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Formation of crystalline aggregates in slowly-cooled starch solutions prepared by steam jet cooking

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Abstract

Spherocrystalline particles were formed in dilute, jet cooked solutions of normal cornstarch, high amylose cornstarch, rice starch and wheat starch, when hot solutions were allowed to slowly cool in insulated Dewar flasks. Yields ranged from approximately 7 to 12%, and particles were composed largely of amylose. Spherocrystals were not obtained from waxy cornstarch, defatted cornstarch or potato starch. Normal cornstarch, high amylose cornstarch and rice starch yielded mixtures of two different particulate species, each having its own unique size and morphology. Both species were strongly birefringent, and no significant loss of birefringence was observed when particles produced from normal cornstarch were heated in water to 97–99°C. Scanning electron microscopy (SEM) showed that smaller-sized particles were disc or torus-shaped and often exhibited spiral surface striations. The larger particles were approximately spherical in shape, and had rough surface textures. Wheat starch yielded only a single spherical small-particle species. X-ray powder diffraction patterns of small particle material matched patterns previously reported for the 6_1 amylose V-helical complex in the hydrated form. In contrast, diffraction patterns for large particle material suggested the 7_1 V-helical conformation for amylose. These results are consistent with the theory that spherocrystalline particles result from crystallization of helical inclusion complexes formed from amylose and the native lipid material present in cereal starch granules. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Spherocrystal; starch; Amylose; Lipid; Complex

1. Introduction

Steam jet cooking is a rapid and continuous process that has been used for decades to prepare aqueous starch solutions for industrial applications (Klem & Brogley, 1981). As part of a continuing research program on starch utilization, we are studying new starch-based compositions prepared by jet cooking mixtures of starch with non-starch materials, such as natural gums, fatty acids, polymers and lipids. In the course of these investigations, we have observed the formation of crystalline particles or spherocrystals in dilute solutions of jet cooked cornstarch, when these solutions were allowed to slowly cool in insulated Dewar flasks. This particulate material is different from retrograded amylose in both size and morphology and is not observed when jet cooked starch solutions are rapidly cooled.

Crystalline aggregates of this general type have been observed previously (Davies, Miller & Procter, 1980; Kitamura, Yoneda & Kuge, 1984; Zobel, 1988; Jane, Kasemsuwan, Chen & Juliano, 1996). Davies et al. [1980] have used the term ‘high temperature retrogradation’ to describe the formation of these spherocrystalline particles and have presented evidence that they result from crystallization of helical inclusion complexes formed from amylose and the native lipid material (particularly fatty acids) normally present in cereal starch granules. In this report, we will expand upon the work of Davies et al. and will show that the spherocrystalline material formed in slowly cooled starch solutions is actually composed of two distinct species that differ in size, morphology, crystal structure and properties.

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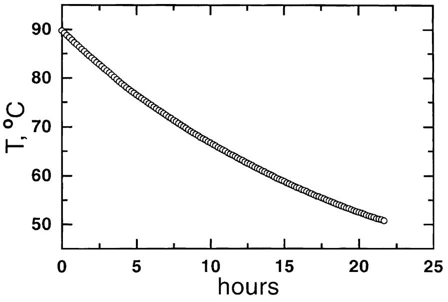

Fig. 1. Plot of time vs temperature for a jet cooked starch solution (approx. 4 kg) collected in a 6l stainless steel Dewar flask and allowed to stand at room temperature for 22 h.

2. Materials and methods

2.1. Materials

Normal, unmodified food grade cornstarch and waxy cornstarch (Waxy No.1) were products of A.E. Staley Mfg.Co., Decatur, Il. High amylose cornstarch (Amylomaize VII) was a product of Cerestar, Hammond, IN. Potato starch, wheat starch and rice starch were purchased from Sigma, St. Louis, MO. Percent moisture was determined by vacuum drying accurately weighed starch samples at 100°C, and all weights of starch are given on a dry weight basis.

Selected starch samples were defatted by extraction with refluxing 85% methanol followed by refluxing 75% *n*-propanol (Fanta, Felker, Shogren & Kunston, 2001; Morrison & Coventry, 1985).

2.2. Jet cooking of starch and isolation of spherocrystalline material

A stirred dispersion of 200 g of starch in 4 l of water was passed through a Penick and Ford Laboratory Model steam jet cooker, operating under excess steam conditions (Klem & Brogley, 1981). Cooking temperature was 140°C (back pressure: 40 psig (2.8 kg/cm^2 gauge pressure) steam), and steam line pressure was 70 psig (4.9 kg/cm^2 gauge pressure). Pumping rate through the cooker was about 1 liter/min. The hot, cooked starch solution (4.0–4.3 kg) was collected in a 6 l stainless steel Dewar flask. Cooked solutions typically contained 4.3 ± 0.1% starch solids, determined by freeze drying an accurately weighed portion of the solution. A thermocouple probe was inserted through the cork cover of the Dewar flask, and the hot dispersion was allowed to stand at room temperature and slowly cool without stirring for a period of 22 h. Plots of time vs temperature during this cooling period were obtained using an OMB TempBook/66 thermocouple data acquisition system purchased from Omega, Stamford, CT. A typical plot is shown in Fig. 1. A 300 g portion of cooled dispersion (temperature 50–55°C) was diluted with 2700 g of water (25°C), stirred for 30 min, and then centrifuged at 25°C for15 min at 3000 rpm (approx. 2000 × *g*) in a Beckman GS-6KR centrifuge. The precipitated solid was washed twice with excess water to remove dissolved starch and was then freeze-dried. Yield was calculated from the weight of freeze-dried solid. This procedure was also repeated on a larger scale to obtain sufficient material for fractionation and characterization. The water-washed, undried precipitate was fractionated with respect to particle size by allowing a water dispersion of the precipitate to partially settle, leaving the smaller particles in suspension. Light microscopy was used to monitor the efficiency of this fractionation procedure.

