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Carbohydrate Polymers 61 (2005) 222–230

Carbohydrate Polymers

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Crystalline particles formed in slowly-cooled cornstarch dispersions prepared by steam jet cooking. The effect of starch concentration, added oil and rate of cooling[☆]

George F. Fanta[a,b,*], Frederick C. Felker[a,b], Randal L. Shogren[b], Jeffrey A. Byars[a], John H. Salch[a,b]

[a] *Cereal Products and Food Science, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, 1815 N. University St., Peoria, IL 61604, USA*

[b] *Plant Polymer Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture, 1815 N. University Street, Peoria, IL 61604, USA*

Received 10 November 2004; revised 25 April 2005; accepted 4 May 2005

Abstract

Spherical/lobed and torus-shaped particles were formed when jet cooked cornstarch dispersions (4–10% starch solids) were slowly cooled for 22 h. When jet cooking was carried out in the presence of mineral oil, the torus-shaped particles did not form, but small spherical particles, about 1–2 μm in diameter, were observed. These small particles resembled those formed in wheat starch dispersions jet cooked in the absence of oil. Dispersions jet cooked without oil and cooled over a 4 h period also yielded 1–2 μm spheres in addition to the spherical/lobed and torus-shaped particles. With 4 h cooling in the presence of oil, the torus-shaped particles were absent, and the 1–2 μm spheres were the only small particles observed. Very few spherical/lobed particles were formed in the presence of oil at starch concentrations of 5 and 4%. Mineral oil droplets could affect the nature of the particles formed by selectively extracting free fatty acids from the native lipid released from cornstarch by steam jet cooking. The remaining native lipid would therefore be richer in lysophospholipids, thus favoring the formation of 1–2 μm spheres, similar to those observed with wheat starch. The rate of cooling could affect the nature of the particles formed because of its effect upon the depletion of native lipid components from the dispersion by the particles that form first at the highest temperature.

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Keywords: Starch; Amylose; Spherulite; Jet cooked; Fatty acids; Phospholipids

1. Introduction

Steam jet cooking is a rapid and continuous process used to prepare aqueous starch dispersions for industrial applications (Klem & Brogley, 1981). At our Research Center, the steam jet cooking process is also being studied as a method for preparing new starch-based composites, such as those formed from starch and water-immiscible oils and lipids. We have found that the high temperature and intense mechanical shear encountered during steam jet cooking not only dissolves starch, but also disperses the oil component into micrometer-sized droplets that do not phase-separate or coalesce, even after prolonged storage or drying (Eskins, Fanta, Felker, & Baker, 1996; Fanta & Eskins, 1995; Fanta & Eskins, 1998; Fanta, Felker, Eskins, & Baker, 1999; Fanta, Felker, Shogren, & Knutson, 2001).

In the course of these investigations, we have observed the formation of crystalline starch particles (spherulites) in dilute, slowly-cooled dispersions of jet cooked cornstarch. Particles of this type have also been observed by other workers (Davies, Miller, & Procter, 1980; Jane, Kasemsuwan, Chen, & Juliano, 1996; Kitamura, Yoneda, & Kuge, 1984; Zobel, 1988). An earlier study of jet cooked cornstarch dispersions, prepared

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[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

[*] Corresponding author. Tel.: +1 309 681 6356; fax: +1 309 681 6685.
E-mail address: fantagf@ncaur.usda.gov (G.F. Fanta).

0144-8617/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.carbpol.2005.05.013

at about 4% starch solids, showed that the mixture of particles formed under these conditions contained two distinct species that differed in size, morphology, and crystal structure (Fanta, Felker, & Shogren, 2002). Both species were strongly birefringent and were composed largely of amylose. SEM and phase contrast microscopy showed that the smaller-sized particles were disc or torus-shaped, whereas the larger particles were more spherical and often exhibited a two-lobed or four-lobed morphology. Wheat starch, however, yielded small, spherical particles with diameters of about 1–2 μm. X-ray powder diffraction patterns of the torus-shaped particles matched patterns previously reported for the 6_1 amylose V-helical complex in the hydrated form. In contrast, diffraction patterns for the spherical/lobed particles suggested a 7_1 V-helical conformation for amylose. These results were consistent with the conclusion of Davies, Miller, and Procter (1980) that these particles result from crystallization of helical inclusion complexes that form in jet cooked dispersions from amylose and the native lipid normally present in cereal starch granules.

We have now observed that the nature of the particles formed in these dispersions is affected by the presence or absence of added oil during the jet cooking process, the concentration of starch, and the rate at which the jet cooked dispersions are cooled. In this report, we will compare the morphologies, birefringence and X-ray diffraction patterns of particles formed in the presence and absence of added mineral oil at several different starch concentrations and at two different cooling rates.

2. Materials and methods

2.1. Materials

Normal, unmodified, food grade cornstarch was a product of A.E. Staley Mfg. Co., Decatur, Il. Percent moisture was determined by vacuum drying weighed starch samples at 100 °C, and all weights of starch are given on a dry-weight basis. Mineral oil (heavy white oil) was purchased from Sigma Diagnostics, Inc., St Louis, MO. Viscosity of the oil at 100° F (37.78 °C) was 340–360 Saybolt universal seconds, and the specific gravity at 77° F (25 °C) was 0.875–0.885.

