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The influence of pH on the viscous behavior of starch–poly(ethylene-co-acrylic acid) complexes

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Starch–poly (ethylene-co-acrylic acid) (EAA) complexes were prepared by jet-cooking mixtures of either cornstarch, waxy cornstarch or high amylose cornstarch with aqueous ammonia dispersions of EAA (4% EAA based on the weight of starch). Viscosities (η) were determined at temperatures ranging from 80°C to 22°C, and plots of log η versus $1/T$ (K^{-1}) were prepared. When cooked with EAA, cornstarch and waxy cornstarch showed major changes in viscous behavior between 50°C and 60°C. Above 50–60°C, viscosity increased markedly with a reduction in temperature; however, viscosity increased slowly below 50–60°C with an apparent activation energy for the process approximating that of water itself. The temperature dependence of the measured viscosity from 80°C to 60°C could be attributed to the large increase in size and complexity of the flowing particles as individual amylopectin molecules were bound together by complexed EAA. Apparently, complexing is essentially complete at 50°C. When high amylose cornstarch was cooked in the absence of EAA, retrogradation produced a sharp increase in log η at temperatures below about 50°C. However, if EAA is present, association between amylose molecules apparently takes place via complex formation rather than retrogradation, since log η increases sharply at about 70–80°C. Also, in contrast to cornstarch and waxy cornstarch, log η versus $1/T$ plots for high amylose cornstarch did not level off at low temperatures. In general, viscosities increased with the pH of the system, particularly when η was measured at high temperatures. This could result from improved complexing ability of EAA under high pH conditions, possibly due to reduced micelle size and maximum extension of polymer chains from micelle surfaces.

INTRODUCTION

Composite systems containing starch and poly(ethylene-co-acrylic acid) (EAA) have been under investigation at the authors' laboratory for a number of years. Research in this area was initiated by Otey and coworkers (Otey *et al.*, 1977, 1980, 1987; Otey & Westhoff, 1984), who prepared both cast- and extrusion-blown films from this two-component polymer system. A large body of evidence has been presented (Fanta *et al.*, 1990; Shogren *et al.*, 1991*a*, 1991*b*) to support the idea that starch and EAA form helical inclusion complexes similar to those formed from starch and fatty acids. Complex formation undoubtedly contributes to the observed compatibility between these two dissimilar polymers and to the excellent film properties that Otey *et al.* have observed for starch–EAA mixtures.

Complex formation between starch and EAA results in a pronounced viscosity increase when aqueous dispersions of the two polymers are mixed. Maxwell (1970) first observed this increase in viscosity while investigating starch–EAA blends intended as water-resistant paper sizes. The authors have examined this system in some detail, initially using a Brabender Amylograph to measure viscosity versus temperature for starch cooked in aqueous ammonia dispersions of EAA (Fanta & Christianson, 1991). In a subsequent study (Christianson *et al.*, 1992), cooking was carried out by passing

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starch and EAA in aqueous ammonia through a steam jet cooker. Viscosities were then continuously measured in a Roto-Visco Viscometer as solutions were cooled. In contrast to the Brabender Amylograph, which heats starch slurries to less than 100°C (and thus yields not only soluble starch but also gelatinized and swollen starch granule fragments), jet cooking is carried out under high shear conditions with high pressure steam and therefore dissolves/disperses starch completely. Swollen granule fragments are not evident in the jet-cooked product. With both cooking procedures, addition of less than 1% EAA, based on the dry weight of starch, caused significant increases in the viscosities of starch dispersions.

During the course of the authors' research on jet-cooked starch–EAA mixtures in aqueous ammonia, it was observed that addition of sodium hydroxide before jet cooking, in an amount equivalent to carboxylic acid substituents present in EAA, dramatically increased the measured viscosity, particularly at high temperatures. The present study was therefore carried out to quantitate these preliminary observations, since this simple method for altering the rheological properties of starch solutions might have practical applications in the area of starch utilization. Also, to enhance knowledge regarding the formation and structure of starch–EAA complexes, plots of log viscosity (η) versus $1/T$ (in K^{-1}) were constructed to estimate apparent activation energies for viscous flow of these 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 cornstarch (Amylomaize VII) was from American Maize Products Co., Hammond, Indiana. All weights are corrected for moisture and are given on a dry basis.

