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Effect of amylopectin on the rheological properties of aqueous dispersions of starch–sodium palmitate complexes[★]

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ABSTRACT

Aqueous dispersions of normal and high-amylose corn starch were steam jet cooked and blended with aqueous solutions of sodium palmitate to give starch containing amylose–sodium palmitate inclusion complexes. Partial conversion of complexed sodium palmitate to palmitic acid by addition of acetic acid led to the formation of gels. Blends of inclusion complexes prepared from normal and high-amylose corn starch were used to vary the amylose:amylopectin ratio of the gels, and the linear viscoelastic moduli were found to decrease with decreasing amylose:amylopectin ratio. Precipitation of the complexed starch at low pH showed that most of the amylopectin was not part of the gel network. The elastic modulus of the gels was shown to decrease sharply between 74 and 85 °C, and the transition temperature increased strongly with decreasing amylose:amylopectin ratio.

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1. Introduction

Starch is extensively used within the food industry as an important functional ingredient to form viscous aqueous dispersions and gels used to improve food formulations and impart desirable rheological, textural and stabilizing attributes (Banerjee & Bhattacharya, 2011; Saha & Bhattacharya, 2010). The determination and understanding of a gel's rheological properties are useful for understanding changes in microstructure and gel formation, which is essential for the development of new products. Gelation of polysaccharides typically occurs through intermolecular associations resulting from conformational changes such as coil-helix transitions and the formation of physical bonds, such as van der Waals attraction and hydrogen bonding. These associations can lead to the subsequent formation of junction zones and molecular aggregation in the developing gel networks. A well-known example of this gelation phenomenon is the retrogradation that can be observed in aqueous solutions of amylose-containing starches. These dispersions are typically not stable, and upon standing at room temperature amylose molecules begin to reassociate and form three-dimensional networks that eventually gel or precipitate depending on concentration and molecular size of the polymer chains (Gidley & Bulpin, 1989; Pfannemüller, 1987). The properties of the gel network structure are determined in part, by the density and stability of the intermolecular junction zones.

The influence of amylose and amylopectin on the rheological properties of gels prepared from nongranular starch has been studied in a number of different systems. Leloup, Colonna, and Buleon (1991) showed that for amylose:amylopectin ratios above 30:70 the elastic modulus and temperature resistance of 8% gels of potato amylose and amylopectin from waxy corn starch were similar to pure amylose gels. They suggested that at these amylose:amylopectin ratios amylose formed a continuous network that entrapped a discontinuous amylopectin phase. Phase separation upon storage at 80 °C between amylose and amylopectin was also shown by Kalichevsky and Ring (1987). Doublier and Llamas (1993) prepared blends of potato amylose and amylopectin from waxy corn starch. Gels formed in samples with 4% solids and amylose:amylopectin ratios as low as 15:85. Since amylose alone did not form a gel at 0.6%, they attributed this behavior to phase separation. For amylose:amylopectin ratios above 15:85, amylose formed the continuous phase and entrapped amylopectin. Jane and Chen (1992) fractionated amylose and amylopectin from different starches and prepared mixed gels with 8% starch and an

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amylose:amylopectin ratio of 20:80. They found that gels formed using amylopectin from high-amylose corn starch containing longer branch chains were stronger than ones prepared using amylopectin from waxy corn. Klucinec and Thompson (1999) compared the temperature dependence of the storage modulus of gels of 7.5% starch from different types of corn. They showed that the storage modulus for nongranular starches decreased much more upon heating than did the modulus for gels prepared using amylose from the same starch. This difference was attributed to amylopectin inhibiting the formation of amylose double helices. They also studied (Klucinec & Thompson, 2002) the effects of amylopectin source and amylose:amylopectin ratio on the gel properties. They found that amylose-amylopectin junction zones had a greater contribution to gelation at higher amylose:amylopectin ratio. Ortega-Ojeda, Larsson, and Eliasson, (2004) prepared blends of potato amylose and high-amylopectin potato starch. Strong gels were formed with amylose:amylopectin ratios above 40:60. This corresponded to a higher amylose concentration than required for amylose alone to form a gel, suggesting that amylopectin prevented the formation of a continuous amylose network.

