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Preparation and properties of amylose complexes prepared from hexadecylamine and its hydrochloride salt☆

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ABSTRACT

Amylose inclusion complexes were prepared from jet-cooked aqueous mixtures of high amylose corn starch and 1-hexadecylamine (HDA). Slow-cooling produced torus/disc-shaped spherulites, whereas aggregates of smaller spherulites were obtained by rapid-cooling in ice. The morphologies and 6_1V X-ray diffraction patterns of these spherulites were similar to those of spherulites obtained previously with palmitic acid, indicating that spherulite morphology is influenced largely by the hydrophobic structure of the carbon chain of the complex-forming ligand and to a lesser extent by the nature of the more polar head group. Water soluble, cationic amylose inclusion complexes were prepared by adding an aqueous solution of the HCl salt of HDA to a jet-cooked dispersion of high amylose starch. The cationic nature of these HDA·HCl complexes suggests possible applications as flocculating agents for water purification and as retention aids in papermaking.

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1. Introduction

Steam jet-cooking at high temperature and pressure is a rapid and continuous process that is widely used to prepare aqueous starch dispersions for commercial applications (Klem & Brogley, 1981). We have used this processing method to prepare amylose inclusion complexes from fatty acids and fatty acid salts and have characterized the spherulites that are formed when the dispersions are cooled (Fanta, Felker, Shogren, & Salch, 2006; Fanta, Felker, Shogren, & Salch, 2008; Fanta, Kenar, Byars, Felker, & Shogren, 2010). To our knowledge, there has been only a limited amount of research related to the formation of inclusion complexes from amylose and organic amines. Kuge and Takeo (1968) reported that diethylamine, triethylamine, diphenylamine and triphenylamine failed to give complexes with amylose. These results are not surprising, since the alkylamines tried are quite soluble in water, while the bulky nature of the aromatic amines may have inhibited complex formation. The formation of inclusion complexes from amylose and dodecylamine was recently reported by Li and coworkers (Li, Li, Zang, & Zou, 2012). Although a longer-chain organic amine was used in this study, the use of steam jet-cooking to prepare amylose complexes from fatty amines and fatty amine salts in quantities large enough to study their properties and potential applications has not been described.

In this study, we have investigated the steam jet-cooking of aqueous mixtures of high amylose starch and 1-hexadecylamine (HDA). HDA is a fatty amine of low water solubility composed of a hydrophobic C_{16} alkyl chain which can be complexed by amylose. HDA is a weak base with a pK_a of 9.9, and the amine group can be protonated by a strong acid (such as HCl) to give the corresponding hexadecylamine hydrochloride salt (HDA·HCl), which is more water soluble due to its positive charge (Slabaugh & Cates, 1955; Sonntag, 1964).

The differences in spherulite morphology that result from slow-cooling vs. rapid-cooling of the hot, jet-cooked dispersions will be described, and the spherulites formed will be compared with those previously obtained when palmitic acid was used as the complex-forming ligand. Since HDA and palmitic acid both have similar C_{16} saturated carbon chains, but differ in the chemical nature of the polar head group (i.e., amine vs. carboxylic acid), comparison of the spherulites formed from these two ligands would enable us to determine the influence of the head group of the complex-forming ligand on the morphologies of the spherulites that form in these cooled, jet-cooked dispersions. The preparation and properties of a water soluble amylose inclusion complex

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from the hydrochloric acid salt of HDA will also be described. The amylose complex formed from this ligand will have cationic properties analogous to those of cationic starches that are prepared by chemical reaction of the hydroxyl groups of starch with cationic reagents, and that are used as flocculating agents for water treatment and as retention aids in papermaking. Although Eliasson and coworkers have prepared cationic amylose inclusion complexes from hexadecyltrimethylammonium bromide and have studied their properties (Eliasson, 1988; Eliasson, Finstad, & Ljunger, 1988; Lundqvist, Eliasson, & Olofsson, 2002), the properties of these quaternary ammonium complexes differ from those prepared from HDA·HCl. The water-soluble HDA·HCl ligand within the amylose helix is converted to water-insoluble HDA under alkaline conditions, and this transformation results in an increase in solution viscosity followed by precipitation of the complex as micrometer-size spherulites at high pH.

The large number of industrial processes and wastewater management issues in which flocculation serves an important purpose has resulted in many research efforts aimed at exploring more cost-effective, efficient, and biodegradable flocculants. Among the broad categories of inorganic salts, synthetic polymers, and natural organic materials, covalently modified starch has received much attention, as detailed in several recent reports (Ghimici & Nichifor, 2010; Lin et al., 2012; Pal, Sen, Ghosh, & Singh, 2012; Shi, Ju, & Zhang, 2012; Zou, Zhu, Wang, Sui, & Fan, 2011; and references therein). The ability of cationic, water-soluble inclusion complexes of amylose with fatty amine salts to be produced from readily available feedstocks by continuous thermomechanical processing would provide a potentially useful alternative to the costly chemical modification of starch, or to the use of synthetic polymers.