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, a M_w of about 18 000, and an M_n of about 7 000 (Dow Chemical Co., 1984).

A 10% dispersion of EAA 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 dispersion, which had lost weight due to loss of volatile ammonia, was then diluted with concentrated ammonium hydroxide to a total weight of 600 g. Brookfield viscosity (No. 1 spindle; 30 rpm) was 5 centipoise (cp), as compared with 2 cp for water (Korson *et al.* (1969) report that the true viscosity of water at 20°C is 1·0020 cp).

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^{-1}.

EAA dispersion needed to obtain either 3% or 5% EAA, based on the dry weight of starch, was weighed into a 1-liter volumetric flask. For systems containing sodium hydroxide, 0·1 N NaOH was added in an amount equivalent to the carboxylic acid content of EAA. The flask was diluted with water to 1 liter, and 66·7 g of starch was suspended in this solution. Starch concentrations higher than 5% were prepared to allow for dilution of cooked dispersions with condensed steam. Mixtures were passed through the jet cooker, and dispersions were collected in a Dewar flask to maintain temperatures above 90°C. Per cent solids were determined by freeze-drying weighed portions of each cooked dispersion. The pH of the cooked dispersions was determined at 25°C.

Viscosity

Viscosities were measured with a Haake Rotovisco model RV 100 viscometer (Fisons Instruments, Inc., Paramus, New Jersey) with MVII cup. The jacketed sample cup was attached to a circulating water bath initially held at 90°C and was covered with flexible plastic wrap to retard evaporation of water from the sample. After the cup (preheated in a 90°C oven) was filled with hot, jet-cooked dispersion, the bath was cooled to 80°C for the first series of viscosity measurements. The temperature of the bath was then lowered in 10°C steps to 30°C and then finally to 22°C, and viscosities were measured at a series of shear rates at each of these temperatures. Viscosities were determined at shear rates of 22·6, 90·2, 180·4, 270·6, 360·8 and 451 s^{-1} (5, 20, 40, 60, 80 and 100% of the maximum shear rate attainable with the MVII cup). Viscometer readings stabilized rapidly with each stepwise increase in shear rate, and stable readings were usually obtained within less than 1 min. Total elapsed time at each temperature (during viscosity measurements at the six different shear rates) was in the order of 15–20 min.

Turbidity determinations

Turbidities of aqueous dispersions of EAA were determined with a Hach Ratio Turbid Meter, Model 18900. Readings are given in Nephelometric Turbidity Units (NTU).

RESULTS

Cornstarch contains amylose and amylopectin in an approximate ratio of 1:3 and was studied initially because it is the most common and inexpensive starch used commercially. Before studying starch-EAA mixtures, the authors first examined the rheological behavior of cornstarch itself in the absence of EAA. Cornstarch was jet cooked at pH values ranging from 8·31 to 10·44 to give solutions containing 5% starch solids. The pH was varied by adding either ammonium hydroxide or a combination of ammonium hydroxide plus sodium hydroxide to starch slurries prior to passing them through the jet cooker. This pH range encompasses that usually obtained when cornstarch is mixed with aqueous alkaline dispersions of EAA.