2.2. Jet cooking and isolation of crystalline particles

A stirred dispersion of either starch or starch/mineral oil in 1500 ml of water was passed through a Penick and Ford Laboratory Model steam jet cooker, operating under excess steam conditions (Klem & Brogley, 1981). Amounts of starch used for nominal starch concentrations of 10, 7.5, 6.25, 5, and 4% were 200, 150, 125, 100 and 75 g, respectively. For experiments carried out in the presence of added oil, 20 parts of mineral oil per 100 parts of starch, by weight, were blended into the dry starch sample prior to steam jet cooking. Samples were cooked at 140 °C (back pressure: 40 psig, 380 KPa steam) with a steam line pressure of 65 psig (550 KPa). Pumping rate through the cooker was about 1-L/min. Hot, jet cooked dispersions were collected in a 1-L stainless steel Dewar flask which was heated to about 100 °C. Weight% starch (or starch/oil) in these dispersions was calculated from the weight of dry solid obtained by freeze-drying weighed portions of jet cooked dispersion. The concentration of starch in oil-containing dispersions was calculated by correcting the weight of freeze-dried solid for the amount of oil added.

Hot, jet-cooked dispersions were allowed to stand and cool for 22 h without stirring. Temperatures during this cooling period were monitored as described earlier (Fanta et al., 2002); and initial and final temperatures in 12 separate experiments were 94.3 ± 1.3 °C, and 51.4 ± 2.3 °C, respectively. After cooling was complete, 300 g portions of cooled dispersion were diluted with 2700 mL of water; and the crystalline particles were isolated by centrifugation and fractionated according to particle size as described earlier (Fanta et al., 2002).

For experiments carried out with 4 h cooling, the rate of cooling was controlled with a Rapid Visco Analyzer (RVA) manufactured by Newport Scientific, Warriewood, NSW, Australia. Hot, jet cooked dispersion (50 mL) was transferred from the Dewar flask to a preheated aluminum sample cup; and the cup was placed in the RVA. The cooling program was begun by stirring for 2 min at 360 rpm and 95 °C to establish a consistent experimental starting point with regard to temperature of the dispersion. Samples were then cooled from 95 to 25 °C over a 4 h period (approximately 0.3 °C/min) in the absence of stirring. The top of the sample cup was lubricated with vacuum grease, and a rubber O-ring was fitted to the stirrer to minimize drying of the sample during cooling. After cooling was complete, the contents of the cup was dispersed in 450 mL of water at 25 °C; and the mixture of particles was isolated and fractionated as described above. Yields were not determined in this series of experiments because of the small volumes of dispersion available.

2.3. Scanning electron microscopy (SEM)

Aqueous dispersions of particles (20 μL) were added to 20 mL of absolute ethanol, and the solids were allowed to settle. Settled solids were washed with ethanol and critical point dried on aluminum stubs using CO_2. Dried specimens were then sputter coated with Au–Pd and examined with a JEOL 6400V scanning electron microscope.

2.4. Light microscopy and birefringence

Undried samples in water dispersion were observed with a Zeiss Axioskop light microscope (Carl Zeiss, Inc., Thornwood NY) using phase contrast optics. Representative fields were photographed using a Nikon D100 digital camera (Nikon Corp., Tokyo, Japan). Birefringence was observed using crossed polarizing filters and a Zeiss bright field light microscope (Carl Zeiss, Inc., Thornwood, NY). Representative fields were photographed with Polaroid #57 film.

2.5. X-ray diffraction

X-ray diffraction was carried out as described previously (Fanta, Shogren, & Salch, 1999). Freeze dried samples were equilibrated at 23 °C and 45% relative humidity for 2 days prior to analysis.

2.6. Determination of mineral oil content by FTIR

Percent mineral oil in freeze dried samples was determined by measuring the midrange absorbencies for mineral oil at 2954 and 2854 cm^{-1}, after subtracting a spectrum of cornstarch to remove interference caused by the starch peak at 2929 cm^{-1}. Both of these mineral oil absorbencies were used for these determinations, and the two results were averaged. Samples of known mass were pulverized in 1-in. steel vials with two spherical steel pestles using a Wig-L-Bug Mixer (Crescent Dental Mfg. Co., Lyons, IL) until the absorbencies reached a maximum and did not change with additional ball-milling. Pulverized solids were then pressed into KBr pellets. Absorbencies per milligram of sample were then calculated, and percent mineral oil was then estimated from standard curves obtained by analyzing starch samples with known mineral oil contents ranging from 3.3 to 30.5%. Standard curves were obtained by linear regression. R^2 was 0.9457 for the 2954 cm^{-1} absorbance and 0.9608 for the 2854 cm^{-1} absorbance. The standard curve was validated by spreading small amounts of mineral oil onto NaCl disks and also between ZnSe discs over the same area as the infrared beam passing through the disks. All of these techniques gave the same values for absorbency per mg of oil. Measurements made on Nicolet Impact 410 and Nicolet Avater 370 spectrometers gave identical absorbency values.

3. Results

Two cooling methods were used for particle preparation. In the first method, jet cooked starch dispersions were allowed to cool for 22 h without stirring in insulated Dewar flasks. In the second method, cooling from 95 to 25 °C was carried out over a 4 h period without stirring in a Rapid Visco Analyzer at a programmed rate of about 0.3 °C per minute. The nominal starch concentration in these jet cooked dispersions was varied from 10 to 4%, by weight; and the amount of mineral oil added was 20 g per 100 g of starch. Mineral oil was used in these experiments to minimize the possibility of helical inclusion complex formation between amylose and added oil. Actual starch concentrations differed from the nominal concentrations because of dilution of the cooked dispersions with variable amounts of condensed steam.

