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Preparation of spherulites from jet cooked mixtures of high amylose starch and fatty acids. Effect of preparative conditions on spherulite morphology and yield ☆

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Abstract

When high amylose cornstarch (amylose content: 70%) was jet cooked with 5% palmitic acid, based on amylose, spherulite yields of approximately 60%, based on total starch, were obtained. Spherulites were characterized by SEM and X-ray diffraction. The types of spherulites formed depended on the method used to cool the hot, jet cooked dispersions. Slow cooling for 22 h with magnetic stirring produced mixtures of torus/disc and spherical/lobed spherulites along with trace amounts of micron and sub-micron sized particles. In the absence of stirring, higher yields of sub-micron particles were observed along with spherulite aggregates that were comprised primarily of large, torus/disc spherulites with only minor amounts of spherical/lobed material. When jet cooked dispersions were rapidly cooled in ice, sub-micron spherical particles were the only particles observed. When defatted high amylose cornstarch was used, it was necessary to add an additional amount of palmitic acid to replace the native lipid removed from the starch sample in order to maximize yields and to avoid gel formation. Amounts of complexed palmitic acid in these spherulites varied from 4.5% to 6.1%, by weight. High yields of spherulites were also obtained when oleic acid was used; and, as observed with palmitic acid, sub-micron spherical particles were the only particles observed when the dispersion was rapidly cooled. Factors that affect the formation and morphology of these spherulites were considered.
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Keywords: Starch; Amylose; Fatty acid; Spherulite; Helical inclusion complex; Excess steam jet cook

1. Introduction

Steam jet cooking is a rapid and continuous process that is widely used to prepare aqueous dispersions of starch for commercial applications (Klem & Brogley, 1981). As part of our research program on starch utilization, we are investigating steam jet cooking as a convenient and inexpensive processing method for preparing new starch-based compositions. In the course of these investigations, we have observed the formation of spherulites when aqueous starch dispersions were jet cooked and then allowed to slowly cool. Spherulite formation in starch dispersions has also been observed by other workers, for example, Davies, Miller, and Procter (1980), Heinemann, Escher, and Conde-Petit (2003), and Heinemann, Zinsli, Escher, and Conde-Petit (2003). In previous studies, we observed two distinct types of spherulites that differed in size, morphology, and crystal structure, when cornstarch was jet cooked at 4% solids (Fanta, Felker, & Shogren, 2002). The smaller of these two spherulite species was disc or torus-shaped; whereas the larger spherulites were more spherical in shape

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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.

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and often exhibited a 2-lobed or 4-lobed appearance. Total yields of spherulites were about 10%, based on total starch, when normal dent cornstarch was used; and somewhat higher yields were observed with high amylose cornstarch. Our findings supported the conclusion of Davies et al. (1980) that these spherulites resulted from crystallization of helical inclusion complexes formed from amylose and the native lipid material normally present in cereal starch granules. High amylose starch contains about 1% native lipid; whereas the lipid content of normal dent cornstarch is somewhat less. This lipid fraction is composed primarily of palmitic, linoleic and oleic acids along with smaller amounts of lysophospholipids (Morrison, 1988). The complexed native lipids in both the torus/disc and the spherical/lobed spherulites have been identified and compared (Peterson, Fanta, Adlof, & Felker, 2005). We have also investigated the influence of fatty acid structure on the morphology of spherulites formed from defatted normal dent cornstarch and a number of pure fatty acids (Fanta, Felker, Shogren, & Salch, 2006).

Possible end-use applications for these spherulites are currently being examined. Since substantial quantities of spherulites will be required for these investigations, this study was carried out to determine whether higher yields of spherulites than those reported previously could be obtained by (1) using high amylose cornstarch in the jet cooking process, and (2) adding a sufficient amount of pure fatty acid to complex all of the amylose in the starch sample. In this report, we will describe the increased yields of spherulites obtained by this technique, and also the effects of stirring and cooling rate on the morphologies of the spherulites formed. Palmitic acid was used in most experiments, and some experiments were also carried out with oleic acid for comparison.

2. Materials and methods

2.1. Materials

High amylose cornstarch (AmyloGel 03003, containing approximately 70% amylose) was a product of Cerestar, Hammond, IN. Percent moisture was calculated from weight loss after drying at 100 °C under vacuum, and all weights of starch are given on a dry weight basis. Starch was defatted by extraction with refluxing 85% methanol–water followed by refluxing 75% *n*-propanol–water (Fanta et al., 2002; Morrison & Coventry, 1985). Palmitic acid and oleic acid (approx. 99%) were purchased from Sigma Chemical Co., St. Louis, MO.

2.2. Jet cooking starch–fatty acid mixtures and isolation of crystallites

In a typical experiment, 2.10 g of palmitic acid (5%, by weight, based on amylose, assuming 70% amylose in the starch sample) was dissolved in about 20 mL of ethanol, and the solution was intimately mixed with 60.0 g of high amylose cornstarch. The ethanol was then allowed to evaporate under ambient conditions. The starch–fatty acid mixture was dispersed in 1200 mL of water, and the dispersion was passed through a Penick & Ford Laboratory Model steam jet cooker, operating under excess steam conditions (Klem & Brogley, 1981). Temperature in the hydroheater was 140 °C, the steam back pressure was 40 lb/in.^{2} (2.8 kg/cm^2) and the steam line pressure from the boiler was 65 lb/in.^{2} (4.6 kg/cm^2). Pumping rate of the aqueous starch dispersion through the jet cooker was about 1-L/min. About 900 ml of jet cooked dispersion was collected in a 1-L stainless steel Dewar flask (Series 3763, Cole-Parmer Instrument Co., Vernon Hills, IL). Prior to collection of the sample, the Dewar flask was heated with hot (100 °C) water from the jet cooker. Percent solids in jet cooked dispersions, determined by freeze-drying weighed portions of dispersion, varied from 4.0% to 4.3%. Variations in percent solids were caused by dilution of cooked dispersions with varying amounts of condensed steam.

