The Effect of Amylose Content from Differing Botanical Sources on the Nonlinear Viscoelastic Properties of Semidilute Solutions of Maize Starches*

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ABSTRACT: The effect of the addition of potato or maize on the shear-thickening behavior of semidilute solutions of maize was examined. The experiments were conducted at 25°C using 90/10 weight-weight dimethyl sulfoxide (DMSO)-water as the solvent. The addition of amylose to maize amylopectin reduced and eventually eliminated the observed shear-thickening behavior of maize amylopectin. When potato amylose was combined with maize amylopectin, the shear-thickening phenomenon was observed up to a total amylose content of 10% by weight. For maize amylose, the shear-thickening behavior was eliminated at an amylose content of 5%. Maize amylose is thus more effective in inhibiting the formation of the structure formed after the shear-thickening region than potato amylose. This result indicates that the amylose obtained from maize. © 1999 John Wiley & Sons, Inc.* J Appl Polym Sci 73: 2429–2436, 1999

Key words: viscoelasticity; semidilute; starch; maize; amylose; amylopectin

INTRODUCTION

Starch is composed of (1-4) linked α -D-glucopyranosyl units and is one of the most widely used polymeric materials. Starch is composed of two different polysaccharides, designated as amylopectin and amylose, respectively. Amylopectin is a randomly branched, very-high-molecular-weight (typically 10,000–300,000 kg/mol) biopolymer. Amylose is a lower-molecular-weight (typically 20–800 kg/mol),

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essentially linear-chain polysaccharide. The most widely produced starch in the USA is obtained from maize. Normal maize (NM) starch is composed of approximately 75% amylopectin and 25% amylose. Waxy maize (WM) starch is composed 98% amylopectin and 2% amylose. High amylose (greater than 70%) containing starches are also known. In its native form, maize starch exists as granules with diameters on the order of 10 μ m. These granules can be dispersed into aqueous media at temperatures of 60 to 80°C.¹ Detailed discussions of the structure of amylopectin and amylose can be found in the literature.^{1,2}

The range of industrial applications for starch is enormous.¹ The utility of these water-soluble polysaccharide polymers is a result of their wide range of functional properties. Of main importance in the characteristics of starch is its ability to modify the properties of the polar solvents that

^{*} Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

it is dissolved into, namely, to thicken, stabilize, swell, and suspend, or to form gels and membranes. These properties have lead to applications for starch ranging from thickeners in foods, explosives, and polishes to blends with synthetic polymers. Starches are natural polymers from renewable resources and physical and chemical properties, such as biocompatibility, biodegradability, and nontoxicity have lead to their increasing exploitation as commercial materials. As a renewable resource, starch also offers lower raw material costs than synthetic polymers. Common maize starches can sell for 10 cents per pound, with higher amylose starches selling for approximately 20 cents per pound. This is in comparison to the 30-50 cents per pound cost of such commodity synthetic polymers as polyethylene and polystyrene. The lower material cost of starch offers attractive pricing benefits for the development of new blend and composite systems. Despite the increasing use of starch in numerous industrial applications, many basic performance characteristics of starch are still poorly understood. In addition, due to the complex interactions that can occur with biopolymer materials with one another as well as with various solvents, predicting the functional performance of such systems is problematical.

Over the past few years, a series of articles have reported on the nonlinear viscoelastic behavior of semidilute solutions of WM starch.³⁻⁷ Shear-thickening behavior for WM starch was observed in a number of different solvents, including a 90% by volume mixture of dimethyl sulfoxide and 10% water, at room temperature. Both phase-contrast microscopy and circular dichroism measurements indicated the presence of a flow-induced structure. Oscillatory shear data indicated that the flow-induced structure was related to a highly entangled, stable network formed in the solution. The nonlinear viscoelastic behavior of WM starch in 90/10 dimethyl sulfoxide (DMSO)-water displays many of the characteristics of onset shear thickening as observed in solutions of dextran⁸⁻¹⁰ and DNA.¹¹ Shear-thickening behavior was not observed for semidilute solutions containing NM starch; indeed, these solutions exhibited exclusively shear-thinning behavior.