3.1. Cooling time of 22 h

Experiments carried out with 22 h cooling are summarized in Table 1. The particles isolated from oil-containing dispersions contained some residual mineral oil, presumably trapped within the particle matrix; and the percentages of oil in these mixtures varied from about 8 to 15%, by weight, as estimated by FTIR. Yields of particles, based on starch, decreased with decreasing starch concentration; and the yields were somewhat lower in the presence of mineral oil. After removing dispersed starch by water washing, the particle mixtures were fractionated according to particle size by dispersing the mixtures in excess water and then allowing the larger particles to settle, leaving the smaller

Table 1
Particles formed with 22-h cooling

Nominal starch percentage	Cooked with oil	Wt.% starch in cooked dispersion	Yield %[a]	Water-insoluble particles			
				Large particles		Small particles	
				Wt.%	Amylose content (%)	Wt.%	Amylose content (%)
10	No	10.2	16	92	88	8	81
10	Yes	9.9	15(11)	97	98	3	–[b]
7.5	No	7.9	12	98	80	2	–[b]
7.5	Yes	7.6	9(13)	88	93	12	–[b]
6.25	No	6.8	12	>99	79	<1	–[b]
6.25	Yes	6.5	9(15)	54	85	46	84
5	No	5.4	11	99	–[b]	1	–[b]
5	Yes	5.3	8(14)	52	–[b]	48	–[b]
4	No	4.1	10	>99	–[b]	<1	–[b]
4	Yes	4.1	7(8)	20	–[b]	80	81

[a] Yields are based on starch. Weight percentages of oil in unfractionated particle mixtures are shown in parentheses.

[b] Not determined.

particles in suspension. Analyses of selected particle fractions showed that amylose was the major component.

Fig. 1 shows SEM, phase contrast and birefringence images of un-fractionated mixtures of particles prepared in the absence of oil. Although particle size increased with increasing starch concentration, the morphologies and birefringence patterns were similar and resembled those of the torus-shaped and spherical/lobed particles reported earlier (Fanta et al., 2002). Only the spherical/lobed spherulites are visible in the birefringence images, because of the relatively small size of the torus-shaped particles. Images of the particles formed with 6.25% starch are not shown because of their similarity to images obtained with 7.5% starch. Two replicate experiments carried out at 4% starch yielded spherical/lobed spherulites having somewhat different morphologies, even though experimental conditions were ostensibly the same (see Fig. 1J–L and their insets). Despite these differences in morphology, similar birefringence patterns were observed; and the patterns were also similar to those of the other spherical/lobed particles in this series. Variations in the morphology of these spherulites in repetitive experiments were noted by us earlier (Fanta et al., 2002) and may be due to the effects of small temperature changes on the rate of crystallite nucleation.

Two previously unobserved particle types were observed with 10% starch. One of these (designated 'a' in Fig. 1B and C) was large and spherical and exhibited a mottled birefringence pattern and a uniform, grey appearance when viewed under phase contrast. The other particle (designated 'b' in Fig. 1A–C) resembled the torus-shaped particles but was larger and exhibited more pronounced surface striations. The b-type particles were mostly located on the surfaces of large spheres, and SEM images at high magnification suggested that they may have grown from these surfaces, as opposed to being loosely attached. The b-type particles were strongly birefringent but exhibited no discernable pattern.

X-ray powder diffraction scans of some of the particle fractions isolated in this series of experiments are shown in Fig. 2. The torus-shaped particles formed with 10% starch (Fig. 2E) exhibited the same V_6 reflections as the torus-shaped particles formed in earlier experiments with 4% starch (Fanta et al., 2002). Diffraction scans of selected spherical/lobed particles (Fig. 2A–D) also showed the same V_7 reflections observed previously for spherulites of this type (Fanta et al., 2002). The diffraction pattern for the spherical/lobed particles formed with 10% starch (Fig. 2D) exhibited low-intensity V_6 reflections in addition to the V_7

