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Properties of aqueous dispersions of amylose–sodium palmitate complexes prepared by steam jet cooking

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ABSTRACT

Aqueous dispersions of high-amylose corn starch were steam jet cooked and blended with aqueous solutions of sodium palmitate to form amylose inclusion complexes for investigation of their bulk properties. The rheological properties of the cooled dispersions depended on the starch concentration and varied from low-viscosity liquids (at 3.75% and 5.00% solids) to gels (at 6.64% solids). Gel formation was not caused by the formation of permanent cross-links. Viscosities of the dispersions increased when they were acidified with 0.02N HCl, and at pH 3.6, about 90% of the dispersed solid precipitated from the aqueous dispersion, due to conversion of complexed sodium palmitate into insoluble palmitic acid. Addition of sodium chloride solution also increased the viscosities of jet-cooked dispersions, and caused the amylose complexes to precipitate. The gelling properties of these preparations suggest practical applications as dispersants for lipids in foods, lotions, and water-based lubricants.

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). We are currently investigating the use of steam jet cooking as an inexpensive processing method for preparing new starch-based compositions, and we have used this method to prepare helical inclusion complexes of amylose by jet-cooking aqueous mixtures of high-amylose starch and fatty acids, such as palmitic and oleic (Fanta, Felker, Shogren, & Salch, 2008). The fatty acid in these complexes occupies the center of an amylose helix that typically has 6 or 7 glucose units per turn of the helix. When analyzed by X-ray diffraction, 6_1V and 7_1V scattering patterns are observed for these amylose complexes (Kawada & Marchessault, 2004; Takeo, Tokumura, & Kuge, 1973). Insoluble spherulites are formed when jet-cooked dispersions of these complexes are cooled, and the size and morphology of these spherulites depends on the fatty acid used and the rate at which the dispersions are cooled (Fanta et al., 2008).

The literature contains numerous reports of helical inclusion complexes that are formed from amylose and the alkali metal salts of fatty acids (Bulpin, Welsh, & Morris, 1982; Eliasson & Kim, 1995; Karkalas & Raphaelides, 1986; Kowblansky, 1985; Tufvesson, Wahlgren, & Eliasson, 2003). Amylose complexes formed from other surface-active anionic ligands, such as sodium dodecyl sulfate, have also been studied (Egermayer & Piculell, 2003; Karlberg, Piculell, & Huang, 2007; Yamamoto, Sano, Harada, & Yasunaga, 1983; Yamamoto, Harada, Nakatsuka, & Sano, 1988), as well as the complexes formed from non-ionic surfactants, such as alkyl polyglucosides (Rodríguez, Alameda, Gallegos, Requena, & López, 2008), and glycerol monostearate (Conde-Petit & Escher, 1992). Studies on the properties and functionalities of these complexes have dealt mostly with their effect on the pasting properties of starch granules (Biliaderis & Tonogai, 1991; Evans, 1986; Ghiasi, Varriano-Marston, & Hoseney, 1982; Mira, Persson, & Villwock, 2007; Svensson, Autio, & Eliasson, 1998), and their ability to retard the retrogradation of starch in baked products (Keetels, van Vliet, Jurgens, & Walstra, 1996).

In this report, we describe the preparation of amylose–sodium palmitate complexes by adding aqueous solutions of sodium palmitate to jet-cooked dispersions of high-amylose starch. Use of this preparative method allowed us to prepare these complexes in quantities sufficient to examine their bulk properties, and therefore consider some of their possible end-use applications. Specifically, we describe: (1) the effect of solids concentration on the viscous properties of the jet-cooked dispersions; (2) a comparison of the titration of sodium palmitate in water dispersion with titrations

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carried out when sodium palmitate is complexed within the amylose helix; (3) the increase in viscosity observed during titration with HCl, and during the addition of sodium chloride solution to the aqueous jet-cooked dispersions; and (4) the X-ray diffraction patterns and microstructure of amylose complexes that precipitate from solution when the jet-cooked dispersions are acidified, and when excess sodium chloride solution is added.

2. Materials and methods

2.1. Materials

High-amylose cornstarch was AmyloGel 03003 from Cargill, Inc., Minneapolis, MN. Although the apparent amylose content of this starch was 70% as determined by potentiometric titration with iodine, the absolute amylose content reported in the literature was only 40%, since long-chain branches of amylopectin also form helical inclusion complexes with iodine (Jane et al., 1999). Percent moisture was determined by weight loss after drying at 100 °C under vacuum over P_2O_5. All weights of starch are given on a dry-weight basis. Sodium palmitate (98.5%) was purchased from Sigma Chemical Co., St. Louis, MO, and was used as received.