Viscosities of these 5% starch solutions (in mPa s) were determined at 80, 70, 60, 50, 40, 30 and 22°C using shear rates in the range 22·6–451 s^{-1} at each temperature. Although viscosities of these samples at pH 8·31 were below about 60 mPa s (a level for which the authors' viscometer does not provide precise data), the order of magnitude of viscosities observed can be indicated. To the precision of the data, the solutions were close to Newtonian in behavior; and at 22, 30 and 40°C, the viscosities observed were 52 ± 6 mPa s, 42 ± 4 mPa s and 31 ± 6 mPa s, respectively. Instrument limitations were such that even more scatter occurred at 50°C and above, where viscosity values were 30 mPa s or less. Under more alkaline conditions (pH 10·44) viscosities were somewhat higher. For this pH range, the viscosity/shear rate plot showed definite non-Newtonian behavior at 22, 30 and 40°C, with slopes of the log viscosity/log shear rate plots being −0·20, −0·22 and −0·11, respectively. At 100 s^{-1}, the corresponding viscosities at 22, 30 and 40°C were 100, 80 and 50 mPa s, respectively. At 50°C, the solution was Newtonian with a viscosity of 35 ± 5 mPa s. At temperatures of 60°C and above, the viscosities were all below 30 mPa s and were, as noted for the pH 8·31 samples, badly scattered.

Addition of EAA to cornstarch at a level of 3%, based on the dry weight of starch, has a major effect on viscosity, as shown in Fig. 1. Since EAA is dispersed in aqueous ammonium hydroxide before mixing with starch and jet cooking, the pH of the cooked dispersion is 8·64. At 80°C, the viscosity is low (about 25 mPa s), and the scatter in the results is similar to that observed with cornstarch solutions cooked in the absence of EAA. To the precision of the data, however, the cornstarch-EAA mixture appears Newtonian at 80°C. At 70°C, the viscosity has increased markedly and is clearly non-Newtonian in behavior, obeying a power law in the shear rate range examined (a slope of −0·3). A further large increase in viscosity occurs when the temperature is lowered to 60°C; however, further decreases in temperature result in comparatively minor increases in viscosity, and the slopes of the log viscosity versus log shear rate plots are constant at −0·5 for 60, 50, 40, 30 and 22°C.

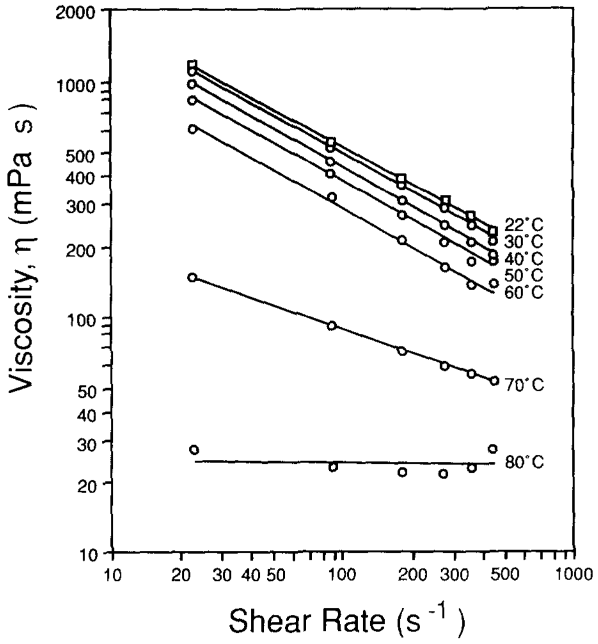

Fig. 1. Effect of the temperature of a cornstarch-EAA dispersion on the relationship between viscosity and shear rate: 5·40% total solids; 3% EAA based on starch; pH 8·64.

Figure 2 shows similar log η versus log (shear rate) plots for 5% cornstarch and 3% EAA, but with NaOH added in an amount equivalent to the carboxylic acid content of EAA. The pH of this jet-cooked dispersion was 9·38. If we compare Figs 1 and 2, we see that addition of NaOH causes a major shift to higher viscosities at 70°C and 80°C. Also, the slope of the power law relation between log η and log (shear rate) at these temperatures is essentially the same as that observed at the lower temperatures. For temperatures in the 22°C to 60°C range, there is a smaller but still significant increase in viscosity with NaOH addition.