If amylose inclusion complexes are formed with amylose and a fatty acid or fatty acid salt, less amylose is available for retrogradation, but the complexed amylose can still interact to form a gel. The effects of fatty acid salt concentration and amylose:amylopectin ratio on the rheology of solutions of potato amylose and waxy corn starch were studied by Raphaelides (1992a). The viscosity of amylose solutions was shown to increase with increasing fatty acid salt concentration, while for mixed systems the viscosity decreased with increasing amylose:amylopectin ratio and a constant fatty acid salt concentration. Gel formation in more concentrated systems of potato amylose and fatty acid salts at pH 12 (Raphaelides, 1992b) was more rapid than in the absence of fatty acid salts, and the final gels were more rigid. Eliasson and Kim (1995) studied the rheological properties of a range of gelatinized starches and complexed lipids. For 5% starch gels, the storage modulus at room temperature varied by almost two orders of magnitude for different starch-lipid systems. A sharp decrease in storage modulus was observed upon heating. The transition temperature depended on the type of starch, the chain length and head group of the lipid, and the salt concentration. These differences were attributed to dissociation of the amylose–lipid complex.

Some of our recent studies (Byars, Fanta, Kenar, & Felker, 2012; Fanta, Kenar, Byars, Felker, & Shrogren, 2010) have shown that materials with a range of properties can be prepared by steam jet cooking high-amylose corn starch and blending it with an aqueous solution of sodium palmitate to form helical inclusion complexes. The rheology of dispersions of these complexes can be controlled by adding acid to adjust the pH. At high pH, electrostatic repulsion from complexed sodium palmitate stabilized the amylose in solution and inhibited intermolecular interactions, resulting in non-turbid, low-viscosity liquids. As the pH was reduced, complexed sodium palmitate was partially converted to palmitic acid complexes, reducing electrostatic repulsion. Junction zones also formed due to associations between palmitic acid complexes, leading to the formation of a gel network. We are interested in preparing these materials by steam jet cooking, since it offers a convenient and industrially-accepted method of preparing materials on a large scale for food and nonfood applications such as the protection and delivery of oxygen sensitive materials (Lalush, Bar, Zakaria, Eichler, & Shimoni, 2005; Lay Ma, Floros, & Ziegler, 2011; Yang, Gu, & Zhang, 2009), water-based thickeners, gels and dispersants for lipids. This work therefore examines the properties of dispersions prepared from less expensive normal corn starch, and studies the effect of amylopectin on the rheology of the gels.

2. Materials and methods

2.1. Materials

Normal corn starch (Pure Food Powdered Corn starch, amylose:amylopectin ∼30:70) was obtained from Tate & Lyle North America, A.E. Staley Mfg. Co., Decatur, IL. High-amylose corn starch (AmyloGel 03003, amylose:amylopectin ∼66:34) was obtained from Cargill, Minneapolis, MN. Moisture contents of starch samples were calculated from weight loss after drying at 100 °C under vacuum. All weights of starch and starch-sodium palmitate complexes are given on a dry weight basis. Sodium palmitate (98.5%) was purchased from Sigma (St. Louis, MO). Acetic acid (Certified ACS grade) was purchased from Fisher Scientific (Waltham, MA).

2.2. Determination of amylose content

The total amylose contents of defatted starches were measured based on the colorimetric method of Morrison and Laignelet (1983). Absorbance was measured at 635 nm with a Shimadzu (Kyoto, Japan) UV-1601 spectrophotometer, and the means of triplicate measurements are reported. Waxy corn starch (7350 Waxy #1, Tate & Lyle Ingredients, Decatur, IL) and amylose fractionated by butanol precipitation from normal corn starch (Schoch, 1942) were used to construct the standard curve. The starches were defatted following a method based on Morrison and Coventry (1985) as described in Fanta, Felker, Shogren, and Knutson (2001).