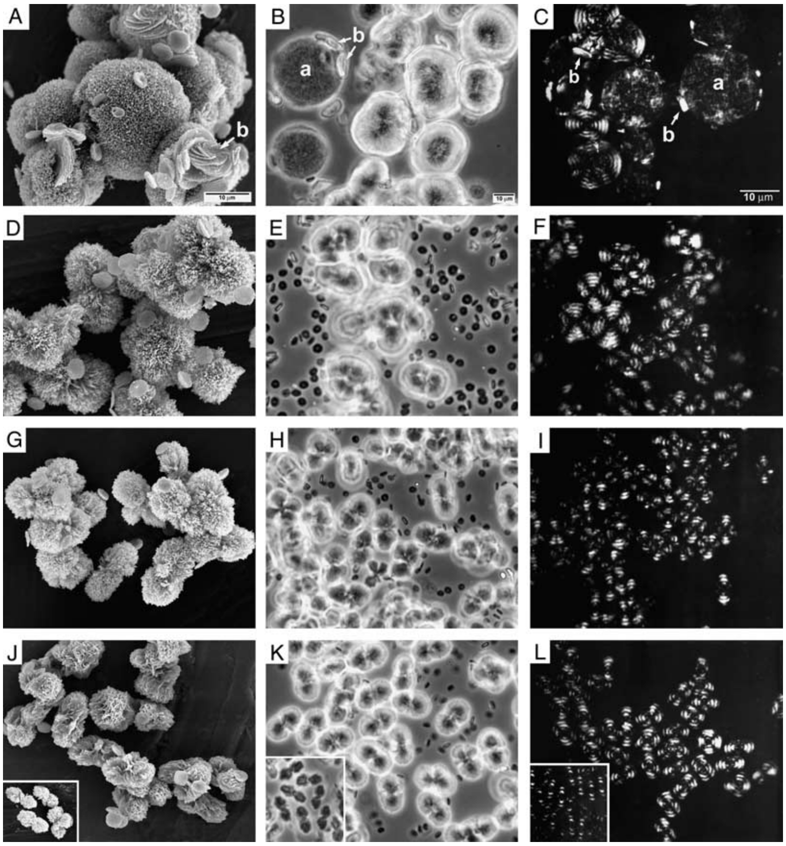

Fig. 1. Micrographs of un-fractionated mixtures of particles formed from jet cooked cornstarch in the absence of oil. Dispersions were slowly cooled for 22 h. (A, D, G and J) SEM images. (B, E, H and K) Phase contrast images. (C, F, I and L) Birefringence images. (A–C) Particles formed with nominal starch concentration of 10%. (D–F) Particles formed with nominal starch concentration of 7.5%. (G–I) Particles formed with nominal starch concentration of 5%. (J–L) Particles formed with nominal starch concentration of 4%. Insets show the particles formed in a replicate experiment.

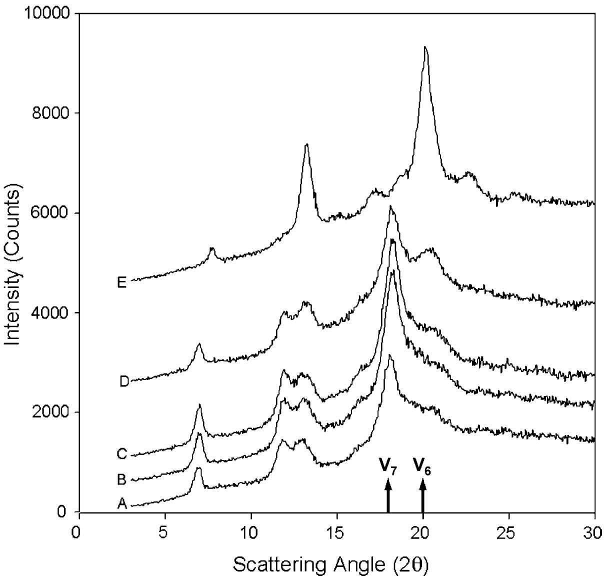

Fig. 2. X-ray powder diffraction scans of particles formed from jet cooked cornstarch in the absence of oil. Dispersions were slowly cooled for 22 h. (A) Spherical/lobed particles formed with nominal starch concentration of 4%. (B) Spherical/lobed particles formed with nominal starch concentration of 6.25%. (C) Spherical/lobed particles formed with nominal starch concentration of 7.5%. (D) Spherical/lobed particles (large particle fraction) formed with nominal starch concentration of 10%. (E) Torus-shaped particles formed with nominal starch concentration of 10%. Arrows refer to major V_6 and V_7 reflections.

scattering pattern. These V_6 reflections may be due to the presence of a-type particles that could not be separated from the spherical/lobed spherulites by selective settling due to the similarity in particle sizes.

The fact that all of the spherical/lobed spherulites formed in this series of experiments exhibited similar birefringence and X-ray diffraction patterns suggests that these particles all have the same basic structure, and differ only in the extent to which they have grown. In a previous study (Peterson, Fanta, Adlof, & Felker, 2005), we observed the formation and growth of these spherulites by jet cooking starch at 4% solids and then removing samples for microscopy at intervals of 2 °C, as the dispersion was allowed to slowly cool. Small, 2- and 4-lobed particles were the first to form at 86 °C, and no torus-shaped particles were seen at this temperature. The lobed spherulites increased in size at 84 °C, and some small torus-shaped particles were also observed at this temperature. A further increase in the size of the lobed particles was observed at 82 °C; however, further cooling did not significantly change their appearance. The observed formation and growth of these spherical/lobed spherulites closely resembles computer simulations of spherulite growth from individual crystalline lamallae (Kalinka & Hinrichsen, 1997).

Fig. 3 shows SEM, phase contrast and birefringence images of the particles formed under the same conditions as those as Fig. 1, but in the presence of mineral oil. With 10% starch, many of the large spheres resembled the a-type particles observed in the absence of oil (see Fig. 1B and C); however, the large particles formed at lower starch concentrations exhibited the usual spherical/lobed morphology. The small particles formed in this series of experiments were not torus-shaped, but were spherical in shape with diameters of about 1–2 μm. SEM images at high magnification suggested that these small, spherical particles were aggregates of even smaller particles with diameters less than 1 μm (see inset for Fig. 3J). Relative amounts of these 1–2 μm particles increased with decreasing starch concentration; and with 4% starch, they comprised about 80% of the total weight of isolated material.

X-ray powder diffraction scans of some of the particle fractions isolated in this series are shown in Fig. 4. The V_6 diffraction patterns observed for the 1–2 μm spherical particles (Fig. 4E and F) were somewhat different than the V_6 patterns observed for torus-shaped particles. Reflections for the 1–2 μm spheres were broader, and the scattering patterns closely resembled patterns previously observed (Fanta et al., 2002) for particles with similar morphology formed from jet cooked wheat starch at 4% solids in the absence of oil (Fig. 4D). Patterns for the spherical/lobed spherulites isolated in the experiments with 6.25 and 7.5% starch (Fig. 4A and B) were similar to the V_7 patterns in Fig. 2 for the analogous spherulites formed in the absence of oil. Reflections for the large spherical particles formed with 10% starch (Fig. 4C) were broad and diffuse and suggested a combination of V_6 and V_7 patterns.

