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Complexes between starch and poly(ethylene-*co*-acrylic acid) — viscosity and gel rheology of jet-cooked dispersions

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Starch-poly(ethylene-*co*-acrylic acid) (EAA) complexes were prepared by jet-cooking cornstarch, waxy cornstarch, high amylose cornstarch (Amylomaize VII), wheat starch and potato starch in the presence of an aqueous ammonia solution of EAA. Much of the excess ammonia is volatilized during jet-cooking, and cooked dispersions had pH values of about 9, depending on the amount of EAA solution used relative to starch. Viscosities were continuously measured as dispersions were cooled from 90 to 22°C. Addition of as little as 0·5% EAA based on starch significantly increased the viscosity of a cooked starch dispersion, and viscosities increased with the amount of EAA added. The maximum viscosity and the shape of the viscosity versus time/temperature curve varied with the particular starch variety used. Hot starch–EAA dispersions were poured into molds to allow the formation of gels on cooling. Gel rigidity was measured by subjecting these gels to uniaxial compression in an Instron testing machine. The ability to form a gel depended on the starch variety used, but more importantly on the presence of EAA and the starch–EAA ratio. The most rigid gel tested was prepared from 5% Amylomaize VII (amylose content 70%) without EAA. Addition of 5% EAA based on starch softened the gel, indicating interference of EAA with amylose retrogradation during gelation. Contrary to these results, cornstarch (containing about 30% amylose) gave a firm gel at 5% solids when cooked with 5% EAA (based on starch), whereas gels too soft for testing were obtained with EAA levels less than 5%. With waxy cornstarch and potato starch, which do not form gels by themselves, EAA levels of 10% (based on starch) were required to obtain gels rigid enough to test. Addition of EAA may, therefore, either increase or decrease gel rigidity depending upon how readily a particular starch will form a gel by itself (through amylose retrogradation) in the absence of additives. Apparent cross-link densities were also calculated from compressional data.

INTRODUCTION

Composite systems containing starch and poly(ethylene-*co*-acrylic acid) (EAA) have been under investigation for a number of years. A series of papers by Otey and coworkers (Otey *et al.*, 1977, 1980; Otey & Westhoff, 1984; Otey *et al.*, 1987) describe the preparation and properties of starch–EAA films, while Maxwell (1970) used blends of the two polymers as water-resistant paper sizes and also observed that addition of an aqueous ammonia solution of EAA to a water solution of starch resulted in a pronounced viscosity increase. Evidence suggests (Fanta *et al.*, 1990, Shogren *et al.*, 1991) that a helical inclusion complex is formed from starch and EAA that is similar to well-known complexes produced from starch and fatty acids.

In earlier work a Brabender amylograph was used to examine paste viscosities of starch dispersions cooked in the presence of aqueous ammonia solutions of EAA (Fanta & Christianson, 1991). The rheology of gels prepared from the resulting pastes (by allowing pastes to stand for 24 h) was also studied. The presence of

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EAA during cooking increased the viscosity of starch dispersions, presumably because the polymeric nature of EAA enables it to complex with more than one starch molecule and thus increase the effective molecular weight of starch through formation of pseudo cross-links. Gel strengths, however, were reduced by the presence of EAA, because the ability of solubilized amylose to retrograde and aggregate for structure development was limited by EAA complexing. Scanning electron micrographs and FTIR analyses suggested that EAA only complexes with the minor percentage of starch (roughly 25%) that has been solubilized and not with the major fraction that is made up of swollen granules and granule fragments.

To determine how EAA influences the viscosity and gel properties of starch when it is totally in solution, the authors turned to jet-cooking of starch–EAA mixtures as a convenient technique for solubilizing starch and also for achieving an intimate mixture of the two polymers. These studies show that addition of less than 1% EAA (based on starch) significantly alters the rheological properties of starch in solution as well as the properties of starch gels. These changes broaden the number of practical applications for aqueous starch dispersions.

EXPERIMENTAL

Materials

Cornstarch (Buffalo 3401) was from CPC International, Inc. Argo, Illinois. Waxy cornstarch (Amioca) was from National Starch and Chemical Corp. Bridgewater, New Jersey. High amylose corn starch (Amylomaize VII) was from American Maize Products Co. Hammond, Indiana. Potato starch was from Sigma Chemical Co. Wheat starch (AYTEX P) was from Ogilvie Mills, Inc. Montreal, Quebec. All weights are corrected for moisture and are given on a dry basis. Gelatin (275 Bloom) was obtained from Atlantic Gelatin Division, General Foods Corp, Woburn, MA, and 10% gels were prepared as described earlier (Bagley *et al.*, 1985).