2.3. Steam jet-cooking of corn starch samples and preparation of starch–sodium palmitate complexes

Starch (150.0 g of normal or high-amylose corn starch) was dispersed in 2700 mL of deionized water, and the slurry was passed through a Penick & Ford laboratory model steam jet cooker (Penford Corp., Englewood, CO) operating under excess steam conditions (Klem & Brogley, 1981). The 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). The flow rate of the dispersion through the jet-cooker was about 1 L/min. The hot, jet-cooked starch dispersion was collected in a tared Waring blender (Waring Products Division, New Hartford, CT) that was previously heated with 100 °C water from the jet cooker, and the jet cooker was flushed with additional water to maximize the amount of starch collected. The weight of hot dispersion in the blender was determined, and the concentration of starch was determined by freeze drying weighed amounts of dispersion. From these values, it was determined that over 90% of the initial weight of starch was recovered in the jet-cooked dispersion. The recovery of starch was not quantitative due to hold-up of small amounts of starch in the plumbing of the steam jet cooker.

Sodium palmitate (7.88 g for high amylose corn starch, or 2.81 g for normal corn starch) was dissolved in 300 mL of water at about 95 °C, and the clear solutions were added to the hot starch dispersions immediately after they were collected from the jet cooker. The resulting dispersions were slowly stirred for about 2 min, and then cooled in an ice-water bath to 25 °C. The cooled solutions were then centrifuged for 1 h at 10,000 rpm (relative centrifugal force of approximately 17,000 × g) using a Beckman (Palo Alto, CA) J2-21 ME centrifuge equipped with a JA-10 rotor. The supernatants were then freeze dried.

2.4. Acidification of aqueous solutions of normal corn starch–sodium palmitate complexes to determine the amount precipitated

Solutions of normal corn starch–sodium palmitate complexes were prepared by dissolving the freeze-dried complex in water at concentrations ranging from 1.0 to 0.025% and then heating the dispersions to 80 °C. Solubility of the complex under these conditions was confirmed by phase contrast microscopy. The solutions were then titrated with 0.1 M acetic acid under various conditions of time and temperature to a final pH of 3.7–3.8. For comparison purposes, 0.1 M acetic acid was also added in one portion, as opposed to dropwise. The acidified dispersions were centrifuged for 1 h at 10,000 rpm (as described above), and the precipitated solid was washed by dispersing in fresh water and centrifuging. The washed solid was then freeze dried and weighed to determine the percentage of the original dissolved product that was precipitated by acidification.

2.5. Preparation of starch–sodium palmitate gels for rheological studies

Solutions at varying concentrations and with varying amylose:amylopectin ratios (total weight of freeze-dried material + deionized water = 45.0 g) were prepared from the freeze-dried high-amylose and/or normal corn starch–sodium palmitate complexes. The amounts of each starch sample were varied to obtain samples at the desired total concentration of amylose while varying the ratio of amylopectin relative to amylose in the samples. The mixtures were stirred and heated to 80 °C to dissolve the freeze-dried materials. While at 80 °C, 0.1 M acetic acid (200–1800 μL) was added to the solution to adjust the pH to different values. The mixtures were then stirred at 80 °C for an additional 15–20 min to allow sufficient mixing and to obtain a homogeneous solution. The solutions were then removed from the heat and allowed to cool slowly to ambient temperature. After cooling, the pH was measured (Orion 8235BN electrode and ThermoOrion 370 meter, Thermo Fisher Scientific, Waltham, MA) and the rheological properties were measured.

