

Influence of Poly (Ethylene-co-Acrylic Acid) on the Paste Viscosity and Gel Rheology of Cornstarch Dispersions

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ABSTRACT

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The rise in viscosity of aqueous starch suspensions during gelatinization was measured with a Brabender amylograph with and without poly (ethylene-co-acrylic acid) (EAA). Increases in paste viscosity were observed with as little EAA as 0.25–0.50 g/30 g of starch. EAA was added as a 5–10% solution in aqueous ammonium hydroxide, thus producing an alkaline pH during pasting. A similar but smaller increase in viscosity was also observed under near-neutral conditions, brought about by the removal of excess ammonia by evaporation. Gelatinization of starch in the presence of either poly (acrylic acid) or stearic acid caused no increase

in viscosity; this is consistent with the theory that EAA increases viscosity by pseudocross-linking starch through formation of helical inclusion complexes with more than one starch macromolecule. Although EAA increases the paste viscosity of aqueous starch dispersions, it reduces the strength of gels formed from starch pastes. Scanning electron micrographs and Fourier transform infrared analyses for EAA suggest that EAA does not promote disruption of starch granules but complexes with starch that has already been solubilized by heating in water.

Composite systems containing starch and poly (ethylene-co-acrylic acid) (EAA) have been under investigation at the Northern Regional Research Center for a number of years, and a series of articles describes their preparation and properties (Otey et al 1977, 1980, 1987; Otey and Westhoff 1984). Applications for starch-EAA films originally centered on biodegradable agricultural mulches for high-value crops; however, current interest in plastic bags and packaging and in conserving petrochemical-based resources by blending with annually renewable natural polymers has further expanded the number of potential uses for composites of this type. It also has stimulated further research on the starch-EAA system.

Starch can be compounded with EAA in the presence of aqueous ammonia or aqueous alkali metal hydroxides, since both polymers are dispersible in these solvent systems and thus can be intimately mixed. Maxwell (1970) used blends of the two polymers as water-resistant paper sizes and observed that adding an aqueous ammonia solution of EAA to a water solution of starch resulted in a pronounced increase in viscosity.

In a previous publication (Fanta et al 1990), we presented evidence that a helical inclusion complex is formed from starch and EAA that is similar to well-known complexes produced from starch and fatty acids. Part of this evidence was the immediate increase in viscosity observed when solutions of starch and EAA were mixed. Viscosity did not increase when the microbial polysaccharide dextran was substituted for starch, presumably because the α -(1 \rightarrow 6) linkage between glucose units in dextran does not permit formation of the required helical structure.

Preliminary work showed that adding even small amounts of EAA greatly increased the paste viscosity of cooked starch dispersions. Since EAA addition seemed such a simple and practical technique for altering the rheological properties of starch, this system was examined in more detail because of its potential for opening up new starch markets.

MATERIALS AND METHODS

Materials

Unmodified cornstarch (Buffalo 3401) was obtained from CPC International, Inc.; all weights were on a dry basis. EAA was Primacor 5981 from Dow Chemical Co. This polymer contains about 20% copolymerized acrylic acid (w/w); its melt index is

300, weight-average mol wt about 18,000, and number-average mol wt about 7,000.

A 5% solution-dispersion of EAA in aqueous ammonium hydroxide was prepared by stirring 25 g of EAA pellets in 500 ml of 50:50 (v/v) concentrated ammonium hydroxide-water in a flask equipped with a reflux condenser. The mixture was heated to 75°C, stirred at 75–85°C for about 6 hr, and allowed to cool. The slightly turbid solution was then diluted with concentrated ammonium hydroxide to a total weight of 500 g. A 10% EAA solution-dispersion was similarly prepared by heating 60 g of EAA in 600 ml of 50:50 (v/v) concentrated ammonium hydroxide-water and then diluting to a weight of 600 g. Because of the low molecular weight of EAA, viscosities of these solutions were only slightly greater than those of water.

The ammonium hydroxide control solution used in experiments performed in the absence of EAA was prepared by a similar heating and diluting procedure, except that no EAA was used.