Because of the similarities between the morphologies and X-ray diffraction patterns of the 1–2 μm spheres formed from cornstarch in the presence of oil and the particles isolated from 4% wheat starch in the absence of oil (Fanta et al., 2002), we jet cooked wheat starch at 6.25% solids in the absence of oil to determine the nature of the particles formed at a higher starch concentration. SEM and phase contrast images are shown in Fig. 5. In addition to the 1–2 μm spherical particles, large aggregates of these small spheres were also observed. The 1–2 μm spheres and the large aggregates both exhibited the same V_6 X-ray diffraction pattern (patterns not shown) previously observed for the wheat starch particles formed at 4% solids. When examined through crossed polarizing filters, the aggregates showed weak birefringence with no discernable pattern, due to the combined birefringence of the individual 1–2 μm spheres (birefringence image not shown).

3.2. Cooling time of 4 h

Jet cooked cornstarch dispersions that were cooled over a period of 4 h yielded particle mixtures that differed from those observed with 22 h cooling. In the absence of mineral oil, and at starch concentrations of 10, 7.5 and 6.25%, the torus-shaped particles were larger and had more pronounced surface striations than those observed with 22 h cooling. SEM and phase contrast images of the particles formed with 7.5% starch are shown in Fig. 6A and B. Some intermediate-sized,

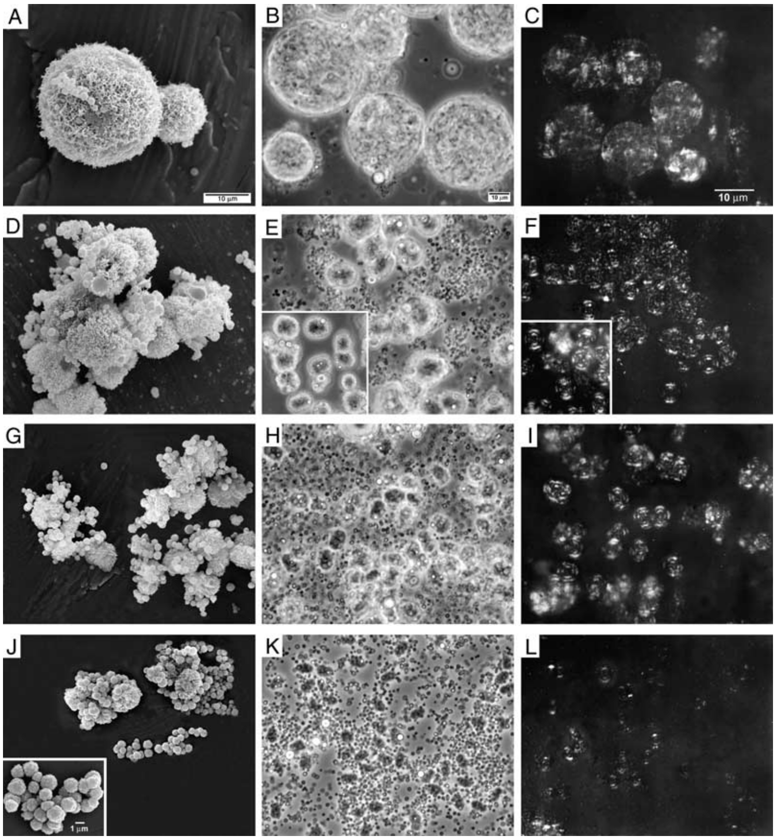

Fig. 3. Micrographs of un-fractionated crystallites formed from cornstarch jet cooked in the presence of mineral oil. Dispersions were slowly cooled for 22 h. (A, D, G and J) SEM images. (B, E, H and K) Phase contrast images. (C, F, I and L) Birefringence images. (A–C) Particles formed with nominal starch concentration of 10%. (D–F) Particles formed with nominal starch concentration of 7.5%. Insets in (E) and (F) show images after removal of the 1–2 μm spherical particles. (G–I) Particles formed with nominal starch concentration of 5%. (J–L) Particles formed with nominal starch concentration of 4%. Inset in (J) is a higher magnification image to better show the structure of the 1–2 μm spheres.

spherical particles, larger than the torus-shaped particles but smaller than the spherical/lobed spherulites, were also observed at this starch concentration. When the concentration of starch was reduced to 5% and then to 4%, the torus-shaped particles were replaced by 1–2 μm spheres, similar in appearance to those described earlier. SEM and phase contrast images of the particle mixture formed with 5% starch are shown in Fig. 6C and D.

Scattering patterns for the spherical/lobed particles formed with 7.5 and 5% starch (patterns not shown) were similar to the V_7 patterns observed for the analogous spherulites formed with 22 h cooling. The birefringence patterns were also similar. Scattering patterns for the torus-shaped particles and the 1–2 μm spheres (patterns not shown) also resembled the patterns shown earlier for these two particle species. The scattering pattern for the intermediate-sized spherical particles formed with 7.5% starch (Fig. 7A) exhibited V_6 reflections; however, the pattern was partially obscured by additional reflections, possibly due to retrograded starch.