Table 1
Yield of spherocrystals from different starch types

Experiment #	Starch type	Yield (%)
1	Normal corn	7.6
2	Normal corn, defatted	0
3	Waxy corn	0
4	High amylose corn	12.0
5	High amylose corn, defatted	0.4
6	Rice	7.9
7	Potato	0
8	Wheat	10.2

2.3. Scanning electron microscopy (SEM)

An aqueous dispersion of particulate material (200 μl) was added to 20 ml of absolute ethanol, and the solid was allowed to settle. The settled solid was washed with ethanol and was then critical point dried on aluminum stubs using supercritical CO$_2$. Dried specimens were sputter coated with gold–palladium and examined with a JEOL 6400 V scanning electron microscope.

2.4. X-ray diffraction

X-ray diffraction was carried out as described previously

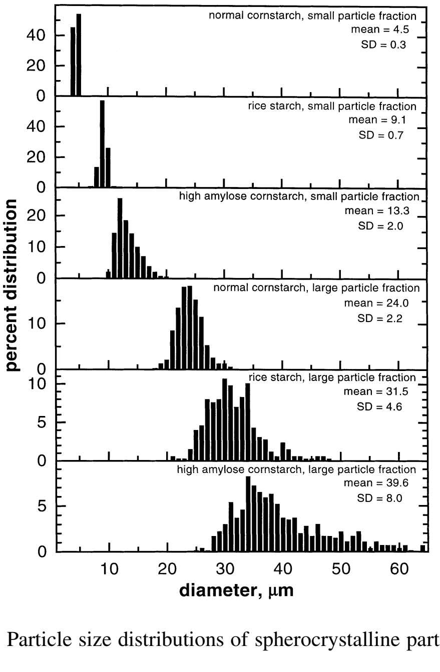

Fig. 2. Particle size distributions of spherocrystalline particles.

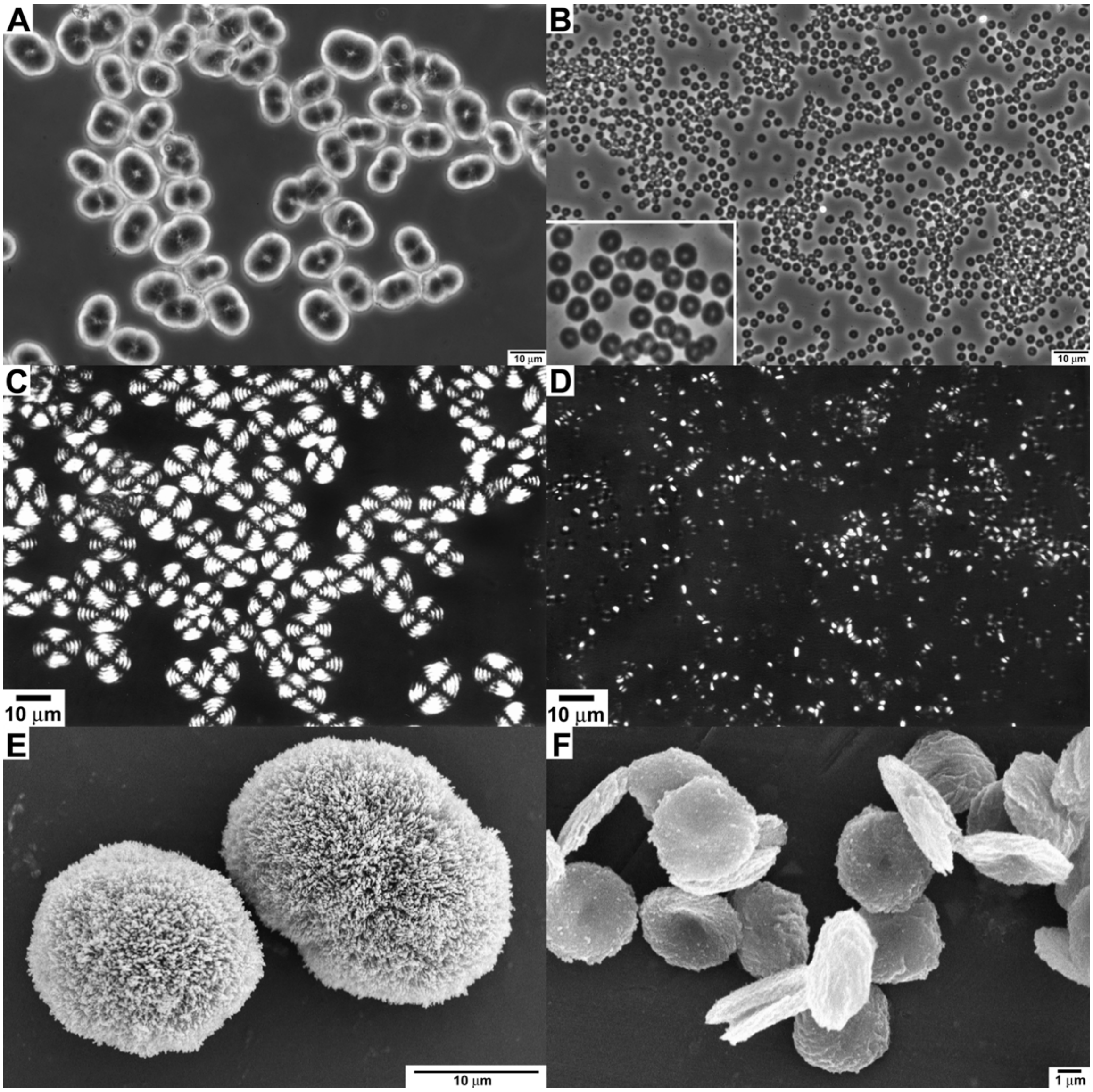

Fig. 3. Micrographs of spherocrystals formed from normal cornstarch (experiment 1, Table 1). (A) Phase contrast light micrograph of large particle spherocrystals. (B) Phase contrast light micrograph of small particle spherocrystals (inset is at higher magnification). (C and D) Same as A and B, except viewed with polarized light. (E) SEM of large particle spherocrystals. (F) SEM of small particle spherocrystals.

