not significantly lower than control PVOH films. Young's modulus and toughness were generally unchanged at lower starch concentrations but increased and decreased, respectively, at higher starch loadings. Iodine staining of thin sections revealed a particulate distribution of starch in films made with Procedure 1, but a continuous, diffuse staining of starch in films made with Procedures 2 and 3, indicating that the gelatinous fragments produced by acidification of sodium palmitate complexes fused together on drying in the presence of PVOH. The significance of this research is shown by the fact that steam jet cooking is a commercially viable method for the large scale production of starch-based submicron particles, and the incorporation of these particles into PVOH films at levels up to 50% does not result in large detrimental effects on tensile properties.

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