

Effects of pH, Sodium Chloride, Polysaccharides, and Surfactants on the Pasting Characteristics of Pea Flours (*Pisum sativum*)

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ABSTRACT

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The effects of concentration, pH, sodium chloride, low-methoxyl sunflower pectin, xanthan gum, guar gum, sodium stearyl lactylate, and soybean lecithin on the pasting characteristics of slurried green and/or yellow field pea flours and powders were investigated on a Brabender Amylograph-Viscograph. Dietary fiber apparently affects slurry viscosity. Thermally ground, dehulled green pea flour imparted the maximum

viscosity at the isoelectric range of the pea globulins. Addition of sodium chloride (e.g., 0.1%) to the green pea flour slurries substantially increased the viscosity. Additions of the above polysaccharides and surfactants to thermally ground, dehulled yellow pea flour affected the pasting characteristics to different degrees; the mechanisms involved are discussed.

Recent years have witnessed a rapid increase in the use of vegetable proteins as functional ingredients in the food industry (Kinsella et al 1985). Although soybean products are still dominant in this respect, efforts have been made to explore possible uses of other legumes for their functional properties. These include field peas, horsebeans, faba beans, Great Northern beans, chickpeas, and cowpeas (Vose 1980, Gueguen 1983, Sosulski and McCurdy 1987, Sathe et al 1981). Field peas (*Pisum sativum*) have been given special attention, because they are already an accepted part of the human diet throughout the world. Therefore, their components can be readily used in the food industry, both as nutritional and functional ingredients.

A patent-pending process has been employed to produce pea flours. In this process, dry, green, or yellow peas are subjected, in a retort, to a temperature of 147°C under steam at 20 psi for 5-7 min and then thermally ground in a hammer mill into powder. Gelatinization of the starch fraction of peas does not occur during the retort cooking process but during thermal grinding. It has also been postulated that starch-oligosaccharide complexing, rather than simple gelatinization of the starch fraction, gives pea flours their functional properties, particularly viscosity, when used in aqueous food systems (Duxbury 1987).

However, Kinsella (1979) reported that although starch fractions are quantitatively dominant in most legume flours, the protein fractions are mainly responsible for numerous functional properties. The main objective of the present study was, therefore, to investigate the mechanisms involved in the viscosity development of slurried pea flours.

MATERIALS AND METHODS

Pea Flours

Five different pea flour products were provided by Dupro Division of Dumas Seed Corp., Golden Valley, MN, and stored at 4°C prior to the test. Table I describes the products and includes typical proximate analysis data taken from the supplier's product specification bulletins.

pH and Sodium Chloride

Adjustments in pH were made by adding 1N reagent grade HCl or NaOH to a series of 12% (w/v) slurries of PC-111 with constant stirring and allowing sufficient time for equilibration. Original slurry pH was 6.7; adjustments were made to pH 4.0, 5.0, 6.0, 8.0, 10.0, and 12.0.

The appropriate quantities of solid reagent grade NaCl were added to a series of 12% (w/v) slurries of PC-111 with constant

stirring to attain NaCl concentrations of 0.1, 0.2, 0.4, 0.6 and 1.0% (w/v).

Polysaccharide Gums and Surfactants

Low-methoxyl pectin was provided by Shanghai Food Research Institute of the People's Republic of China. Xanthan gum (G-1253) and guar gum (G-4129) were purchased from Sigma Chemical Company, St. Louis, MO. Sodium stearyl-2-lactylate (SSL), brand name Emplex, was obtained from Patco Products, Kansas City, MO, and soybean lecithin (Lecigram 5750) from Riceland, Stuttgart, AR. The appropriate amount of each of the above was weighed and hydrated in 450 ml of distilled water. These mixtures were combined with pea flour PC-311 to make five series of 12% (w/v) pea solids slurries containing 0-2.0% (w/v) pectin or lecithin and 0-3.0% (w/v) xanthan, guar, or SSL.

Viscosity Measurements

Viscosity of pea slurries was measured on a Brabender Amylograph-Viscograph, Type AV-30 (Brabender Corp., Rochelle Park, NJ) using a standard cartridge of 350 CM/GRS (cm·g) and a rotation speed of 75 rpm. The measurement procedure was as follows. A series of pea slurries of different concentrations (8, 10, 12, 14, 16%, dry basis, w/v) was made by weighing appropriate amounts of each pea flour in a 500-ml beaker. The weighed portion was hydrated in 450 ml of distilled water (or in a 450-ml additive solution) in a water bath preheated to 30°C for 30 min. After transferring the slurry to a test bowl, the heating cycle was conducted by elevating the heating temperature at a rate of 1.5°C per min from 30 to 93°C, and the paste was stirred and cooked at this temperature for 60 min. Then, the cooling cycle was carried out by lowering the temperature at the same rate down to 50°C, and the paste was stirred at this temperature for 60 min.