The hot, jet cooked dispersions were allowed to slowly cool in covered Dewar flasks for 22 h. Dispersions that were stirred during cooling were stirred with a magnetic stirring bar. Temperatures during the 22 h cooling period were monitored with an OMB TempBook/66 thermocouple data acquisition system from Omega, Stamford, CT. Initial and final temperatures were about 93 ± 1 °C and 46 ± 2.5 °C, respectively. Dispersions that were rapidly cooled were poured into a 2-L beaker and cooled to about 25 °C in an ice-water bath, while gently stirring with a spatula. Cooling times varied from 7 to 12 min.

Cooled dispersions were diluted with water to give a 10-fold reduction in solids concentration, and the spherulites were isolated by centrifugation in a Beckman GS-6KR centrifuge at 3000 rpm (approx. 2000*g*). Dissolved starch was removed from the precipitated spherulites by washing three times with excess water followed by centrifugation. Percent yield was determined by freeze drying the water-washed spherulites isolated from a weighed portion of jet cooked dispersion. Spherulite mixtures were fractionated according to particle size by diluting with excess water and then allowing the dispersions to partially settle, leaving the smaller spherulites in suspension. The spherulite fractions were then isolated by freeze drying. The efficiency of this fractionation procedure was monitored by light microscopy.

2.3. Microscopy

Aqueous dispersions of spherulites (about 40 μL) were added to about 20 mL of absolute ethanol, and the spherulites were allowed to settle. The settled particles were washed with ethanol and critical point dried with CO_2onto aluminum stubs. Dried specimens were sputter coated with gold and were examined and photographed with a JEOL 6400 V scanning electron microscope.

2.4. X-ray diffraction

X-ray diffraction patterns of freeze dried samples were obtained as described previously (Fanta, Shogren, & Salch, 1999). Samples were equilibrated at 23 °C and 45% relative humidity for 2 days prior to analysis.

2.5. Determination of complexed palmitic acid

Percentages of palmitic acid, by weight, in freeze dried spherulite fractions was determined by FTIR as described previously (Fanta et al., 2006).

3. Results

Mixtures of high amylose cornstarch and fatty acid (either palmitic or oleic) were steam jet cooked, and the hot dispersions were allowed to slowly cool, with and without stirring, for 22 h. Alternatively, the dispersions were rapidly cooled in an ice bath. The spherulites were then isolated from the cooled dispersions, and their yields and morphologies were determined.

Experiment 1 and replicate Experiments 2a and 2b, Table 1, were carried out to determine the yields of spherulites formed, with and without stirring, in the absence of added fatty acid, where the only lipid available for complex formation was the native lipid present in high amylose cornstarch. Yields of torus/disc and spherical/lobed spherulites were 16–17%. Although X-ray diffraction patterns (not shown) were similar to patterns previously observed for these two spherulite species (Fanta et al., 2002), comparison of SEM images (Fig. 1A and B) with the images published earlier (Fanta et al., 2002) showed that the spherulites formed in the present investigation were smaller and more irregular in shape and surface morphology. These differences are probably caused by variations in cooling rates due to the different sized Dewar flasks (1-L vs. 6-L) and dispersion volumes used in the two studies. Representative plots of temperature vs. time under these two different experimental conditions are shown in Fig. 2. We also observed trace amounts of a small

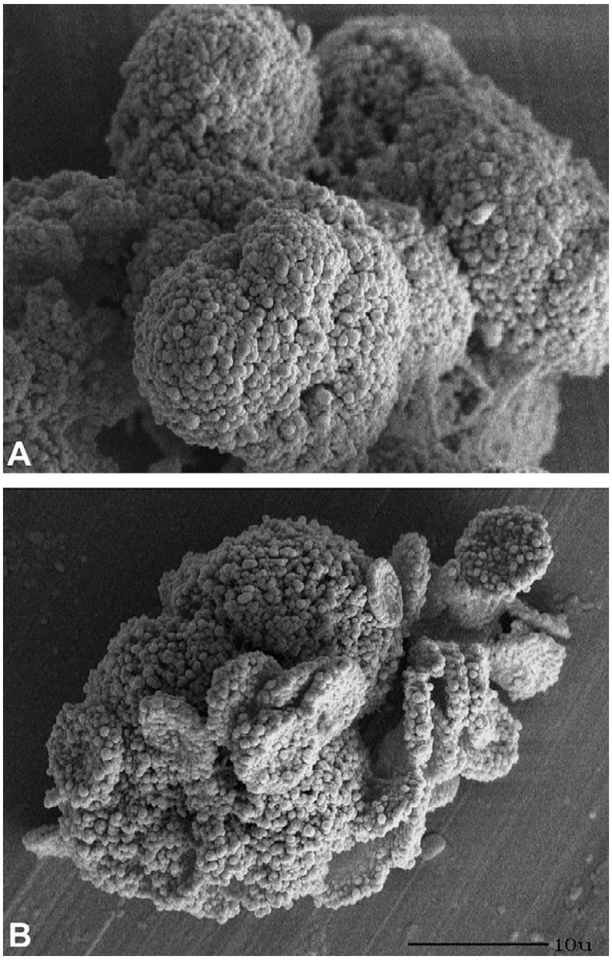

Fig. 1. SEM images of spherulites formed from high amylose cornstarch in the absence of added palmitic acid. (A) Jet cooked dispersion slowly cooled with stirring (Experiment 1, Table 1). (B) Jet cooked dispersion slowly cooled without stirring (Experiment 2b, Table 1).