Two poly (acrylic acid) samples (about 5,000 and 50,000 mol wt) were obtained from Polysciences as 50 and 25% solutions in water, respectively. An amount of poly (acrylic acid) solution needed to give 20 g of dry polymer was diluted to a total weight of 200 g by adding 50:50 (v/v) concentrated ammonium hydroxide-water.

A solution of stearic acid in aqueous ammonia was prepared by suspending 0.50 g of stearic acid (from Fisher Scientific Co.) in 500 ml of water containing 20.0 g of concentrated ammonium hydroxide and then warming the suspension to about 65°C.

Starch Gelatinization

Solutions used to gelatinize starch were prepared by weighing either 5 or 10% EAA solution or the control solution of ammonium hydroxide-water into a 500-ml volumetric flask and diluting with water.

EAA solution in the absence of excess ammonia was prepared by first diluting 5 g of 10% EAA solution to 500 ml and then heating this solution in an open baker for about 2 hr at 80–85°C to reduce the volume to about 350 ml. The resulting solution had a pH of 7.8 after diluting to 500 ml. Adding 30 g of starch further reduced the pH to 7 or below. Minor pH adjustments could then be made by adding a few drops of ammonium hydroxide solution.

A viscoamylograph (model VA-1B, C. W. Brabender Instruments, Inc.) was used to gelatinize starch and to record viscosities as a function of time and temperature. Slurries were stirred at 75 rpm and heated at 1.5°C/min to 85°C (95°C in a few experiments), held at this temperature for 30 min, and cooled to 50°C. Stirring was continued for 30 min at 50°C, and the cooked dispersions were cooled to 30°C. In most experiments, the presence of ammonium hydroxide limited the maximum temperature to 85°C, since release of gaseous ammonia caused the paste to foam out of the sample bowl.

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To determine solubles in cooked starch pastes recovered from the amylograph, 20 g of paste was diluted to 200 g with water, stirred with a magnetic stirrer overnight at room temperature, and centrifuged (20 min at 10,000 × g). Accurately weighed samples of the clear supernatant and the uncentrifuged starch dispersion were allowed to evaporate to dryness at room temperature in tared aluminum pans; the percent of solubles was calculated from weights of dry solids after drying the pans overnight in a vacuum oven at 40°C. Experiments were run in duplicate. Insoluble gel fractions were diluted to 200 g with fresh water, stirred for 1 hr, and separated by centrifugation before analysis by scanning electron microscopy and Fourier transform infrared analysis. Fourier transform infrared analyses for percent of EAA in the soluble and insoluble fractions were performed as described in an earlier publication (Fanta and Salch 1991).

Scanning Electron Microscopy

Specimens were fixed overnight at 4°C in glutaraldehyde (2% in 0.1M phosphate buffer, pH 7.4) and then dehydrated by successive washing in 10, 20, 30, 40, 50, 75, 85, 95, and 100% ethyl alcohol. Samples were critical point dried (Bulla et al 1973), coated with a thin layer of gold-palladium, and viewed in a microscope (Cambridge Stereoscan Mark VI).

Gel Rheology

Starch and starch-EAA samples prepared in the amylograph were poured (at 30°C) into cylindrical polyvinyl chloride disk molds with an internal diameter of 77 mm and a nominal height of 10 mm. Rings were placed on Saran-covered Lucite blocks. Molds were overfilled with dispersion and covered with another Saran-wrapped block, and the excess paste was forced out. A 1-kg weight was placed on the upper block, and samples were allowed to stand for 24 hr at ambient temperature before compression testing. Mold rings were removed, and gels were compressed (by lubricated uniaxial compression) with a testing machine (Instron Universal, model 1122) with a 50-kg load cell (Christianson et al 1985). Tests were performed beyond the fracture point of the gel at 0.5 cm/min cross-head speed. Stress (Pa) was plotted against strain ($\Delta h/h$), where h is the actual height of the gel disk after compression by an amount Δh . Gel strength is defined as the stress at the point of fracture.