The viscosity of the paste was characterized by the following parameters. Pasting temperature was the initial temperature at which the viscosity was recorded before the heating temperature reached 93°C. Viscosities were expressed (as Brabender units) upon reaching 93°C, after 60 min stirring and cooking at 93°C, upon reaching 50°C and after 60 min stirring at 50°C.

RESULTS AND DISCUSSION

Composition of Pea Flours

Typical analysis data in Table I show similar protein, fat, and total carbohydrate contents in the five pea flour products. The lower moisture content in PC-111, PC-200, and PC-311 compared to the other two products is possibly related to the thermal grinding process employed in producing the former. Dehulling prior to grinding reduced the total dietary fiber content more than 90% (PC-111 and PC-311 vs. the other three products). Dehulling also resulted in a substantial decrease in ash content in the finished products.

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Effect of Concentration on Viscosity

It is noteworthy that none of the additive solutions, per se, even at the highest concentration tested, registered a viscosity value on the Brabender meter. Both viscosity (Fig. 1) and pasting temperature (Fig. 2) of the pea pastes are concentration-dependent. Apparently, the higher the concentration, the greater the viscosity and the lower the pasting temperature. This can possibly be explained as follows. With respect to the principle of Brabender measurement, the viscosity observed is proportional to the energy required to align the molecules parallel to the direction of flow. Therefore, at high concentrations, the disturbance of flow pattern around one molecule will overlap or interact with the disturbance of flow pattern around another molecule and

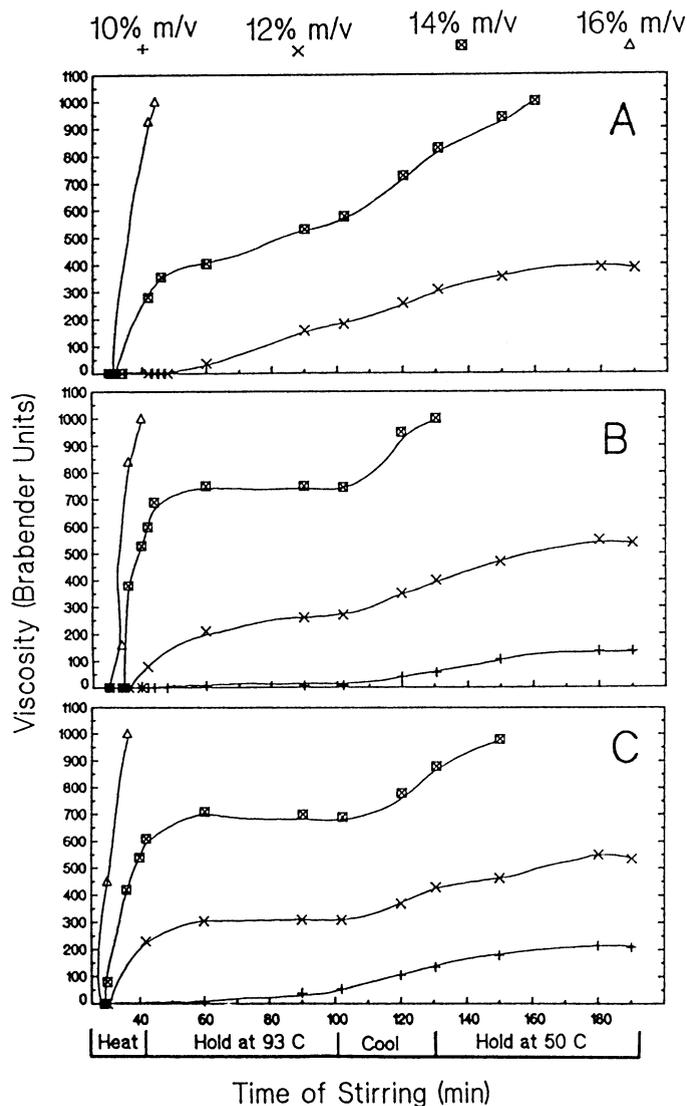


Fig. 1. Effects of pea flour concentrations and Brabender heating, holding, cooling, and holding regime on viscosity of slurries: A, PC-100; B, PC-111; C, PC-200.

thus increase the frictional force. Consequently, the viscosity increases.

Alternatively, if the hypothesis of complex formation is correct, high concentrations of reactants can enhance complexing and therefore increase the viscosity as well.

It should be noted that PC-100 exhibited the highest pasting temperature, whereas PC-200 showed the lowest one at all of the concentrations tested. Also, PC-100 showed the lowest viscosities at all of the concentrations tested and at all of the temperatures and times (Fig. 3). Because the upper limit of the amylograph scale is 1,000, all values of 1,000 in Figure 3 represent values of 1,000 or greater. With respect to their similar chemical compositions, their different pasting characteristics seem to be due to the thermal grinding process. This process brings about gelatinization of the starch fraction and denaturation of the protein fraction and other possible interactions that apparently reduce the pasting temperature and increase the viscosity of pea paste.

