lower than 64% could not be used with Hylon V because the samples could not be handled during rheological measurements. Only 82% moisture could be used for amylose because, below that moisture content, the sample did not form a homogeneous semisolid material, which is necessary for rheological measurements.

Reactor Studies

Precooking of samples using reactor bomb. Amioca and amioca-protein samples at moisture contents of 55, 64, and 82% were heated to 64, 72, and 100°C using a reactor bomb, with a 300-ml chamber volume obtained from the Parr Instrument Company, Moline, IL. Hylon V and Hylon V-protein as well as potato amylose and potato amylose-protein mixtures were studied only at 82% moisture at 100°C using the same reactor bomb because the broken gel structure of the samples did not allow subsequent rheological measurements at other conditions. A constant headspace pressure of 50 psig was used to prevent vapor flash-off at the higher temperature. The bomb does not provide a constant heating rate; however, a uniform heating profile could be maintained. The suspensions were held at the desired temperature for 10 min before being cooled to room temperature. They then were immediately used for rheological study.

Rheological measurements. Rheological measurements were conducted at room temperature on the cooled samples immediately after preparation. Measurements were performed in triplicate using the parallel plate geometry of the Rheometrics mechanical spectrometer (Rheometrics, Inc., Piscataway, NJ) with a gap of 2 mm.

To prevent moisture loss during experimentation, the measurement chamber was kept at saturated moisture conditions with the use of a stainless steel cover and sponges saturated with water in the interior of the chamber.

During small-amplitude oscillatory measurements, strain sweeps were first conducted at a frequency of 1.0 rad/sec for each sample to determine the linear region where the complex viscosity is independent of the magnitude of the imposed strain. Frequency sweeps then were conducted from 0.1 to 100 rad/sec at the selected magnitude of strain.

Time-temperature studies with a mechanical spectrometer. To measure rheological properties as a function of temperature and time in the Rheometrics mechanical spectrometer, starch-protein suspensions were heated at a rate of 3°C/min from 30 to 100°C and then held at 100°C for 10 min while the complex viscosity $|\eta^*|$ was being simultaneously measured at a frequency of 10 rad/sec. Parallel plates, 25 mm in diameter, were used with a 2-mm gap. Measurements were conducted in triplicate, and their averages are reported here.

Moisture loss of the samples during the heating process was reduced by lubricating the edges between the plates with a silicone oil as suggested by Szczesniak et al (1983). Actual moisture loss determination of the samples showed that moisture losses ranged between 2 and 3%. The results are therefore reported with errors in moistures in the range of 2–3%. Because the moisture loss is the same for starch and starch-protein mixtures, this experimental error does not cloud the conclusions.

RESULTS AND DISCUSSION

Isothermal Rheological Measurements

Amylopectin (amioca) and protein systems. The complex viscosities versus frequency for amylopectin and amylopectin-protein systems are shown in Table I. The four treatments included amioca at 64% moisture heated in a Parr bomb to 64°C for 10 min and then cooled to 25°C, heated to 64°C for 20 min and then cooled to 25°C, heated to 72°C for 10 min and then cooled to 25°C, and heated to 100°C for 10 min and then cooled to 25°C. At 64°C and 10 min, the amylopectin-water system gave the highest complex viscosity $|\eta^*|$ at both frequencies. All amylopectin-protein mixtures had lower complex viscosities over the entire frequency range. The temperature of 64°C is slightly below the gelatinization point of amylopectin starch (Breslauer et al 1990). The presence of the protein decreases viscosity because large starch molecules are diluted by smaller protein molecules.

Increasing the residence time at this temperature did not have a significant effect. The complex viscosity versus frequency curves of all of the protein-added systems at 64% moisture content cooked at 64°C for 20 min and then cooled to 25°C also show lower complex viscosities than does the curve of amioca alone. Increasing the residence time did not result in increases in viscosities of starch with the addition of protein.