RESULTS AND DISCUSSION

Paste Viscosity

The increase in viscosity caused by the presence of EAA during starch gelatinization is apparent from the two amylograph curves shown in Figure 1. A starch concentration of 12.5 g (dry basis) in 500 ml was chosen so that the entire pasting curve would

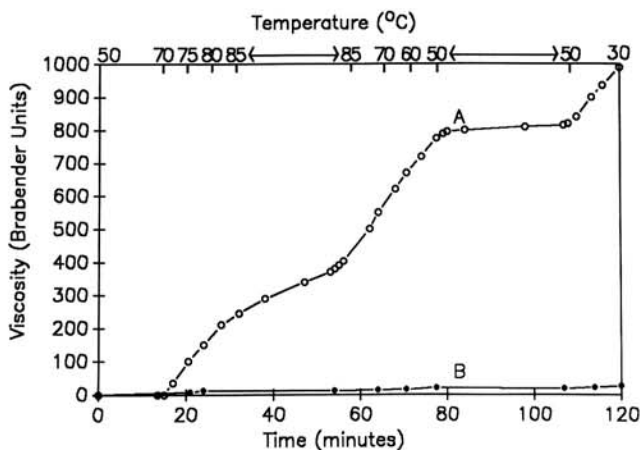


Fig. 1. Effect of poly (ethylene-co-acrylic acid) (EAA) on paste viscosity of starch shown by amylograph runs made with 12.5 g of starch in a total volume of 500 ml of aqueous solution. Curve A: Solution contains 100 g of 5% EAA solution; final pH, 10.54. Curve B: Solution contains 100 g of aqueous ammonia control solution; final pH, 10.77.

be on scale when EAA was added. The dry weight of EAA added amounted to 5 g/12.5 g of starch; both dispersions contained the same amount of ammonium hydroxide. In the absence of EAA, starch showed only a negligible increase in viscosity when heated under these conditions, whereas addition of EAA produced a final viscosity of about 1,000 BU at the end of the heating and cooling cycle. The high viscosity imparted to the system by EAA confirms the work of Maxwell (1970), as well as our earlier study (Fanta et al 1990), in which a helical complex between starch and EAA was first proposed.

Since gelatinization of starch was performed under alkaline conditions (because ammonium hydroxide was used to dissolve EAA), we needed to single out the effect of ammonium hydroxide on gelatinization and paste viscosity of starch in the absence of EAA. Figure 2 shows a series of amylographs obtained with 30 g of starch in 500 ml of water containing varying amounts of our ammonium hydroxide control solution (see materials and methods section). It is apparent that even a small amount of ammonium hydroxide promotes chemical gelatinization and therefore increases the paste viscosity of starch. The amount of soluble starch is also approximately doubled. However, paste viscosities and the percent of solubles do not change in an amount

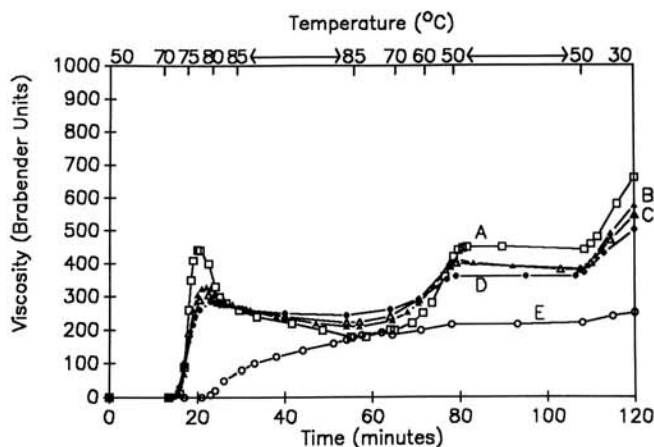


Fig. 2. Effect of ammonium hydroxide on paste viscosity of starch shown by amylograph runs made with 30 g of starch in a solution prepared by diluting X g of aqueous ammonia control solution with water to a total volume of 500 ml. Curve A: X = 100; final pH, 10.50. Curve B: X = 10; final pH, 9.78; 26% solubles. Curve C: X = 5; final pH, 9.54; 23% solubles. Curve D: X = 2; final pH, 9.25. Curve E: X = 0; final pH, 4.95; 11% solubles.