Table 1
Effect of palmitic acid addition and cooling conditions on yield and morphology of spherulites

Experiment	% Palmitic acid[a]	Cooling conditions	Spherulite yield[b] (%)	Spherulites formed, % of total spherulite weight	
				Small particles	Torus/disc + spherical/lobed spherulites[c]
1	0	Slow cool, stirred	16	Trace	100 (8:92)
2a	0	Slow cool, not stirred	17	Trace	100 (13:87)
2b	0	Slow cool, not stirred	16	Trace	100 (15:85)
3	2.5	Slow cool, stirred	41	Trace	100 (17:83)
4a	5	Slow cool, stirred	58	Trace	100 (6:94)
4b	5	Slow cool, stirred	58	Trace	100 (44:56)
4c	5	Slow cool, stirred	58	1	99 (9:91)
5	10	Slow cool, stirred	56	Trace	100 (14:86)
6a	5	Slow cool, not stirred	59	28	72 (ND[d])
6b	5	Slow cool, not stirred	58	9	91 (ND)
7a	5	Rapid cool in ice	63	100	0
7b	5	Rapid cool in ice	62	100	0

[a] Based on the amylose content of the starch sample.

[b] Based on total starch.

[c] Weight ratios of torus/disc:spherical/lobed spherulites are shown in parentheses.

[d] Not determined, due to aggregation of spherulites.

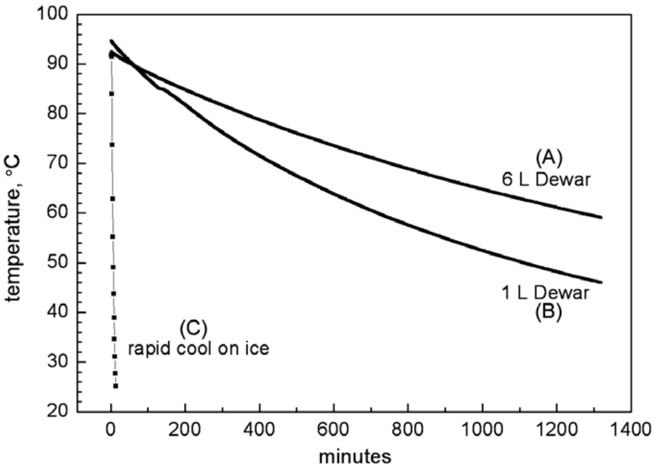

Fig. 2. Representative plots of temperature vs. time under the following experimental cooling conditions: (A) About 4-L of jet cooked dispersion was collected in a 6-L Dewar flask and allowed to cool without stirring. (B) About 900 mL of jet cooked dispersion was collected in a 1-L Dewar flask and allowed to cool without stirring. (C) About 900 mL of jet cooked dispersion was cooled rapidly in an ice bath with slow stirring.

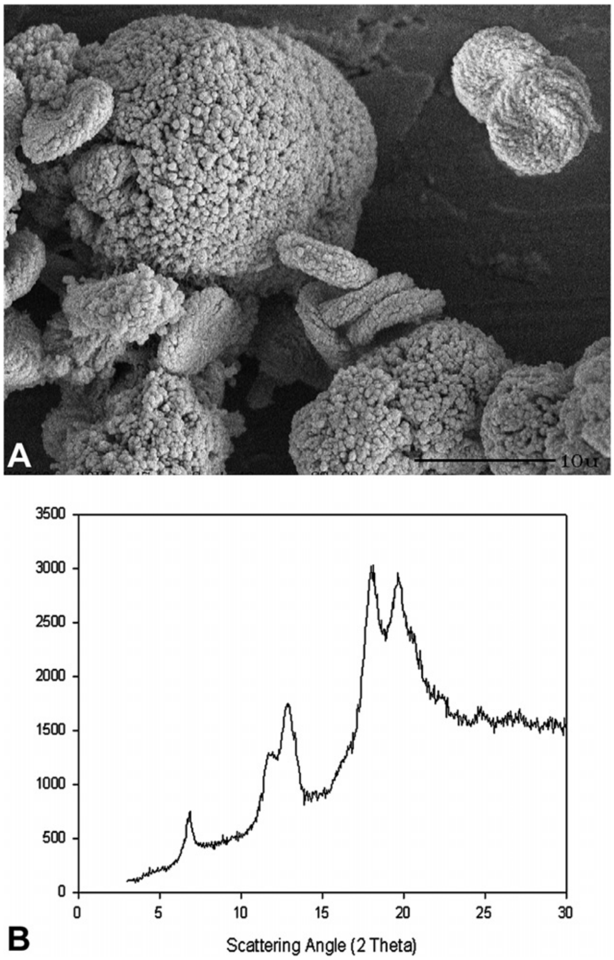

Fig. 3. (A) SEM image of spherulite mixture formed in Experiment 4c (Table 1), 5% palmitic acid, based on amylose. Jet cooked dispersion slowly cooled with stirring. (B) X-ray diffraction pattern of the spherical/lobed spherulite fraction isolated in Experiment 4c (Table 1).

particle fraction comprised of micron- and sub-micron-sized particles and thin, two-lobed particles that were almost rod-like in appearance. This small-particle fraction was not quantitatively determined but was estimated at about 1% of the total spherulite mixture.

In Experiments 3 through 5, Table 1, the jet cooked dispersions were stirred during the 22 h cooling period, and this series of experiments shows the higher yields of spherulites obtained when starch was jet cooked with increasing amounts of palmitic acid. Addition of palmitic acid in amounts equal to 2.5% (Experiment 3) and 5% (replicate Experiments 4a–c) of the weight of amylose in the starch sample increased the yield to 41% and 58%, respectively, based on total starch. Since an additional increase in yield was not observed with 10% palmitic acid (Experiment 5), subsequent experiments were carried out at the 5% level of addition. Consistent with the high yields of spherulites observed, jet cooked dispersions prepared with 5% palmitic acid did not form gels after standing overnight at room temperature, indicating that most of the amylose was converted to the palmitic acid complex. An SEM image (Fig. 3A) of the torus/disc and spherical/lobed spherulites obtained with 5% palmitic acid (Experiment 4c) showed that the spherulites were larger and had more ordered structures than those in Fig. 1A where no palmitic acid was added. Small particles, similar to those formed in Experiments 1 and 2, were also formed in small amounts. The 6_1V X-ray diffraction pattern for the torus/disc spherulites in Experiment 4c (pattern not shown) was similar to that observed previously for this spherulite species (Fanta et al., 2002). The diffraction pattern for the spherical/lobed spherulites (Fig. 3B) showed reflections for both the 6_1V and 7_1V conformations. Although the same yields were obtained in replicate Experiments (4a–c), large variations were observed in the relative amounts of torus/disc and spherical/lobed spherulites. Similar variations in replicate experiments were reported by us earlier (Fanta et al., 2002; Fanta, Felker, Shogren, Byars, & Salch, 2005).