2. Materials and methods

2.1. Materials

High-amylose corn starch (AmyloGel 03003) containing 70% apparent amylose and a moisture content of 10% was a product of Cargill, Minneapolis, MN. Percent moisture was calculated from weight-loss after drying at 100 °C under vacuum, and all starch weights are given on a dry weight basis. Starch was defatted by extraction with 85% methanol–water followed by refluxing 75% *n*-propanol-water (Fanta, Felker, & Shogren, 2002; Morrison & Coventry, 1985). 1-Hexadecylamine (HDA), 98%, was purchased from Aldrich, Milwaukee, WI.

2.2. Preparation of amylose–HDA complexes by steam jet-cooking and isolation of spherulites from cooled, jet-cooked dispersions

Mixtures of high amylose corn starch and HDA were prepared by dissolving 3.15 g of HDA in 20 mL of ethanol and then mixing the solution with 60.0 g of high amylose corn starch. The ethanol was then allowed to evaporate at room temperature. This weight of HDA corresponds to 7.5% of the weight of amylose in 60 g of starch with an apparent amylose content of 70%. The starch–HDA mixtures were dispersed in 1200 mL of water, and the dispersions were passed through a Penick & Ford Laboratory Model steam jet-cooker (Penford Corp., Englewood, CO) operating under excess steam conditions (Klem & Brogley, 1981). Temperature in the hydroheater was 140 °C, the steam back pressure was 380 kPa (40 psig), and the steam line pressure from the boiler was 550 kPa (65 psig). Pumping rate through the jet-cooker was 1 L/min. The jet-cooked dispersion was collected in an insulated Dewar flask that was previously heated with 100 °C water from the jet-cooker. The wt% of solids in the jet-cooked dispersion was determined by freeze-drying weighed portions of dispersion. Values for % solids were on the order of 4%; however, variations in % solids were observed due to dilution of the mixtures with varying amounts of condensed steam.

To form spherulites under slow-cooling conditions, the insulated Dewar flask containing the jet-cooked dispersion was allowed to stand at ambient room temperature without stirring for 22 h. Temperatures during cooling were recorded with an OMB TempBook/66 thermocouple data acquisition system (Omega, Stamford, CT). Initial and final temperatures were 93 °C and 53 °C, respectively. After the 22 h cooling period, the dispersions were cooled to 30 °C and then diluted with water to give a 10-fold reduction in concentration. Spherulites were isolated from the diluted dispersions by centrifugation (Sorvall Legend centrifuge equipped with Fiberlite F14-6X250 rotor, Thermo Fisher Scientific, Hanover Park, IL). Centrifugation time was 30 min at 3500 rpm (1900 × *g*). To remove soluble starch, the spherulites were washed twice by dispersing in 100 mL of fresh water followed by centrifugation. The washed spherulites were then freeze-dried. In addition to the spherulites, some small particulate material was also observed in these preparations, and this material was separated by dispersing the solid in water and then allowing the larger spherulites to settle, leaving the small particles in suspension. The weight of small particulate material was 1–2% of the total weight of solid.

To form spherulites under rapid-cooling conditions, the hot, jet-cooked dispersions were transferred to a 2 L beaker and cooled to 25 °C in an ice-water bath. The time required for cooling was 10 min. The cooled dispersions were diluted 10-fold with water, and the spherulites were isolated as described above.

2.3. Preparation of the hydrochloric acid salt of HDA (HDA·HCl) and preparation of amylose complex by addition of a water solution of HDA·HCl to jet-cooked high amylose corn starch

A water solution of HDA·HCl was prepared by dispersing 2.625 g of HDA in 108.7 g of 0.1 N HCl (the theoretical amount of HCl needed to convert HDA to HDA·HCl). This weight of HDA corresponds to 7.5% of the weight of amylose in 50.0 g of starch with an apparent amylose content of 70%. The mixture was then stirred and heated to 95 °C to obtain a clear solution.

High amylose starch (50.0 g) was dispersed in 900 mL of water and the dispersion was jet-cooked under the operating conditions described above. The hot, jet-cooked starch dispersion was collected in a pre-weighed Waring stainless steel blending container (Waring Products Division, New Hartford, CT) that was previously heated with 100 °C water from the jet cooker. Excess water was passed through the jet-cooker to maximize the recovery of starch, and the wt.% of starch solids in the cooked dispersion was determined by freeze-drying weighed portions of the dispersion. Based on the weight of starch dispersion collected and the % solids in the collected dispersion, 97% of the initial weight of starch was collected. The hot solution of HDA·HCl was added to the hot starch dispersion in the blending container, and the dispersion was slowly stirred for 1 min. The dispersion was then transferred to a 2 L beaker and rapidly cooled in ice-water to 25 °C. The cooled dispersion was centrifuged (1 h at 10,000 rpm; 15,300 × *g*) to remove a small amount of insoluble solid, equal to 0.36% of the total weight of solid in the dispersion. A portion of the centrifuged dispersion was saved for titration, and the remainder was freeze-dried for use in future experiments.