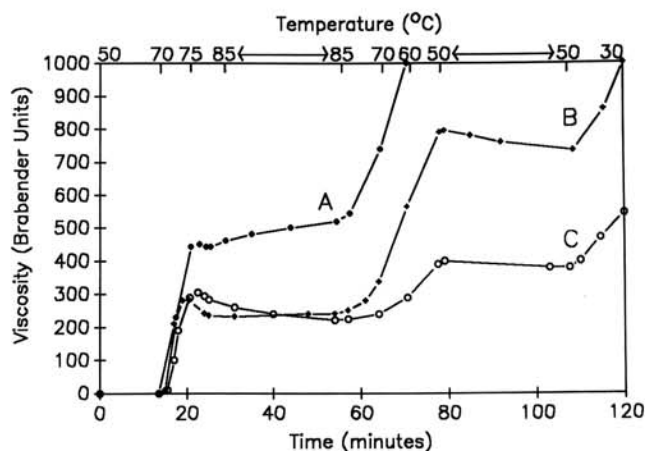


Fig. 3. Effect of poly (ethylene-co-acrylic acid) (EAA) on paste viscosity of starch shown by amylograph runs made with 30 g of starch in a total volume of 500 ml of aqueous solution. Curve A: Solution contains 5 g of 10% EAA solution; final pH, 9.34; 18% solubles. Curve B: Solution contains 5 g of 5% EAA solution; final pH, 9.50; 25% solubles. Curve C: Solution contains 5 g of aqueous ammonia control solution; final pH, 9.54; 23% solubles.

proportional to the weight of ammonium hydroxide solution added, but stay fairly constant. This is especially true for 2–10 g of added ammonium hydroxide solution. Properties of starch pastes thus seem to depend primarily on pH, which does not vary greatly with the amount of ammonium hydroxide in the system.

Figure 3 shows that significant increases in paste viscosity can be achieved by adding as little EAA as 0.25–0.50 g/30 g of starch. Although paste viscosities in the presence of 0.25 g of EAA were not greatly different from those of the control at temperatures up to 85°C, the viscosity of the cooled starch-EAA paste was significantly higher. Addition of 0.5 g of EAA increased viscosities throughout the entire heating and cooling cycle. The percent of solubles in starch pastes containing 0, 0.25, and 0.5 g of EAA were 26, 25, and 18, respectively.

Since amylographs up to this point were performed in the presence of ammonium hydroxide at alkaline pH, we now needed to determine whether EAA would also cause an increase in viscosity at a pH near neutrality. Perhaps the most obvious way to lower the pH of an EAA solution in aqueous ammonia is to remove excess ammonia by evaporation. Although this technique causes EAA to precipitate from a 10% solution, the polymer

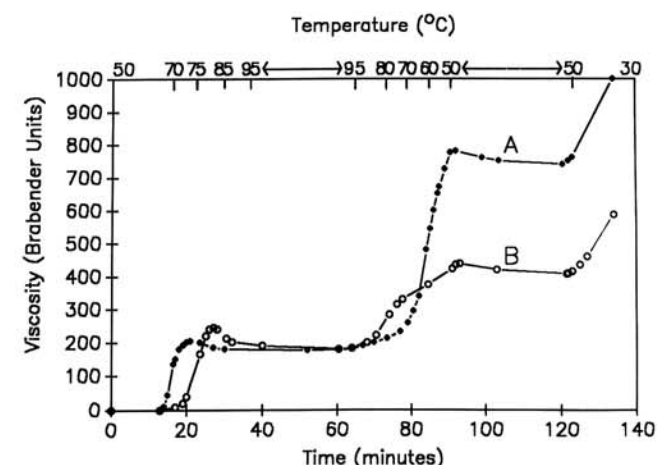


Fig. 4. Effect of poly (ethylene-co-acrylic acid) (EAA) on paste viscosity of starch at near-neutral pH shown by amylograph runs made with 30 g of starch in a total volume of 500 ml of aqueous solution. Curve A: Solution contains 5 g of 10% EAA solution; final pH, 6.77; 18% solubles. Curve B: No EAA; final pH, 7.00; 20% solubles.