Replicate Experiments 6a and 6b, were carried out under conditions similar to those used in Experiments 4a through 4c; however, the dispersions were not stirred during the 22 h cooling period. Under these conditions, a fraction comprised of small particles that were roughly spherical in shape and less than 1 μm in diameter were formed in addition to the usual torus/disc and spherical/lobed material. These particles amounted to 28% and 9%, by weight, of the total spherulite mixture. The SEM (Fig. 4A) and the 6_1V X-ray diffraction pattern (Fig. 4B) of these small particles (isolated in Experiment 6a) resembled those of particles observed by us earlier in jet cooked and slowly-cooled dispersions of wheat starch (Fanta et al., 2002) and in jet cooked dispersions of cornstarch that were either cooled over a 4 h period or jet cooked in the presence of paraffin oil (Fanta et al., 2005). The torus/disc and spherical/lobed spherulites formed in Experiments 6a and 6b were aggregated together and could not be separated

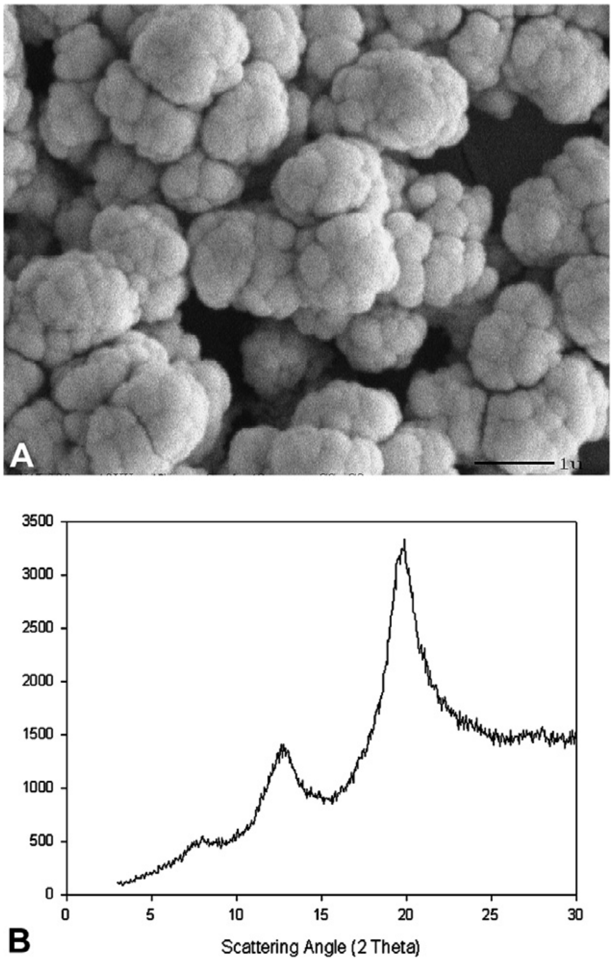

Fig. 4. (A) SEM image of small-particle fraction (28% of total spherulite weight) isolated in Experiment 6a (Table 1). Jet cooked dispersion slowly cooled without stirring. (B) X-ray diffraction pattern of the fraction shown in (A).

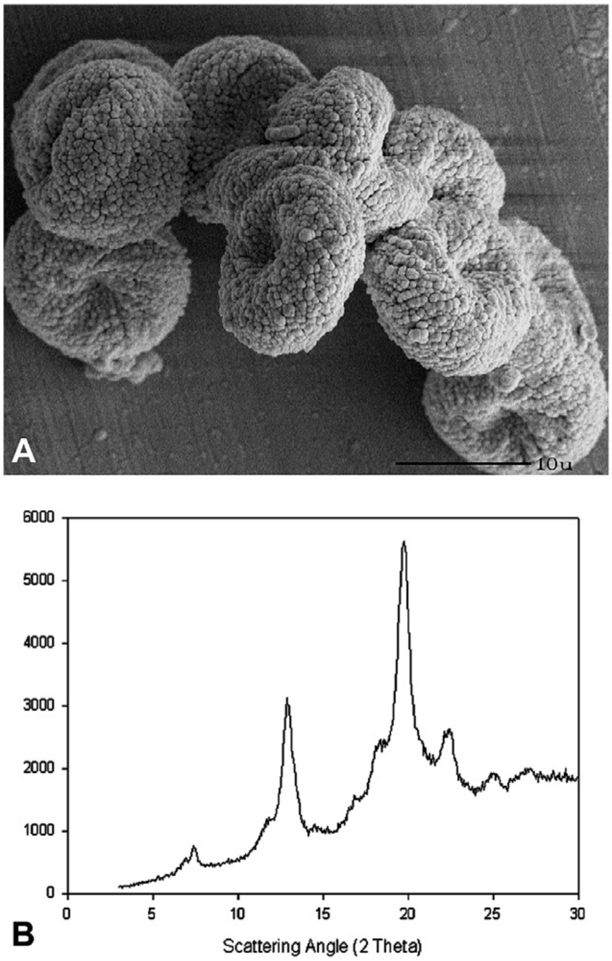

Fig. 5. (A) SEM image of spherulite aggregates formed in Experiment 6a (Table 1). Jet cooked dispersion slowly cooled without stirring. (B) X-ray diffraction pattern of the spherulite aggregates shown in (A).

by selective settling. SEM of the aggregates isolated in Experiment 6a (Fig. 5A) showed that they were comprised mostly of large torus/disc spherulites with only minor amounts of spherical/lobed material. This conclusion was substantiated by the X-ray diffraction pattern (Fig. 5B), which showed that the predominant conformation was 6_1V.