EAA was Primacor 5981 from Dow Chemical Co. Midland, Michigan. This polymer, which contains about 20% copolymerized acrylic acid by weight, has a melt index of 300, M_w of about 18 000, and M_n of about 7000.

A 10% EAA solution in aqueous ammonium hydroxide was prepared by stirring 60 g of EAA in 600 ml of 50/50 (by volume) concentrated ammonium hydroxide/water in a flask equipped with reflux condenser. The mixture was heated under gentle reflux (about 65–85°C) for 8 h, and was then allowed to cool. The slightly turbid solution was then diluted with concentrated ammonium hydroxide to a total weight of 600 g. Brookfield viscosity of this solution (No. 1 spindle; 30 rpm) was 5 cp, as compared with 2 cp for water.

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

Jet-cooking

Jet-cooking (Winfrey & Black, 1964) was carried out with a Penick & Ford laboratory model continuous cooker operated with 65 psig line pressure steam. Cooking was carried out at 140°C (40 psig steam) with a pumping rate of about 1·1 liter/min.

The required amount of 10% EAA solution was diluted with water to 1 liter, and starch was suspended in the resulting solution. All percentage EAA values reported for starch dispersion compositions are based on dry weight of starch. Mixtures were passed through the jet-cooker, and dispersions were collected in a Dewar flask to maintain the temperature above 90°C. Somewhat higher starch concentrations than those desired were used to allow for dilution of the cooked dispersions with condensed steam. For example, 66·7 g of starch in 1 liter of aqueous EAA solution was used to obtain a final starch concentration of 5%.

Per cent solids in each cooked dispersion were determined by freeze-drying a weighed portion of the paste. Actual per cent solids were within 0·35% of the desired values.

Viscosity

Viscosities were measured with a Rotovisco model RV 100 viscometer with MV II bob. The jacketed sample cup was attached to a circulating water bath initially held at 90°C. After the cup was filled with hot, jet-cooked dispersion, the bath was cooled to 22°C at 0·97°C per min, and viscosity was recorded as a function of time and temperature. A low shear rate ($10\ s^{-1}$) was used to minimize mechanical degradation of the starch–EAA complex. The viscometer was then allowed to run for about 80 min at 22°C to record any viscosity changes with time. Since the viscometer has no provision for determining actual temperature of the sample, it was necessary to use bath temperature as an estimate of sample temperature with the realization that minor differences will exist between these two temperature values.

Gel rheology

Hot (about 90°C) jet-cooked dispersions were poured into cylindrical PVC disc molds having 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 h at ambient temperature before compressional testing. Mold rings were removed, and gels were compressed (lubricated uniaxial compression) using an Instron Universal Testing Machine (Model 1122) with a 50-kg load cell (Christianson *et al.*, 1985). Tests were carried out at 0·5 cm/min crosshead speed. Stress (Pa) was plotted against strain ($\Delta h/h$), where h is the actual height of the gel disc after compression by an amount Δh. Δh is defined as h_0 (initial gel height) minus h.

RESULTS AND DISCUSSION

Paste viscosity

Jet-cooking (Winfrey & Black, 1964) has been used commercially for decades to prepare starch solutions. The method involves pumping an aqueous starch slurry through an orifice where it contacts a jet of high pressure steam. Under these high temperature, high shear conditions, the starch granule structure is totally disrupted; little or no insoluble starch is found in the final dispersion. In the present study, EAA was added to starch–water slurries as a 10% solution in aqueous ammonia, and the resulting two-component mixture was then jet-cooked. Although much of the excess ammonia is volatilized during jet-cooking, starch–EAA dispersions are still mildly alkaline and show a pH of about 9, depending on the amount of EAA solution used relative to starch. Starch–EAA dispersions are fluid at high temperatures but thicken rapidly on cooling, developing higher viscosities than dispersions of starch itself. Viscosities were, therefore, continuously measured as dispersions were uniformly cooled from a maximum temperature of 90°C and are reported as a function of both time and temperature. In the absence of starch, EAA in aqueous ammonia exhibits a viscosity not much greater than that of water.