As the temperature was raised to 72°C, the protein-added systems, with the exception of amylopectin-zein, had higher complex viscosities than did amioca-water, as seen in Table I. At this temperature, differential scanning calorimetry has shown (Breslauer et al 1990) that gelatinization of amylopectin starch readily occurs. This temperature also is above the denaturation temperature of all of the proteins studied. Therefore, as starch gelatinizes and proteins denature, it is possible that entanglements develop a network structure (De Gennes 1971) and result in synergistic increases in viscosity. It would, however, be expected that such synergism also would depend on the compatibility (or solubility) of one polymer with the other. Clearly, starch and the hydrophilic cereal proteins are insoluble in one another. The reason that the viscosity of the amylopectin-zein system is still comparable to the viscosity of amioca appears to be attributable to the fact that zein is the most hydrophobic protein among the four proteins studied and, therefore, has the lowest compatibility with starch. With increasing hydrogen bond density on the protein, increasing compatibility with starch would be expected, resulting in the synergistic interactions observed with other proteins.

Amylopectin starch in amylopectin-protein samples with 64%

TABLE I
Complex Viscosity (η^*, in P) Versus Frequency at 64% Moisture for Amioca and Amico-Protein

	Frequency, rad/sec							
	Amioca		Amioca + Zein		Amioca + Gliadin		Amioca + Glutenin	
Treatment	1	10	1	10	1	10	1	10
Heated to 64°C for 10 min, cooled to 25°C	7.0×10^4	7.0×10^3	2.0×10^4	2.5×10^3	3.0×10^4	3.8×10^3	5.2×10^4	7.0×10^3
Heated to 64°C for 20 min, cooled to 25°C	4.8×10^4	6.0×10^3	1.0×10^4	1.5×10^3	3.2×10^4	4.8×10^3	1.9×10^4	3.1×10^3
Heated to 72°C for 10 min, cooled to 25°C	2.5×10^4	3.1×10^3	2.0×10^4	2.5×10^3	4.2×10^4	5.6×10^3	4.0×10^4	7.0×10^3
Heated to 100°C for 10 min, cooled to 25°C	2.2×10^5	5.3×10^4	3.6×10^5	4.8×10^4	1.02×10^6	2.5×10^5	1.05×10^6	2.4×10^5

TABLE II
Complex Viscosity (η^*, in P) Versus Frequency at 82% Moisture for Hylon V and Hylon V-Protein

	Frequency, rad/sec							
	Hylon V		Hylon V + Zein		Hylon V + Gliadin		Hylon V + Glutenin	
Treatment	1	10	1	10	1	10	1	10
Heated to 100°C for 10 min, cooled to 25°C	2.1×10^5	2.6×10^4	7.3×10^4	9.5×10^3	6.5×10^4	8.5×10^3	1.04×10^5	1.08×10^4

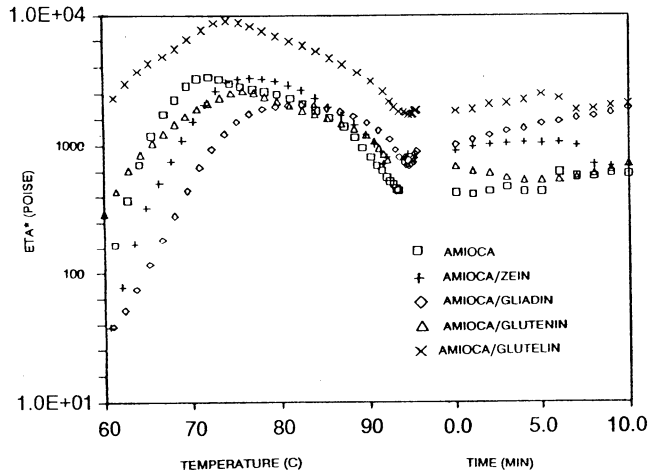

Fig. 1. Amioca and amioca-protein at 55% moisture: Complex viscosity (η^*) vs. temperature and time.