2.4. Potentiometric titration of the amylose–HDA·HCl complex with 0.02 N NaOH

Jet-cooked high amylose starch-HDA·HCl dispersion, previously centrifuged to remove insoluble solid, was diluted with water to obtain 200 g of dispersion with a solids content of 1.0 wt.%.

Examination of the dispersion (pH 3.54) by phase contrast light microscopy confirmed the absence of insoluble material. The mixture was stirred with a magnetic stir bar and titrated at 25 °C with 0.02 N NaOH. The pH during the titration was measured with an Orion Research pH/millivolt meter 811 (Orion Research, Inc., Cambridge, MA) using a glass electrode (Number 910400 from Thermo Orion, Thermo Fisher Scientific, Waltham, MA). The viscosity of the dispersion during the titration was monitored with a Brookfield Synchro-Lectric Viscometer, Model LVT (Brookfield Engineering Laboratories, Stoughton, MA), operating at 30 rpm, with a number 2 spindle. When the titration was complete at pH 9.42, the mixture was centrifuged for 1 h at 10,000 rpm (15,300 × *g*). The settled solid was washed twice by re-dispersing in fresh water followed by centrifugation. The washed solid was isolated by freeze-drying, and the weight of precipitated solid was determined.

A 1% solution was also prepared by dispersing 2.00 g of freeze-dried high amylose starch–HDA·HCl in water to give a total weight of 200 g, heating the dispersion for 5 min at 65 °C and then cooling the dispersion to 25 °C. Examination of the cooled dispersion by phase contrast light microscopy confirmed the absence of insoluble material. The dispersion was titrated at 25 °C with 0.02 N NaOH, and the precipitated solid was isolated as described above.

2.5. Conversion of complexed HDA in amylose–HDA spherulites to HDA·HCl and determination of water-solubility of the resulting product

Spherulites used in this experiment were those isolated from the rapidly cooled, jet-cooked starch–HDA dispersion obtained with non-defatted high amylose starch. A dispersion of freeze-dried spherulites was prepared by dispersing 1.00 g of freeze-dried spherulites in 100 g of water that contained the theoretical amount of HCl needed to convert complexed HDA to the hydrochloride salt. The dispersion was heated at 65 °C for 5 min and then cooled to 25 °C. When the resulting dispersion was centrifuged for 1 h at 10,000 rpm (15,300 × *g*), 79% of the initial weight of spherulites was recovered as an insoluble solid.

2.6. Microscopy

For scanning electron microscopy (SEM), 100 μL of an aqueous dispersion of spherulites was added to 20 mL of absolute ethanol, and the spherulites were allowed to settle overnight at room temperature. The settled spherulites were washed by re-suspending in ethanol followed by overnight settling, and the ethanol-wet settled solid was critical point dried with CO_2 onto aluminum stubs. Dried specimens were sputter coated with gold and were examined and photographed with a JEOL 6400 V scanning electron microscope (JEOL, Peabody, MA).

For light microscopy, aqueous dispersions of spherulites were observed and photographed with a Zeiss Axioskop light microscope equipped with an Axiocam ICc digital camera (Carl Zeiss, Inc., Thornwood, NY) using phase contrast optics. For the examination of aqueous dispersions of amylose–HDA·HCl complexes, the microscope slides and cover slips used were washed with 0.5 N HCl followed by distilled water. If this washing procedure was not used, visual artifacts were observed due to neutralization and precipitation of the acidic amylose–HDA·HCl complex onto the relatively alkaline glass surfaces.

2.7. X-ray diffraction

X-ray diffraction patterns of freeze-dried samples were obtained as previously described (Fanta, Shogren, & Salch, 1999).

3. Results and discussion

Amylose inclusion complexes were prepared from high amylose corn starch (70% apparent amylose) and HDA by steam jet-cooking mixtures of the two components at high temperature and pressure. Experiments were carried out with both defatted starch and starch that still contained native lipid. The amount of HDA used was 7.5%, based on the weight of apparent amylose in the starch sample. Spherulites were formed from the amylose–HDA complexes when the hot, jet-cooked dispersions were cooled, and the sizes and morphologies of these spherulites depended on whether the dispersions were allowed to slowly cool or whether they were rapidly cooled in ice. Slow-cooling of the dispersions was carried out by collecting the hot dispersions in an insulated Dewar flask and then allowing them to cool from 93 °C to 53 °C over a period of 22 h without stirring. The yields of spherulites obtained under these conditions, based on the starting weight of starch, were 60% with defatted high amylose corn starch and 67% with high amylose starch that still contained native lipid. The higher yield of spherulites obtained with native high amylose starch could be due to the higher total percentage ligand available for complex formation (i.e., native lipid plus HDA).