As observed with 22 h cooling, the presence of mineral oil changed the nature of the particle mixture formed. Large spherical particles were observed at starch concentrations of 10 and 7.5%, and phase contrast images of these particles were similar in appearance to those shown in Fig. 3B and to those of particles observed by us in an earlier study (Byars, Fanta, & Felker, 2005). Torus-shaped particles were not formed in these experiments; and the 1–2 μm spheres were the only small particles observed. SEM and phase contrast images of the mixture of particles obtained with 7.5% starch in the presence of oil are shown in Fig. 6E and F, respectively. When the concentration of starch was reduced to 5 and 4%, few (if any) large particles were formed, and the 1–2 μm spheres were the only particles observed. The 1–2 μm spheres and the large spherical particles isolated from the experiment with 7.5% starch both exhibited V_6 X-ray diffraction patterns; however, the scattering pattern for the large spheres was partially obscured by additional reflections, possibly due to the presence of retrograded starch (Fig. 7B).

4. Discussion and conclusions

The native lipid component in cornstarch contains mainly free fatty acids, along with smaller amounts of lysophospholipids (Morrison, 1988). Linoleic, palmitic and

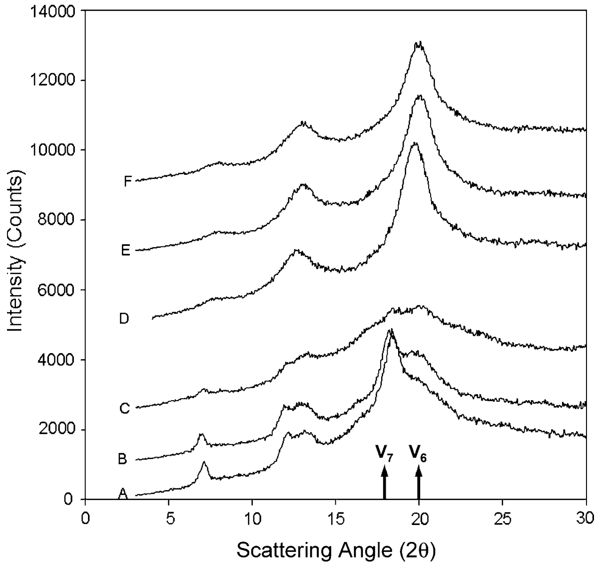

Fig. 4. X-ray powder diffraction scans of particles formed with 22 h cooling. (A) Large particle fraction formed from cornstarch in the presence of mineral oil with nominal starch concentration of 6.25%. (B) Large particle fraction formed from cornstarch in the presence of mineral oil with nominal starch concentration of 7.5%. (C) Large particle fraction formed from cornstarch in the presence of mineral oil with nominal starch concentration of 10%. (D) Particles formed from wheat starch in the absence of oil with nominal starch concentration of 4%. (E) Small particle fraction formed from cornstarch in the presence of mineral oil with nominal starch concentration of 4%. (F) Small particle fraction formed from cornstarch in the presence of mineral oil with nominal starch concentration of 6.25%. Arrows refer to major V_6 and V_7 reflections.

oleic acids are the fatty acids present in largest amounts. When cornstarch is dispersed by steam jet cooking, helical inclusion complexes are formed between amylose and native lipid; and these complexes then crystallize to form the particles observed. Separation of aqueous amylose and amylopectin phases takes place in mixed solutions of amylose and amylopectin (Kalichevsky & Ring, 1987). It is not known at this time whether spherulite formation takes place prior to phase separation or within the separated amylose-rich phase.

The two types of particles observed when cornstarch was jet cooked at concentrations of 4–10% in the absence of mineral oil and then allowed to slowly cool for 22 h were (1) large, spherical/lobed spherulites that exhibited 7_1 V-helical X-ray diffraction patterns, and (2) smaller, torus-shaped particles with 6_1 V-helical patterns. In an earlier study of the particles formed at a starch concentration of 4% (Peterson et al., 2005), we showed that free fatty acids comprised the major portion of the complexed lipids, and that both particle species contained the same mixture of lipids, although the individual lipids were present in different relative amounts.

When cornstarch was jet cooked in the presence of mineral oil and then allowed to slowly cool for 22 h, small, spherical aggregates with diameters of 1–2 μm were also observed in addition to the spherical/lobed and the torus-shaped particles. Amounts of these 1–2 μm spheres increased with decreasing starch concentration; and with 4% starch, they comprised about 80%, by weight, of the mixture of particles isolated. The morphologies and X-ray diffraction patterns of these 1–2 μm spheres were similar to those of particles isolated from jet cooked dispersions of wheat starch in the absence of added oil. In contrast to cornstarch, the native lipid component of wheat starch contains mainly lysophospholipids, rather than free fatty acids (Morrison, 1988).