moisture heated at 100°C for 10 min was completely gelatinized (Breslauer et al 1990). At 64% moisture, all of the protein and starch mixtures (including amylopectin-zein) had higher complex viscosity values than did amylopectin alone. The amioca-gliadin and the amioca-glutenin systems showed the highest complex viscosity values, which are almost a decade higher than amylopectin, followed closely by amylopectin-glutelin and amylopectin-zein. The temperature of 100°C is well above the denaturation temperature of all proteins. The proteins are known to undergo transitions from α-helix to β-pleated sheet structure and their hydrophilic amino acids are exposed (Bauman and Breslauer 1988). This makes the proteins more compatible with starch and results in increasing synergism. Consistent with the previous explanation, the more hydrophobic corn proteins glutelin and zein result in the smallest degree of synergistic behavior, resulting in comparatively lower viscosities than do gliadin and glutenin.

Hylon V and Hylon V-protein systems. For Hylon V-water and Hylon V-protein-water mixtures, the complex viscosities for Hylon V were higher than those for amylopectin at 100°C, as shown in Table II. This is attributable to the fact that Hylon V contains approximately 50% amylose, and amioca contains only about 2%. Leaching and retrogradation of amylose molecules also significantly contribute to viscosity in gelatinized starch systems containing large amounts of amylose (Eliasson 1985).

At the moisture content of 82%, Hylon V had the largest complex viscosity, followed by Hylon V-glutenin. Hylon V-glutenin, Hylon V-zein, and Hylon V-gliadin all had lower viscosities than did Hylon V. Clearly, the presence of approximately 50% amylose affected the synergistic interactions between protein and carbohydrate observed with amylopectin starch at this temperature and residence time. This might be associated with the linear nature of amylose. It is known, for example, that branched-chain polymers entangle a great deal more than do linear polymers (Graessley 1977). Therefore, above the gelatinization temperature of starch, the likelihood of entanglement formation with protein is much higher with amylopectin than with amylose. Furthermore, the long side branches of amylopectin enhance the potential for interaction with the hydrophilic-compatible portions of the protein molecule.

TABLE III
Amioca[a] Versus Amioca-Protein Systems: Peak Viscosity as a Function of Moisture Content

Moisture Content (%)	Average Peak Viscosity, P				
	Amioca	Amioca-Zein	Amioca-Gliadin	Amioca-Glutenin	Amioca-Glutelin
55	3,389	3,307	2,061	2,651	9,132
64	2,453	2,023	283	2,695	2,555
82	331	223	257	469	459

[a] 98% amylopectin.

TABLE IV
Amioca[a] Versus Amioca-Protein Systems: Peak Viscosity as a Function of Moisture Content

Moisture Content (%)	Maximum Viscosity Temperature, °C				
	Amioca	Amioca-Zein	Amioca-Gliadin	Amioca-Glutenin	Amioca-Glutelin
55	72.0	76.7	82.4	75.8	76.5
64	77.5	78.3	80.9	77.4	76.2
82	75.1	76.2	76.5	74.8	75.4

[a] 98% amylopectin.

Time-Temperature Studies of Starch-Protein Systems

Amioca (98% amylopectin)-protein. At 55% moisture, a close examination of the actual magnitudes of the peak viscosity and the peak viscosity temperature in Figure 1 clearly shows that they are affected by the addition of protein, as shown in Tables III and IV. The addition of all proteins increased the peak viscosity temperature for amioca. The presence of protein retards the gelatinization process, possibly by competing for the available water.

Isothermal viscosity measurements at 100°C at the end of the heating cycle for 10 min showed that viscosity of the starch-protein mixtures was higher than that of amylopectin-water mixtures alone.