2.2. Preparation of amylose complexes by steam jet cooking

High-amylose starch (either 50, 75 or 100 g) was dispersed in 900 mL of water, and the slurry was passed through a Penick & Ford (Penford Corp., Englewood, CO) 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 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 hot, jet-cooked starch dispersion was collected in a tared Waring stainless steel blending container (Waring Products Division, New Hartford, CT) that was previously heated with 100 °C water from the jet-cooker, and the weight of jet-cooked dispersion in the container was calculated. In each experiment, the jet-cooker was flushed with excess water to maximize the amount of starch collected. The calculated weight of hot dispersion in the blending container was typically 1400 g. The percent starch solids in the cooked dispersion was determined by removing a small amount of the hot dispersion and then freeze-drying weighed portions of this material. The value for percent solids was then used to calculate the total weight of starch collected. In all experiments, over 95% of the initial weight of starch was collected in the jet-cooked dispersion.

The weight of sodium palmitate used was equal to 7.5% of the weight of apparent amylose in the starch sample initially weighed out for cooking, assuming a 70:30 weight ratio of apparent amylose:amylopectin. The sodium palmitate was dissolved in 100 mL of water at 92–95 °C, and the resulting clear solution was added to the hot starch dispersion immediately after it was collected from the cooker. The resulting dispersion was slowly stirred for 2 min, and the dispersion was then transferred to a 2-L beaker and allowed to cool for 20–24 h from 95 °C to 20–25 °C, without stirring, under ambient room temperature conditions. Percent solids was then determined by freeze-drying weighed portions of the cooled dispersion.

2.3. Potentiometric titration of high-amylose starch–sodium palmitate dispersions with 0.02N HCl

The sodium palmitate dispersion used for control titrations in the absence of starch, or the solution obtained when the dispersion was heated to 70 °C, was prepared by dissolving 0.500 g of sodium palmitate in 500 mL of water at 85–90 °C. The solution was washed into a 1-L volumetric flask, cooled to 20–25 °C and diluted to the mark.

Cooled dispersions of jet-cooked starch–sodium palmitate were diluted with water to 1% solids, and the diluted dispersions were stirred overnight using a magnetic stir-bar. The gelled dispersion obtained from 100 g of starch was first stirred briefly at low speed in a Waring blendor to break up large gel fragments. Weighed portions (175 g) of the diluted dispersions at 1% solids were then titrated at either 25 °C or 70 °C with 0.02N HCl, while stirring continuously with a magnetic stir-bar. 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, using a number 2 spindle.

Acidified dispersions after titrating with HCl (pH 3.6) were centrifuged (60 min at a relative centrifugal force of 2060 × g), and the settled solids were washed with water and isolated by freeze-drying.

2.4. Addition of sodium chloride solution to high-amylose starch–sodium palmitate dispersions and measurement of viscosity increase

Starch–sodium palmitate dispersions (175 g of a 1% solids dispersion) were prepared as described above for potentiometric titrations. The dispersions were stirred magnetically, and 0.50 M NaCl was slowly added to the stirred solutions from a burette. Changes in Brookfield viscosity during addition were monitored as described above. After the Brookfield viscosity reached its maximum, 3 additional mL of 0.50 M NaCl was added, and the dispersion was centrifuged. The settled solid was then washed with a solution having a sodium chloride concentration similar to that in the dispersion prior to centrifugation. The settled solid was then freeze-dried.

2.5. Flow property measurements

Small amplitude oscillatory shear flow measurements of the storage modulus, G', loss modulus, G'', and loss tangent, $\tan\delta = G''/G'$, were measured with an ARES LS1 controlled strain fluids rheometer (TA Instruments, New Castle, DE). Tests were performed with a 50 mm diameter stainless steel parallel plate geometry. A Peltier plate was used to maintain the temperature at 25.0 ± 0.1 °C, and humidity covers were used to prevent drying of the samples.

2.6. GPC-MALLS

Jet-cooked starch dispersions were diluted with water to 0.2–0.4% and filtered through 0.22 μm nylon filters prior to analysis. Solids concentrations before and after filtration were calculated from the weights of dry solids obtained by drying known weights of filtered and un-filtered dispersions. High-amylose starch samples without added sodium palmitate were filtered while still hot, and then injected immediately into the GPC system to avoid retrogradation. Cooled, jet-cooked samples prepared with sodium palmitate were slowly stirred with a magnetic stir-bar at room temperature for 1 day after dilution and were then stored under refrigeration for 1–3 days prior to analysis.

GPC-MALLS was carried out using a Waters (Milford, MA) 1525 HPLC system, a Waters 717 plus autosampler, a Waters 2414 refractive index detector and a Wyatt Technologies (Santa Barbara, CA) Dawn EOS light scattering detector. GPC analyses were per-

Table 1
High-amylose starch–sodium palmitate dispersions prepared by steam jet cooking.