In replicate Experiments 7a and 7b, the jet cooked dispersions were rapidly cooled in an ice bath to 25 °C with gentle stirring over a period of about 10 min. Under these cooling conditions, the only particles formed were sub-micron spherical particles (and aggregates of these particles) that were similar to those formed in lesser amounts in Experiments 6a and 6b. Fig. 6A shows an SEM image of the particles formed in Experiment 7a. Fewer aggregates and more individual particles were observed when the mixtures were stirred under high-shear during cooling. The X-ray diffraction pattern of the particles formed in Experiment 7a (Fig. 6B) was similar to the 6_1V pattern shown in Fig. 3B for the small particle fraction in Experiment 6a.

Experiments were also carried out with mixtures of palmitic acid and defatted high amylose cornstarch (Table 2). In these experiments, an additional 1% palmitic acid, based on total starch, was added in addition to the usual 5%, based on amylose, in order to replace the native lipid removed when the starch sample was defatted. In the absence of this additional palmitic acid, the jet cooked dispersions gelled when they were cooled, indicating that the dispersions contained significant amounts of un-complexed amylose. Yields obtained under these conditions were similar to those observed with non-defatted starch. SEM (Fig. 7A) of the spherulites obtained in Experiment 1 (slow cooled with stirring) showed that the morphologies of these particles resembled those of the spherulites formed with non-defatted starch. The torus/disc spherulites showed the expected 6_1V X-ray diffraction pattern (pattern not shown); whereas the spherical/lobed spherulites showed a mixture of the 6_1V and 7_1V conformations (Fig. 7B). In the absence of stirring (Experiment 2), spherulite aggregates were formed that resembled those obtained with non-defatted starch. These aggregates were comprised largely of torus/disc material, as shown by the SEM in

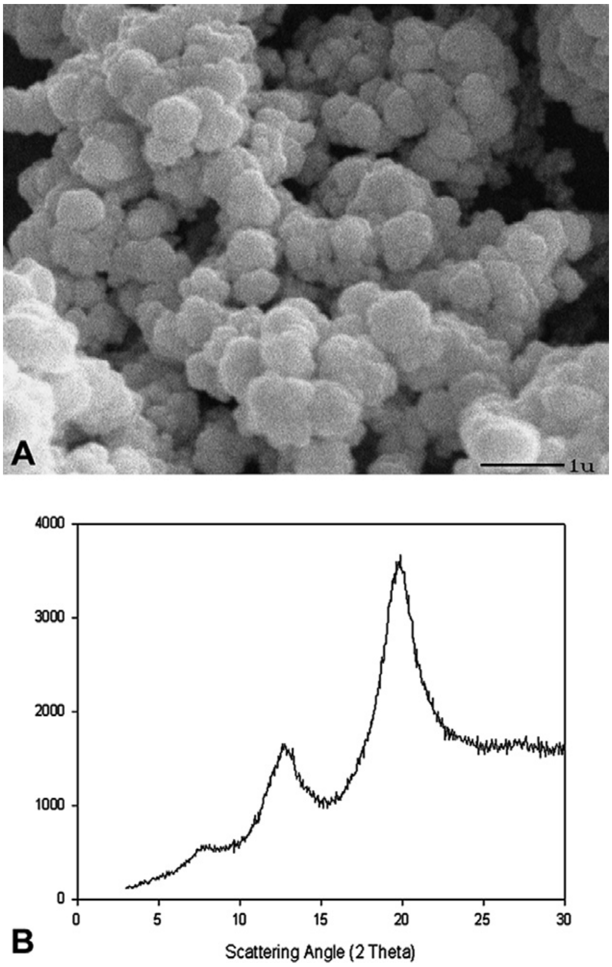

Fig. 6. (A) SEM image of particles formed in Experiment 7a (Table 1). Jet cooked dispersion rapidly cooled in ice. (B) X-ray diffraction pattern of the particles shown in (A).

Fig. 8A. The X-ray diffraction pattern shown in Fig. 8B also showed the 6_1V conformation usually observed for this spherulite species. The spherulite mixture also contained about 4% of a fraction comprised of small, spherical particles, similar to those obtained with non-defatted starch under the same cooling conditions. As observed with non-defatted starch, sub-micron spherical particles were the only particles formed when the jet cooked dispersion was rapidly cooled in ice. The weight percentages of palmitic acid in the different spherulite fractions shown in Table 2 varied from 4.5% to 6.1%, as determined by FTIR.

Experiments carried out with oleic acid (Table 3) gave spherulite yields comparable to those observed with palmitic acid. Slow cooling with stirring (Experiment 1) yielded a spherulite mixture that contained 99% spherical lobed material and about 1% of a small particle fraction that was comprised mostly of small torus/disc spherulites and thin, rod-like particles that were similar to those observed with palmitic acid. The SEM (Fig. 9A) and the 7_1V X-ray diffraction pattern of the spherical/lobed material (pattern not shown) resembled those observed previously for spherulites of this type. When the mixture was cooled without stirring (Experiment 2), the spherulite mixture contained about 2% of a small-particle fraction; plus a mixture of torus/disc and spherical/lobed particles in a weight ratio of 7:93. An SEM of this spherulite mixture is shown in Fig. 9B. X-ray diffraction patterns of the torus/disc and spherical/lobed spherulites (not shown) resembled the 6_1V and 7_1V patterns observed earlier for these two species. As observed with palmitic acid, spherical, sub-micron particles (and aggregates of these particles) were the only particles observed when the dispersion was rapidly cooled in ice. The SEM (Fig. 10A) and X-ray diffraction pattern of this material (Fig. 10B) resembled those observed with palmitic acid.