With common cornstarch, the large viscosity increases caused by addition of EAA made it necessary to carry out experiments at three different starch concentrations. A high starch concentration (10% solids) was used (Fig. 1) to detect differences between dispersions containing 1% EAA or less; however, with increasing amounts of EAA, viscosities became too high for accurate measurement. The effect on viscosity of 1–10% EAA is best seen at 5% starch solids (Fig. 2). EAA levels of up to 20% could only be measured at low starch solids, e.g. 2·5% (Fig. 3). Curves show a steady increase in viscosity with decreasing temperature, and some samples also show a loss in viscosity with prolonged stirring at 22°C. Although 0·25% EAA (based on starch) at 10% starch solids (curve D, Fig. 1) gave little or no increase in viscosity over the control with 0% EAA (curve E), a significant viscosity increase was observed with 0·5% EAA (curve B). Maximum viscosities occurred at stirring times of about 70 min or longer (i.e. after samples had reached room temperature).

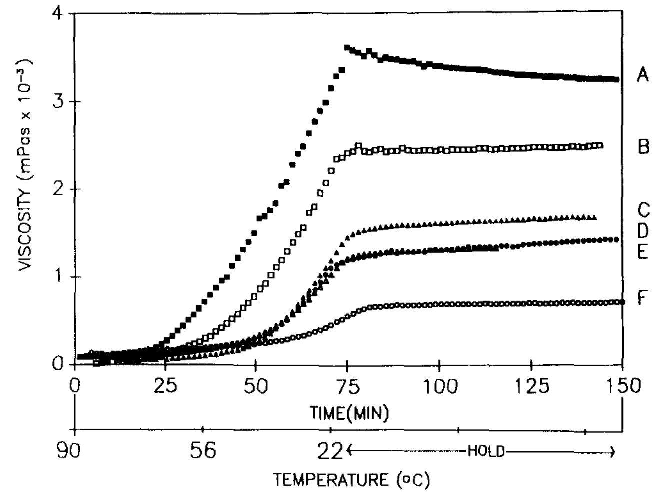

Fig. 1. Effect of time/temperature on viscosities of starch–EAA complexes. Starch jet-cooked at 10% solids. Curve A: 1% EAA based on starch; final pH 8·48. Curve B: 0·5% EAA based on starch; final pH 8·15. Curve C: No EAA; NH_4OH/H_2O control solution equal to the weight of EAA solution used for Curve A; final pH 8·85. Curve D: 0·25% EAA based on starch; final pH 7·75. Curve E: No EAA; NH_4OH/H_2O control solution equal to the weight of EAA solution used for Curve D; final pH 8·15. Curve F: No EAA; no NH_4OH/H_2O control solution; final pH 5·03.

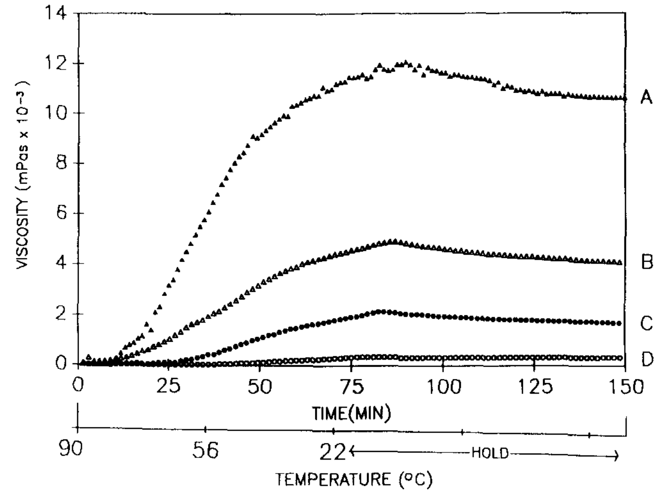

Fig. 2. Effect of time/temperature on viscosities of starch–EAA complexes. Starch jet-cooked at 5% solids. Curve A: 10% EAA based on starch; final pH 8·83. Curve B: 5% EAA based on starch; final pH 8·85. Curve C: 3% EAA based on starch; final pH 8·80. Curve D: 1% EAA based on starch; final pH 8·40.

For control experiments in the absence of EAA (Fig. 1), a volume of ammonium hydroxide-water solution equal to the volume of 10% EAA was used.