(Fanta et al., 1999). Freeze-dried samples were equilibrated at 23°C and 45% relative humidity for 2 days prior to analysis.

2.5. *Differential scanning calorimetry*

Thermograms were obtained with a Perkin–Elmer DSC7 instrument equipped with a CCA7 liquid nitrogen cooling accessory. The melting temperatures and enthalpies of indium and water were used for calibration. Starch samples (approx.10 mg) were added to stainless steel, high pressure DSC pans followed by addition of about 40 mg of distilled water. Pans were allowed to equilibrate overnight prior to DSC testing. Samples were heated in the DSC from 20 to180°C at 10°C/min. Melting temperatures and enthalpies were calculated using DSC7 software.

2.6. *Determination of amylose*

Lipid was extracted from spherocrystal samples prior to colorimetric analysis by heating 0.2–0.4 g of sample for 2 h under reflux with 50 ml of 75% *n*-propanol–water. Solid was separated by filtration, and the extraction procedure was repeated two additional times under the same conditions. The extracted solid was allowed to air-dry overnight and was then vacuum dried at 55°C for 6–7 h. Percent amylose was determined by measuring the absorbence of the blue amylose–iodine complex in urea–dimethylsulfoxide solution (Morrison & Laignelet, 1983). A standard curve of absorbence vs % amylose was prepared by analyzing known mixtures of corn amylose (same used by Knutson, 1986) and waxy cornstarch.

2.7. Effect of heating on birefringence

A water dispersion of spherocrystals prepared from normal food grade cornstarch was heated to 97°C at 2°C/min on a covered glass microscope slide using an Instec STC200 hot-stage and temperature controller (Instec, Broomfield, CO). A sample of the same material was also heated for 10 min at 98–99° in a boiling water bath and then examined for birefringence.

2.8. Particle size analysis

Particle diameter was measured by digital analysis of representative phase contrast micrographs of washed, fractionated samples using Origin software (Microcal, Northampton, MA). The number of particles analyzed ranged from 327 to 982 per sample.

3. Results and discussion

Spherocrystalline particles were formed from normal cornstarch, high amylose cornstarch, rice starch and wheat starch, when jet cooked solutions of these starches were collected in insulated Dewar flasks and allowed to slowly cool. Yields ranged from about 7 to 12% (Table 1). Spherocrystals were not observed when defatted normal cornstarch, waxy cornstarch and potato starch were jet cooked and cooled under the same conditions. In contrast to experiment 1 in the table, only a 0.25% yield of insoluble solid (which appeared to consist largely of retrograded amylose) was obtained when a jet-cooked solution of normal cornstarch was allowed to rapidly cool in a non-insulated stainless steel beaker (data not shown).

Although Davies et al. [1980] reported only one type of spherocrystalline particle, microscopy of particulate material isolated from normal cornstarch, high amylose cornstarch and rice starch revealed that two distinct particle types, widely different in both size and morphology, are formed from each of these starch varieties. These two species could be conveniently separated according to particle size by dispersing the material in excess water and then allowing the large particle fraction to rapidly settle, leaving the smaller particles in suspension. Particle size distributions of the various fractions are shown in Fig. 2, along with calculated values for mean particle size and standard deviation. Although both species were strongly birefringent, experiments carried out with normal cornstarch showed that gentle pressure on the cover slip caused the large particle material to fracture and fragment, thus altering and reducing the intensity of the birefringence pattern. Similar observations were reported by Davies et al. [1980]. The small particle fraction was not as easily fractured. Heating aqueous dispersions of these two fractions for10 min at 97–99°C resulted in no significant loss of birefringence. The observation of birefringence in these spherocrystals (i.e. maltese cross pattern) implies that polysaccharide chains are oriented (compare with native starch granules, in which chains are oriented radially).

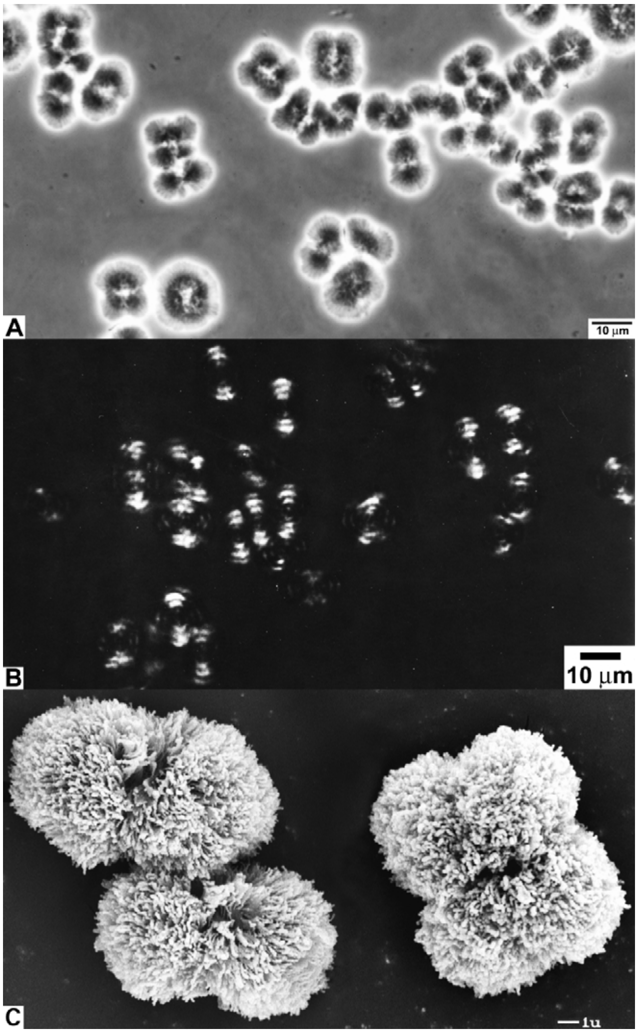

Fig. 4. Micrographs of large particle spherocrystals formed from normal cornstarch. About half the amount of starch solution was collected in the Dewar flask to provide a more rapid rate of cooling. (A) Phase contrast light micrograph. (B) Same as A, except viewed with polarized light. (C) SEM.