4. Discussion and conclusions

When high amylose cornstarch (amylose content: 70%) was jet cooked with 5% palmitic acid (based on amylose) spherulite yields of approximately 60%, based on total starch, were obtained. Essentially all of the amylose was converted to amylose–lipid complex, as indicated by the high yields of spherulites and the absence of gel in the cooled dispersions. The types of spherulites formed depended on the method used for cooling. Slow cooling for 22 h. in a 1-L Dewar flask with magnetic stirring produced mixtures of torus/disc and spherical/lobed spherulites. Small amounts (about 1% of the total spherulite weight) of micron- and sub-micron sized particles were also observed. When dispersions were allowed to cool for 22 h without stirring, higher yields of sub-micron particles were observed along with aggregates of spherulites that could

Table 2
Spherulites formed from defatted high amylose starch and palmitic acid

Experiment[a]	Cooling conditions	Spherulite yield[b] (%)	Spherulites formed, % of total spherulite weight	
			Small particles	Torus/disc + spherical/lobed spherulites[c]
1	Slow cool, stirred	58	1	99 [18(5.7%):81(5.9%)]
2	Slow cool, not stirred	58	4 (4.5%)	96[d] (5.8%)
3	Rapid cool in ice	60	100 (6.1%)	0

[a] Starch jet cooked with 1% palmitic acid, based on total starch, plus 5% palmitic acid, based on amylose (by weight).

[b] Based on total starch.

[c] Weight ratios of torus/disc:spherical/lobed spherulites are shown in brackets. Weight% palmitic acid in spherulites is shown in parentheses.

[d] Weight ratio of torus/disc:spherical/lobed particles was not determined due to aggregation of spherulites.

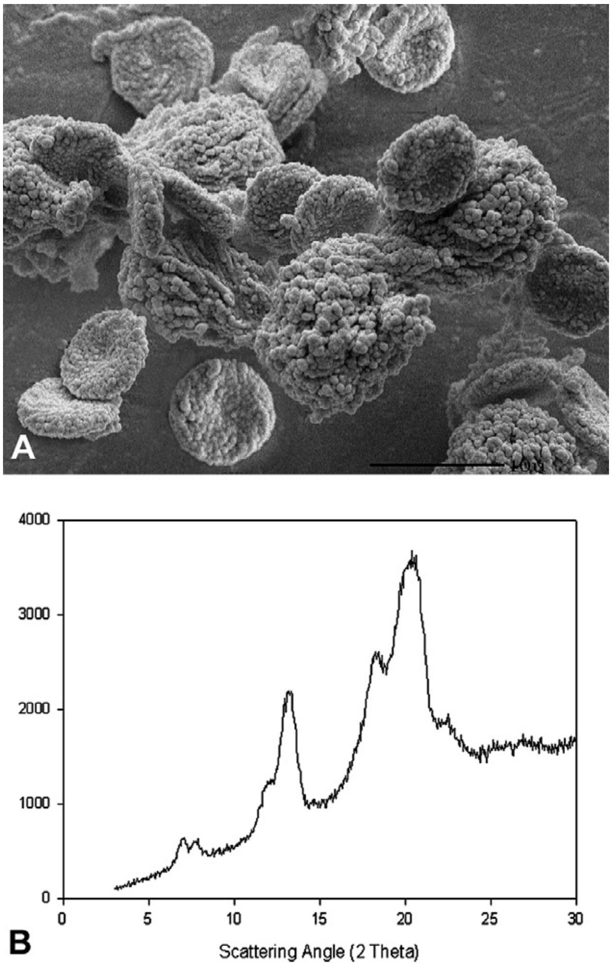

Fig. 7. (A) SEM image of the spherulite mixture formed in Experiment 1 (Table 2). Defatted high amylose starch. Jet cooked dispersion slowly cooled with stirring. (B) X-ray diffraction pattern of the spherical/lobed spherulite fraction isolated in Experiment 1 (Table 2).

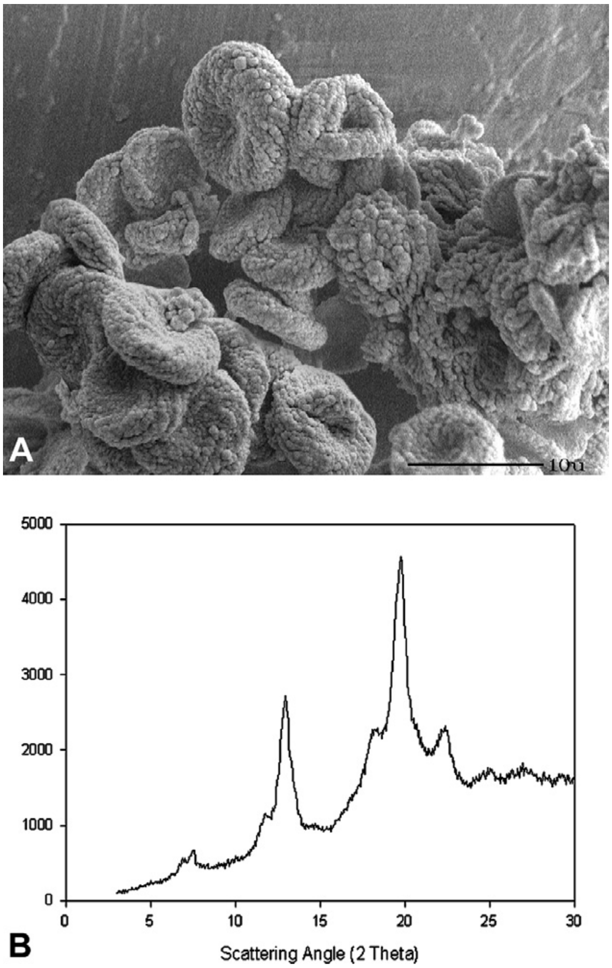

Fig. 8. (A) SEM image of spherulite aggregates formed in Experiment 2 (Table 2). Defatted high amylose starch. Jet cooked dispersions slowly cooled without stirring. (B) X-ray diffraction pattern of the spherulite aggregates shown in (A).

