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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