In addition to its lower pasting temperature in comparison to that of PC-111 at all of the concentrations tested, PC-200 also showed higher viscosity than PC-111 at low concentration (i.e., 12%) at most of the temperatures and times of stirring. Because both products were subjected to the same thermal grinding process, their different viscosity characteristics seem to be due to their different chemical compositions, particularly their total dietary fiber contents (2.1% for PC-111 vs. 24.9% for PC-200, Table I). These results suggest that total dietary fiber may play a role in the viscosity of pea paste, particularly at low concentrations.

The viscosity and pasting data in Figures 1 and 2 suggest differences due to thermal grinding and fiber content. The data in Table I indicate no gross compositional differences between green and yellow pea flours. Therefore, a thermally ground, dehulled green pea flour (PC-111) was used in the pH and NaCl studies and a similarly processed yellow pea flour (PC-311) was used in the gum and surfactant studies.

Effects of pH on Viscosity

The effects of pH on the viscosity of pea pastes (PC-111)

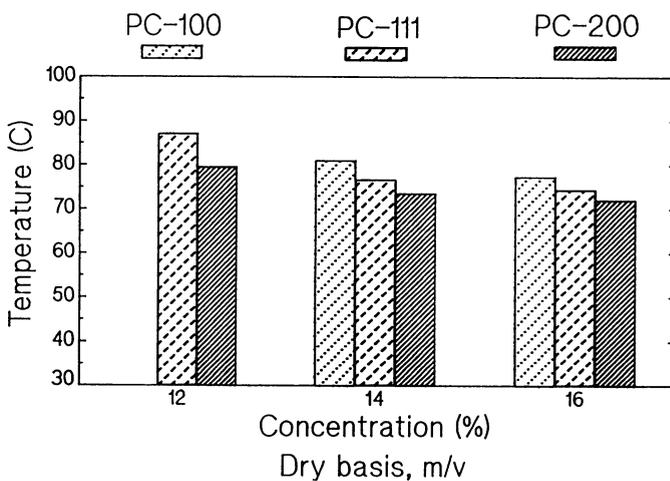


Fig. 2. Effects of concentration of three pea flours on pasting temperatures of slurries.

TABLE I
Description and Typical Analysis of Five Pea Flour Products

Product	Pea Type	Thermally Ground	Dehulled	Proximate Analysis (%)					
				Moisture	Protein	Fat	Ash (as-is)	Total Dietary Fiber	Total Carbohydrate ^a
PC-100	Green	No	No	8.0	25.0	1.0	2.4	23.9	63.8
PC-111	Green	Yes	Yes	4.0	28.3	1.0	1.4	2.1	65.3
PC-200	Green	Yes	No	4.0	26.0	1.0	2.5	24.9	66.4
PC-300	Yellow	No	No	8.0	25.0	1.0	2.4	23.9	63.8
PC-311	Yellow	Yes	Yes	4.0	28.3	1.0	1.4	2.1	65.3

^aCalculated as difference.