2.6. Rheological property measurements

Measurements in small amplitude oscillatory shear flow were conducted on an ARES LS1 (TA Instruments, New Castle, DE) controlled strain fluids rheometer. Tests were performed with a 25 or 50 mm diameter parallel plate geometry at strains within the linear viscoelastic region for all samples. Samples were loaded carefully to minimize damage to the gel structure, and samples were allowed to stand for 5 min before beginning measurements. A Peltier plate was used to maintain the temperature at 25.0 ± 0.1 °C or to conduct temperature ramps at 1 °C/min. Sample edges were coated with mineral oil, and humidity covers were used to prevent drying of the samples.

3. Results and discussion

We have previously reported the properties of dispersions of starch–sodium palmitate complexes prepared from jet-cooked high-amylose corn starch (Byars et al., 2012; Fanta et al., 2010). Granular starch was rapidly solubilized under the high-temperature and high-shear conditions of excess steam jet cooking, and mixed with sodium palmitate at a concentration of 7.94% based on apparent amylose, which was sufficiently high to prevent retrogradation. Samples of normal corn starch–sodium palmitate complexes used in this study were similarly prepared. Samples with a range of amylose:amylopectin ratios were prepared by dispersing varying amounts of freeze-dried amylose complexes at 80 °C and adding acetic acid to adjust the pH and induce gelation. The samples were then allowed to stand at ambient temperature for at least 2 h to cool to room temperature and allow the gel network to develop further. The pH and rheological properties were then measured, and subsequent measurements showed that they did not change significantly over at least 24 h. The rate of gel formation in these systems is much more rapid than observed for gels formed by amylose retrogradation (Doublier & Llamas, 1993).

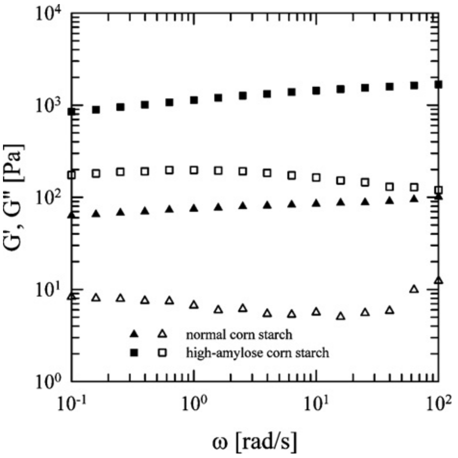

Fig. 1. Storage modulus, G′, (solid symbols) and loss modulus, G″, (open symbols) for samples containing 3% starch–sodium palmitate complexes.

The amylose content of the defatted starch was 29.8% for normal corn starch and 66.4% for high amylose corn starch. Similar values for defatted starches have been reported by Morrison and Laignelet (1983) and Jane et al. (1999). The starches used to prepare the starch–sodium palmitate complexes were not defatted, so a portion of the amylose is expected to be complexed by native lipids. Although amylose that is complexed by native lipids cannot be complexed by sodium palmitate, amylose–native lipid complexes are expected to participate in gel formation similarly to amylose–palmitic acid complexes obtained during the neutralization of amylose–sodium palmitate complexes, and we therefore base our calculations on the total amylose content of the defatted starches.

The linear viscoelastic properties of a dispersion containing 3% of normal corn starch–sodium palmitate complexes at pH 6.35 are shown in Fig. 1. The formation of a strong gel is indicated by the weak frequency dependence of the moduli, and the fact that the storage modulus (G′) was higher than the loss modulus (G″) for all frequencies. For comparison, our previous results for a dispersion of 3% high-amylose corn starch–sodium palmitate complexes at pH 6.49 are also shown. The modulus values for the normal corn starch sample are more than an order of magnitude lower, but the results indicate that qualitatively similar gels were formed despite the lower amylose concentration. A dispersion of 3% jet-cooked normal corn starch without sodium palmitate was also prepared and allowed to cool to room temperature. This dispersion did not form a gel (data not shown), but instead gave a turbid, low-viscosity liquid. We envision that association and hydrogen bonding between insoluble amylose–palmitic acid complexes resulting from partial neutralization of amylose–sodium palmitate complexes by the addition of acetic acid allow junction zones to develop that give rise to a network structure and gel properties in a manner similar to what we have reported for high-amylose corn starch–sodium palmitate complexes (Byars et al., 2012; Fanta et al., 2010). Although these junction zones may be weaker than double helices formed by amylose retrogradation, Fig. 1 indicates that the interactions are strong enough to form a gel network at low amylose concentrations.