Starting materials			Jet-cooked dispersions	
Experiment	Starch (g/900 mL)	Na palmitate (g)[a]	% Solids (starch + Na palmitate)	% Na palmitate (based on amylose)
1	50	2.62	3.75	8.16
2	75	3.94	5.00	7.88
3	100	5.25	6.64	7.67

[a] 7.5%, by weight, based on apparent amylose, assuming an amylose:amylopectin weight ratio of 70:30.

formed using a Polymer Labs (Varian Instruments, Walnut Creek, CA) aquagel-OH 60 column (300 mm × 7.5 mm), an injection volume of 50 μL of 0.2–0.4% solutions and a temperature of 30 °C. The HPLC was set to an isocratic flow rate of 0.60 mL/min using ultrafiltered, deionized water. A value of 0.145 mL/g was used for the refractive index increment (dn/dc) for starches (Yoo & Jane, 2002). Weight-average molecular weights and *z-average* radii of gyration were calculated using Wyatt Astra software (version 5.3.2.15). Samples were run in duplicate.

2.7. Microscopy

For scanning electron microscopy (SEM), 100 μL portions of aqueous dispersions of solid particles (after washing with either water or dilute NaCl) were added to 20 mL of absolute ethanol, and the precipitated solid was allowed to settle overnight. The settled solid was washed twice more with ethanol by dispersing and settling, and the ethanol-wet precipitate was critical-point-dried with CO_2 onto aluminum stubs. Dried specimens were sputter-coated with gold and examined and photographed with a JEOL 6400 V scanning electron microscope (JEOL, USA, Peabody, MA). For light microscopy, particles were observed with a Zeiss Axioskop light microscope (Carl Zeiss, Inc., Thornwood, NY) using bright-field or phase-contrast optics. Representative fields were photographed using a Nikon D100 digital camera (Nikon Corp., Tokyo, Japan).

2.8. X-ray diffraction

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

2.9. Spray-drying

Aqueous dispersions of jet-cooked starch–sodium palmitate (5.0% total solids) were spray-dried using a Niro Spray Drier (GEA Niro Atomizer Inc., Columbia, MD) equipped with a Mobile Minor co-current two-fluid atomization nozzle (GEA Process Engineering Inc., Columbia, MD). The two-fluid atomization nozzle gap was set using a 3 mm Teflon^{TM} spacer. Drying conditions were: 125–135 °C inlet and 50–65 °C outlet temperatures, 20–25 mL/min product feed rate, and 1.5–2.0 bar air pressure for operation of the nozzle. The resulting spray-dried powders had a moisture content of 4% and were stored in sealed glass jars at room temperature until use. Recovery yields observed with this pilot scale spray drier were typically 70%.

3. Results and discussion

Jet-cooking experiments carried out with varying concentrations of high-amylose starch and sodium palmitate in water are shown in Table 1. The amount of sodium palmitate used was 7.5%, based on the weight of apparent amylose in the starch sample, assuming a 70:30 weight ratio of apparent amylose to amylopectin. With this weight percentage of sodium palmitate, there was no visual evidence of retrogradation of non-complexed amylose. With 6% sodium palmitate based on amylose, some cloudiness was observed when the dispersion was allowed to stand overnight at room temperature, suggesting that retrogradation of non-complexed amylose was taking place. The absence of amylose retrogradation in the presence of sodium palmitate is consistent with a study of the amylose–sodium dodecyl sulfate system (Karlberg et al., 2007), in which the authors concluded that formation of a helical inclusion complex with an anionic fatty acid salt gives amylose the properties of a polyelectrolyte, and that the complex remains water soluble due to electrostatic repulsion between anionic charges. Formation of the expected amylose–sodium palmitate inclusion complex was confirmed by the 6_1V X-ray diffraction pattern (Fig. 1A) observed for a freeze-dried sample of jet-cooked dispersion.

Although amylose inclusion complexes were previously prepared by steam jet-cooking aqueous mixtures of starch and free fatty acids (Fanta et al., 2008), this technique could not be used in the present study because of foam formation, due to the surface-active properties of sodium palmitate when it was passed through the steam jet-cooker along with starch. As a result of this excess foam, uncooked starch granules were still observed in our jet-cooked dispersions (in amounts that sometimes exceeded 10% of the initial weight of starch) despite the high temperature of the cooking process (140 °C). Weak birefringence was even observed in a few of these uncooked granules. Starch granules apparently became trapped within micro-bubbles of foam as they passed through the hydroheater and, therefore, did not come in contact with the hot liquid water necessary for gelatinization and disruption. To avoid this problem, starch was first jet-cooked in the absence of sodium palmitate, and hot aqueous solutions of sodium palmitate were then blended into the hot starch dispersions imme-