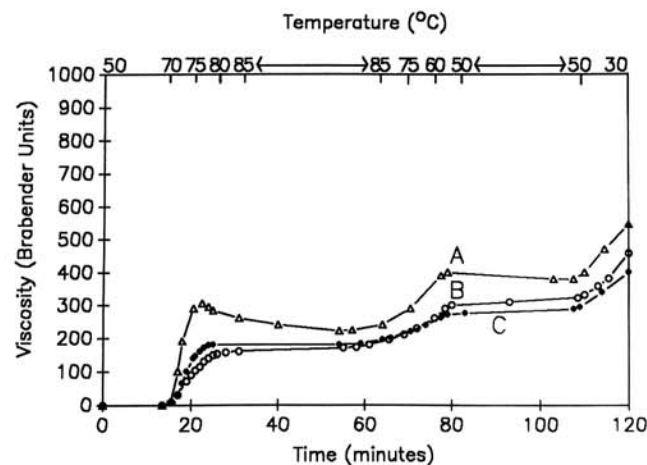


Fig. 5. Effect of poly (acrylic acid) on paste viscosity of starch shown by amylograph runs made with 30 g of starch in a total volume of 500 ml of aqueous solution. Curve A: Solution contains 5 g of aqueous ammonia control solution; final pH, 9.54; 23% solubles. Curve B: Solution contains 5 g of 10% poly (acrylic acid), approximately 50,000 mol wt; final pH, 9.16; 24% solubles. Curve C: Solution contains 5 g of 10% poly (acrylic acid), approximately 5,000 mol wt; final pH, 9.30; 24% solubles.

remains soluble if 5 g of 10% EAA is first diluted with water to 500 ml and then allowed to evaporate to about two thirds of its volume in an open baker on a hot plate. A suspension of 30 g of starch and 0.5 g of EAA in 500 ml of water at pH 7 can therefore easily be prepared with this technique. Figure 4 shows the amylograph curve of this mixture and the curve of a control run without EAA. Since no excess ammonia is present, starch slurries could be heated to 95°C in these two runs. The initial rise in viscosity occurred at a lower temperature in the solution with EAA than in the control, and the viscosity of the cooled paste was significantly higher. However, viscosities at 95°C were not greatly different, and solubles in both runs amounted to 18–20%. Comparison of figures 3 and 4 shows that EAA has a greater effect on viscosity at high pH than at low pH, which is in agreement with the work of Maxwell (1970).

To support our view (Fanta et al 1990) that EAA increases the viscosity of starch pastes by forming a helical inclusion complex rather than through some simple interaction between the hydroxyl substituents of starch and the carboxyl substituents of EAA, poly (acrylic acid) of approximately 5,000 and 50,000 mol wt were substituted for EAA. If carboxyl substituents alone were responsible for interaction between starch and synthetic polymer, poly (acrylic acid) should cause a rise in viscosity equal to or greater than that observed with EAA. Comparison of the pasting curves shown in Figure 5, however, indicates that addition of poly (acrylic acid) to starch actually lowers rather than raises the viscosity throughout the heating and cooling cycle.

Gelatinization of starch in the amylograph was also performed in the presence of an aqueous ammonia solution of stearic acid to compare its behavior with that of EAA (Figure 6). Stearic acid was more difficult to dissolve than EAA and thus required a higher concentration of ammonium hydroxide than that used in most previous runs. Amylograph curves for starch-EAA and for starch alone were therefore repeated under more alkaline conditions so that a direct comparison could be made. Although stearic acid is known to form a helical inclusion complex with starch and might thus be considered a monomeric analogue of EAA, its behavior was greatly different. Instead of acting like EAA to increase the viscosity of starch, stearic acid reduced the viscosity over most of the pasting curve, which is in agreement with the work of Gray and Schoch (1962). The unique behavior of EAA when it is allowed to interact with starch is probably due to its polymeric nature and thus its ability to form pseudocross-links by complexing with more than one starch macromolecule.