Phase contrast light micrographs and SEM images of the two particulate species formed from normal cornstarch (experiment 1, Table 1) are shown in Fig. 3, along with birefringent patterns observed under polarized light. Critical point drying of specimens prior to examination by SEM revealed details in morphology not seen in earlier SEM images published by Davies et al. (1980). Spherocrystals comprising the small particle fraction (mean diameter 4.5 μm) were disc-shaped with depressions in the center, and a regular surface striation pattern was faintly visible. In contrast, spherocrystals comprising the large particle fraction (mean diameter 24.0 μm) were approximately spherical, and surface textures were coarse and rough.

Size, morphology and amounts of the two particulate species varied with minor (and sometimes very subtle) changes in experimental conditions. For example, when a

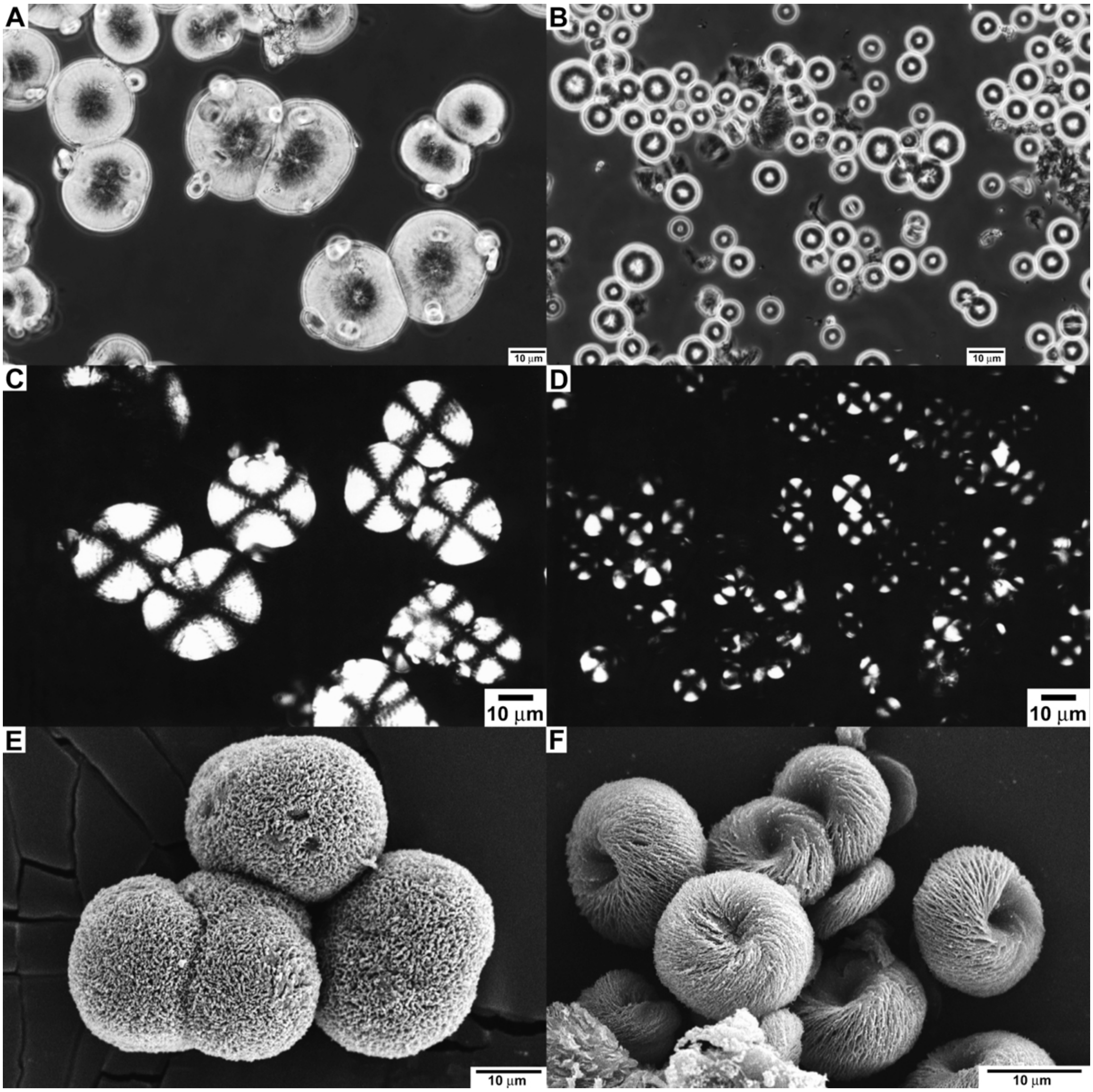

Fig. 5. Micrographs of spherocrystals formed from high amylose cornstarch (experiment 4, Table 1). (A) Phase contrast light micrograph of large particle spherocrystals. (B) Phase contrast light micrograph of small particle spherocrystals. (C and D) Same as A and B, except viewed with polarized light. (E) SEM of large particle spherocrystals. (F) SEM of small particle spherocrystals.

jet cooked normal cornstarch solution prepared as in experiment 1, Table 1, was magnetically stirred during the 22 h cooling period, the small, disc-shaped particles had a more flattened appearance. Also the large particle material was smaller in size (roughly 15 μm; mean diameter not determined), and some particles were oblong in appearance. When experiment 1 was repeated with about half the amount of starch solution (to provide a more rapid cooling rate) some of the large particle material had a two-lobed or four-lobed appearance (Fig. 4). A wide variation in the weight ratio of large and small spherocrystals (11.7/1 and 0.45/1) was also observed in two repeat experiments carried out under the conditions of experiment 1, despite the fact that the conditions used were outwardly identical.