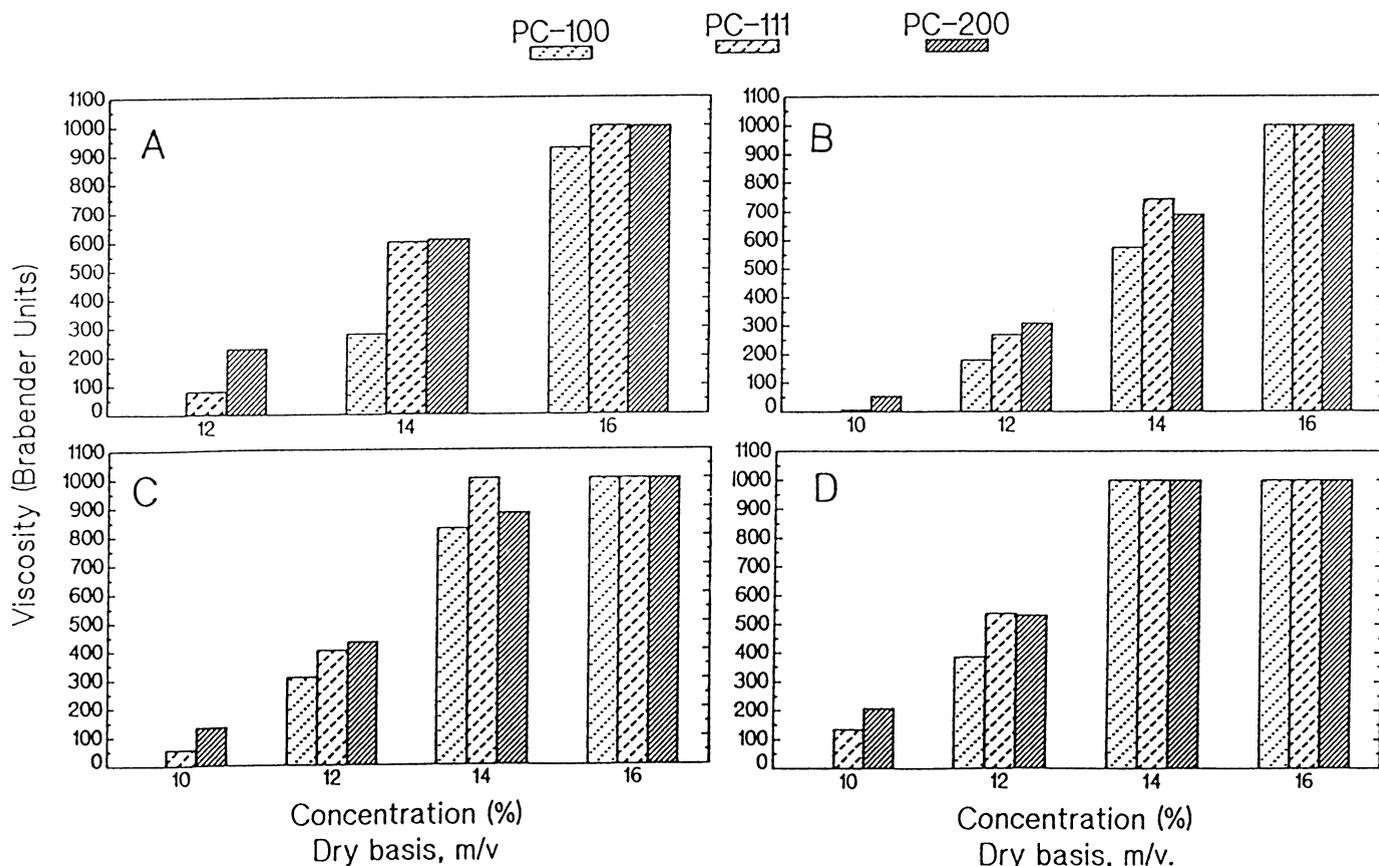


Fig. 3. Effects of pea flour concentrations on viscosity of slurries; A, upon stirring/heating to 93°C; B, after stirring/holding at 93°C for 60 min; C, upon stirring/cooling to 50°C; D, after stirring/holding at 50°C for 30 min.

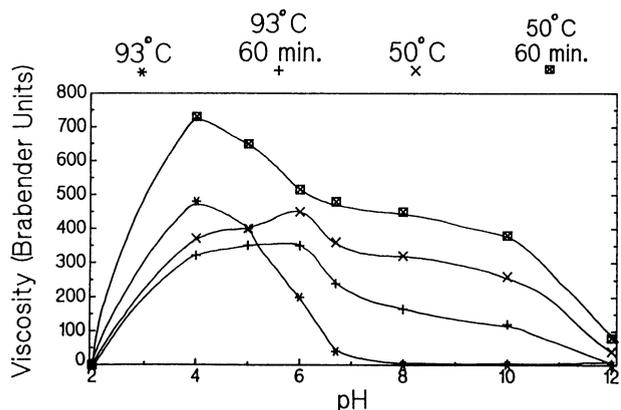


Fig. 4. Effects of pH and Brabender heating, holding, cooling, and holding regime on viscosity of pea flour PC-111 12% (w/v) slurries.

measured at different temperatures and at different times of stirring are shown in Figure 4. The viscosity reached a maximum at pH 4-6 at all of the temperatures and stirring times observed. The pasting temperatures were 75.8, 77.2, 78.8, and 87.8°C, respectively, at pH 4, 5, 6, and 6.7 (Fig. 5).

Zobel (1984) reported that alkaline compounds and organic acids decrease or increase starch gelatinization temperatures and determine the extent of gelatinization. For instance, starch gelatinizes at a lower temperature under alkaline compared with acidic conditions. However, at pH values in the range of 4-7, the acid concentration has little effect on starch gelatinization (Whistler and Daniel 1987). Therefore, it is unlikely that gelatinization of the starch fraction accounts for the maximum viscosity observed.

The main storage proteins of peas are vicilin (conglycinin) and legumin (glycinin), which are similar in physical and chemical properties to their counterparts in soybeans (Derbyshire et al 1978). Lee and Rha (1979) reported that the viscosity of soy protein

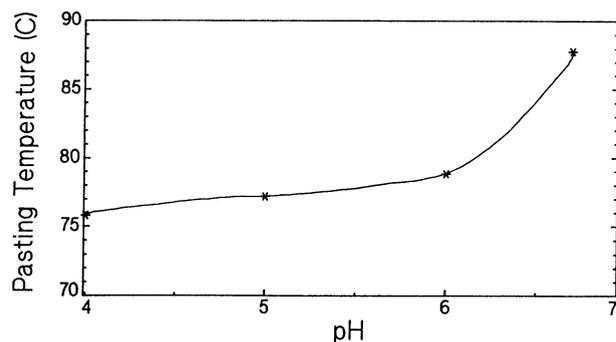


Fig. 5. Effects of pH on pasting temperature of pea flour PC-111 12% (w/v) slurries.

dispersions increased below pH 3.5 and above pH 6.0. Thanh and Shibasaki (1976) also reported that the apparent viscosity showed a minimum at pH 4.0 and 6.0 and that these two minima might correspond to the isoelectric pH values of the glycinin and conglycinin. The above observations are in accord with the theoretical consideration of protein chemistry, i.e., protein molecules show minimum viscosity at their pI values due to minimum hydration.