Fig. 2 shows the effect of pH on the rheology of the normal corn starch–sodium palmitate complexes at a concentration of 3%. For comparison, our previous results for 2% and 3% high-amylose corn starch–sodium palmitate complexes are also shown. The value of the storage modulus at a frequency of 1 rad/s is presented as a

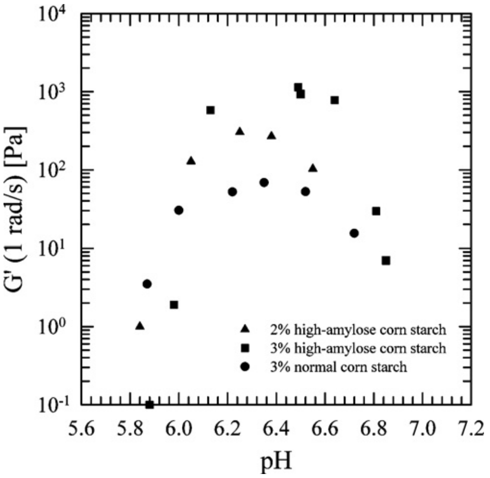

Fig. 2. Storage modulus at 1 rad/s for different starch–sodium palmitate samples as a function of pH.

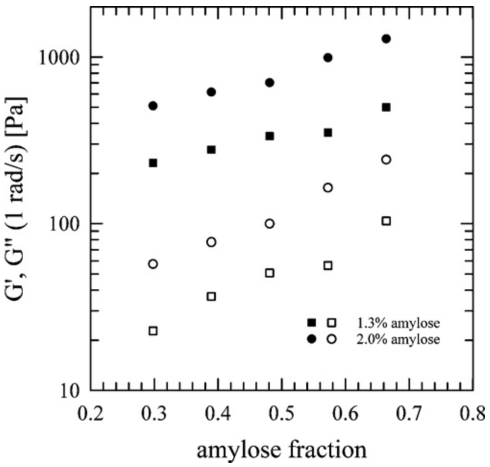

Fig. 3. Storage modulus, G′, (solid symbols) and loss modulus, G″, (open symbols) at 1 rad/s for samples with constant amylose concentrations of 1.3 and 2.0%.

characteristic measure of the gel strength for each sample. The pH dependence for the 3% normal corn starch sample is similar to the high-amylose corn starch sample, verifying that the same gelation mechanism is likely occurring. As discussed above, lowering the pH to ~6.3 gave the maximum gel strength as electrostatic repulsion was reduced and junction zones were formed. As the pH was further decreased, the complexed sodium palmitate was completely converted to palmitic acid, which produced insoluble aggregates, similar to those observed when palmitic acid was used directly to complex amylose (Fanta, Felker, Shrogren, & Salch, 2008). These aggregates subsequently precipitate from solution and do not contribute to the modulus value of the gel.

In order to examine the influence of amylopectin on the gel properties of these amylose–sodium palmitate complexes, a range of compositions containing blends of normal corn starch–sodium palmitate complexes and high-amylose corn starch–sodium palmitate complexes were prepared and examined at the pH where the highest storage modulus values were obtained. For each composition, samples were prepared at multiple pH values to ensure that a sample was obtained near the peak of the G′ vs. pH curve. Samples were typically prepared at pH increments of ~0.15, and the pH for the maximum storage modulus was in the range of 6.1–6.3.