The effects of temperature can be conveniently summarized by plotting log η versus $1/T$, and plots of this type were constructed for the two cornstarch-EAA dispersions prepared at pH 8·64 and 9·38 (Fig. 3). Values of log η used in the construction of Fig. 3 were obtained from the straight-line plots in Figs 1 and 2 and are for an arbitrary shear rate of 100 s^{-1}. Vertical bars in curve B show the variation in log η values for three separate experiments carried out under identical conditions of cooking and viscosity determination. At the higher pH, where NaOH was added (Fig. 2), this arbitrary choice of shear rate does not affect the result, since the double logarithmic plots of viscosity versus shear rate are linear and essentially parallel over the range investigated. However, for the experiments in which NaOH was not added, the 70 and 80°C curves of Fig. 1 are not parallel to the viscosity/shear rate plots at

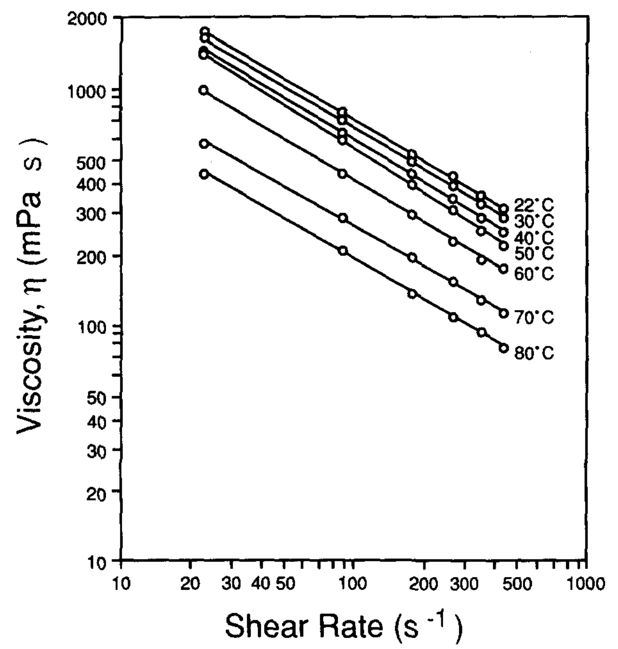

Fig. 2. Effect of the temperature of a cornstarch–EAA dispersion on the relationship between viscosity and shear rate: 5·40% total solids; 3% EAA based on starch; NaOH added to raise the pH to 9·38.

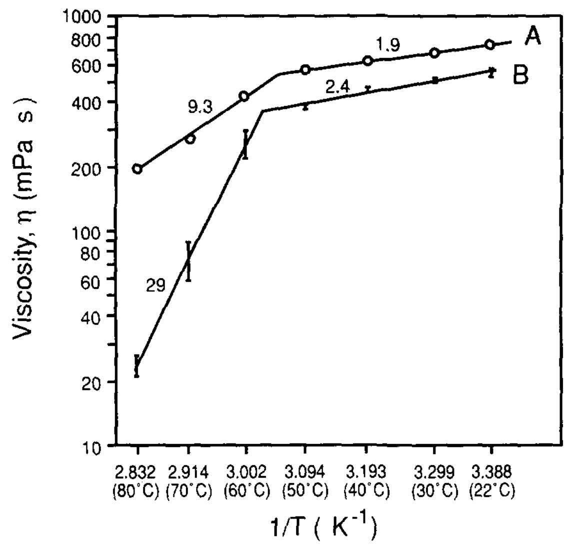

Fig. 3. Plots of log viscosity (η at 100 s^{-1}) versus $1/T$ (K^{-1}) for cornstarch–EAA dispersions. (A) NaOH added; 5·40% total solids; 3% EAA based on starch; pH 9·38. (B) No NaOH added. Vertical bars show the variation in the following three experiments: (1) 5·40% total solids, 3% EAA based on starch, pH 8·64; (2) 5·38% total solids, 3% EAA based on starch, pH 8·63; (3) 5·29% total solids, 3% EAA based on starch, pH 8·64. Numbers assigned to various portions of the curves are Arrhenius apparent energies of activation in kcal mol^{-1}, and these values are equal to $2{\cdot}303R\,[\Delta \log \eta/\Delta\,(1/T)]\,10^{-3}$, where R is the gas constant (1·987 cal degree^{-1} mol^{-1}), T is the temperature (K), η is the viscosity (mPa s), and $\Delta \log \eta/\Delta\,(1/T)$ is the slope of the experimentally determined plot of log η versus $1/T$.