However, the present results apparently contradict the above observation and the theory, which can be explained as follows. The complexity of pea flour composition precludes the possibility of using classical thermodynamic theory to describe its viscosity behavior. For the same reason, it is not practical to attribute its viscosity directly to starch gelatinization or protein denaturation, per se. More likely, a complex may be formed during the thermal grinding process or viscosity measurement that accounts primarily for the viscosity. Although at this stage it is not clear which food components are involved in the formation of the complex or the mechanism of its formation, the present results

strongly indicate the involvement of the protein fraction. This is because its formation is pH-dependent and the pH range corresponding to the maximum viscosity coincides with the pI values of the proteins.

The above hypothesis seems in accord with results reported by Ganz (1974), wherein the viscosity of protein-carboxymethyl cellulose systems increased because of the formation of a soluble complex as the pH was decreased to values approaching the isoelectric points of the proteins. Taking the dietary fiber content of the pea flour into consideration, it is likely that a soluble complex might be formed between the polysaccharide and protein fractions. This is dependent on the charge carried by the macromolecules; the interaction reaches its maximum at minimal net charge. Furthermore, this prediction is in keeping with the observation mentioned previously that PC-200 (rich in dietary fiber) exhibited lower pasting temperature and higher viscosity than PC-111 (containing much less dietary fiber) although both products were subjected to the identical process.

Effects of Sodium Chloride Concentration on Viscosity

Addition of 0.1% sodium chloride to PC-111 slurries was found to increase viscosity at 93°C by nearly six times and to decrease the pasting temperature by almost 10°C in comparison with the slurry without NaCl (Figs. 6 and 7). These results support the above hypothesis of complex formation.

Although sodium chloride at low levels does not ordinarily interfere with starch functionality, it has been used to raise the gelatinization temperature of starch being derivatized (Moore et al 1984). The fact that viscosity increased drastically and pasting temperature dropped substantially up to the NaCl level of 0.1% as observed in the present study strongly suggests that other interactions in addition to starch gelatinization may have taken place.

It is reported that addition of sodium chloride decreases the apparent viscosity of soy protein dispersions, primarily by decreasing protein hydration via neutralization of charges by counterions (Joubert 1955). However, in the present study, the

viscosity actually increased as a consequence of NaCl addition. This apparently abnormal phenomenon supports the hypothesis of complex formation. As indicated by Ledward (1979), although the formation is very dependent on electrostatic forces, some longer range cooperative forces are involved in yielding a stable, high molecular weight soluble complex. These forces possibly include hydrogen bonds and Van der Waal's associations (Ganz 1974). The maximum viscosity apparently coincides with either zero (at the pI) or low (by addition of NaCl) net charges on protein molecules. Hence, electrostatic repulsion between molecules is reduced, which possibly promotes complex formation.

Alternatively, the above phenomenon can possibly be due to the unique ionic strength-dependent association-dissociation characteristic of conglycinin. For instance, the conglycinin fraction of *Pisum sativum* separates, at low ionic strength in the ultracentrifuge, into two molecular species (Circle et al 1964). Theoretical considerations and experimental findings suggest that the most important factor affecting the viscosity of a protein solution is the shape of the protein molecules (Kinsella et al 1985); therefore, association-dissociation will affect the viscosity. The addition of NaCl to pea paste may cause such an association-dissociation and hence affect the viscosity of the paste either directly or indirectly through its effect on the complex formation.

Effects of Polysaccharides on Viscosity

The addition of low-methoxyl sunflower pectin, guar gum, and xanthan gum increased the viscosity of PC-311 paste (Figs. 8 and 9) and reduced the pasting temperatures (Figs. 10 and 11.) Xanthan gum produced the greatest effect and guar gum the least.

Although the mechanisms of interactions between starch and other polysaccharides and proteins are not fully understood, it has been postulated that mainly electrostatic forces are involved in the reactions between low-methoxyl pectin and myofibrillar protein or whey protein concentrates (Bernal et al 1987). The negatively charged carboxylate groups of the polysaccharides interact with some, or all, of the positively charged protein residues, i.e., α -amino, ϵ -amino, guanidinium, and imidazole (Imeson et al 1977, Ledward 1979). The actual strength of the interactions is related to the conformations of the macromolecules as well as the overall charge on the protein (Ledward 1979). A protein molecule at any pH above its pI value carries a net negative charge (as is the case for PC-111 in the present study). Therefore, the accumulation of negative charge brought about by the attachment of polysaccharides to protein molecules may cause electrostatic repulsion and inhibit further interactions. This might explain why the viscosity of PC-311 paste reached a maximum at 1.5% pectin addition and did not increase with further addition (Fig. 8).