Since we might expect the rheological properties of these gels to be determined primarily by the concentration of junction zones in the partially-acidified amylose complex, two series of experiments were performed at constant amylose concentrations of 1.3 and 2.0%, but with increasing amounts of amylopectin added to the dispersions to determine the effect on the rheological properties (Fig. 3). The amylopectin concentration in the samples was increased by preparing blends containing increased amounts of the amylose complex prepared from normal corn starch (~70% amylopectin) while decreasing the amount of amylose complex prepared from high-amylose corn starch (~34% amylopectin). If the amylose concentration is held constant, then the total concentration of starch in these dispersions must increase as the concentration of amylopectin increases. Therefore, the results obtained for samples at a constant amylose concentration of 2.0% ranged from 3% total starch solids for high-amylose corn starch complexes to 6.7% total starch solids for normal corn starch complexes. For samples prepared with a constant amylose concentration of 1.3%, the total starch concentration ranged from 2 to 4.5%. The rheological results for these series of samples are summarized in Fig. 3, which shows the storage and loss moduli at a frequency of 1 rad/s for each sample. For each amylose level, the highest modulus values were obtained for high-amylose corn starch (amylose:amylopectin = 66:34, shown here as amylose fraction = 0.66). As the amylopectin concentration was increased in the blended samples, similar trends were observed for amylose concentrations of both 1.3 and 2.0% from an amylose fraction of 0.66 down to 0.30. The storage modulus decreased by a factor of 2.5 over this range for 2.0% amylose, and by a factor of 2.2 for 1.3% amylose. Because the loss modulus decreased even more strongly as the amylose fraction decreased, the loss tangent, tan $\delta = G''/G'$, decreased from 0.19 to 0.11 for 2.0% amylose, and from 0.21 to 0.10 for 1.3% amylose. At amylose fractions of 0.39 and lower, the linear viscoelastic spectra for the samples began to change qualitatively from the behavior shown in Fig. 1 to become more characteristic of weaker gels. The storage modulus increased slightly with frequency across the entire measurement range, and the loss modulus increased more strongly with frequency at high frequencies, although a plateau value was obtained for all samples below a frequency of 1 rad/s. Although the mechanism of network formation is different in this system than for amylose retrogradation, an amylose network entrapping amylopectin is also consistent with our results. Since intermolecular junction zone formation is required to form a network, if the amylopectin acts to sterically interfere with contact between amylose molecules, a weaker gel would result. Interaction between amylose and amylopectin has also been shown to affect the properties of starch gels (Klucinec & Thompson, 2002). Junction zones can form between complexed amylose and amylopectin if complex formation with sodium palmitate also takes places with the outer branches of amylopectin. Amylopectin could thus act as part of a gel network by forming junction zones with multiple amylose molecules. However, if there are relatively few amylose complex–amylopectin complex associations, the role of amylopectin would simply be to interfere and decrease the amount of amylose junction zones that could form.

To better understand the interaction between amylopectin and the amylose gel network, a series of precipitation experiments was conducted to determine the percentage of total starch precipitated when dispersions of the sodium palmitate complexes were acidified. The rheology results in Fig. 3 were obtained at pH values giving the optimum equilibrium between sodium palmitate and palmitic acid within the amylose helices to allow the formation of junction zones while allowing swelling of the amylose network to give the maximum gel strength. When acetic acid was added to reduce the pH to ~3.8, complexed sodium palmitate was completely converted to palmitic acid, and the complexed starch precipitated as insoluble aggregates. The amount of precipitated starch recovered by centrifugation should include all of the complexed amylose, any amylopectin entrapped within the amylose network, and any

Table 1
Effect of concentration on acid precipitation of starch–sodium palmitate complexes at 25 °C.