Light micrographs and SEM images of the spherulites formed from defatted- and native high amylose starch under slow-cooling conditions are shown in Fig. 1, along with images that show the birefringence of these spherulites when viewed with polarized light. The spherulites formed from native high amylose starch were larger than those formed from defatted starch, and maltese cross birefringence patterns can be readily seen in these larger spherulites. Although the spherulites formed from native high amylose starch were larger than those formed from defatted starch, similar torus/disc morphologies were observed in these two preparations. A small percentage of the amylose–HDA spherulites (not shown in SEM images) were larger than the rest and exhibited a more spherical morphology. However, due to aggregation of individual particles, no attempt was made to fractionate these mixtures according to particle size.

The morphologies of the amylose–HDA spherulites resembled the morphologies previously observed for the spherulites formed in jet-cooked, slowly cooled mixtures of starch and palmitic acid (Fanta et al., 2008). The absence of major differences in morphology between the spherulites formed from HDA and those formed from palmitic acid indicates that spherulite morphology is influenced mainly by the structure of the hydrophobic carbon chain of the complex-forming ligand (e.g., chain length and degree of unsaturation), and not by the chemical nature of the polar head group (e.g., amine vs. carboxylic acid). The 6_1V X-ray diffraction patterns obtained for the spherulites formed from HDA (Fig. 2) showed reflections at 7.5°, 13° and 20° 2θ and resembled the scattering patterns previously observed for the 6_1V spherulites obtained with palmitic acid (Fanta et al., 2008).

Rapid-cooling of the hot, jet-cooked dispersions was carried out by stirring the dispersions in an ice-water bath, and a final temperature of 25 °C was reached in 10 min. The yield of spherulites was 73% with defatted high amylose starch, and 79% with high amylose starch that still contained native lipid. Yields greater than the 70% apparent amylose content of high amylose starch could be due to entanglement and hydrogen bonding between amylose and amylopectin under the rapid-cooling conditions used. In contrast to the slow-cooling experiments, rapid-cooling produced aggregates of micron-sized spherulites with surface morphologies suggesting that they may have been formed by aggregation of smaller nanometer-size particles. Light micrographs and SEM images of these spherulites are shown in Fig. 3. Native- and defatted high amylose starch produced spherulites with similar morphologies; and because of their small size, polarized light revealed no