60°C and below, and hence the slopes of the log viscosity versus $1/T$ plots are affected by the choice of shear rate.

It is evident in Fig. 3 that both with and without NaOH present, there is a major change in the behavior of these systems occurring between 60 and 50°C. Below this temperature range, the viscosity changes slowly with decreasing temperature, with an apparent energy of activation for the process of 1·9 and 2·4 kcal mol^{-1} at pH 9·38 and 8·64, respectively. Water alone in this temperature range has apparent energies of activation for flow ranging from about 4 to 3·1 kcal mol^{-1} (Korson *et al.*, 1969). Thus, to a first approximation, the temperature dependence of these starch–EAA dispersions is attributable to the temperature dependence of the suspending medium, water. This in turn implies that the starch–EAA complex is acting as a filler and contributes to viscous effects only through the contributions resulting from the volume fraction occupied by the complex. Above the 50–60°C transition range, the temperature dependence of the measured viscosity becomes very marked, with apparent energies of activation of 9·3 and 29 kcal mol^{-1} for pH 9·38 and 8·64, respectively. This appears to be a reflection of the complexing occurring between starch molecules and EAA, although a detailed explanation of these results obviously requires further study of these complexes in solution/dispersion (as well as a study of starch solutions in the absence of EAA).

The same general pattern of behavior is seen in comparable experiments carried out with waxy cornstarch (Fig. 4). This is not unexpected, since waxy cornstarch contains about 100% amylopectin, as compared with about 75% amylopectin in cornstarch. Despite similarities between the two starches, log η values are lower for waxy cornstarch throughout the entire range of temperatures. Moreover, slopes of the curves are somewhat lower for waxy cornstarch in the 60–80°C range. An increase in EAA level from 3% (curve B) to 5% (curve A) produced higher viscosities but did not greatly change the shape of the curve.

Similar experiments were next carried out with a commercial high amylose cornstarch containing 70% amylose. Experiments were not run with pure amylose, because the authors wished to confine the study to native starches in granule form to remove any variability that might be associated with the isolation of starch components before jet cooking.

Log η versus $1/T$ plots for high amylose cornstarch (Fig. 5) are dramatically different from those obtained for cornstarch and waxy cornstarch. Whereas viscosities of cornstarch and waxy cornstarch in the absence of EAA remain too low for accurate measurement throughout the entire temperature range, the viscosity of high amylose cornstarch increases sharply below 50°C, as an expected result of amylose retrogradation (see curves C and D). When high amylose cornstarch is

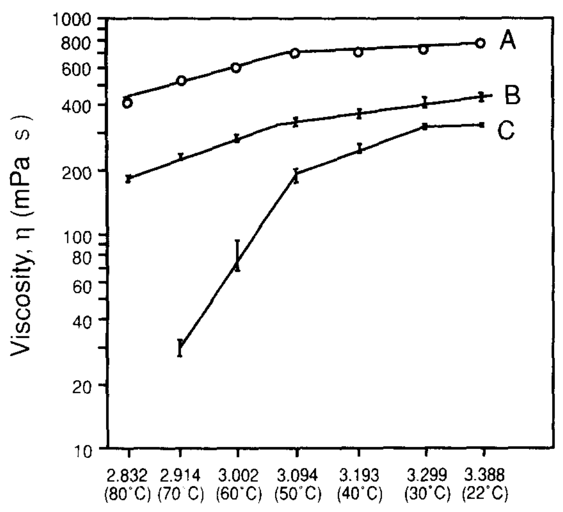

Fig. 4. Plots of log viscosity (η at 100 s^{-1}) versus $1/T$ (K^{-1}) for waxy cornstarch-EAA dispersions: (A) NaOH added, 5·53% total solids, 5% EAA based on starch; (B) NaOH added. Vertical bars show the variation in the following two experiments: (1) 5·45% total solids, 3% EAA based on starch, pH 9·61; (2) 5·33% total solids, 3% EAA based on starch, pH 9·86. (C) No NaOH added. Vertical bars show the variation in the following two experiments: (1) 5·45% total solids, 3% EAA based on starch, pH 8·86; (2) 5·45% total solids, 3% EAA based on starch, pH 8·97.