Complex concentration (%)	Method of acid addition	Final pH	% of starch precipitated
1.0	Dropwise	3.80	91.8
1.0	One portion	3.68	91.5
0.1	Dropwise	3.73	89.0
0.05	Dropwise	3.73	83.8
0.025	Dropwise	3.75	59.3

amylopectin that formed junction zones with amylose due to complex formation with its outer branches. Table 1 shows the results of the precipitation experiments at different concentrations of normal corn starch-sodium palmitate complexes. At 1% solids, over 91% of the total starch was recovered by precipitation, whether the acid was added quickly in one portion to the dispersion of complexed starch, or titrated dropwise over a period of 10 min. When lower concentration dispersions were precipitated, the amount of recovered starch decreased to as low as 59.3% for an initial concentration of 0.025%. These results can be interpreted by considering the concentration of amylopectin in solution. Byars (2003) found the intrinsic viscosity, [η], of jet cooked waxy corn starch in 90% DMSO to be 115 mL/g. The overlap concentration of amylopectin can be estimated as 1/[η] (Larson, 1999), or 0.12% for normal corn starch with 70% amylopectin. Above this concentration, the entire volume of the sample contains amylopectin, so any amylose network would necessarily include some amylopectin, even if there is no interaction between the amylose and amylopectin. At lower concentrations, however, portions of the sample would not contain amylopectin, and if there was no interaction between amylose and amylopectin, the amount of starch recovered when the amylose network collapses upon acidification would be reduced. If it is assumed that all of the amylose (30% of normal corn starch) is recovered by precipitation, the results of Table 1 indicate that 88, 77 and 42% of the amylopectin is recovered for initial concentrations of 1.0, 0.05 and 0.025%, respectively. Although this experiment cannot determine whether the precipitated amylopectin is entrapped in an amylose network or interacts more strongly with the amylose, it does suggest that over half of the amylopectin does not interact directly with the amylose. This suggests that steric interference of the amylose network by amylopectin is an important contribution to the reduction of modulus values with increasing amylopectin concentration.

We have shown previously (Byars et al., 2012) that gels formed from high-amylose corn starch–sodium palmitate complexes were characterized by weak temperature dependence up to a transition temperature above which the linear viscoelastic properties rapidly decreased. Similar behavior was observed at higher amylopectin concentration, as shown in Fig. 4 for samples with an amylose concentration of 2.0% and varying amylose fraction. The gel network recovered quickly upon cooling, and although some hysteresis was observed, the samples returned to their initial values after cooling at 1 °C/min. The transition temperature was estimated by extrapolating the G′ values at low and high temperatures, where log G′ vs. T was linear, and calculating the intersection of the two lines. These results are summarized in Fig. 5, which shows that the transition temperature depended strongly on the amylose fraction of the sample, but not on the concentration of amylose in the dispersion, which was held constant at 1.3 or 2.0%. Since each of the samples was at nearly the same pH, each sample should have the same fraction of palmitic acid complexed within the amylose helices and thus available to form junction zones. However, if the effect of increased amylopectin concentration is to inhibit network formation, it may be that only the strongest junction zones are present in the samples with the lowest amylose fraction. Although the modulus values decrease with an increase in temperature due to fewer junction zones, the gels could still be less temperature sensitive due to more stable junction zones. Experiments to determine the percentage of starch precipitated were also conducted at higher temperatures to determine the effects of the breakdown of the gel network at high temperature on the amount of precipitated starch. Table 2 shows the amount of starch precipitated at 75 and 85 °C for 1% dispersions of normal corn starch–sodium palmitate complexes. Because starch hydrolysis can occur at elevated temperatures and low pH (Hoover, 2000), samples were either cooled quickly after adding the acid, or held at high temperature for 5 min before cooling to estimate the amount of acid hydrolysis occurring. At 75 °C, the amount of starch precipitated was independent of the