The effect of added oil on the types of crystallites formed could be due to the ability of micrometer-sized oil droplets to alter the composition of the native lipid by selectively extracting the free fatty acid components. The greater hydrophobicity of the fatty acids relative to the

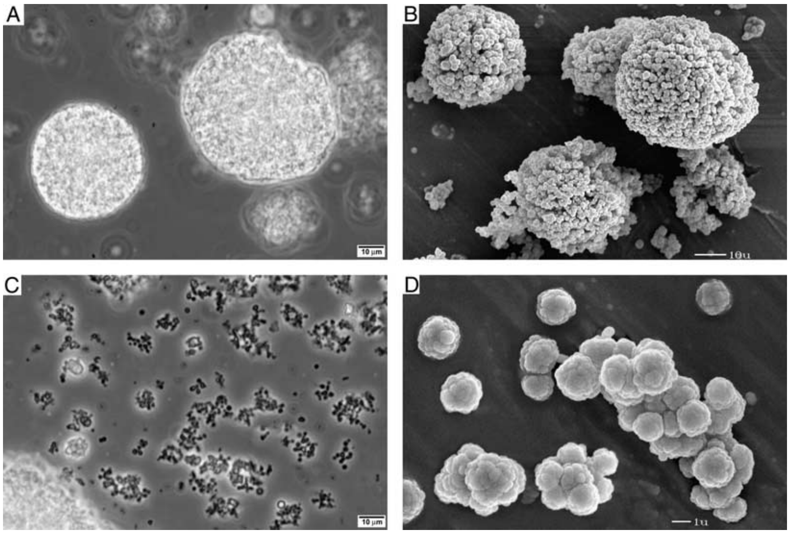

Fig. 5. Micrographs of particles formed from wheat starch jet cooked in the absence of mineral oil. Dispersion was slowly cooled for 22 h. Nominal starch concentration was 6.25%. (A and C) Phase contrast images. (B and D) SEM images. (A and B) Aggregates of 1–2 μm spherical particles. (C and D) Individual 1–2 μm spherical particles.

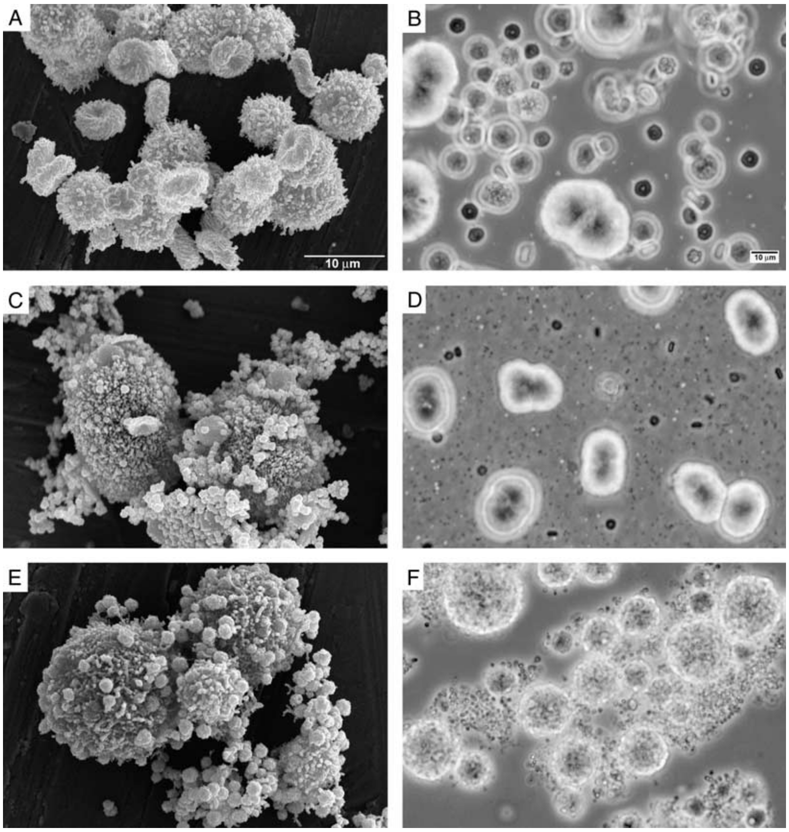

Fig. 6. Micrographs of particles formed from jet cooked cornstarch. Dispersions were cooled for 4 h. (A, C and E) SEM images. (B, D and F) Phase contrast images. (A and B) Particles formed in the absence of oil with nominal starch concentration of 7.5%. (C and D) Particles formed in the absence of oil with nominal starch concentration of 5%. (E and F) Particles formed in the presence of mineral oil with nominal starch concentration of 7.5%.

lysophospholipids (due to esterified glycerol in the lysophospholipids) makes this a reasonable supposition. The lipid droplets could also provide a hydrophobic surface for adsorption of amylose–fatty acid complexes. Removal of free fatty acids from jet cooked dispersions would increase the relative abundance of lysophospholipids in the native lipid that remains, thus favoring formation of the 1–2 µm spheres that we observe when wheat starch is jet cooked in the absence of added oil. Spherical/lobed spherulites are also observed in these cornstarch–oil dispersions because they are the first to form at the highest temperature, where the absorption of free fatty acids by mineral oil is minimal.

Particles with the same 1–2 µm spherical morphology were also observed when cornstarch was jet cooked in the absence of added mineral oil and then cooled over a 4 h period, as opposed to 22 h. The rate at which these dispersions are cooled can influence the types of particles formed, because growth of the first-formed particles (i.e. the spherical/lobed spherulites followed by the torus-shaped particles) removes mainly free fatty acids (along with minor amounts of lysophospholipids) from the jet cooked dispersion, thus altering the composition of the native lipid available for complex formation and crystallization at lower temperatures. Although not verified experimentally, the 1–2 µm spherical particles are probably formed at a lower temperature than the other particles, because lysophospholipids, which likely comprise much of the complexed lipid in these small spheres, are more hydrophilic than free fatty acids because of esterified glycerol. Slow cooling over 22 h favors growth of the first-formed