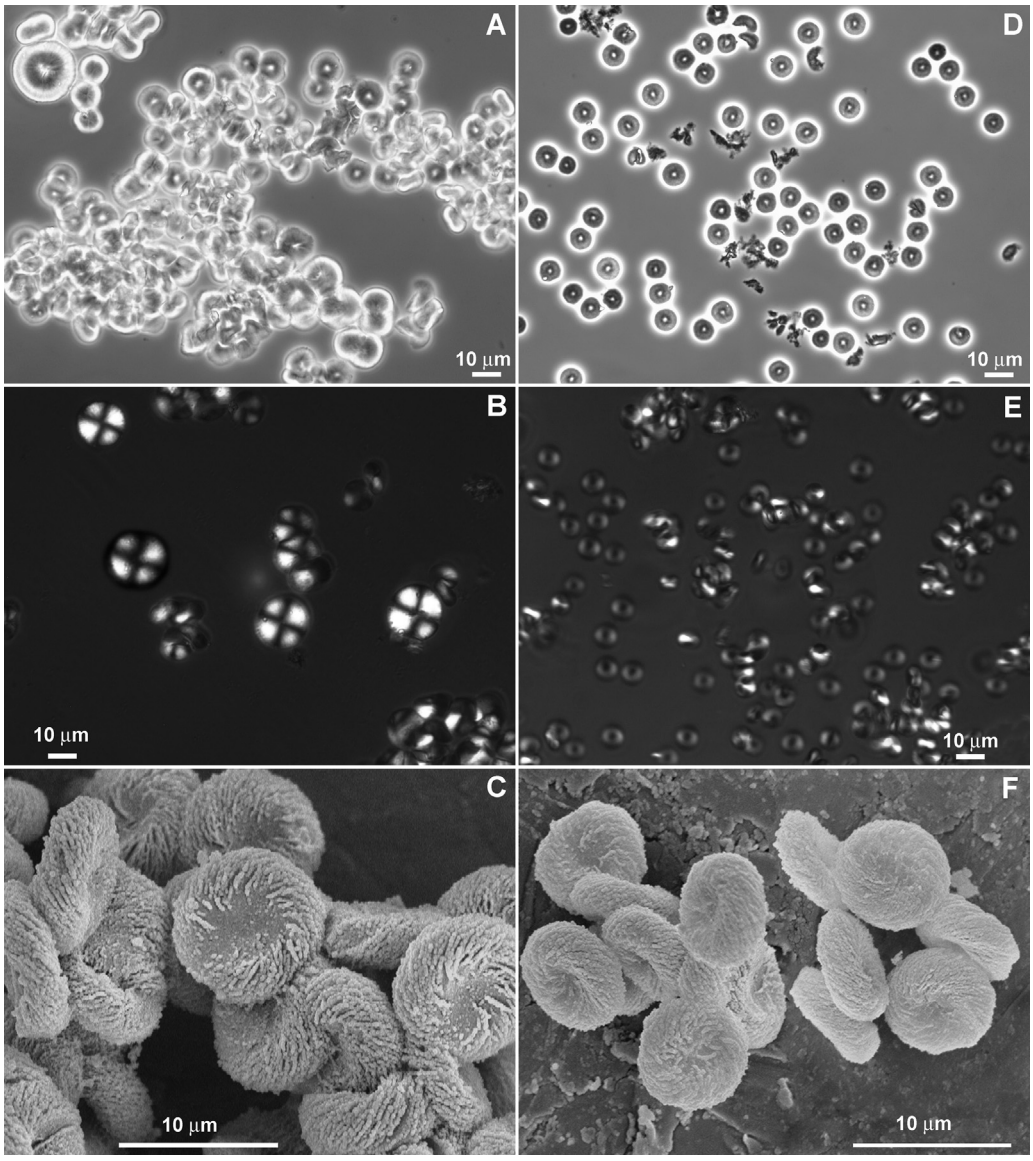

Fig. 1. Micrographs of amylose–HDA spherulites obtained from native- and defatted high amylose corn starch under slow-cooling conditions. (A) and (D) are phase contrast images. (B) and (E) were photographed under polarized light. (C) and (F) are SEM images. (A), (B) and (C) are images of spherulites obtained from native high amylose corn starch. (D), (E) and (F) are images of spherulites obtained from defatted high amylose corn starch.

apparent birefringence. The 6_1V X-ray diffraction patterns for these amylose–HDA spherulites are shown in Fig. 4A and B. The broader diffraction peaks in Fig. 4, compared with those shown in Fig. 2, could be due to the formation of smaller crystallites in the rapidly cooled samples.

In a second phase of this study, a water solution of the HCl salt of HDA was combined with a hot, jet-cooked dispersion of high amylose starch to determine whether a water soluble amylose–HDA·HCl complex could be prepared by this method. A similar procedure was successfully used to prepare inclusion complexes from high amylose starch and sodium palmitate (Fanta et al., 2010). The expected amylose–HDA·HCl complex was indeed formed under these conditions, as confirmed by the 6_1V X-ray diffraction pattern of a freeze-dried sample (Fig. 4C). This scattering pattern was similar to the scattering patterns observed for the spherulites isolated from jet-cooked mixtures of starch and HDA under rapid-cooling conditions. The freeze-dried amylose–HDA·HCl complex could be easily re-dissolved in water at 65 °C, since the complexed fatty amine salt gives the amylose complex the properties of a cationic polyelectrolyte, and retrogradation is inhibited due to electrostatic repulsion between amylose helices. Water-solubility of dried samples of these cationic complexes is an essential property of these materials if they are to find use as flocculating agents and as retention aids in papermaking. Initial experiments carried out with 1% dispersions of talc and kaolin clay confirmed the functionality of these complexes as flocculants.

To determine whether aqueous solutions of amylose–HDA·HCl could also be prepared from acidified samples of freeze-dried starch-HDA spherulites, a 1% dispersion of spherulites (isolated from a rapidly-cooled, jet-cooked dispersion) was heated for 5 min at 65 °C in a water solution containing an amount of HCl sufficient to convert complexed HDA to HDA·HCl. When the dispersion was cooled, 79% of the starting material was recovered by centrifugation as an insoluble solid, indicating that water solutions of amylose–HDA·HCl cannot be prepared in this manner. Apparently, the hydrogen bonding between amylose helices that occurs when the amylose–HDA spherulites precipitate from solution and are then freeze-dried inhibits their re-solubility, even when the complexed HDA is converted to a water-soluble acid salt.

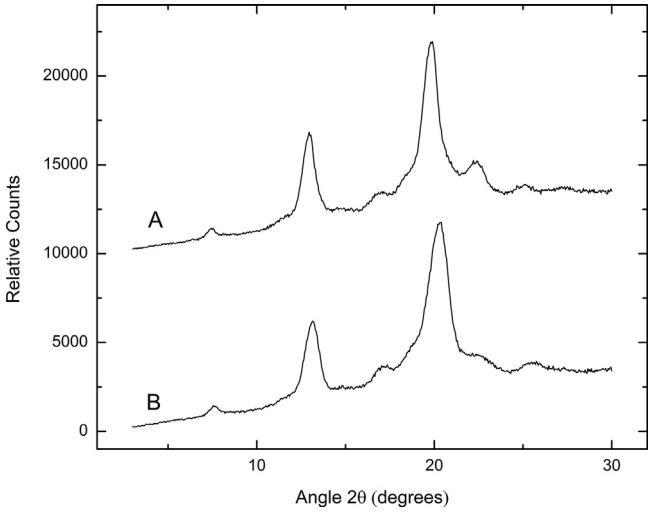

Fig. 2. X-ray powder diffraction scans of spherulites obtained under slow-cooling conditions from: (A) defatted high amylose corn starch and (B) native high amylose corn starch.