Gel Rheology

On completion of amylograph runs, pastes at 30°C were poured

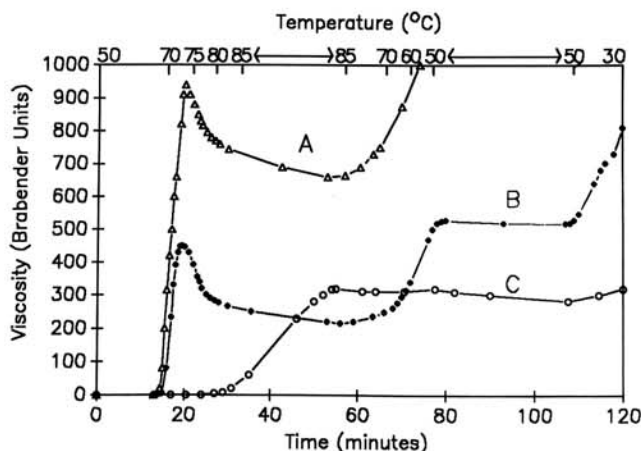


Fig. 6. Effect of stearic acid vs poly (ethylene-co-acrylic acid) (EAA) on paste viscosity of starch shown by amylograph runs made with 30 g of starch in a total volume of 500 ml of aqueous solution. Curve A: Solution contains 0.50 g of EAA; final pH, 10.10; 18% solubles. Curve B: Control run with no EAA or stearic acid; final pH, 10.31; 21% solubles. Curve C: Solution contains 0.50 g of stearic acid; final pH, 10.17; 13% solubles.

into molds and allowed to stand for 24 hr to permit the pastes to form gels firm enough for testing (Christianson et al 1985). Instron tests were then performed to determine gel strength and rigidity.

Figure 7 is a plot of the compressional stress-strain data of gels prepared from the starch pastes shown in Figure 2. Starch granules heated to 85°C at pH 4.95 are fully swollen and closely packed at this concentration, with only a small amount of exudate surrounding them (Christianson and Bagley 1983). However, when starch is both chemically and thermally gelatinized at 85°C, granule disruption and solubility increase, and a progressive increase in gel strength can be observed up to a pH of 9.54. Beyond this PH, the gel softens, as shown by a reduction in the rigidity modulus and in gel strength.

The effect of EAA on the compressional stress-strain behavior of starch gels prepared at 85°C and at pH 9.34-9.54 is shown in Figure 8. Gels in this figure were cast from starch and starch-EAA pastes recovered from amylograph runs shown in Figure 3. Figure 8 indicates that adding as little EAA as 0.25 g/30 g of starch reduces the strength of the resulting gel. A further reduction in gel strength was observed with the addition of EAA at 0.50 g/30 g of starch.

Stress-strain plots in Figure 9 of starch and starch-EAA gels cooked at 95°C at near-neutral pH (see amylograph curves in Figure 4) are not greatly different from comparable plots (Fig. 8) obtained at lower temperature and higher pH. Although starch in the absence of EAA exhibited a higher gel strength when cooked at the higher temperature, the gel strength of starch-EAA was nearly independent of cooking temperature and pH.

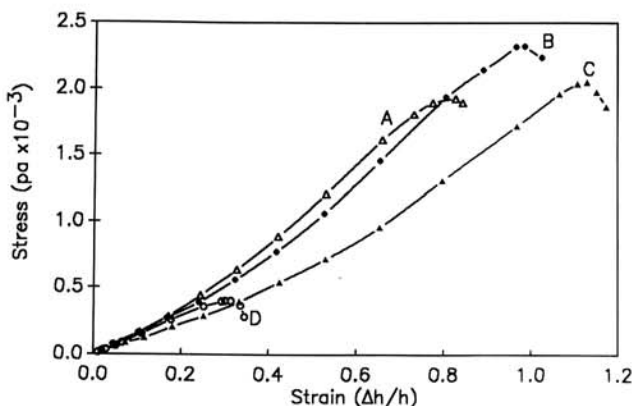


Fig. 7. Effect of ammonium hydroxide on gel rheology of starch. Pastes were recovered from amylograph runs shown in Figure 2. Curve A: 2 g of aqueous ammonia control solution; pH, 9.25. Curve B: 5 g of aqueous ammonia control solution; pH, 9.54. Curve C: 10 g of aqueous ammonia control solution; pH, 9.78. Curve D: No aqueous ammonia; pH, 4.95.