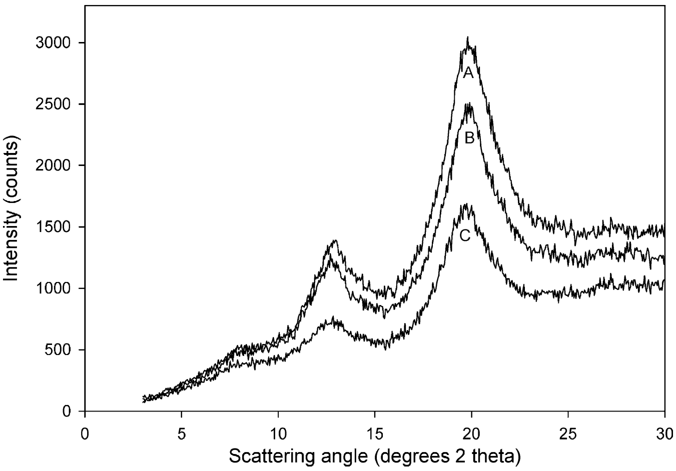

Fig. 1. X-ray diffraction patterns of (A) freeze-dried sample of the jet-cooked dispersion obtained in Experiment 2, Table 1; (B) freeze-dried sample of the precipitated solid isolated by acidifying a 1% solids dispersion of the jet-cooked dispersion obtained in Experiment 2, Table 1; (C) freeze-dried sample of the precipitated solid isolated by adding excess sodium chloride solution to a 1% solids dispersion of the jet-cooked dispersion obtained in Experiment 2, Table 1.

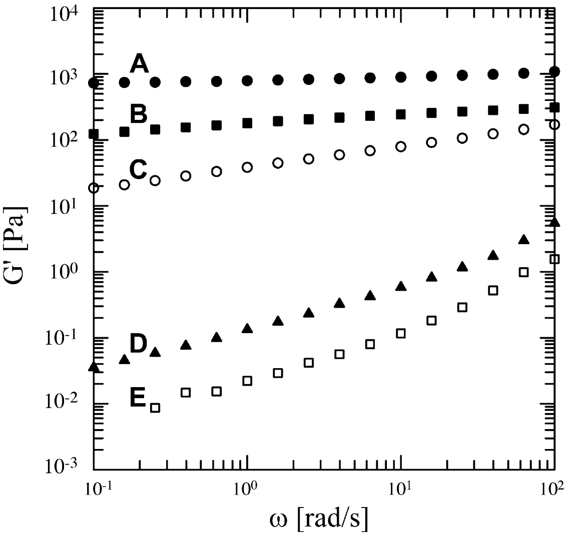

Fig. 2. Storage moduli (G') of high-amylose starch–sodium palmitate dispersions. (A) 6.64% solids dispersion obtained in Experiment 3, Table 1. (B) 4.98% solids dispersion obtained by diluting the dispersion from Experiment 3. (C) 7.74% solids dispersion obtained by concentrating a dispersion prepared from 50 g of starch as in Experiment 1. (D) 3.32% solids dispersion obtained by diluting the dispersion from Experiment 3. (E) 5.00% solids dispersion obtained in Experiment 2.

diately after cooking. When this procedure was used, however, the actual percentages of sodium palmitate in the jet-cooked products were somewhat higher than the calculated value of 7.5%, based on the starting weight of amylose; since the recovery of starch passing through the jet-cooker during the collection period is less than 100%. The actual percentages of sodium palmitate, based on apparent amylose, that were calculated from percent solids determinations are shown in Table 1.

The solids contents of the jet-cooked dispersions prepared with 50 g and 75 g of starch (Experiments 1 and 2, Table 1) were 3.75% and 5.00%, respectively, and both of these dispersions were low-viscosity liquids at room temperature. However, the dispersion with 6.64% solids (prepared in Experiment 3 with 100 g of starch) behaved differently and formed a translucent gel when it was allowed to cool to room temperature. The flow properties of these dispersions were characterized by small amplitude oscillatory shear flow measurements of the storage modulus (G'), the loss modulus (G'') and the loss tangent ($\tan\delta = G''/G'$). Storage moduli of selected samples are shown in Fig. 2 (loss moduli are not shown in the figure for clarity). These measurements confirmed our initial observation that the flow properties were highly dependent on concentration, and that a strong gel was formed at the highest concentration of 6.64%. Both G' and G'' for this gelled sample (Fig. 2A) were almost independent of frequency, and at a frequency of 1 rad/s, $\tan\delta$ was 0.28. To determine the effect of dilution on the flow properties of this sample, the gelled dispersion was diluted to 4.98% and 3.32% solids by adding distilled water and gently stirring by hand, followed by rolling the sample container for 24 h at room temperature. At 4.98% solids, the G' values decreased (Fig. 2B), but the sample remained gel-like ($\tan\delta$ at 1 rad/s = 0.25). However, further dilution to 3.32% (Fig. 2D) dramatically changed the material properties, and the diluted dispersion became a thin, pourable liquid. The loss modulus G'' of this sample had a frequency dependence similar to that of the storage modulus; and the sample was much less elastic, as shown by the increase in $\tan\delta$ to 1.55 at 1 rad/s. The effect of the initial concentration of starch used in these preparations was also shown by the flow properties of the dispersion prepared with 75 g of starch. This sample, with a solids content of 5.00% (Fig. 2E), was a lower viscosity liquid than the sample at 3.32% solids that was prepared by dilution of the dispersion prepared with 100 g of starch (Fig. 2D). Moreover, when a jet-cooked dispersion prepared with 50 g of starch was concentrated on a rotary evaporator to a solids concentration of 7.74%, the concentrated sample (Fig. 2C) was a very weak gel ($\tan\delta$ at 1 rad/s = 0.59) with lower modulus values than those observed for the 6.64% solids dispersion prepared with 100 g of starch (Fig. 2A), despite the fact that the concentration of solids was higher.