However, in the presence of calcium, chelation takes place between carboxyl, sulfhydryl, and amino groups, and the interactions can be further complicated. Both proteins and polysaccharides can interact on their own, with calcium ions or with

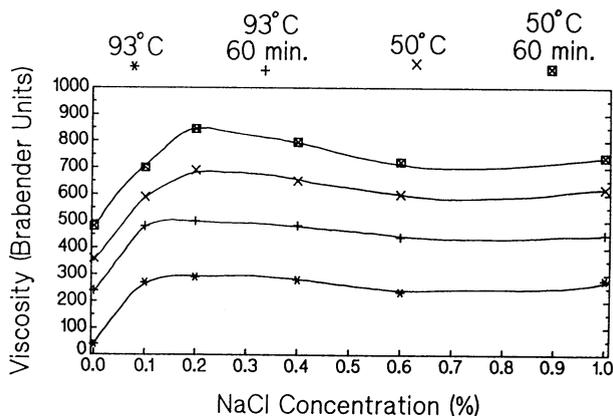


Fig. 6. Effects of NaCl concentration and Brabender heating, holding, cooling, and holding regime on viscosity of pea flour PC-111 12% (w/v) slurries.

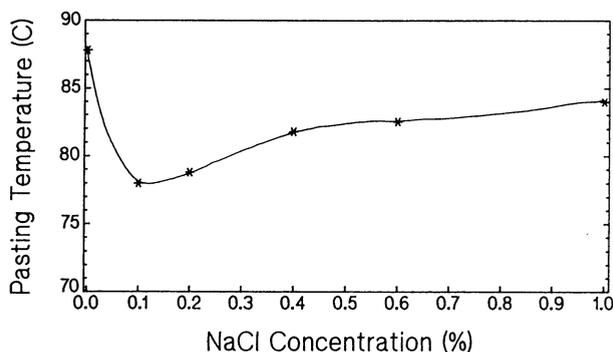


Fig. 7. Effects of NaCl concentration on pasting temperature of pea flour PC-111 12% (w/v) slurries.

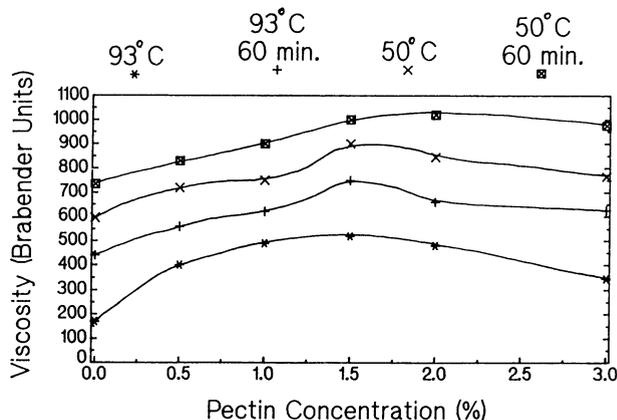


Fig. 8. Effects of low-methoxyl sunflower pectin concentration and Brabender heating, holding, cooling, and holding regime on viscosity of pea flour PC-311 12% (w/v) slurries.

each other, with or without calcium involvement (Hughes et al 1980). Since dehulled field peas were found to contain about 0.3% calcium on a dry basis (Sosulski and McCurdy 1987), the viscosity enhancement observed above in pea paste with the addition of guar gum and pectin could have also been influenced by calcium ions.

In addition, hydrogen bonding may also take place within and/or between polysaccharides, proteins, and starches, which could enhance complex formation. However, this contribution may be effective to a lesser extent in comparison to those caused by the above interactions, because the bond energy involved is weaker. This could explain why guar gum had the least effect on viscosity. Taking the structure of guar gum into consideration, it is very likely that hydrogen bonding might be the sole mechanism of the interaction, if any, between it and proteins or starches.

Effects of Surfactants on Viscosity

Figure 12 shows the effects of SSL and soybean lecithin on the viscosity of PC-311 slurries. An addition of 0.5% of SSL

exhibited no effect on the viscosity. However, at addition levels of 1.0 and 2.0%, the viscosity curves were characterized by a sharp increase, which reached the maximum at 124 and 122 min, respectively, after the initial time and then decreased rapidly. At addition levels of 2.0 and 3.0% of lecithin, the maximum viscosity was reached, respectively, at 107 and 111 min after the initial time. No decrease in viscosity was observed thereafter.