not be separated into their individual components. SEM and X-ray diffraction showed that these aggregates were comprised primarily of large, torus/disc spherulites with only minor amounts of spherical/lobed material. When jet cooked dispersions were rapidly cooled in ice, sub-micron spherical particles were the only particles observed. Spherulites formed from mixtures of defatted high amylose cornstarch and palmitic acid resembled those obtained with non-defatted starch. To maximize yields and to avoid gel formation in these experiments, it was necessary to add an additional amount of palmitic acid to replace the native lipid removed from the starch sample. Amounts of complexed palmitic acid in these spherulites varied from 4.5% to 6.1%, by weight. High yields of spherulites were also obtained when oleic acid was substituted for palmitic. Slow cooling the starch/oleic acid dispersion for 22 h with stirring yielded spherical/lobed spherulites, and no torus/disc spherulites were observed. In the absence of stirring, torus/disc and spherical lobed spherulites were formed in a weight ratio of 7:93. As observed with palmitic acid, sub-micron spherical particles were the only particles observed when the dispersion was rapidly cooled in ice.

The spherulites formed from amylose–fatty acid complexes are comprised of chain-folded crystalline lamellae with the amylose helices oriented perpendicular to the plane of each lamella (Manley, 1964; Yamashita, 1965; Yamashita & Hirai, 1966). Computer simulations have shown that variations in spherulite morphology can result from imperfect stacking of lamellae and also from the branching of lamellae during spherulite growth (Kalinka & Hinrichsen, 1997). The morphologies and relative amounts of the different spherulite species formed in our experiments are determined by a number of factors. Fatty acid structure is one such factor, since the conformation of the amylose helix (i.e., 6_1V or 7_1V) is determined by the molecular size or bulkiness of the complexed fatty acid; and the conformation of the helical complexes will influence the formation, stacking and branching of the individual lamellae. The presence of fatty acid dimers, or other multimers, within the amylose helix (as opposed to single fatty acid molecules) would also influence the conformation of the amylose helix.

Table 3
Spherulites formed from high amylose starch and oleic acid

Experiment[a]	Cooling conditions	Spherulite yield[b] (%)	Spherulites formed, % of total spherulite weight	
			Small particles	Torus/disc + spherical/lobed spherulites[c]
1	Slow cool, stirred	59	1	99 (0:100)
2	Slow cool, not stirred	58	2	98 (7:93)
3	Rapid cool in ice	65	100	0

[a] High amylose starch (not defatted) jet cooked with 5% oleic acid, based on amylose (by weight).
[b] Based on total starch.
[c] Weight ratios of torus/disc:spherical/lobed spherulites are shown in parentheses.

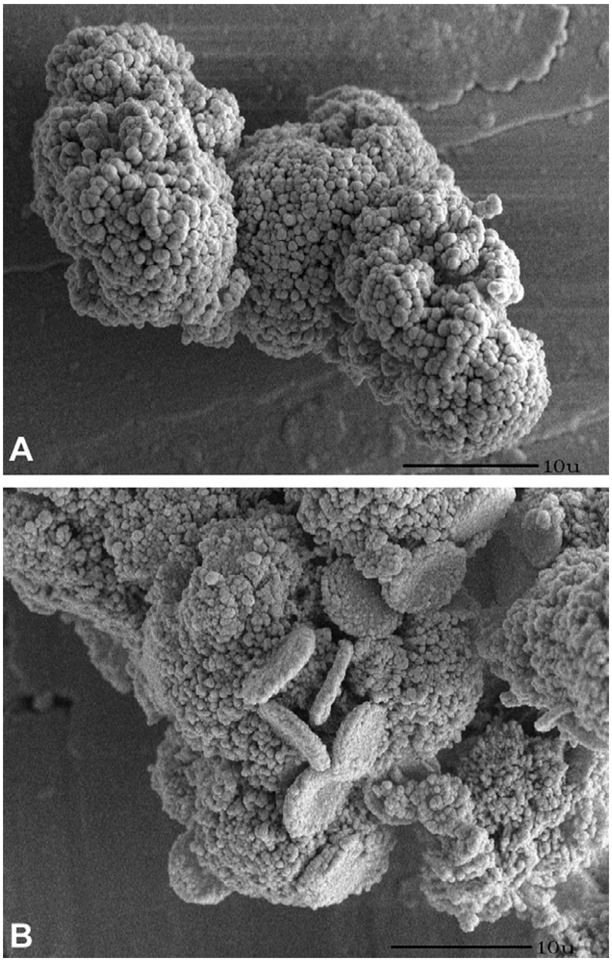

Fig. 9. SEM image of spherical/lobed spherulites formed with oleic acid (Experiment 1, Table 3). Jet cooked dispersion slowly cooled with stirring. (B) SEM image of the spherulite mixture formed with oleic acid (Experiment 2, Table 3). Jet cooked dispersion slowly cooled without stirring.