When the jet-cooked dispersions from Experiments 1 and 3 (prepared at the lowest and highest solids concentrations) were diluted to 0.2% solids, both dispersions could be filtered through 0.2 μm syringe filters without loss of dispersed solids, indicating that little or no residual microgel remained in either of these highly diluted samples. GPC-MALLS was then used to quantitatively compare the 0.2% dispersions obtained from Experiments 1 and 3 with a dispersion of high-amylose starch that was prepared by jet cooking in the absence of palmitic acid under the same conditions used in Experiment 1. The results of these experiments are shown in Table 2. The dispersion of high-amylose starch had an overall M_w of $3.7 \pm 0.5 \times 10^6$, and M_w values for the amylopectin and amylose components were $11 \pm 1.1 \times 10^6$ and $1.2 \pm 0.17 \times 10^6$, respectively. These values may be compared with previous estimates of M_w for high-amylose cornstarch (dissolved under more gentle conditions) of $70–200 \times 10^6$ for amylopectin and $1.4–2.7 \times 10^6$ for amylose (Aberle, Burchard, Vorwerg, & Radosta; Han & Lim, 2004; Yoo & Jane, 2002). Thus, the amylopectin component of high-amylose corn starch was apparently reduced considerably in molecular weight by the high-temperature, high-shear conditions of the steam jet-cooking process, while the M_w of amylose was reduced only slightly. For the high-amylose starch–sodium palmitate preparations, molecular weights were not greatly different than those observed for high-amylose starch alone. For the dispersion obtained with 50 g of starch (Experiment 1), M_w values were $7.1 \pm 1.3 \times 10^6$ and $1.2 \pm 0.3 \times 10^6$ for amylopectin and amylose, respectively. For the dispersion obtained with 100 g of starch (Experiment 3), similar values for M_w were obtained ($6.8 \pm 1.3 \times 10^6$ and $1.2 \pm 0.2 \times 10^6$ for amylopectin and amylose, respectively). There was, however, a somewhat larger fraction of higher molecular weight material in the sample prepared with 100 g of starch, which could be due to the presence of some residual aggregated starch–fatty acid complexes. In addition, there was some reduction in the size of the amylopectin peak over time (1–2 days) for the sample prepared from 100 g of starch, suggesting that some slow dissociation of aggregates may be occurring. In summary, the GPC-MALLS data indicate that the amylose–fatty acid salt complexes are predominantly molecularly dispersed when they are diluted with water to low concentrations.

Although more than one factor could contribute to the formation of gel when the concentrations of jet-cooked dispersions exceed a certain critical value, gel formation is apparently not caused by permanent associations or cross-links between starch molecules; since GPC-MALLS showed that molecular dispersions were obtained when the jet-cooked dispersions were diluted to low concentrations with gentle stirring. Sodium palmitate is therefore not acting as a cross-linking agent by forming complexes between two adjacent amylose helices, as suggested in a previous study of amylose complexes prepared from free fatty acids (Kawada & Marchessault, 2004; Lebail, Buleon, Shiftan, & Marchessault, 2000). One explanation for the flow properties observed for these jet-cooked dispersions is that association between molecules of amylose complex occurs when they are forced into close proximity to each other when the concentration exceeds a certain critical value. In a study of the flow properties of star polymers, it has been shown that near the overlap concentration, these polymers also form gels near the close-packing volume fraction (Roovers, 1994). However, when the starch–sodium palmitate dispersions are diluted to a sufficiently low concentration,

Table 2
Comparison of structural parameters from GPC-MALLS for jet-cooked high-amylose corn starch with and without Na palmitate.

Starch, g/900 mL	Na palmitate added	Amylopectin			Amylose		
		M_w	Rg (nm)	Wt. fr.[a]	M_w	Rg (nm)	Wt. fr.[a]
50	No	$11.0 \pm 1.1 \times 10^6$	66 ± 2	0.26 ± 0.04	$1.2 \pm 0.2 \times 10^6$	69 ± 5	0.74 ± 0.04
50[b]	Yes	$7.1 \pm 1.3 \times 10^6$	60 ± 5	0.29 ± 0.01	$1.2 \pm 0.3 \times 10^6$	62 ± 7	0.71 ± 0.01
100[c]	Yes	$6.8 \pm 1.3 \times 10^6$	63 ± 4	0.34 ± 0.01	$1.2 \pm 0.2 \times 10^6$	69 ± 1	0.66 ± 0.01

[a] Obtained from integration of refractive index peaks.
[b] Dispersion from Experiment 1, Table 1.
[c] Dispersion from Experiment 3, Table 1.

molecular dispersions are formed from the hydrogen-bonded aggregates.