The purpose of the work reported herein was to investigate the role of amylose in the observed shear-thickening behavior of WM starch. One of the major differences between NM and WM starches is the amount of amylose present in each of the materials. In this work, amylose from two different botanical sources (maize and potatoes) was blended with maize amylopectin. The solution rheological behavior of the resulting blend was then investigated to explore the role of amylose content in inhibiting the shear-thickening behavior of WM starch.

EXPERIMENTAL

Materials

Various starches were used in this study. NM starch, designated as Buffalo® Starch 3401, and consisting of 25% amylose and 75% amylopectin was obtained from CPC International, Corn Products Division (Summit-Argo, IL). A waxy maize (WM) starch, designated as Amioca, consisting of about 98% amylopectin was obtained from American Maize Products Company (Hammond, IN). Purified high-amylose maize starch, designated as Amylon VII, consisting of 68.2% amylose was obtained from C. Knutson (USDA ARS NCAUR, Peoria, IL). High amylose potato starch consisting of 80% amylose was obtained from Sigma Chemical Company (St. Louis, MO) and designated as lot A-0512. The amylose content of the above materials was checked using the method of Knutson and coworkers.¹² Dimethyl sulfoxide (DMSO) was obtained from Aldrich Chemical Company (Milwaukee, WI) and designated as lot 67-68-5. All the materials were used as received.

Moisture Content

The moisture contents of the starches were measured using a gravimetric method prior to the preparation of the solutions. Approximately 10 g of starch was weighed on an analytical balance. The material was then placed in a vacuum oven at 100°C for 1 h, removed, and then reweighed. The process was repeated until a steady weight was obtained. The weight difference was used to calculate the amount of moisture in the starch. The starting moisture contents for WM starch, maize amylose, and potato amylose were 10.9 ± 1 , 11.2 ± 0.9 , and $8.9 \pm 0.8\%$, respectively.

Solution Preparation

Solutions for the rheological measurements were prepared by dispersing an appropriate quantity of the desired starches into a volumetric flask containing 10 mL of distilled water and stirring gently with a stirring bar at 30 rpm to wet and disperse the granules thoroughly. The amount of the high amylose starch used was calculated to adjust the total content of amylose in the sample to the desired percentage. The stirring was continued and 60 mL of DMSO were added. The flask was then heated gradually for 20-30 min until the solution was at 80°C for 5 min. As the starch dissolved into solution, the originally opaque dispersions became clear with time. The solution was then cooled to room temperature, and additional DMSO was added to bring the total final volume to 100 mL. Initially, solutions of the materials were made at a 5% by weight concentration. This stock solution was then diluted with 90/10 DMSO/water to a concentration of 2% by weight.

The intrinsic viscosities of the WM and NM starches used in this investigation are 209 ± 4 and 178 ± 2 mL/g, respectively.⁷ These values for the intrinsic viscosities leads to values of the critical overlap concentrations (c^*) for WM and NM starch of 0.014 and 0.017 g/mL, respectively. The intrinsic viscosities for the maize and potato amylose samples were 77 \pm 0.8 and 33 \pm 1 mL/g, respectively. The concentrations of the solutions used in the intrinsic viscosity studies were measured using the method of Dintzis and Tobin.¹³

Rheological Measurements

Rheological properties were measured at 25°C using a CarriMed® CSL^2 500 controlled-stress rheometer with a cone-and-plate fixture. All the rheological studies were conducted using a 6-cm-diameter, 4° cone. The temperature of the sample was controlled using a Peltier plate that enabled the chamber of the viscometer to be controlled to within ± 0.1 °C. The cone was accelerated uniformly from rest to a shear rate of 250 s⁻¹ over a 2-min time period and then, without delay, decelerated uniformly back to 0 s⁻¹ over the same time period. This cycle was repeated immediately.