For 64% moisture, the amylopectin and amylopectin-protein complex viscosity versus temperature-time curves are shown in Figure 2. With the exception of the gliadin-added systems, all of the amioca and amioca-protein systems showed fairly close peak viscosity values, as seen in Table III. The values for peak viscosity temperature were not significantly changed and varied by about 2°C, as seen in Table IV.

Isothermal viscosity measurements conducted at 100°C showed approximately constant viscosity values for all protein-starch mixtures higher than those for amylopectin starch alone. This is consistent with the studies of amylopectin starch-protein systems discussed earlier.

At 82% moisture content, water was in excess for amylopectin starch (Baumann and Breslauer 1988). Here, the peak complex viscosity and viscosity decay occurred over a short temperature range relative to 55% moisture (Fig. 3). The temperature at which the peak complex viscosity occurred was not significantly affected by protein addition (Table IV). The peak viscosities were higher than those of amylopectin when glutelin and glutenin were added and lower when zein and gliadin were added (Table III). However, isothermal measurements of amylopectin with glutelin or glutenin continued to have higher complex viscosities than did amylopectin alone.

Hylon V-Hylon V + proteins. The comparisons of the rheological behavior of Hylon V and Hylon V-protein systems at 64 and 82% moisture are shown in Figures 4 and 5 and Tables V and VI, respectively. At 64% moisture, the addition of zein to Hylon V did not significantly alter the peak complex viscosity. The addition of glutelin and glutenin to Hylon V increased the peak viscosity. The addition of gliadin, on the other hand, decreased the value for peak viscosity by close to one third that of Hylon V alone. The reason for this is not well understood; however, the experiment is reproducible.

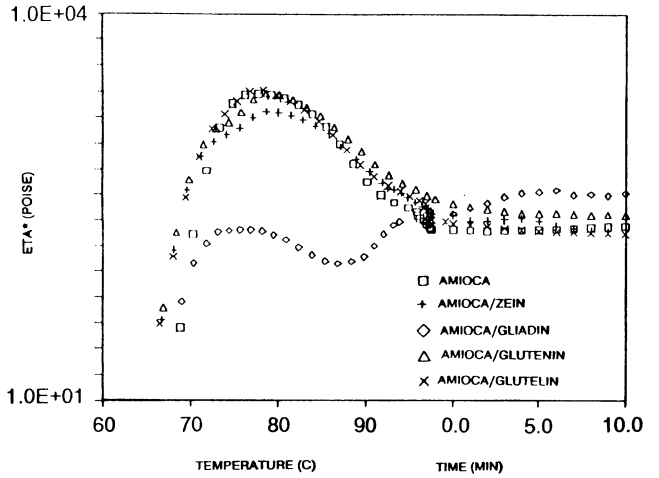

Fig. 2. Amioca and amioca-protein at 64% moisture: Complex viscosity (η^*) vs. temperature and time.

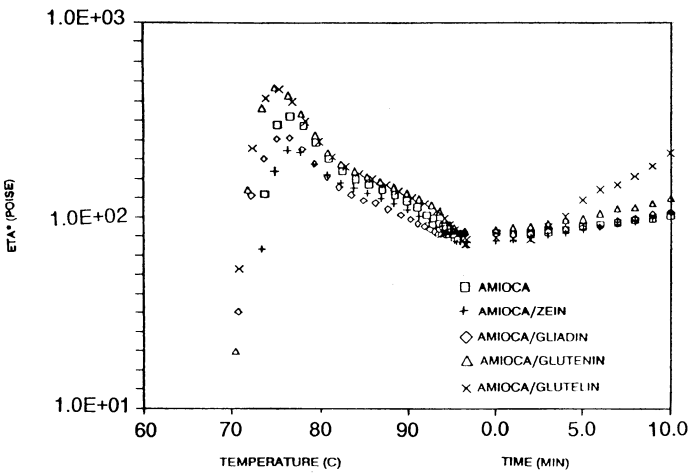

Fig. 3. Amioca and amioca-protein at 82% moisture: Complex viscosity (η^*) vs. temperature and time.