High amylose cornstarch (experiment 4, Table 1) yielded particles having a somewhat different size and morphology than those obtained from normal cornstarch (Fig. 5). The small particle species was thicker and more rounded than its normal cornstarch Analogue, and the mean diameter of this fraction was 13.3 μm. Also, depressions in the centers of these particles were more pronounced, giving them a torus-like appearance. Particle surfaces showed distinct, regularly spaced striations having a uniform spiral pattern. The larger, more spherical species had a mean diameter of 39.6 μm; and some of these particles had smaller, torus-shaped particles imbedded in their surfaces. Fig. 6 shows the interior of one of these large particles that was fractured during the isolation procedure.

Spherocrystals were also formed in slowly cooled solutions of rice starch (experiment 6, Table 1); and

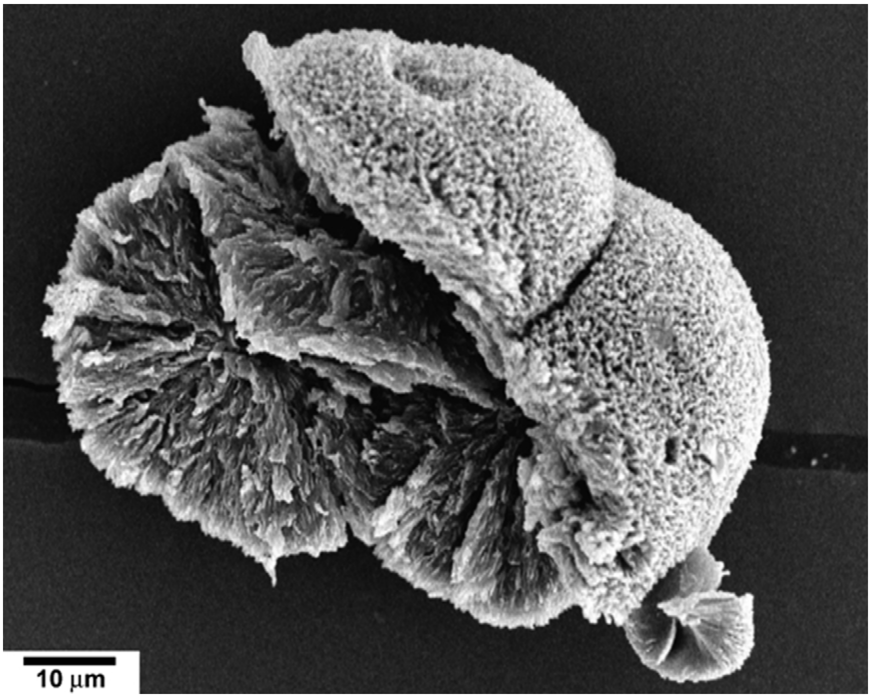

Fig. 6. SEM image of large particle spherocrystals formed from high amylose cornstarch (experiment 4, Table 1). Particles were fractured during the isolation procedure.

micrographs of the two particulate materials formed are shown in Fig. 7. The small particle material had a mean particle diameter of 9.1 μm; and, except for slight differences in surface morphology, were similar in appearance to analogous material isolated from high amylose cornstarch. The larger, more spherical particles were similar in surface morphology to those formed from cornstarch and had a mean diameter of 31.5 μm.

Although wheat starch (experiment 8, Table 1) yielded a solid precipitate in amounts roughly comparable to the other cereal starches, only a single particulate species was observed. These particles were roughly spherical in shape and had diameters of only about 1 μm (Fig. 8; mean diameter not determined). The surface morphology of these particles suggests that they might have formed through aggregation of smaller sub-micron material.

The fact that neither waxy cornstarch (experiment 3, Table 1) nor defatted normal cornstarch (experiment 2, Table 1) formed spherocrystals in slowly cooled, jet-cooked solutions substantiates the conclusion of Davies et al. (1980) that these particles result from crystallization of helical inclusion complexes formed from amylose and native lipid associated with the cereal starch granule. The composition and amount of native lipid material present in various cereal starches has been discussed by Morrison (1988). Potato starch, which contains about 21% amylose but only about 0.05% lipid (Swinkels, 1985), also did not yield any spherocrystalline material (experiment 7, Table 1). A small amount of insoluble solid (0.4% yield) was isolated from a jet-cooked dispersion of defatted high amylose cornstarch (experiment 5, Table 1); however, the particles were irregular in shape and exhibited a B-type X-ray diffraction pattern, suggesting that this material is largely retrograded amylose. Additional evidence that spherocrystals are formed by crystallization of amylose inclusion complexes is provided by the data in Table 2, which shows that spherocrystal fractions isolated from normal cornstarch, high amylose cornstarch, rice starch, and wheat starch are composed largely of amylose. Percentages in excess of 100% probably result from subtle differences in structure and iodine binding capacity between amylose in the spherocrystals and the corn amylose used to prepare the standard curve for the analytical procedure.

X-ray powder diffraction scans of small and large particle spherocrystal fractions isolated from normal and high amylose cornstarch are shown in Figs. 9 and 10, respectively. For both starch varieties, the small particle fractions exhibited X-ray reflections at 7.5, 12.9, 19.8 and 22.3° two theta with corresponding *d* spacings of 11.8, 6.86, 4.48 and 3.98 Å, respectively. These data match closely the pattern found previously for the well-known 6_1 amylose V-helical complex in the hydrate form (Mikus, Hixon & Rundle, 1946; Zobel, French & Hinkle, 1967; Zobel, 1988). When indexed as an orthorhombic unit cell, the second reflection has $hkl = 200$; and the helix diameter is thus $2 \times 6.86 = 13.7$ Å, in agreement with literature values (Mikus et al., 1946; Zobel et al., 1967; Zobel, 1988).