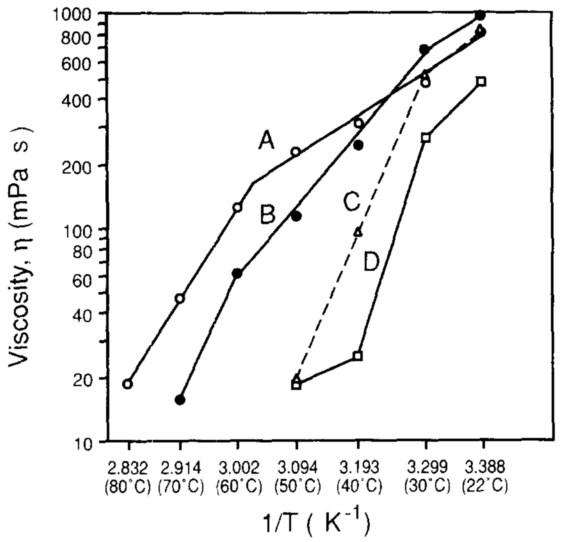

Fig. 5. Plots of log viscosity (η at 100 s^{-1}) versus $1/T$ (K^{-1}) for high amylose cornstarch and high amylose cornstarch-EAA dispersions. (A) NaOH added, 5·33% total solids, 3% EAA based on starch, pH 9·50. (B) No NaOH added, 5·45% total solids, 3% EAA based on starch, pH 8·47. (C) No NaOH added, 5·24% starch solids, no EAA used, pH 8·32. (D) NaOH added, 5·31% starch solids, no EAA used, pH 9·78.

cooked with EAA (curves A and B, Fig. 5), the sharp rise in viscosity occurs at a higher temperature than in the absence of EAA, and the slopes of the curves are reduced. Analogous to cornstarch and waxy cornstarch, addition of sodium hydroxide to the high amylose cornstarch-EAA system (curve A) increases the viscosity over most of the temperature range. However, unlike the other starch varieties, the viscosity of high amylose cornstarch-EAA-NaOH is lower than that of high amylose cornstarch-EAA (curve B), when measured below about 35°C. Other differences in the behavior of high amylose cornstarch and the other two starch varieties are also apparent, especially when cooking is carried out with EAA at high pH (i.e. in the presence of added sodium hydroxide). While cornstarch (Fig. 3, curve A) and waxy cornstarch (Fig. 4, curve B) exhibit η values in excess of 170 mPa s over the entire temperature range, η for high amylose cornstarch (Fig. 5, curve A) is less than 20 mPa s at 80°C, and then increases sharply as the temperature is lowered.

With each of the three cornstarch varieties examined, addition of sodium hydroxide to the aqueous ammonia dispersion of starch and EAA before jet cooking causes a significant increase in log η, particularly at high temperatures. This viscosity increase might simply be due to the higher pH of the sodium hydroxide-containing system; however, it could also result in some manner from formation of the sodium carboxylate salt of EAA at the expense of the ammonium salt. To distinguish between these two possibilities, waxy cornstarch was jet-cooked with EAA that had been dispersed in a higher than usual concentration of ammonium hydroxide, so that the final pH of the cooked mixture would approximate that obtained with sodium hydroxide. The log η versus $1/T$ plot for this mixture (Fig. 6, curve A) was not greatly different from curve B obtained with added sodium hydroxide. Therefore, the most important factor that controls rheological behavior is the pH of the cooked dispersion and not the nature of the carboxylate counterion.