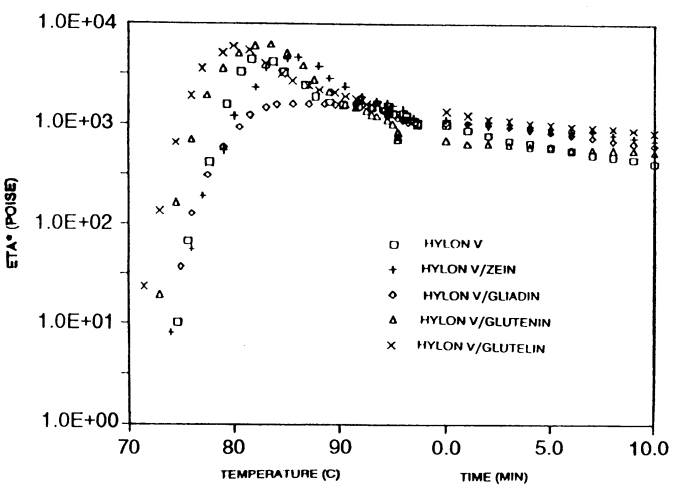

Fig. 4. Hylon V and Hylon V-protein at 64% moisture: Complex viscosity (η^*) vs. temperature and time.

The isothermal 100°C/10 min measurements showed that all four Hylon V-protein systems had higher viscosities than did Hylon V alone. The Hylon V-glutelin system continued to display the highest complex viscosity, but the Hylon V-glutenin system, which had the highest peak viscosity, had only a slightly higher viscosity than Hylon V-zein. Hylon V-gliadin systems are in between the Hylon V and the Hylon V-glutenin systems. The presence of significant amounts of amylopectin in Hylon V and the increase in the heating time to approximately 30 min allowed for the interaction observed with amylopectin in isothermal experiments.

At 82% moisture, the addition of protein reduced the peak viscosity in all four cases. The addition of glutelin had the least effect. Hylon V-zein and Hylon V-glutelin showed an approximate 30% decrease. Hylon V-gliadin showed the lowest peak viscosity, with a 56% drop, as it did in the 64% moisture measurements. Isothermal 100°C measurements at this moisture content showed lower viscosities for all protein-added systems when compared with Hylon V alone. This is most likely attributable to an excess moisture environment. Essentially, the excess moisture completely hydrates any source of interaction between starch and protein of hydrophilic nature, and the potential for entanglement and interaction decreases.

The comparison of amylopectin to amylose with regard to protein addition is markedly different. For most of the high-amylopectin systems studied at 82% moisture content, the effect of the addition of protein was positive, whereas none of the proteins had a positive effect on the viscosity of Hylon V.

Potato amylose vs. potato amylose-protein systems. Figure 6 shows the results obtained from analysis of potato amylose and

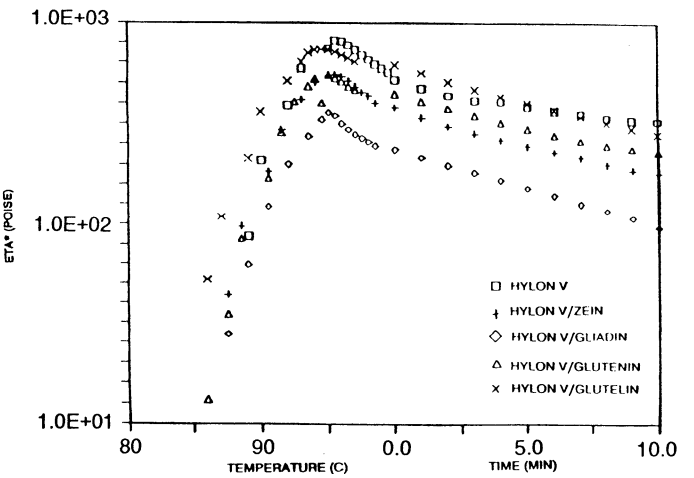

Fig. 5. Hylon V and Hylon V-protein at 82% moisture: Complex viscosity (η^*) vs. temperature and time.