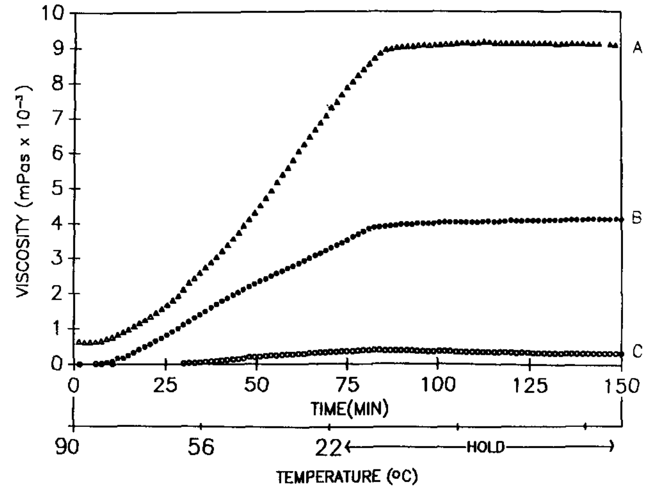

Fig. 3. Effect of time/temperature on viscosities of starch-EAA complexes. Starch jet-cooked at 2·5% solids. Curve A: 20% EAA based on starch; final pH 9·02. Curve B: 10% EAA based on starch; final pH 8·85. Curve C: 5% EAA based on starch; final pH 8·75.

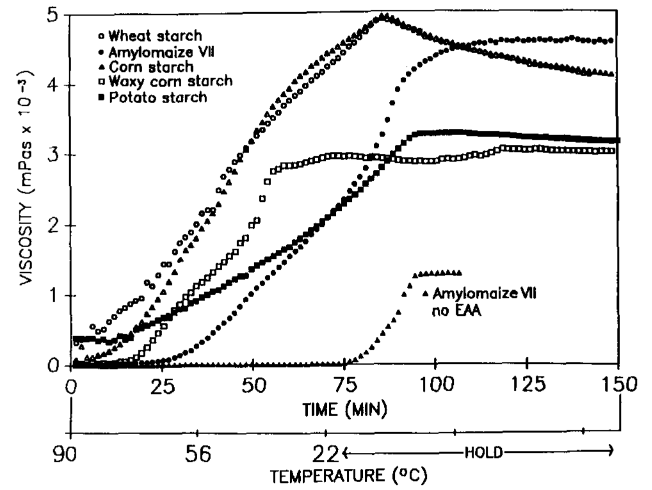

Fig. 4. Effect of time/temperature on viscosities of starch-EAA complexes. Starch jet-cooked at 5% solids with 5% EAA based on starch. A comparison of starch varieties.

Although this technique was used so that pH values with and without EAA would be similar, observed pH values were always somewhat higher in the absence of EAA.

In Fig. 4, the rheological behavior of cornstarch-EAA may be directly compared with that of similar mixtures prepared from waxy cornstarch, high amylose cornstarch (Amylomaize VII), wheat starch and potato starch. The result for Amylomaize VII in the absence of EAA is also presented in Fig. 4. Note that the viscosity of this high amylose sample does not develop until the paste has reached room temperature and begins to retrograde. When EAA is present, viscosity starts increasing at a much higher temperature and continues to rise rapidly as temperature falls.

Large differences are seen between waxy (98% amylopectin) and Amylomaize VII (70–75% amylose) cornstarches (Fig. 4) with respect to both maximum viscosity and the time/temperature at which maxima occur. Waxy cornstarch-EAA attains its maximum viscosity at about 35°C, whereas the maximum for high amylose cornstarch-EAA does not occur until dispersions are stirred for about 30 min at 22°C. Although waxy cornstarch-EAA develops viscosity rapidly on cooling, the maximum value was only about 3000 mPa, as compared with 4600 mPa for the high amylose variety. These results may reflect differences caused by the complexing of EAA with the many short chains of highly-branched amylopectin, as opposed to complexing with a starch polymer that is largely linear.

The two cereal starches, corn and wheat (Fig. 4), gave similar curves for viscosity versus time/temperature, whereas potato starch-EAA exhibited a significantly lower maximum viscosity.