Curve C in Fig. 6 shows the effect of sodium chloride addition on the viscous behavior of the waxy cornstarch-EAA-sodium hydroxide system. As expected for a polyelectrolyte, addition of salt greatly reduces the viscosity throughout the entire range of temperatures.

DISCUSSION

Although EAA is a water-insoluble polymer, it is dispersible in aqueous ammonium hydroxide; and these opalescent dispersions can be diluted with water (prior to mixing with starch and jet cooking) without causing the polymer to precipitate. Despite the fact that the acrylic acid content of EAA is not sufficiently high to give a true aqueous solution of polymer under these conditions, conversion of carboxylic acid to ammonium carboxylate renders EAA sufficiently hydrophilic to form micelles (Dow Chemical Co., 1984; Shogren *et al.*, 1991*a*). Polymer segments having the highest concentration of carboxylate groups are located on micelle

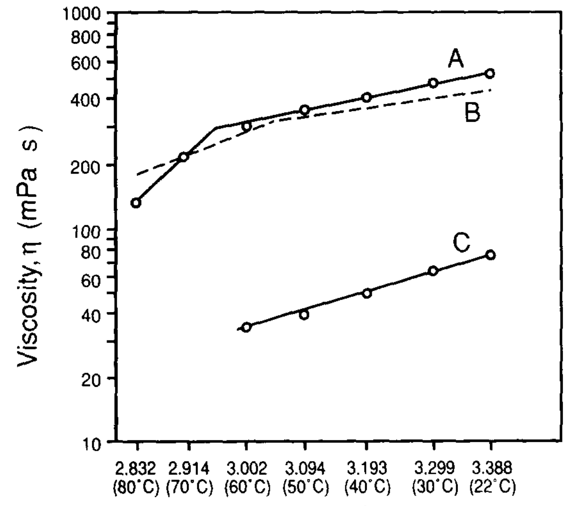

Fig. 6. Plots of log viscosity (η at 100 s^{-1}) versus $1/T$ (K^{-1}) for waxy cornstarch–EAA dispersions. (A) No NaOH added, pH raised by adding additional NH_4OH, 5·55% total solids, 3% EAA based on starch, pH 9·88. (B) NaOH added; curve B of Fig. 4. (C) NaOH added; same conditions as curve B of Fig. 4 except cooking carried out in 0·1N NaCl, 5·76% total solids, pH 9·71.

surfaces, and the more hydrophobic polyethylene-rich segments are in the interior. Complex formation probably takes place between starch and carboxylate-containing EAA chains that extend out from micelle surfaces.

Since ammonia is easily lost by volatilization, jet cooking with high pressure steam lowers the pH of the dispersion and could thus cause ammonium carboxylate substituents to revert back to carboxylic acid. A lower carboxylate salt content would inhibit the extension of polymer chains from the surfaces of EAA micelles, and the individual micelles could even begin to coagulate. The ability of EAA to form complexes with starch would thus be reduced. In the presence of additional alkali, however, loss of ammonia through volatilization would have relatively little effect. In fact, the high temperatures encountered during jet cooking should facilitate the dispersion of EAA in water, leading to reduced micelle size and perhaps even to some solubility for the lowest molecular weight EAA fractions.

Evidence supporting the idea that ammonia loss due to jet cooking leads to coagulation or enlargement of EAA micelles was obtained by jet cooking an aqueous solution of EAA and measuring the changes in pH and turbidity as a result of cooking. At a concentration of 1·56 g of EAA per liter, a turbidity reading of 5 NTU was obtained for an uncooked EAA dispersion at pH 10·22. After jet cooking, the dispersion had a higher turbidity (30 NTU), and the pH was reduced to 9·38. When an equivalent amount of sodium hydroxide was added to the EAA dispersion (based on the carboxylic acid content of EAA), turbidity values for uncooked and cooked dispersions were 5 and 9 NTU, respectively; while the pH values were 10·65 and 10·35.