It is believed that the main mechanism by which surfactants increase viscosity in pea slurries is by enhancing the interactions

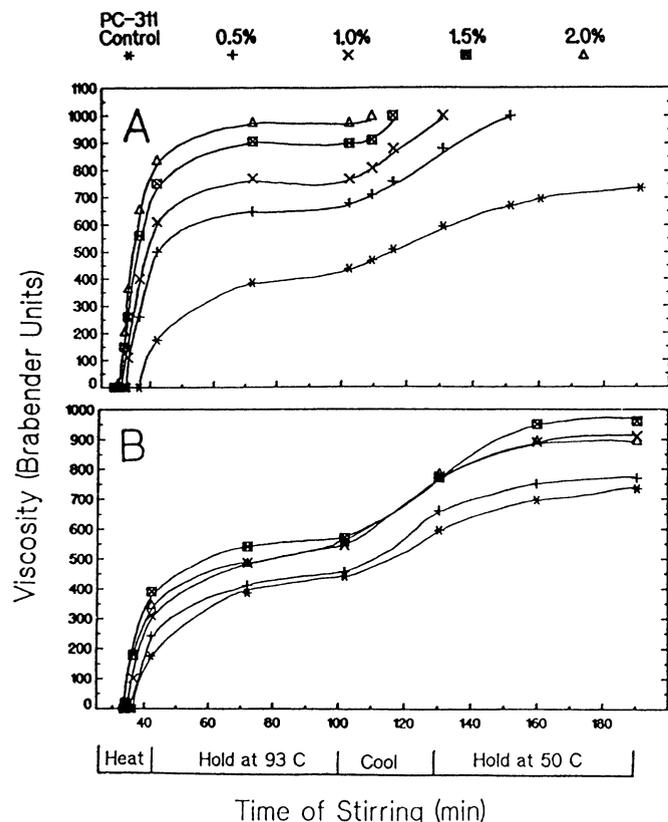


Fig. 9. Effects of polysaccharide concentrations and Brabender heating, holding, cooling, and holding regime on viscosity of pea flour PC-311 12% (w/v) slurries: A, xanthan gum; B, guar gum.

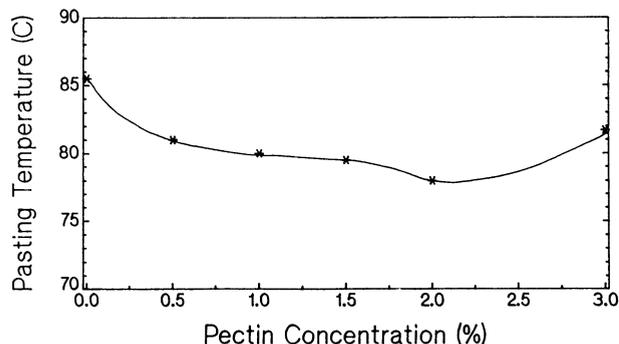


Fig. 10. Effects of low-methoxyl sunflower pectin concentration on pasting temperature of pea flour PC-311 12% (w/v) slurries.

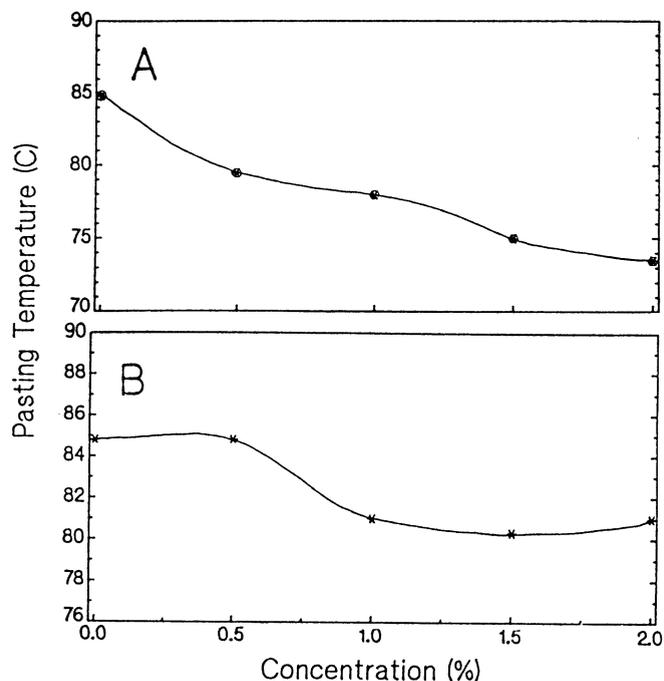


Fig. 11. Effects of polysaccharide concentrations on pasting temperature of pea flour PC-311 12% (w/v) slurries: A, xanthan gum; B, guar gum.