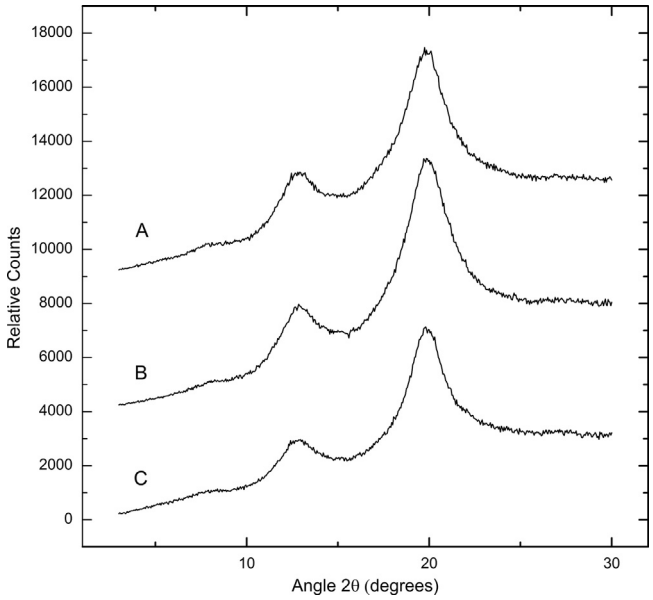

Fig. 4. X-ray powder diffraction scans of spherulites obtained under rapid-cooling conditions from (A) defatted high amylose corn starch and (B) native high amylose corn starch. (C) X-ray powder diffraction scan of freeze-dried amylose–HDA·HCl.

Since increases in viscosity were previously observed when aqueous solutions of amylose–sodium palmitate complexes were titrated with 0.02 N HCl (Byars, Fanta, Kenar, & Felker, 2012; Fanta et al., 2010), titrations of the amylose–HDA·HCl complex were carried out with 0.02 N NaOH to determine whether similar increases in viscosity would be observed. Solutions at solids concentrations of 1% were prepared by dissolving a freeze-dried sample of the complex and also by diluting an un-dried, jet-cooked dispersion. A Brookfield viscometer was used to rapidly monitor the changes in viscosity during the titrations. Increases in viscosity were indeed observed, and the titration curves and viscosities observed in these two experiments are shown in Fig. 5. The pH changed gradually during these titrations, and large increases in viscosity were observed between pH 8.35 and 8.5. The viscosity increase observed when complexed HDA·HCl is partially neutralized is consistent with increased hydrogen bonding between complexed amylose helices, caused by a reduction in electrostatic repulsion resulting from partial conversion of complexed HDA·HCl to water-insoluble HDA. When the titrations were complete at pH 9.4, the yields of insoluble complex precipitated from solution due to the conversion of complexed HDA·HCl to water-insoluble HDA were