When viscosities of jet-cooked starch–EAA dispersions are studied over a wide range of temperatures and shear rates, it is apparent that the viscosity of these starch–EAA systems is as highly dependent upon pH as the behavior of EAA micelles. Viscosities are significantly higher, particularly at high temperatures, when the pH is increased by adding either sodium hydroxide (in an amount equivalent to the carboxylic acid content of EAA) or sufficient ammonium hydroxide to achieve a comparable pH. The pH dependence of the relationship between log η and $1/T$ is particularly evident for the amylopectin component of starch (Fig. 4).

Since the viscosity of starch–EAA and the formation of EAA micelles are both governed by the pH of the system, it is reasonable to propose a relationship between viscosity and micelle structure. The shift in log η versus $1/T$ plots to higher viscosities with an increase in pH can thus be explained if EAA is simply better dispersed in a jet-cooked aqueous starch system under high pH conditions and is thus in a form that complexes with starch more effectively (i.e. reduced micelle size and maximum extension of polymer chains from micelle surfaces). These optimum conditions for complex formation should also allow complexation to occur at high temperature, even though the higher thermal energy of the system tends to cause separation of the complex into its individual polymer components. In agreement with this theory, Shogren *et al.* (1991*a*) showed that amylose-EAA mixtures showed smaller changes in optical rotation (i.e. less V-type complex) at pH 7 than at a pH above 9, and differences were attributed to increased aggregation of EAA micelles at the lower pH.

Slopes of log η $1/T$ plots provide some insight into the structure of starch–EAA complexes. In the case of amylopectin (i.e. waxy cornstarch; Fig. 4), molecular weight of the polysaccharide is in the order of several million, the polymer is highly branched, and intermolecular association (i.e. retrogradation) occurs slowly. The extensive branching present in amylopectin molecules suggests that these molecules behave as swollen gel particles, rotating as a whole rather than moving by the segmental or reptation processes usually associated with flow of linear high polymer in solution. The 25% amylose present in cornstarch samples would be expected to contribute in a relatively minor way to the viscosity, because of the low molecular weight of amylose compared to amylopectin.

A gel particle in a shear field is rotating at an angular velocity of (shear rate/2). It undergoes oscillatory distortion, and the viscosity (rate of dissipation of energy per cc per sec) will depend on the relaxation time distribution of the particle. As the temperature of the starch–EAA dispersion drops, the decrease in thermal energy makes the interaction of EAA with the outer branches of amylopectin to form a complex more probable. If EAA ties together two or more amylopectin molecules, the distribution of relaxation times for the combined complex will be broadened by the introduction of longer relaxation times. This, in turn, will increase the viscosity dramatically.

The rapid increase in viscosity shown in curve C of Fig. 4 (and also in curve B of Fig. 3) in going from 80°C to 60°C can thus be attributed to the very large increase in size and complexity of the flowing particles as amylopectin molecules are bound together by EAA. This complexing process is essentially complete at 50°C, and a further reduction in temperature results in only minor changes in viscosity, associated with the temperature dependence of the suspending medium, water.

For the situation in which NaOH is present (curve A of Fig. 3 and curve B of Fig. 4), the initial viscosity of starch–EAA observed at 80°C is high. In addition to making EAA micelles more amenable to complex formation, raising the pH of the system can also cause amylopectin molecules to expand in solution, thus making the outer branches more accessible to interaction with EAA.

In the case of amylose, represented by high amylose starch in Fig. 5, the molecular weight is lower than that of amylopectin by over a factor of 10; also, amylose contains few branches. In the absence of EAA (curves C and D), association between amylose molecules in solution (i.e. retrogradation) can thus occur rapidly to give sharp increases in viscosity at $T < 50°C$, and ultimately precipitation of the polymer from solution. The steep slopes of these curves at temperatures below 50°C are indicative of the retrogradation process. With EAA in the system (curves A and B), interaction between polysaccharide molecules can take place via complex formation, and this manner of pseudo-crosslinking (as opposed to retrogradation) could cause the sharp increase in log η to occur at temperatures higher than 50°C. In contrast to amylopectin (Fig. 4), log η versus $1/T$ plots do not level off, and slopes remain high even at low temperatures.

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