Gel rheology

As might be expected, jet-cooked starch in the absence of EAA gave molded samples which were qualitatively similar to the 121°C (stirred) samples previously reported (Christianson *et al.*, 1986), with the exception of high amylose starch (Amylomaize VII) which formed a firm gel even at 5% solids, due to amylose retrogradation. Properties of the various gels depended on the particular variety of starch used; but more importantly, it was observed that gel properties could be greatly changed by the addition of varying amounts of EAA to the formulations. At 5% starch solids and 5% EAA (based on starch), wheat and cornstarches as well as Amylomaize VII gave firm gels. Gels prepared from 5% cornstarch, however, were too soft to be tested when EAA levels were less than 5%. Waxy cornstarch and potato starch at 5% starch solids and 5% EAA based on starch also did not give gels sufficiently rigid for testing, and for these two starches it was necessary to increase the EAA level to 10% to obtain meaningful test results.

When starch is not fully solubilized, but has the swollen starch granules and granule fragments present, fracture occurs in lubricated uniaxial compression in a comparatively simple way. A few large, sharp and well-delineated cracks form, and fairly reproducible maxima on stress/strain curves are seen. Gels formed from starch totally dissolved by jet-cooking in the presence of EAA show quite different fracture behavior in that the gels tend to shatter. A multitude of fractures form, and further compression reduces the sample to numerous small pieces. This shattering tendency leads to poor reproducibility near the fracture point and precludes any precise estimate of gel strength.

Figure 5 shows stress (Pa) versus strain (defined here as $(h_0 - h)/h$) curves for the series of gels examined. The most rigid gel tested was 5% Amylomaize VII without EAA, more rigid in fact than the 10% gels of

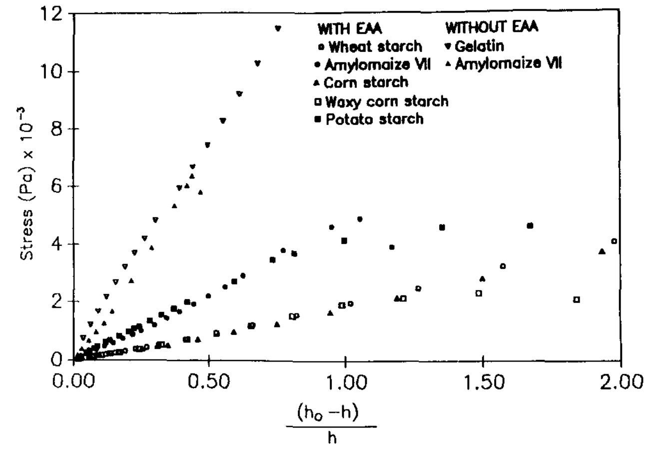

Fig. 5. Stress versus strain plots for starch–EAA gels. Starch was jet-cooked at 5% solids. Cornstarch, wheat starch, and Amylomaize VII gels contain 5% EAA based on starch. Waxy cornstarch and potato starch gels contain 10% EAA.

corn, wheat or rice prepared earlier (Christianson *et al.*, 1986) at 80°C, 94°C and 121°C (static). A gelatin sample, included in Fig. 5 for comparative purposes, was prepared from a 10% gelatin solution, and the stress/strain plot is almost identical to that of Amylomaize VII at 5% solids. Figure 5 shows that addition of 5% EAA softens the Amylomaize VII gel, producing a gel modulus (defined as the slope of the stress/strain curve) less than half that of the 5% Amylomaize VII gel alone. This is in sharp contrast to the other starch varieties, where addition of EAA acts to strengthen the gel. Potato starch at 5% solids and 10% EAA based on starch falls on about the same curve as Amylomaize VII with 5% EAA. Lower modulus gels are formed from corn and wheat starches with 5% EAA and from waxy cornstarch with 10% EAA; and interestingly, gels from these three formulations give similar stress/strain plots.

The data of Fig. 5 are replotted in Fig. 6 to show the initial neo-Hookean behavior of all the gels at low deformation. The apparent cross-link density, as estimated by the intercept on the vertical axis, is highest for gelatin, with Amylomaize VII giving a significantly lower value of the intercept. The intercept for gelatin was about 3·3 × 10^4 Pa, in reasonable agreement with another gelatin gel reported by Bagley *et al.* (1985). The other gels all fall at 10^4 Pa or lower (half the value for Amylomaize VII). In addition, both gelatin and Amylomaize VII show steep rises in these plots once the neo-Hookean region is passed. The other gels, with EAA, do not show this steep rise in slope after the initial neo-Hookean region.