X-ray patterns for the large particle fractions showed major reflections at 6.83, 11.7, 12.9, 18.1 and 20° two theta ($d = 12.9$, 7.5, 6.8, 4.9 and 4.5 Å). This pattern

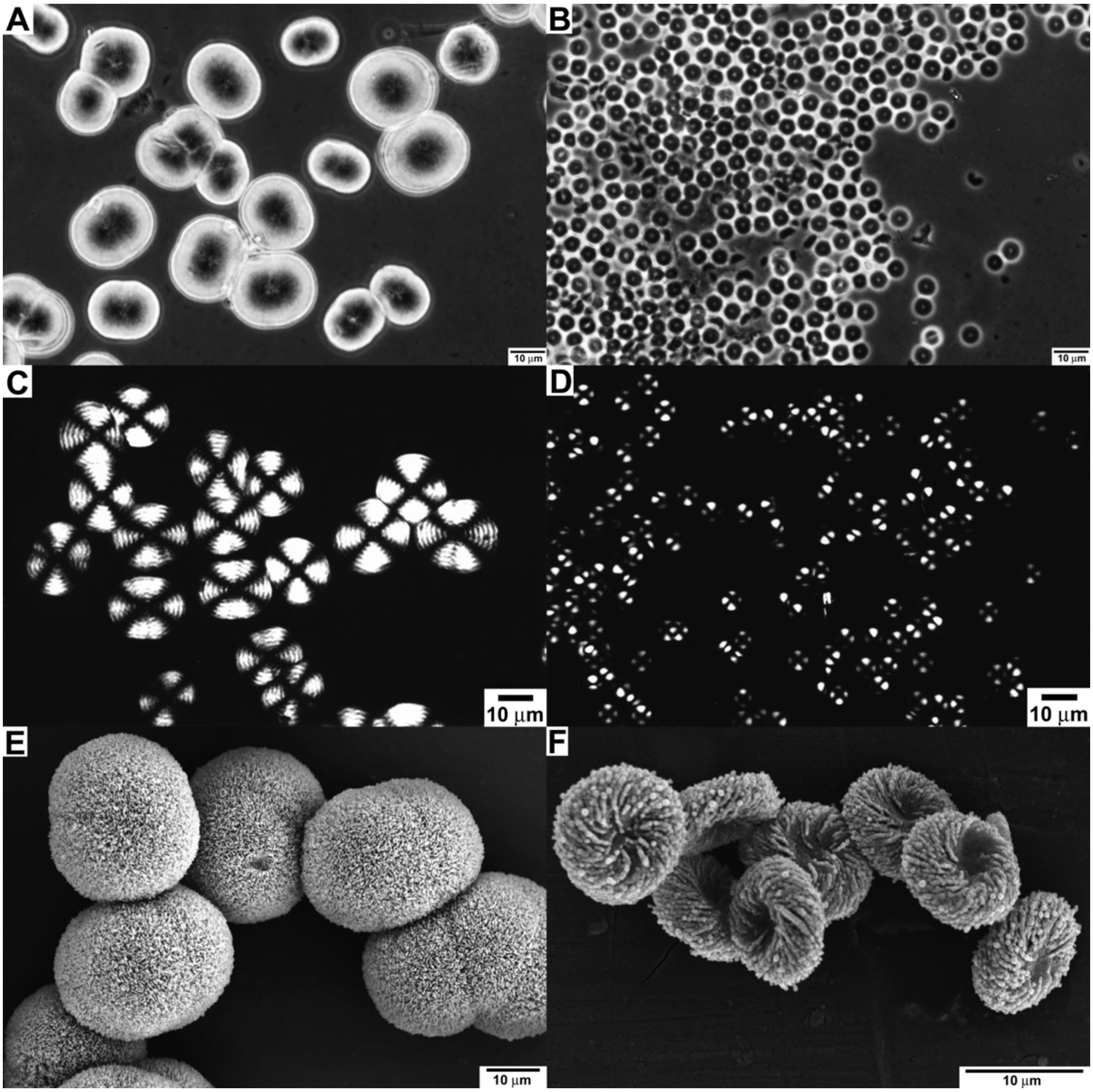

Fig. 7. Micrographs of spherocrystals formed from rice starch (experiment 6, Table 1). (A) Phase contrast light micrograph of large particle spherocrystals. (B) Phase contrast light micrograph of small particle spherocrystals. (C and D) Same as A and B, except viewed with polarized light. (E) SEM of large particle spherocrystals. (F) SEM of small particle spherocrystals.

resembles the V pattern, except that reflections are in part shifted to smaller scattering angles, indicating that helix spacings have increased. These findings thus suggest that the larger diameter spherocrystals contain amylose in the 7_1 V-helical conformation. This conclusion is supported by previous studies of amylose in the purported 7_1 (wet) form which showed major reflections at approximately 6.8, 11–13, 18 and 20° two theta (Yamashita & Hirai, 1966; Yamashita, Ryugo & Monobe, 1973; Takeo, Tokumura & Kuge, 1973). The 7_1 V-helical form is commonly found when amylose forms complexes with bulky molecules such as *i*-propanol or *t*-butanol. The helix diameter calculated from our data is $2 \times 7.5 = 15Å$, and this value is in agreement with a value of 15.0 Å reported previously (Takeo et al., 1973). Yamashita and coworkers (Yamashita & Monobe, 1971; Yamashita et al., 1973) also provided evidence that single crystals of amylose complexed with α-naphthol and quinoline were in the 8_1 V-helical conformation.

More detailed diffraction studies would be needed to confirm the supposition that large diameter spherocrystals contain amylose in the 7_1 V-helical conformation. As pointed out by French and Murphy (1977), detailed diffraction intensity calculations have not been carried out for such V-patterns; and atomic positions have thus not been ascertained. However, French and Murphy further state that there is no reason to doubt that such 7_1 V-helical conformations exist; and that only small changes in glycosidic torsion angles are required to effect the change from a 6_1 to 7_1 helix. Recent electron diffraction studies of amylose–α-napthol complexes by Winter, Chanzy, Putaux and Helbert