Potentiometric titrations of 1% dispersions of the jet-cooked starch–sodium palmitate complexes were carried out with 0.02N HCl to determine whether sodium palmitate had been partially converted to free palmitic acid during the jet-cooking process, possibly due to the slight acidity of the high-amylose cornstarch used. Titrations of aqueous dispersions of sodium palmitate that were not complexed with amylose were first carried out at concentrations comparable those in the jet-cooked dispersions. Fig. 3 shows that although complete titration of sodium palmitate was not achieved at room temperature, about 95% of the theoretical amount of 0.02N HCl was consumed when the titration was carried out at 70 °C, a temperature at which sodium palmitate is completely soluble in water. The incomplete titration of sodium palmitate at room temperature is thus due to its incomplete solubility. Free palmitic acid formed during the titration can also coat the surfaces of insoluble sodium palmitate particles and thus further inhibit the reaction with HCl.

Fig. 4 shows titration curves carried out at both room temperature and 70 °C for the 1% starch–palmitic acid dispersion obtained in Experiment 2. Similar titration curves (not shown) were obtained for the other dispersions in Table 1. In contrast to the titrations carried out with non-complexed sodium palmitate, there was little difference between the titrations carried out at room temperature and at 70 °C. Complexed sodium palmitate apparently reacts rapidly and completely with HCl solution at room temperature, and it is not necessary to heat the dispersion to 70 °C to achieve solubility. Titration of sodium palmitate as a complex within the amylose helix also changed the shape of the titration curve. Whereas a sharp inflection in the titration curve occurred at the end-point for uncomplexed sodium palmitate, a more gradual slope in the curve was observed for the complex. These differences could result from hydrogen-bonding between carboxyl groups and starch hydoxyls, and could also be caused by precipitation of the amylose complex from solution due to conversion of sodium palmitate to free palmitic acid during the titration. Titrations of all three samples described in Table 1 showed that 85–89% of the theoretical amount of HCl was required to fully neutralize the sodium palmitate, indicating that there were only small variations in the percentages of sodium palmitate converted into free palmitic acid during the jet-cooking process.

An increase in viscosity was observed as the end-point of the titration was approached, and a Brookfield viscometer was used to rapidly monitor these viscosity changes. Viscosities measured during the titration are shown along with the titration curves in Fig. 4. These increases in viscosity could be caused by non-covalent, hydrophobic association between complexed molecules of free palmitic acid formed during the titration (Yamamoto et al., 1988). Since the end-point of the titration has not yet been reached, there is enough remaining sodium palmitate to inhibit the precipitation of the complex.

At the end of the titration, complexed sodium palmitate was completely converted into insoluble palmitic acid; and at pH 3.6, about 90% of the dispersed solid precipitated from the dispersion and was isolated by centrifugation. SEM of this insoluble material (Fig. 5A) showed aggregates of small spherical particles that were similar in appearance to the spherulite aggregates formed when jet-cooked mixtures of starch and free palmitic acid were rapidly cooled (Fanta et al., 2008). The insoluble material isolated after acidification also exhibited an X-ray diffraction pattern (Fig. 1B) similar to that observed for the spherulites obtained from a rapidly cooled dispersions of starch and free palmitic acid. The fact that the

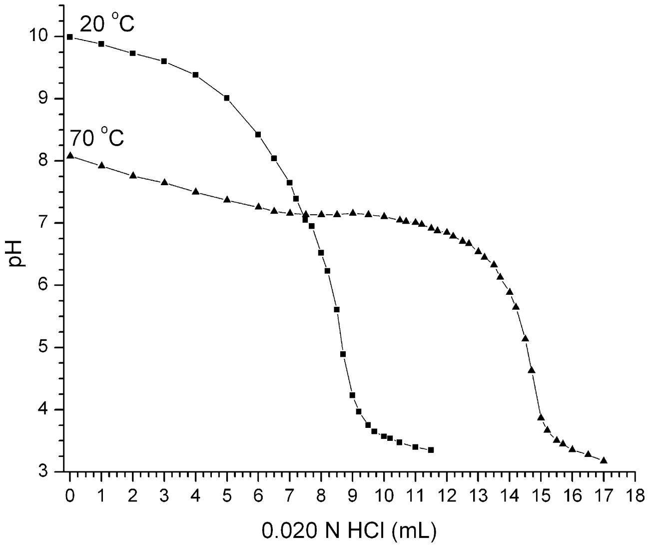

Fig. 3. Titration of 175 g of 0.495 M sodium palmitate with 0.02N HCl at 20 °C and 70 °C.