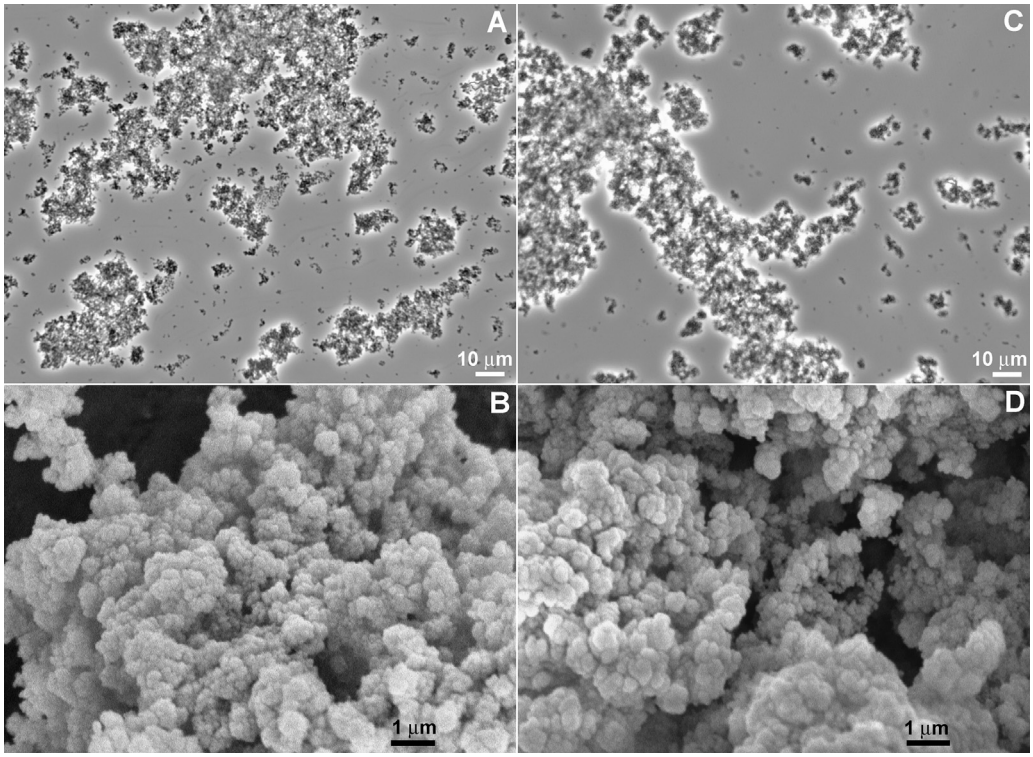

Fig. 3. Micrographs of amylose–HDA spherulites obtained from native- and defatted high amylose corn starch under rapid-cooling conditions. (A) and (C) are phase contrast images; (B) and (D) are SEM images. (A) and (B) are images obtained from native high amylose starch; (C) and (D) are images obtained from defatted high amylose starch.

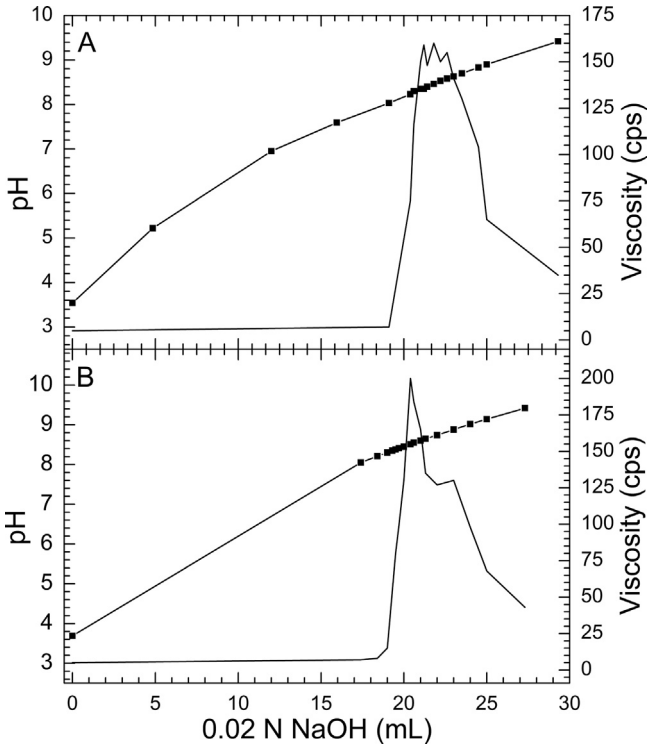

Fig. 5. Titrations of 1% solids dispersions of amylose–HDA·HCl with 0.02 N NaOH at 25 °C. (A) Dispersion prepared by diluting an un-dried jet-cooked dispersion. (B) Dispersion prepared by dissolving a freeze-dried sample of amylose–HDA·HCl.

79.8% from the diluted, undried jet cooked solution and 78.9% from the re-dissolved freeze dried sample. The 6_1V X-ray diffraction patterns of the precipitated solids isolated from these two titrations (not shown) showed reflections at 7.5°, 13° and 20° 2θ and closely resembled the scattering patterns shown in Fig. 4 for the amylose–HDA complexes isolated from rapidly cooled, jet-cooked dispersions. Yields higher than the 70% apparent amylose content of the starting starch indicates that a portion of the amylopectin was precipitated along with amylose, possibly due to the formation of inclusion complexes with the outer branches of amylopectin, or to chain entanglement or hydrogen bonding with amylose.

4. Summary and conclusions

Amylose inclusion complexes were prepared from high amylose corn starch and HDA by steam jet-cooking mixtures of the two components, and the spherulites formed from these complexes were isolated and characterized. Experiments were carried out with both native- and defatted high amylose starch. The sizes and morphologies of the spherulites formed in these experiments varied, depending on how rapidly the jet-cooked dispersions were cooled. The morphologies of these spherulites resembled the morphologies of spherulites previously obtained from palmitic acid under similar conditions. The absence of major differences in morphologies between the amylose–HDA spherulites and those formed from palmitic acid suggests that spherulite morphology is influenced mainly by the structure of the hydrophobic carbon chain of the complex-forming ligand, and not by the chemical nature of the polar head group (e.g., amine vs. carboxylic acid). The similar 6_1V X-ray diffraction patterns observed for the spherulites prepared from HDA and those obtained from palmitic acid is consistent with this conclusion.