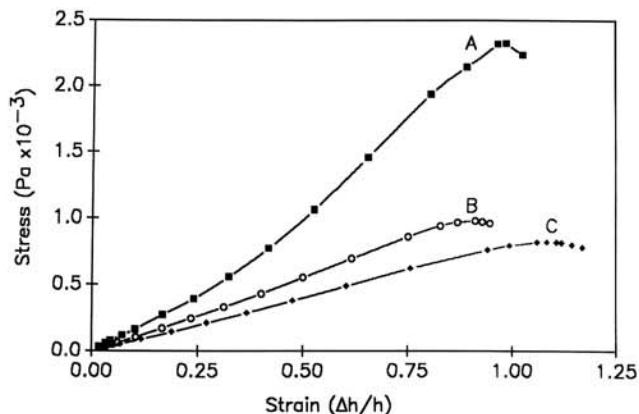


Fig. 8. Effect of poly (ethylene-co-acrylic acid) (EAA) on gel rheology of starch. Pastes were recovered from amylograph runs shown in Figure 3. Curve A: No EAA; pH, 9.54. Curve B: Mixture contains 5 g of 5% EAA solution; pH, 9.50. Curve C: Mixture contains 5 g of 10% EAA solution; pH 9.34.

Analysis of Pasted Starch-EAA Samples

To determine whether the presence of EAA during cooking has any significant effect on degree of gelatinization and granule disruption of starch, the insoluble fractions isolated from runs A and C of Figure 3 were critical point dried and examined by scanning electron microscopy. The two scanning electron micrographs in Figure 10 appeared similar, suggesting that EAA

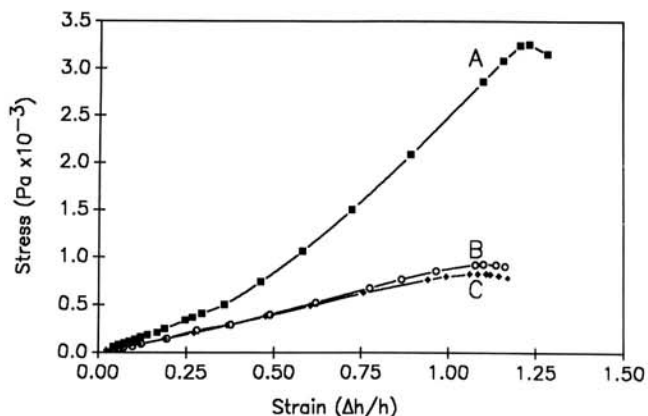


Fig. 9. Effect of poly (ethylene-co-acrylic acid) (EAA) on gel rheology of starch at near-neutral pH. Pastes were recovered from amylograph runs shown in Figure 4. Curve A: No EAA; pH, 7.00. Curve B: Mixture contains 5 g of 10% EAA solution; pH, 6.77. Curve C: Mixture contains 5 g of 10% EAA solution; pH, 9.34.