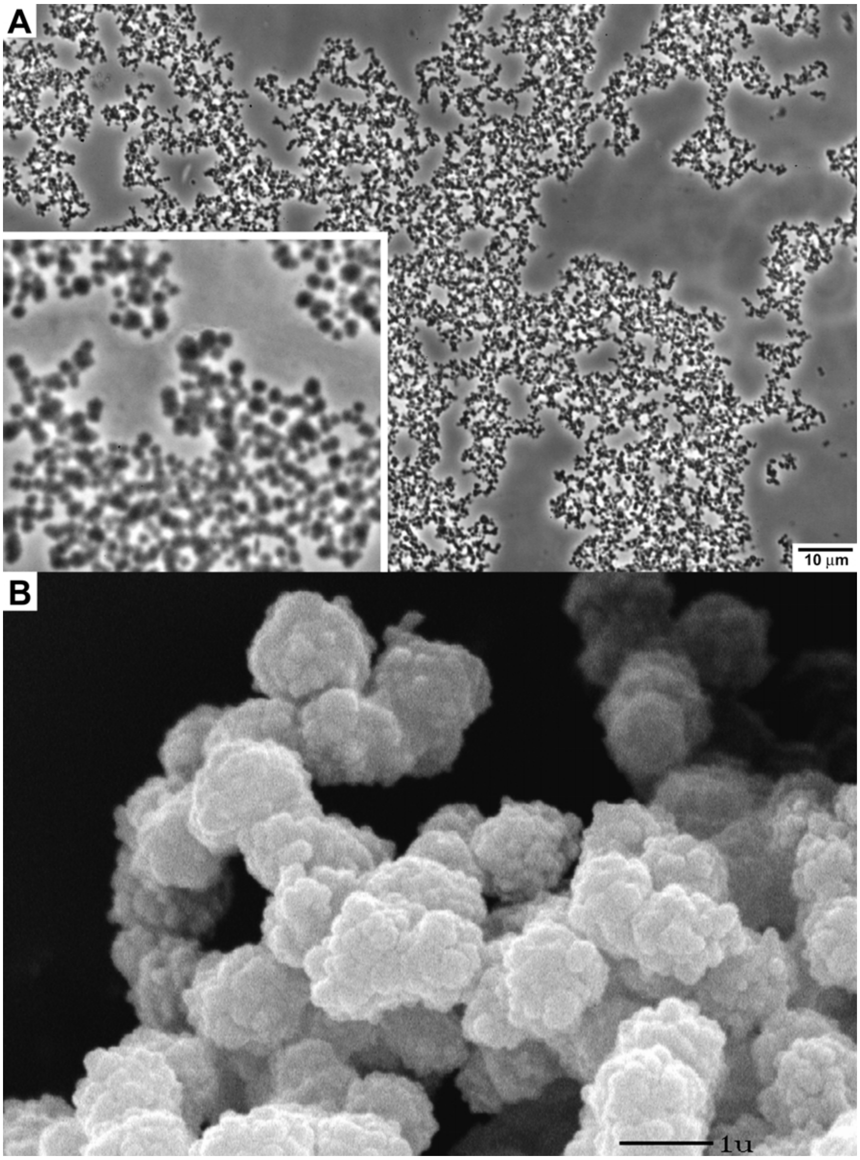

Fig. 8. Micrographs of spherocrystals formed from wheat starch (experiment 8, Table 1). (A) Phase contrast light micrograph (inset is at higher magnification). (B) SEM.

(1998) have provided atomic level detail of 8_1 amylose V helices, indicating that large diameter amylose complexes do indeed exist.

X-ray diffraction patterns for small- and large particle spherocrystal fractions isolated from jet cooked rice starch (patterns not shown) were similar to those shown in Fig. 9 for normal cornstarch. The diffraction pattern for the precipitated solid isolated from wheat starch (pattern not shown) was also similar to the pattern for the small particle cornstarch fraction in Fig. 9, except for the fact that the wheat starch diffraction peaks were wider, indicating a smaller crystallite size.

Table 2
Amylose content of spherocrystal fractions

Starch	Fraction	% Amylose
Normal corn	Small particle	97
	Large particle	96
High amylose corn	Small particle	110
	Large particle	109
Rice	Small particle	94
	Large particle	98
Wheat		103

DSC heating curves for small- and large particle spherocrystal fractions isolated from normal and high amylose cornstarch are shown in Fig. 11. The small, sharp endotherms seen in some of the thermograms are probably due to a small amount of water movement and condensation in the stainless steel pans. This should not, however, affect the starch melting temperatures or enthalpies described below. Single melting endotherms were seen for the small

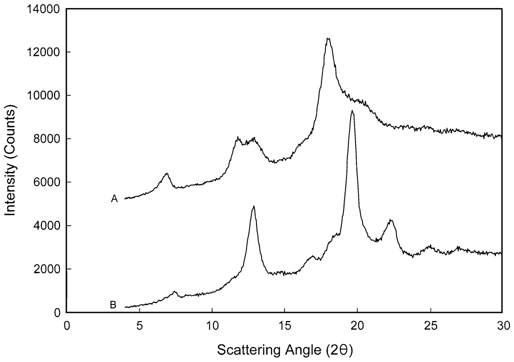

Fig. 9. X-ray powder diffraction scans of spherocrystals isolated from normal cornstarch (experiment 1, Table 1). (A) Large particle fraction. (B) Small particle fraction.

particle fractions at about 115°C. This is similar to melting temperatures of 114–121°C published previously for amylose–stearic acid complexes which had been formed at high temperatures (80–90°C) (Karkalas, Ma, Morrison & Pethrick, 1995). For the large-diameter fractions, two endotherms were observed, one at 90–105°C and another at about 115°C. The lower temperature peak may be due to melting of the 7_1 amylose V-complex crystals followed by recrystallization to the 6_1 form and melting of the latter. A mixture of both forms, however, cannot be ruled out. DSC studies of 7_1 amylose V-complexes have not been previously reported in the literature. Modeling of 7_1 and 8_1 amylose V-helices has suggested that these may by less stable than the 6_1 helix due to longer H-bond distances and more strained glycosidic angles in the expanded helices (French & Murphy, 1977; Winter et al., 1998). Thus, a lower melting temperature might be expected for the 7_1 and 8_1 amylose V-complexes than for 6_1 helices.