The above data show that EAA may have different qualitative effects on the behavior of starch solutions and on the resulting gels prepared from these solutions, depending on the particular starch variety examined. EAA invariably increases starch solution viscosity, presumably because EAA, in complexing with starch, increases the effective molecular weight of the polysaccharide. One of the effects of added EAA on gels is illustrated by the Amylomaize VII results in Fig. 6. Here Amylomaize VII in the absence of EAA has an apparent cross-link density (ordinate intercept) of 2 × 10^4 Pa, caused by retrogradation of amylose. With EAA present, however, this intercept falls to less than 9 × 10^3 Pa, confirming the hypothesis that EAA interferes with amylose retrogradation during gelation by complexing with amylose. On the other hand, for starches containing more amylopectin than amylose, complexing with EAA (and the corresponding increase in effective molecular weight) serves to enhance physical cross-linking and the resulting formation of rigid gels, even in starches which by themselves do not form significant gel structures. We thus have the interesting observation that the addition of EAA can either increase or decrease gel rigidity depending on how readily a particular starch will form a gel by itself (through amylose retrogradation) in the absence of additives.

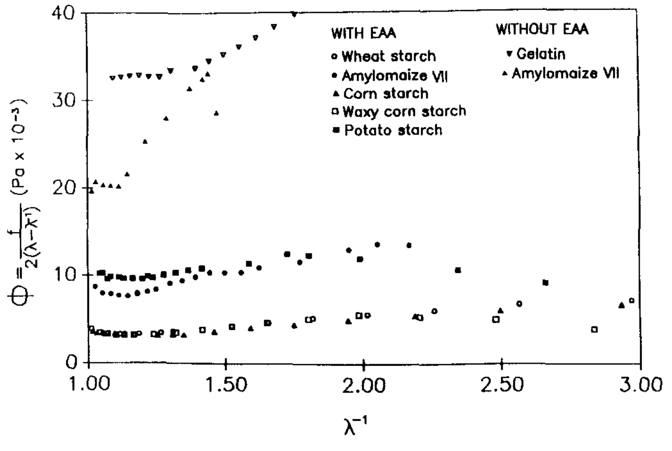

Fig. 6. Mooney-Rivlin plots of compressional data for starch–EAA gels. EAA content of gels is the same as for Fig. 5.

CONCLUSIONS

Starch–EAA complexes may be conveniently prepared by jet-cooking starch in the presence of an aqueous ammonia solution of EAA. Much of the excess ammonia is volatilized during jet-cooking, and aqueous starch–EAA dispersions have pH values of about 9, depending on the amount of EAA solution used relative to starch. Starch–EAA dispersions are fluid at high temperatures but thicken rapidly on cooling. The relationship between viscosity and temperature may be observed by continuously measuring the viscosity under low shear as dispersions are cooled from 90°C to 22°C.

The maximum viscosity and the shape of the viscosity versus time/temperature curve vary with the particular starch variety used. Complexes prepared from cornstarch, high amylose cornstarch, wheat starch, and potato starch do not reach their maximum viscosity until after they have cooled to room temperature, while waxy cornstarch attains its maximum viscosity at about 35°C. The maximum viscosity of starch–EAA complexes increase as the amount of EAA is increased relative to starch. With cornstarch, as little as 0·5% EAA based on starch gives a significant increase in viscosity over that observed in a control experiment carried out in the absence of EAA.

The rigidity of gels formed by allowing starch–EAA dispersions to stand for 24 h may be measured by subjecting these gels to lubricated uniaxial compression in an Instron testing machine. The ability of starch and EAA to form a gel rigid enough for testing depends on both the starch variety used and the starch:EAA ratio. Wheat starch, cornstarch, and high amylose cornstarch give firm gels with 5% starch solids and 5% EAA based on starch. Waxy cornstarch and potato starch require 10% EAA to form gels of comparable firmness. High amylose cornstarch with no added EAA gives the most rigid gel, while potato starch with 10% EAA and high amylose starch with 5% EAA rank second and third in gel rigidity. Wheat starch, cornstarch (both with 5% EAA) and waxy cornstarch (with 10% EAA) are all more elastic and less rigid than the other three samples and fall on about the same stress versus strain curve. The gel rigidities observed are consistent with known properties of the various starches and also with the expected behavior due to complexing with EAA.

Mooney-Rivlin plots of the various starch–EAA gels show an initial region where the slope is essentially zero, thus permitting calculation of apparent cross-link densities. Addition of EAA to high amylose starch reduces the value for apparent cross-linking by about 50%, suggesting that the EAA complex formed with amylose prevents its retrogradation and aggregation.

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