RESULTS AND DISCUSSION

The thixotropic loop behavior of blends of WM and high amylose content potato starch is illustrated in Figure 1. For WM starch, a region of shear-thickening behavior is observed around $40-100 \text{ s}^{-1}$, as has been reported previously. The downward cycle of the thixotropic loop preformed on WM starch exhibits a viscosity for the solution that is markedly higher than that measured dur-

ing the upward loop prior to the shear-thickening regime. This difference in the starting and ending viscosities is caused by the formation of a stable flow-induced structure, as has been discussed elsewhere.³⁻⁵ The shear-thickening region was found to be independent of the shear-ramp speed, as has been discussed in an earlier report.⁷ When the total amylose content in the solution is brought to 5%, a region of shear-thickening can still be observed at a similar onset shear rate to that obtained with WM starch, namely, 40 s^{-1} . The downward cycle of the thixotropic loop experiment also displays a viscosity that is greater than that measured during the initial upward cycle. However, the difference between the starting and ending viscosities are not as great as for WM starch. This indicates that the presence of the additional potato amylose interferes with the effective formation of the flow-induced structure. When the total concentration of amylose in the solution was 10% (data not shown), shear thickening behavior is observed; however, the magnitude of the viscosity increase in the shear-thickening region is lessened in comparison with the data obtained at 5%. At a total amylose concentration of 15% in the solution, the shear-thickening regime has disappeared, and only shear-thinning behavior is observed. The upward and downward loops overlap with one another within the error of the experiment. This result indicates the absence of any flow-induced structure generated in the solution, such as that observed in the WM solution. Similar results are observed for the solution with a total amylose content of 30% by weight.

The thixotropic loop behavior of blends of WM and high-amylose-content maize starch is illustrated in Figure 2. The data obtained for WM starch solution is reproduced in the figure for reference. When the total content of amylose in the solution is brought to 5% by weight, the shearthickening regime is no longer evident, and only shear-thinning behavior is observed over the entire shear rate range. In addition, the viscosity of the solution prior to and after the imposition of the thixotropic loop experiment is unchanged. This result indicates that the flow-induced structure formed with WM starch is no longer produced. In an earlier report,⁷ evidence was presented that the flow-induced structure was caused by the development of a highly entangled network in the solution. The entangled network is formed by the high-molecular-weight, randomly branched amylopectin macromolecules. The pres-



Figure 1 The effect of the addition of potato amylose on the observed shear-thickening behavior of WM starch. The addition of potato amylose to the WM starch solution causes the observed shear-thickening region to gradually disappear. When the total concentration of amylose in the solution is 15%, only shear-thinning behavior is observed. The data illustrated in the figure were obtained at 25°C.

ence of the smaller linear chain amylose polymers disrupts the formation of the network and thereby inhibits the shear-thickening phenomenon.

If the results presented in Figures 1 and 2 are compared, it becomes apparent that the amylose obtained from maize is more effective in eliminating the shear-thickening behavior in WM starch than the amylose obtained from potatoes. The explanation for this observation is not known currently. However, it is obvious from the experimental data that the interactions between maize amylopectin and maize amylose differ from those between maize amylopectin and potato amylose. The result could be due to the higher molecular weight of maize amylose as compared to potato amylose.¹⁴ The longer maize amylose chains can interfere with the formation of the entangled network to a greater degree than can the shorter potato amylose chains.