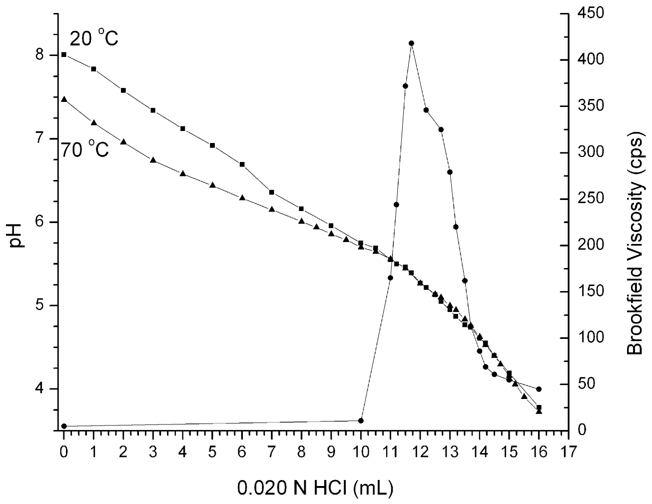

Fig. 4. Titration of 175 g of a 1% solids dispersion of the jet-cooked dispersion obtained in Experiment 2, Table 1. Titrations were carried out at 20 °C and 70 °C. Brookfield viscosities were measured during the titration at 20 °C.

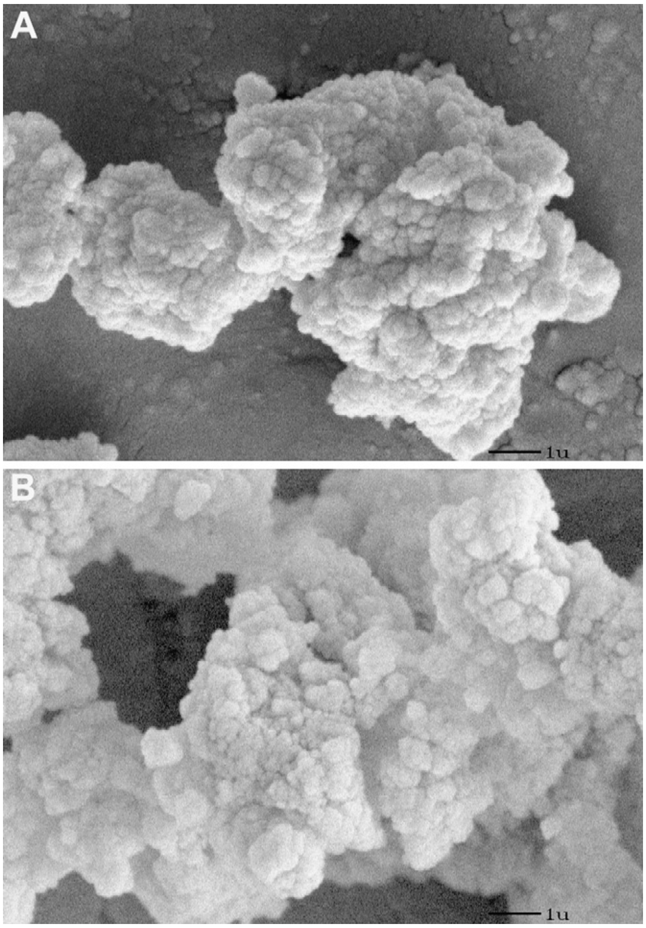

Fig. 5. Scanning electron micrographs of precipitated solids isolated from 1% solids dispersions of the jet-cooked dispersion obtained in Experiment 2. (A) Solid isolated after acidification. (B) Solid isolated after adding excess NaCl.

yield of insoluble precipitate after acidification was greater than the percentage of apparent amylose in the starch sample indicates that some amylopectin was precipitated along with the amylose complex, possibly due to hydrogen-bonding or chain entanglement with the amylose complex, or complex formation with the outer branches of amylopectin (Eliasson & Ljunger, 1988).

Addition of sodium chloride solution to an aqueous dispersion of the sodium palmitate complex also increased the Brookfield viscosity of the dispersion, although the viscosity increase was less than that observed during titration with HCl. Fig. 6 shows the viscosities observed when increasing amounts of 0.50 M NaCl were added to a 1% dispersion of the complex obtained in Experiment 2 (Table 1). Similar viscosity increases (not shown) were observed for the other dispersions. The viscosity reached a maximum when 9.5 mL of sodium chloride solution was added, and then slowly decreased. At maximum viscosity, the NaCl concentration in the dispersion was 0.0257 M. When the addition of sodium chloride solution was complete (12.5 mL added), the NaCl concentration was 0.0333 M, and the pH was 7.35. When the dispersion was centrifuged, 90% of the dispersed solid was isolated as an insoluble precipitate. An SEM image of this precipitate (Fig. 5B) was similar to the image shown in Fig. 5A for the acid-precipitated material. Low concentrations of dissolved electrolyte therefore exert large effects on the flow properties of these jet-cooked dispersions, apparently by reducing the anionic charge repulsion between the complexes, thus causing them to form hydrogen-bonded aggregates that precipitate from the dispersion when excess sodium chloride is added. The 6_1V X-ray diffraction pattern for the precipitated solid (Fig. 1C) was similar to the diffraction pattern shown in Fig. 1B for the insoluble material precipitated by HCl.