Reasons why these amylose–lipid complexes form precipitates having different crystalline and morphological forms at high annealing temperatures are unknown. The various factors involved may include lipid type, ratio of lipid to amylose, temperature, and viscosity (i.e. starch concentration in water). For example, Collona, Buleon and Mercier (1987) found that extrusion of cornstarch at 22% moisture and temperatures of >170°C gave X-ray patterns similar to that of amylose complexed with *t*-butanol, which these authors termed the ‘E-type’ structure. Reconditioning the product to >30% moisture always transformed the E-type to the more stable V-type structure. Karkalas et al. (1995) found that complexes of amylose with *cis*-unsatuated fatty acids melt at lower temperatures than complexes formed from saturated fatty acids. They advanced the hypothesis that the bent *cis*-fatty acids may be bulky enough to cause the formation of enlarged 7_1 amylose complexes, but no evidence for this was presented. They also found that ternary mixtures of amylose with stearic acid and linoleic acid tend to form separate complexes when cooled. Since the native lipid in cornstarch consists of a mixture of about 62% free fatty acids (about 2/3 of which are unsaturated) and about 25% lysophospholipid (Karkalas et al., 1995; Galliard & Bowler, 1987), the opportunity exists for the formation and crystallization of different spherocrystalline types. It has also been shown that the type of V-complex can be changed by varying the ratio of amylose to *n*-propionic acid (Takeo et al., 1973) or salicylic acid (Oguchi, Yamasato, Limmatvapirat, Yonemochi & Yamamoto, 1998).

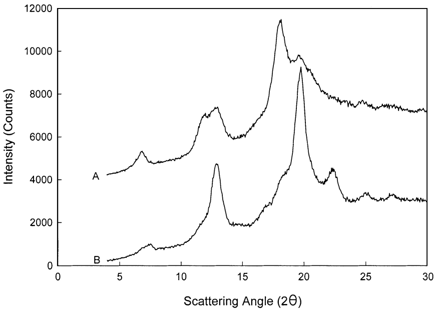

Fig. 10. X-ray powder diffraction scans of spherocrystals isolated from high amylose cornstarch (experiment 4, Table 1). (A) Large particle fraction. (B) Small particle fraction.

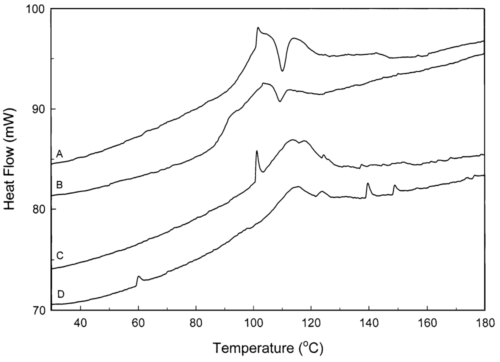

Fig. 11. DSC heating curves for spherocrystals isolated from normal and high amylose cornstarch. (A) Large particle fraction from high amylose cornstarch. (B) Large particle fraction from normal cornstarch. (C) Small particle fraction from high-amylose cornstarch. (D) Small particle fraction from normal cornstarch.

Work on the structure and properties of these spherocrystalline materials is continuing, and future research will center on the identification of lipids responsible for the formation of different morphological species.

4. Summary and conclusions

Spherocrystalline aggregates were formed in dilute, jet-cooked solutions of normal cornstarch, high amylose cornstarch, rice starch and wheat starch, when these solutions were allowed to cool slowly in insulated Dewar flasks. Yields ranged from approximately 7 to 12%. Spherocrystals were not obtained from dispersions of waxy cornstarch, defatted cornstarch or potato starch. Since amylose and native lipid both seem to be essential for spherocrystal formation, these materials apparently result from crystallization of helical inclusion complexes formed from amylose and the native lipid normally present in cereal starch granules. Also, colorimetric analyses of these spherocrystalline aggretates showed that they are composed primarily of amylose.

Normal cornstarch, high amylose cornstarch and rice starch each yielded two different spherocrystalline species; and each of these species exhibited its own unique size distribution and morphology. The smaller of the two species was disc or torus-shaped, and spiral surface striations were often observed. The larger particles were approximately spherical in shape, and surface textures were coarse and rough. Spherocrystals were strongly birefringent, and birefringence was not lost when water dispersions were heated. The exact size, shape and relative amounts of these two species varied with experimental conditions and were influenced by minor variations in the cooking and cooling process. A single small-particle species was formed from wheat starch, and the morphology of this material was different from that of particles formed from the other cereal starches.

X-ray powder diffraction scans of small particle spherocrystals isolated from normal cornstarch, high-amylose cornstarch and rice starch closely matched patterns found previously for the 6_1 amylose V-helical complex in the hydrate form. In contrast, X-ray diffraction patterns for large particle spherocrystals suggest that amylose is in the 7_1 V-helical conformation. The X-ray diffraction pattern for wheat starch spherocrystals was similar to patterns observed for small particle spherocrystals formed from other cereal starches, except that the diffraction peaks for the wheat starch product were wider, indicating a smaller crystallite size.

DSC heating curves for the small particle spherocrystals formed from normal and high amylose cornstarch showed single melting endotherms with melting temperatures similar to those published previously for amylose–stearic acid complexes. Two endotherms were observed for the large particle fractions, one of which may be due to melting of the 7_1 amylose V-complex.

This study confirms the earlier conclusion of Davies et al. [1980] that spherocrystals formed in slowly cooled cereal starch dispersions result from crystallization of helical inclusion complexes formed from amylose and native lipid components of the cereal starch granule. Questions that remain to be answered are: (1) what are the chemical structures of lipids complexed with amylose in the two different spherocrystalline species? (2) What factors are responsible for the unique morphologies observed for these materials? (3) How are amylose chains ordered, and what is the amylose chain length? (4) Can cooling conditions be altered to favor either small or large spherocrystals? (5) Can lipids be added to increase yields? (6) Are there commercial applications for these spherocrystals? Work is currently in progress to provide answers to these questions.

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