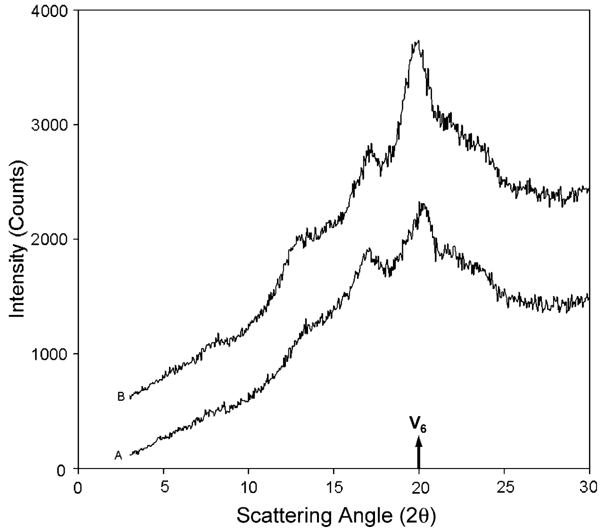

Fig. 7. X-ray powder diffraction scans of particles formed from jet cooked cornstarch at nominal starch concentration of 7.5%. Dispersions were cooled for 4 h. (A) Intermediate-sized spherical particles formed in the absence of oil. (B) Large, spherical particles formed in the presence of mineral oil. Arrow refers to the major V_6 reflection.

crystallites, i.e. the spherical/lobed and torus-shaped particles; and the 1–2 μm spheres are not observed, because most of the native lipid originally present in the dispersion (including some lysophospholipid) has been consumed due to the prolonged time period available for particle growth at the higher temperatures. When dispersions are cooled more rapidly (i.e. 4 h), the initially-formed spherical/lobed and torus-shaped particles have a shorter time period in which to grow; and more native lipid is thus available for complex formation and spherulite growth at lower temperatures. Due to preferential depletion of the fatty acid components, the remaining native lipid also contains the high percentage of lysophospholipids needed for formation of the 1–2 μm spheres.

Acknowledgements

We are grateful to Dr A.R. Thompson for scanning electron micrographs and to S.A. Lyle and J.K. Lingenfelter for technical assistance.

References

Byars, J.A., Fanta, G.F., & Felker, F.C. (2005). The influence of oil on the properties of slowly-cooled jet cooked normal corn starch dispersions. Submitted for publication.

Davies, T., Miller, D. C., & Procter, A. A. (1980). Inclusion complexes of free fatty acids with amylose. *Starch/Starke*, *32*, 149–158.

Eskins, K., Fanta, G. F., Felker, F. C., & Baker, F. L. (1996). Ultrastructural studies on microencapsulated oil droplets in aqueous gels and dried films of a new starch–oil composite. *Carbohydrate Polymers*, *29*, 233–239.

Fanta, G. F., & Eskins, K. (1995). Stable starch–lipid compositions prepared by steam jet cooking. *Carbohydrate Polymers*, *28*, 171–175.

Fanta, G. F., & Eskins, K. (1998). Starch–oil composites prepared by steam jet cooking: Preparations, properties and applications. In D. J. Sessa, & J. L. Willett (Eds.), *Paradigm for successful utilization of renewable resources* (pp. 266–286). Champaign, IL: AOCS Press.

Fanta, G. F., Felker, F. C., Eskins, K., & Baker, F. L. (1999). Aqueous starch–oil dispersions prepared by steam jet cooking. Starch films at the oil–water interface. *Carbohydrate Polymers*, *39*, 25–35.

Fanta, G. F., Felker, F. C., & Shogren, R. L. (2002). Formation of crystalline aggregates in slowly-cooled starch solutions prepared by steam jet cooking. *Carbohydrate Polymers*, *48*, 161–170.

Fanta, G. F., Felker, F. C., Shogren, R. L., & Knutson, C. A. (2001). Starch–paraffin wax compositions prepared by steam jet cooking. Examination of starch adsorbed at the paraffin–water interface. *Carbohydrate Polymers*, *46*, 29–38.

Fanta, G. F., Shogren, R. L., & Salch, J. H. (1999). Steam jet cooking of high amylose starch–fatty acid mixtures. An investigation of complex formation. *Carbohydrate Polymers*, *38*, 1–6.

Jane, J., Kasemsuwan, T., Chen, J. F., & Juliano, B. O. (1996). Phosphorus in rice and other starches. *Cereal Foods World*, *41*(11), 827–832.

Kalichevsky, M. T., & Ring, S. G. (1987). Incompatibility of amylose and amylopectin in aqueous solution. *Carbohydrate Research*, *162*, 323–328.

Kalinka, G., & Hinrichsen, G. (1997). Two-dimensional computer simulation of spherulite formation by branching lamellae. *Acta Polymer.*, *48*, 256–261.

Kitamura, S., Yoneda, S., & Kuge, T. (1984). Study on the retrogradation of starch. I. Particle size and its distribution of amylose retrograded from aqueous solutions. *Carbohydrate Polymers*, *4*, 127–136.

Klem, R. E., & Brogley, D. A. (1981). Methods for selecting the optimum starch binder preparation system. *Pulp & Paper*, *55*, 98–103.

Morrison, W. R. (1988). Lipids in cereal starches: A review. *Journal of Cereal Science*, *8*, 1–15.

Peterson, S.C., Fanta, G.F., Adlof, R.O., & Felker, F.C (2005). Identification of complexed native lipids in crystallites formed from jet cooked cornstarch. Carbohydrate Polymers, in press.

Zobel, H. F. (1988). Starch crystal transformations and their industrial importance. *Starch/Starke*, *40*, 1–7.