Water soluble amylose–HDA·HCl inclusion complexes were prepared by adding water solutions of the HCl salt of HDA to hot, jet-cooked dispersions of high amylose corn starch. Formation of the complex was confirmed by the 6_1V X-ray diffraction pattern of a freeze-dried sample. The water solubility and cationic nature of the amylose–HDA·HCl complex suggests possible applications as flocculating agents for water purification and as retention aids in papermaking. In contrast to the cationic starches currently produced by chemically reacting the hydroxyl groups of starch, the amylose inclusion complexes prepared in this study are obtained by the more environmentally friendly method of steam jet-cooking followed by blending with a cationic, complex-forming ligand. Sharp increases in viscosity were observed when water solutions of the amylose complex were titrated with 0.02 N NaOH, and complete neutralization at high pH caused the amylose complex to precipitate from solution. An attempt to prepare a water solution of amylose–HDA·HCl by heating a freeze-dried sample of starch–HDA spherulites in dilute HCl was unsuccessful, and 79% of the spherulite sample remained insoluble. The associations between complexed amylose helices when these spherulites precipitate from solution and are dried are apparently strong enough to inhibit solution, even when the complexed HDA is converted to the water-soluble acid salt.

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References

Byars, J. A., Fanta, G. F., Kenar, J. A., & Felker, F. C. (2012). Influence of pH and temperature on the rheological properties of aqueous dispersions of starch–sodium palmitate complexes. *Carbohydrate Polymers*, *88*, 91–95.

Eliasson, A.-C. (1988). On the thermal transitions of the amylose–cetyltrimethylammomium bromide complex. *Carbohydrate Research*, *172*, 83–95.

Eliasson, A.-C., Finstad, H., & Ljunger, G. (1988). A study of starch–lipid interactions for some native and modified maize starches. *Starch/Stärke*, *40*, 95–100.

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., & Salch, J. H. (2006). Effect of fatty acid structure on the morphology of spherulites formed from jet cooked mixtures of fatty acids and defatted cornstarch. *Carbohydrate Polymers*, *66*, 60–70.

Fanta, G. F., Felker, F. C., Shogren, R. L., & Salch, J. H. (2008). Preparation of spherulites from jet cooked mixtures of high amylose starch and fatty acids. Effect of preparative conditions on spherulite morphology and yield. *Carbohydrate Polymers*, *71*, 253–262.

Fanta, G. F., Kenar, J. A., Byars, J. A., Felker, F. C., & Shogren, R. L. (2010). Properties of aqueous dispersions of amylose–sodium palmitate complexes prepared by steam jet cooking. *Carbohydrate Polymers*, *81*, 645–651.

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.

Ghimici, L., & Nichifor, M. (2010). Novel biodegradable flocculating agents based on cationic amphiphilic polysaccharides. *Bioresource Technology*, *101*, 8549–8554.

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

Kuge, T., & Takeo, K. (1968). Complexes of starchy materials with organic compounds. Part II. Complex formation in aqueous solution and fractionation of starch by l-menthone. *Agricultural and Biological Chemistry*, *32*, 1232–1238.

Li, H., Li, B., Zang, S., & Zou, J. (2012). Complexation of starch with dodecylamine. *Journal of Central South University (English Edition)*, *19*, 1817–1822.

Lin, Q., Qian, S., Li, C., Pan, H., Wu, Z., & Liu, G. (2012). Synthesis, flocculation and adsorption performance of amphoteric starch. *Carbohydrate Polymers*, *90*, 275–283.

Lundqvist, H., Eliasson, A.-C., & Olofsson, G. (2002). Binding of hexadecyltrimethylammonium bromide to starch polysaccharides. Part I. Surface tension measurements. *Carbohydrate Polymers*, *49*, 43–55.

Morrison, W. R., & Coventry, A. M. (1985). Extraction of lipids from cereal starches with hot, aqueous alcohols. *Starch/Stärke*, *37*, 83–87.

Pal, S., Sen, G., Ghosh, S., & Singh, R. P. (2012). High performance polymeric flocculants based on modified polysaccharides – microwave assisted synthesis. *Carbohydrate Polymers*, *87*, 336–342.

Shi, Y., Ju, B., & Zhang, S. (2012). Flocculation behavior of a new recyclable flocculant based on pH responsive tertiary amine starch ether. *Carbohydrate Polymers*, *88*, 132–138.

Slabaugh, W. H., & Cates, V. E. (1955). Hydrolysis constants of n-aliphatic amine salts. *Analytical Chemistry*, *27*, 151–152.

Sonntag, N. O. V. (1964). Nitrogen derivatives. In K. S. Markley (Ed.), *Fatty acids, part 3* (pp. 1551–1715). New York: Interscience Publishers.

Zou, J., Zhu, H., Wang, F., Sui, H., & Fan, J. (2011). Preparation of a new inorganic-organic composite flocculant used in solid–liquid separation for waste drilling fluid. *Chemical Engineering Journal*, *171*, 350–356.