TABLE V
Maximum Viscosity Temperature as a Function of Moisture Content

Moisture Content (%)	Average Temperature, °C				
	Hylon V	Hylon V-Zein	Hylon V-Gliadin	Hylon V-Glutenin	Hylon V-Glutelin
64	76.5	86.0	87.0	83.5	80.0
82	95.5	95.5	95.0	94.0	94.5

TABLE VI
Average Maximum Viscosity as a Function of Moisture Content

Moisture Content (%)	Average Maximum Viscosity, P				
	Hylon V	Hylon V-Zein	Hylon V-Gliadin	Hylon V-Glutenin	Hylon V-Glutelin
64	4,370	4,612	1,775	6,198	5,927
82	810	551	357	525	735

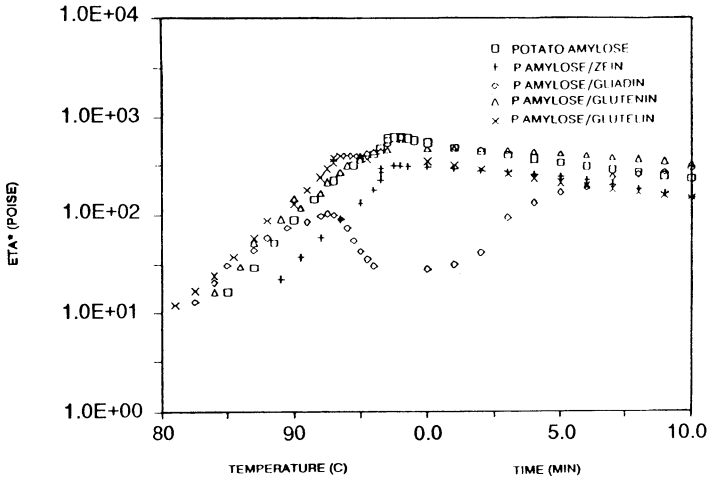

Fig. 6. Potato amylose and amylose-protein at 82% moisture: Complex viscosity (η^*) vs. temperature and time.

TABLE VII
Potato Amylose and Potato Amylose-Protein Systems: Maximum Viscosity as a Function of Moisture Content

System	Peak Temperature (°C)	Peak Viscosity (P)
Potato amylose	98.0	646
Potato amylose-zein	97.5	320
Potato amylose-gliadin	92.5	103
Potato amylose-glutenin	95.5	486
Potato amylose-glutelin	94.0	404

potato amylose plus protein systems at 82% moisture content. Except for the case of potato amylose-gliadin protein, amylose systems showed a steady increase in complex viscosity up to a maximum temperature. This was followed by a plateau region during the time the temperature was held at 100°C. Very little setback was observed. The presence of the proteins decreased the peak viscosity of potato amylose. This is in contrast to amylopectin-protein mixtures, where the mixtures were found to have higher peak viscosities than did amylopectin alone. The major difference between amylose and amylopectin is the branched-chain nature of amylopectin. It is possible that, because amylose-amylose interactions are favored in the absence of side branches, the potential for interaction between amylose and proteins is reduced. The values for the peak viscosity and the temperature corresponding to the peak viscosity are given in Table VII. The addition of protein also tended to lower the temperature at which peak viscosity occurred.

In conclusion, it was shown that starch viscosity was significantly affected by the presence of protein. The amylose-amylopectin ratio, the type of protein, and temperature, coupled with residence time and moisture content, appeared to affect the extent of viscosity change. Amylopectin starch favored increases in viscosity above the gelatinization temperature, presumably due to the branched nature of amylopectin. With amylose starch, amylose-amylose interactions appeared to be favored to a greater extent than were amylose-protein interactions.

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