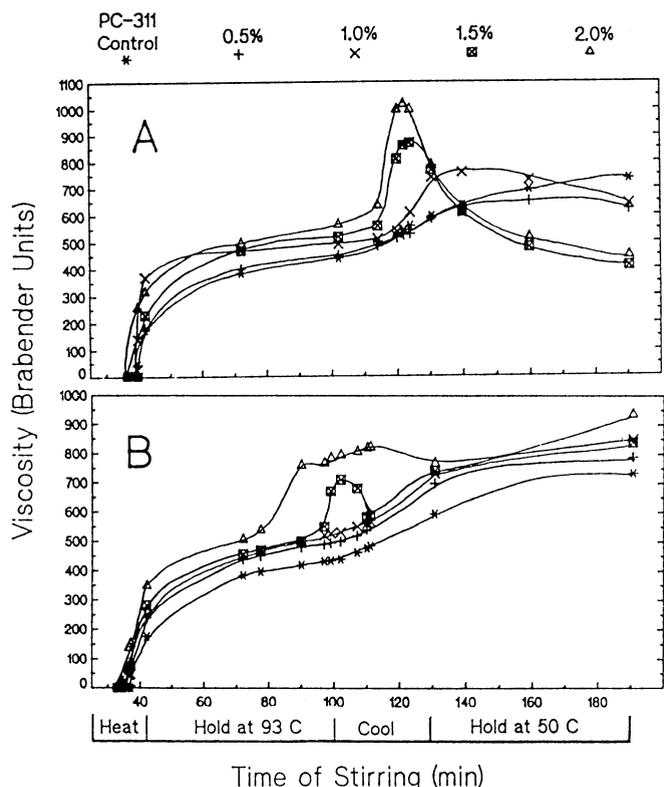


Fig. 12. Effects of surfactant concentrations and Brabender heating, holding, cooling, and holding regime on viscosity of pea flour PC-311 12% (w/v) slurries: A, sodium stearyl-2-lactylate; B, lecithin.

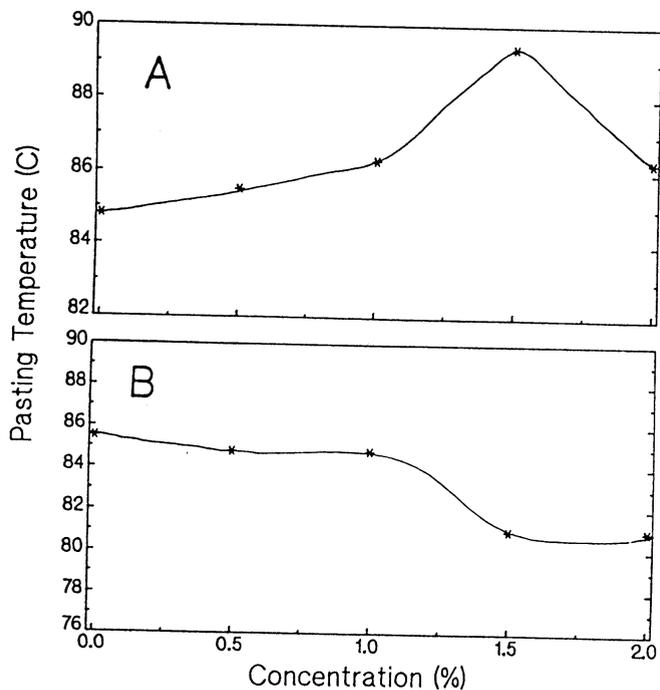


Fig. 13. Effects of surfactant concentrations on pasting temperature of PC-311 12% (w/v) slurries; A, sodium stearyl-2-lactylate; B, lecithin.

between hydrophilic and hydrophobic residues in food components. It has been proved by NMR studies that ionic surfactants can be bound by both hydrophobic and hydrophilic substituents of protein and starch to form a complex (Tu 1971). Since thermal denaturation unfolds globulin molecules and consequently exposes hydrophobic residues that were originally buried inside the molecules, more hydrophobic sites become available for surfactant molecules to bind. Also, it has been reported that elevated temperature enhances the hydrophilic and hydrophobic binding of an ionic surfactant to protein and starch (Tu 1971). This might explain why the maximum viscosity was reached after completion of the heating cycle. However, due to their different chemical structures, the specific mechanisms of interaction between these two surfactants and proteins, starches, and other food components might be different. This is supported by their different effects on the pasting temperature; i.e., SSL, in general, increased the pasting temperature whereas lecithin reduced it (Fig. 13).

SUMMARY

The present work indicates that the viscosity of pea slurries cannot be attributed to starch gelatinization or protein denaturation per se, but rather to the formation of a complex consisting of a protein fraction and other food components. This complex formation can be enhanced at pH 4-6 (the pI value of the main storage proteins of *Pisum sativum*) and high ionic strength (e.g., above 0.1% NaCl). Also, the viscosity of pea paste can be greatly increased by adding polysaccharides such as pectin and xanthan gum and surfactants such as SSL and lecithin. Further studies using model systems consisting of purified, isolated pea starch, protein, and fiber and their combinations would be required to verify complex formation and would be useful in studying effects of other variables.

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