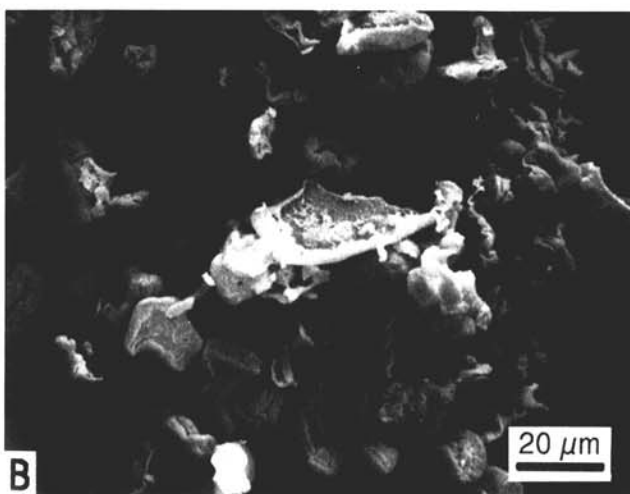
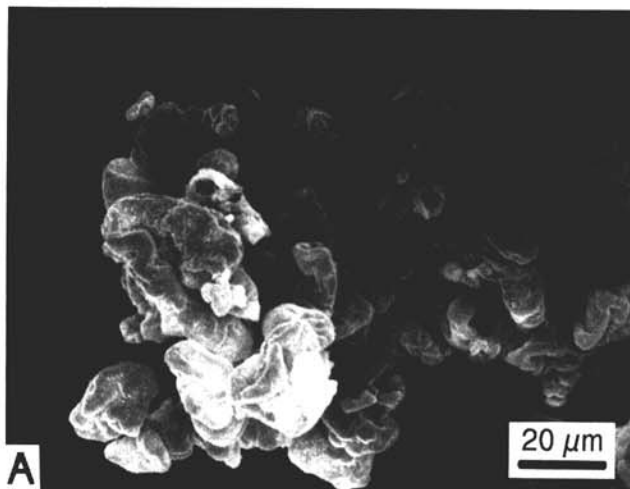


Fig. 10. Scanning electron micrographs of insoluble starch granule fragments. A, no poly (ethylene-co-acrylic acid) (EAA); insolubles were recovered from amylograph C shown in Figure 3; B, mixture contained 5 g of 10% EAA solution; insolubles were recovered from amylograph A shown in Figure 3.

does not promote disruption of starch granules during the pasting process. Thus, the increases in viscosity and decreases in gel strength that we observed when EAA was added seem largely due to complexing of EAA with the starch fraction already solubilized by heating in water.

This conclusion was confirmed by Fourier transform infrared analyses of soluble versus insoluble fractions isolated from run A in Figures 3 and 4. In both runs, the insoluble starch-granule fragments contained only traces of EAA, whereas the soluble fractions contained 3–5% of EAA. The amount of EAA in the soluble fraction that was actually complexed with starch was not determined.

CONCLUSIONS

The viscosity and gel rheology of cooked starch pastes can be easily altered by adding EAA (as a 5–10% solution in aqueous ammonia) to aqueous starch dispersions before cooking. Significant increases in paste viscosity are achieved with as little EAA as 0.25–0.50 g/30 g of starch. Viscosity increases not only under alkaline conditions (caused by ammonium hydroxide) but under neutral conditions as well. In addition to increasing viscosity, EAA in cooked starch pastes reduces the strength of gels formed when the pastes are allowed to stand at ambient temperature.

The influence of EAA on the viscosity and gel rheology of starch dispersions is apparently due to complexing between the two polymers in a manner similar to the well-known complexing between starch and fatty acids, e.g., stearic acid. However, the presence of stearic acid during cooking did not increase the viscosity of starch dispersions, presumably because of its monomeric nature and thus its inability to form pseudocross-links through complex formation with more than one starch molecule.

Scanning electron microscopy of insoluble starch-granule fragments suggests that EAA does not promote granule disruption during the pasting process. Thus, the increases in viscosity and decreases in gel strength seem largely due to complexing of EAA with starch that has already been solubilized by heating in water. This theory is supported by Fourier transform infrared spectra that show only traces of EAA in the insoluble starch fraction.

Although the compressional stress-strain behavior of starch-EAA gels might seem to contradict our data on paste viscosity (i.e., EAA addition decreases gel strength but at the same time increases paste viscosity), we can offer an explanation that is consistent with all of our experimental results and also with the known properties of starch. When starch is gelatinized in water, amylose is dissolved in preference to amylopectin, and the

insoluble granules remaining in suspension imbibe most of the excess water as they swell. The soluble amylose fraction is thus largely located in the interstitial solution surrounding the water-swollen granules. Complexing of EAA with this soluble starch fraction occurs rapidly, and the viscosity therefore sharply increases. However, starch gels form slowly through hydrogen bonding between linear amylose molecules, and the interstitial amylose solution forms a gel network strong enough for Instron testing only after standing for a period of hours. Although complex formation with EAA increases viscosity, it sterically inhibits the gradual hydrogen bonding between amylose molecules and thus reduces the measured strength and rigidity of the gels.

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