A possible explanation for the decrease and loss of the shear-thickening behavior with increasing amylose content is simply that the concentration of amylopectin in the solution is reduced below the critical concentration required for shear thickening. In a previous report,⁷ it was noted that shear-thickening behavior in WM starch was observed at concentrations down to c^* . Below c^* , the shear thickening behavior was not evident. At a concentration of 2% by weight and a



Figure 2 The effect of the addition of maize amylose on the observed shear-thickening behavior of WM starch. The addition of maize amylose to the WM starch solution causes the observed shear-thickening region to gradually disappear. When the total concentration of amylose in the solution is 5%, only shear-thinning behavior is observed. The disappearance of the shear-thickening behavior occurs at a lower total concentration of amylose when maize is used than was observed using potato amylose. The data illustrated in the figure were obtained at 25°C.

total weight percentage of amylose of 15%, the concentration of amylopectin in the solution would be 1.7% with is above the value for c^* . Therefore, the disappearance of the shear-thickening behavior in these solutions cannot be explained by the decrease in amylopectin concentration. To support this point, the viscosity versus shear rate for a 2% by weight solution (85% maize amylopectin-15% maize amylose with a total solution concentration of 1.7% maize amylopectin) is compared to a 1.5% solution of WM starch in Figure 3. Evidence for the onset of shear thickening is apparent in the 1.5% WM starch solution but is absent in the blend. Thus, the disappearance of the shear-thickening regime cannot be ascribed to the lower concentration of amylopectin in the blends.

The NM starch used in this study is composed of 25% maize amylose and 75% maize amylopectin. A comparison between the rheological behavior of NM and a blend of 80% WM starch and 20% maize amylose is presented in Figure 4. The rheological behavior of the two solutions is identical within the error of the experiment. In semidilute solutions, the flow properties of NM starch may be interpreted as a simple mixture of amylose and



Figure 3 A comparison of the thixotropic loop behavior of WM starch at a concentration of 1.5% and a mixture of WM and maize amylose with a total amylose content of 15%. The two solutions were produced so that the total concentration of amylopectin would be the same. For WM starch, the region of shear thickening behavior is evident. For the blend of WM starch and maize amylose, the shear-thickening regions is not observed. This observation indicates that the absence of shear thickening in the WM starch-maize amylose blend cannot be contributed to concentration effects. The data illustrated in the figure were obtained at 25°C.

amylopectin. This result, combined with the results discussed above, indicate that the lack of shear-thickening behavior in NM starch solutions is due to the presence of amylose in the solution, which inhibits the formation of the flow-induced structure.

CONCLUSIONS

The effect of the addition of amylose from potato, or maize, on the shear-thickening behavior of WM starch was examined. The addition of amylose to maize amylopectin reduced and eventually eliminated the observed shear-thickening behavior of WM starch. When potato amylose was combined with maize amylopectin, the shear-thickening phenomenon was observed up to a total amylose content of 10% by weight. For maize amylose, the shear-thickening behavior was eliminated at a total amylose content of 5%. Maize amylose is more effective in inhibiting the formation of the entangled network formed after the shear-thickening region than is potato amylose. This result indicates that



Figure 4 A comparison of the thixotropic loop behavior of NM starch and a mixture of WM starch and maize amylose with a total amylose content of 20%. The total starch concentration for both solutions was 2% by weight. The two thixotropic loop curves agree with one another within experimental error. This result indicates that NM starch in solution acts as a simple mixture of maize amylopectin and amylose. The data illustrated in the figure were obtained at 25°C.

the amylose obtained from potatoes interacts differently, or entangles differently, with maize amylopectin than does the amylose obtained from maize. This may be related to the difference in molecular weight between potato and maize amylose.

The original purpose of this work was to explore the role of amylose in the nonlinear viscoelastic behavior of WM starch in semidilute solutions. The results presented in this article indicate some of the complexity of dealing with biological macromolecules and open more questions than they answer. Not only does amylose, a linear polysaccharide, interact with the randomly branched amylopectin to inhibit the formation of the shear-induced entangled network, but the botanical source for the amylose also plays an important role. Despite many excellent studies on the rheological properties of starch solutions, many unanswered questions remain regarding the specific interactions of the components of various starches under an applied deformation. In addition, the differences in end-use functional properties between starches from differing botanical sources are also not understood completely.

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