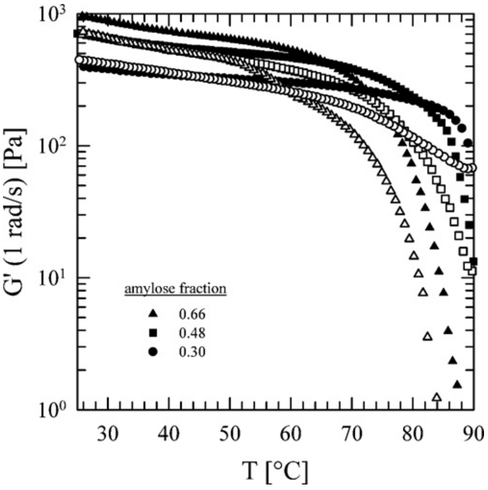

Fig. 4. Storage modulus at 1 rad/s for samples with amylose concentration of 2.0% during heating (solid symbols) and cooling (open symbols).

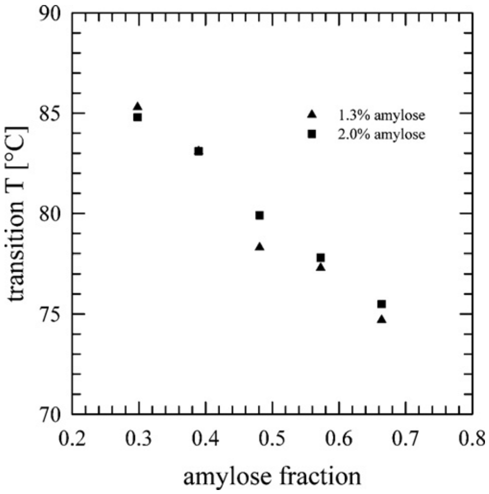

Fig. 5. Transition temperature during heating as a function of amylose fraction.

Table 2
Effect of temperature on acid precipitation of 1 wt% starch–sodium palmitate complexes.

Temperature (°C)	Time at temperature	Final pH	% of starch precipitated
75	10 s	3.65	86.1
75	5 min	3.73	86.1
85	<10 s	3.74	72.6
85	5 min	3.80	62.1

time at high temperature, indicating that hydrolysis was not occurring. The amount of precipitated starch at 75 °C was lower than the amount at 25 °C at 1% from Table 1. This supports the results of the temperature ramp experiment of Fig. 4, which suggest that a weaker amylose network due to decreased junction zones at high temperature entraps less amylopectin upon precipitation. A further decrease in precipitated starch would therefore be expected at higher temperatures, and this was observed at 85 °C for the sample cooled immediately after adding the acid. However, for the sample held at 85 °C for 5 min after adding acid, there was a much greater decrease in the amount of precipitated starch. This suggests that the amylose network may be weakened by acid hydrolysis in addition to junction zone disruption due to temperature, and that a portion of the decrease in precipitation observed with immediate cooling may also be the result of hydrolysis.

4. Conclusions

Aqueous dispersions of normal corn starch and high-amylose corn starch were steam jet cooked and blended with aqueous solutions of sodium palmitate to form amylose inclusion complexes. Blends of these starch–sodium palmitate complex dispersions were prepared to determine the effects of amylopectin concentration on their rheological properties. Acetic acid was added to lower the pH and partially convert complexed sodium palmitate to palmitic acid. This led to the formation of junction zones and the reduction of electrostatic repulsion, and resulted in gel formation. The linear viscoelastic properties of the gels depended on pH, and samples were compared at the pH yielding the highest value of the storage modulus. In order to maintain a constant concentration of amylose inclusion complexes, samples were prepared with 1.3 and 2.0% amylose. For each amylose concentration, the linear viscoelastic properties decreased as the amylose:amylopectin ratio decreased. Precipitation experiments showed that the amylopectin was not part of the gel network, suggesting that the decrease in modulus values was due to steric interference by the amylopectin. Upon heating, the modulus values dropped sharply above a transition temperature. The transition temperature decreased strongly with increasing amylose:amylopectin ratio. The gelling properties of these materials suggest practical applications as thickeners and as dispersants for lipids in foods, lotions and water-based lubricants.

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