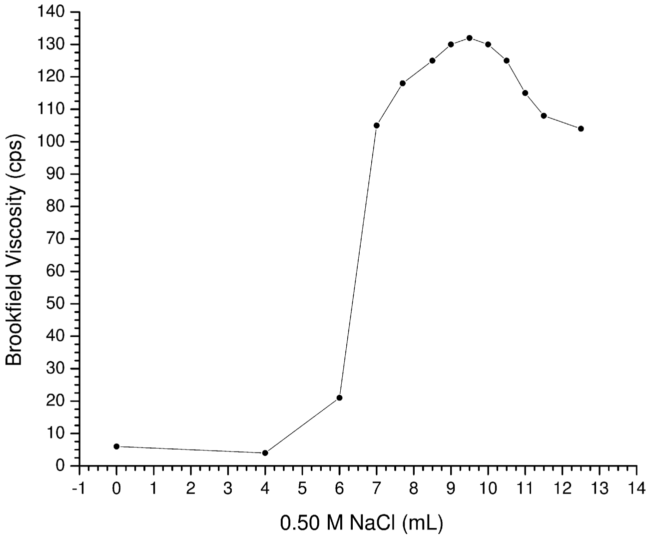

Fig. 6. Viscosity changes resulting from addition of addition of 0.50 M NaCl to 175 g of a 1% solids dispersion of the jet-cooked dispersion obtained in Experiment 2, Table 1.

Although freeze-drying was used to isolate these amylose complexes in small amounts, initial experiments carried out with jet-cooked dispersions prepared as in Experiment 2 (Table 1) showed that the more practical process of spray-drying could also be used when larger quantities of material were required for studies of properties and end-use applications. The spray-dried solid, with a moisture content about 4%, could be easily dispersed in water with gentle stirring at room temperature; and at 1% solids, less than 1% of the dispersed material remained insoluble after centrifugation for 30 min at 10,800 × g. After centrifugation, further dilution to 0.2% solids yielded a solution that could be filtered through a 0.2 μm syringe filter with no significant reduction in solids content, indicating the absence of residual microgel in this highly diluted sample. When a 1% solids dispersion of the spray-dried powder was titrated with 0.02N HCl, the titration curve and increase in viscosity were similar to those observed in Fig. 4 for the un-dried dispersion (data not shown). A viscosity increase, similar to that shown in Fig. 6 for the un-dried dispersion, was also observed when 0.50 M sodium chloride solution was added (data not shown). Spray-drying therefore does not appear to alter the properties of the amylose complex.

Initial experiments showed that the jet-cooked dispersions functioned as dispersants for lipids such as soybean oil, when the oil was blended into the aqueous dispersions under high-shear conditions. Also, acidification of the resulting blends yielded aqueous gels containing high concentrations of dispersed oil droplets. These oil-in-water dispersions could have practical applications in foods, lotions and water-based lubricants; and their properties will be described in future publications.

4. Summary and conclusions

Aqueous dispersions of high-amylose starch were steam jet-cooked at three different concentrations and blended with aqueous solutions of sodium palmitate to form amylose inclusion complexes. The rheological properties of the cooled dispersions were dependent upon the starch concentrations used in the jet-cooking process. Jet-cooked dispersions with solids contents of 3.75% and 5.00% were low-viscosity liquids at room temperature; whereas a gel was obtained at 6.64% solids. Despite these differences in flow properties, dissociation of hydrogen-bonded aggregates in these jet-cooked dispersions appeared to be complete, regardless of the initial solids concentration, when the samples were diluted to about 0.2% solids, indicating the absence of permanent cross-links.

Titration of sodium palmitate in these amylose complexes was carried out with 0.02N HCl at both room temperature and 70 °C, and the titrations showed that about 11–15% of the sodium palmitate was converted to free palmitic acid during the jet-cooking process, probably due to the slight acidity of the high-amylose starch used. Although non-complexed sodium palmitate could not be titrated at room temperature due to its incomplete solubility in water, complete titration was observed at 70 °C. Whereas a sharp inflection point in the titration curve was observed at the end-point for non-complexed sodium palmitate at 70 °C, a more gradual slope was observed for the amylose complex.

The viscosity of the jet-cooked starch–sodium palmitate dispersion increased during the titration with 0.02N HCl. When the titration was complete at pH 3.6, about 90% of the dispersed solid precipitated from the aqueous dispersion, due to conversion of sodium palmitate in the complex to insoluble palmitic acid. The 90% yield of insoluble precipitate indicates that a portion of the amylopectin was precipitated along with amylose, possibly due to hydrogen-bonding or chain entanglement with the amylose, or the formation of complexes with the outer branches of amylopectin. Addition of 0.5 M sodium chloride solution also increased the viscosity of the jet-cooked dispersions, and 90% of the dispersed solid precipitated from the dispersion when excess sodium chloride was added.

Initial experiments showed that spray-drying could be used to isolate larger quantities of these amylose complexes than could be easily obtained by freeze-drying. The spray-dried solid could be easily redispersed in water at room temperature, and the properties of the resulting dispersions were similar to those of jet-cooked dispersions that had never been dried.

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