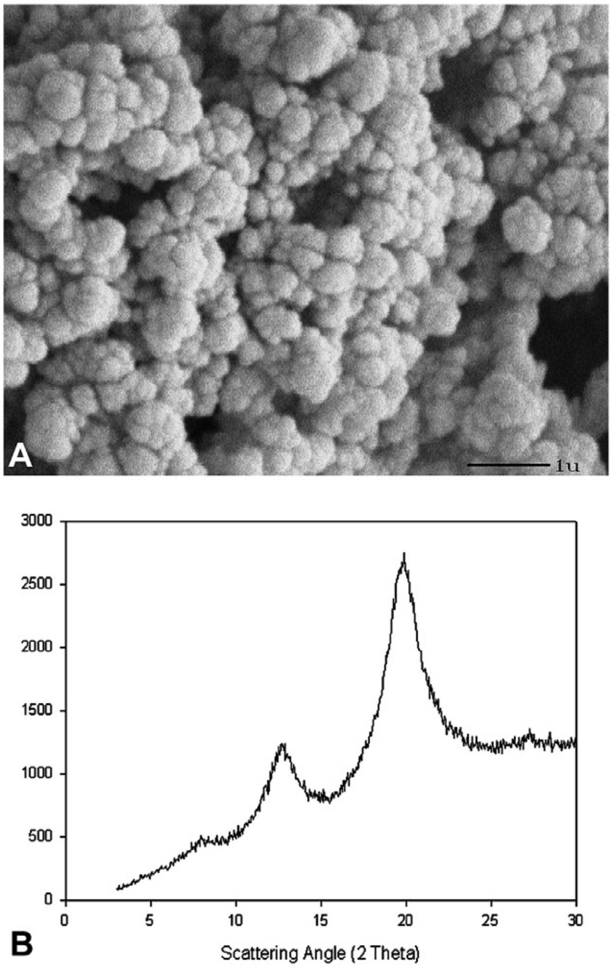

Fig. 10. (A) SEM image of particles formed in Experiment 3 (Table 1). Jet cooked dispersion rapidly cooled in ice. (B) X-ray diffraction pattern of the particles shown in (A).

In a previous study carried out with defatted normal dent cornstarch and a number of pure fatty acids (Fanta et al., 2006), we showed that spherulite morphology can also be influenced by factors other than fatty acid structure. In experiments carried out with palmitic acid, we observed that lower concentrations of palmitic acid yielded mostly the torus/disc species; whereas spherical/lobed and torus/disc spherulites were both formed when the concentration of palmitic acid was increased. X-ray diffraction patterns of the spherical/lobed material showed reflections for both the 6_1V and 7_1V conformations, indicating that it was not necessary that the amylose complexes be in 7_1V conformation for spherulites of this type to form. We also observed that stearic acid and myristic acid yielded spherulite mixtures that were different than those obtained with palmitic acid, even though all of these fatty acids were saturated, straight chain materials and differed only in the length of the alkyl chain. To explain these results, it was suggested that spherulite morphology was also influenced by the rate at which the spherulites are formed, which, in turn, would depend upon factors such as water solubility of the fatty acid, rate of cooling, and the amount of fatty acid used relative to starch. Separation of jet cooked starch dispersions into amylose-rich and amylopectin-rich phases (Kalichevsky & Ring, 1987) would also affect the rate of spherulite formation.

Our previous observation that the spherical/lobed spherulites were the first to form at the highest temperature, whereas the torus/disc spherulites were observed at a lower temperature (Peterson et al., 2005), is consistent with the theory that the rate of spherulite formation plays an important role in the determination of spherulite morphology. When spherulites first begin to form in the slowly-cooled dispersions, spherulite growth is relatively rapid, because the amylose/fatty acid complex is at its maximum concentration. Conversely, as the dispersion cools, less complex is available for spherulite formation; and the formation and growth of spherulites occurs more slowly. The change in morphology from spherical/lobed to torus/disc as the temperature is reduced may thus result from the reduced rate of spherulite formation, and it is possible that the torus/disc morphology is the more thermodynamically stable form of these amylose/fatty acid spherulites. The fact that a greater number large torus/disc spherulites were formed when the jet cooked dispersions were not stirred during the 22 h cooling period may be due to a reduction in the number of spherical/lobed spherulites that rapidly form at high temperature, because of the slow diffusion of amylose/fatty acid complexes in the jet cooked dispersion in the absence of stirring. Under these conditions, more amylose/fatty acid complex would be available for slower formation of the torus/disc species at lower temperatures.

Spherical particles approximately 1 μm or less in diameter were formed when jet cooked dispersions prepared with either palmitic acid or oleic acid were rapidly cooled in ice. These particles resembled those previously observed in slowly cooled dispersions of wheat starch (Fanta et al., 2002), in which the major native lipid components are lysophospholipids rather than fatty acids, and in dispersions of normal dent cornstarch that were either jet cooked with mineral oil or cooled over a period of 4 h (Fanta et al., 2005). In these earlier studies, it was assumed that amylose/lysophospholipid complexes were responsible for the sizes and morphologies of these small particles. In the present study, however, we observed that similar particles were also formed when defatted high amylose starch was jet cooked with either palmitic or oleic acid, indicating that lysophospholipids were not necessary for their formation. It now appears that when the dispersions are cooled rapidly, there is insufficient time for the formation and growth of spherical/lobed and torus/disc spherulites; and precipitation occurs at a lower temperature to form this small-particle species. Precipitation of the amylose–lysophospholipid complexes formed from wheat starch probably occurs at a low temperature, even under slow-cooling conditions, because lysophospholipids are less hydrophobic than fatty acids. Rapid precipitation of amylose/lipid complexes at low temperature might be expected to produce small, poorly-organized clusters of crystallites, as opposed to the ordered structures observed for the spherical/lobed and torus/disc spherulites formed during slow cooling. The broad 6_1V reflections observed in X-ray diffraction patterns of these small particles are consistent with structures of this type. In the present study, small spherical particles were also observed in significant amounts when jet cooked dispersions were not stirred during the 22 h cooling period. As suggested above, diffusion of amylose/fatty acid complexes in these jet cooked dispersions would be relatively slow; and cooling would occur before the complexes could be completely incorporated into the larger spherulites. Significant amounts of the amylose complex would thus be available for low temperature precipitation as micron- and sub-micron particles.

In summary, spherulite morphology appears to be governed by complex interactions between a number of different variables, all of which can be affected by changes in experimental conditions and procedure. Therefore, it should not be surprising that differences in the morphologies and relative amounts of the various spherulite species were observed under different experimental conditions (and even in replicate experiments carried out under similar conditions). Although additional research is needed to fully understand the many factors that influence spherulite formation, our ability to prepare these spherulites in high yields and our increased understanding of the effects of preparative conditions on particle size and morphology will provide a basis for future investigations of end-use applications.

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