

## Some Rheological Properties of Sodium Caseinate–Starch Gels

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The influence of sodium caseinate on the thermal and rheological properties of starch gels at different concentrations and from different botanical sources was evaluated. In sodium caseinate–starch gels, for all starches with the exception of potato starch, the sodium caseinate promoted an increase in the storage modulus and in the viscosity of the composite gel when compared with starch gels. The addition of sodium caseinate resulted in an increase in the onset temperature, the gelatinization temperature, and the end temperature, and there was a significant interaction between starch and sodium caseinate for the onset temperature, the peak temperature, and the end temperature. Microscopy results suggested that sodium caseinate promoted an increase in the homogeneity in the matrix of cereal starch gels.

**KEYWORDS:** Starch; milk protein; caseinate; interaction; potato; rheology; gelatinization; gel

### INTRODUCTION

In the food industry, polysaccharides are largely used as gelling agents, emulsifiers, and stabilizers, to modify food texture, films, and coatings (1, 2). Because of their wide application in food formulation, interest in protein–polysaccharide systems has been growing over recent years (1–5). In a protein–polysaccharide system, the interactions between macromolecules are usually governed by phase separation phenomena and thermodynamic interactions (6). Consequently, the pH in the system, the presence of salts, the sugar content, the processing temperature, the thermal history of the sample, the molecular weight and chain length of polymers, and the substitution of functional sites (2) play a decisive role in these interactions.

Starch is the polysaccharide most commonly used to produce the protein–polysaccharide gels used in the food industry. In the dairy industry, the use of starch in the formulation of some dairy products has improved their texture and viscosity and promoted significant cost savings. Interactions between starch and milk proteins are expected to have great influence on the rheological properties of food systems (3), markedly changing the gel network structure and the rheological profile (4). The thermomechanical properties and the permeability of films made from blends of soluble starch–sodium caseinate–polyols have indicated potential use in food, packaging, or coating applications (5).

Despite the fact that starch and casein are involved in many food formulations, few studies about their interactions have been done. The understanding of the caseinate–starch interactions is an important tool that could be used to manipulate the

rheological properties of food systems and to provide an alternative for the development of new products. The present work aimed to provide the basis for future research focused on the choice of starches in the formulation of dairy products. Some rheological properties of starch–sodium caseinate gels were evaluated by comparing starches from different botanic sources at several concentrations.

### MATERIALS AND METHODS

**Sample Preparation.** Starch samples from different botanical sources (cassava, potato, Amylomais corn, waxy corn, and wheat) were provided by Penford (Englewood, CO). Rice starch and sodium caseinate were supplied by Sigma (St. Louis, MO).

A 10% sodium caseinate solution was prepared under constant agitation at 40 °C and was hydrated at 5 °C overnight.

**Chemical Analysis.** Samples were equilibrated under vacuum conditions using saturated K<sub>2</sub>CO<sub>3</sub> solution. The final moisture contents of all of the samples were constant. The values were in a range from 11.5 to 12%, according with each sample. Moisture contents of samples were measured using AOAC method 925.59 (7). These samples were used for all analyses and to prepare the gels.

The protein levels in the starch samples were estimated according to AACC method 46-30 by nitrogen combustion (%N × 5.70) (8). The amylose/amylopectin ratios were determined using a Megazyme assay kit (Am/Amp 7/98) (Megazyme International Ireland Ltd., Wicklow, Ireland). Starch samples were defatted using an accelerated solvent extractor (ASE200, Dionex Corp., Sunnyvale, CA), with 2-propanol/water 3:1, at 100 °C for 20 min (9), repeating this cycle three times.

The phosphorus, calcium, sodium, potassium, and magnesium contents of the samples were determined using inductively coupled plasma–atomic emission spectroscopy (ICP-AES) (10). These analyses were performed on samples before and after defatting.

**Rheological Measurements.** The starch samples, at several concentrations (3, 5, and 7% w/w for cassava, potato, and waxy corn starches and 5, 7, and 9% w/w for corn, wheat, and rice starches), were suspended in 10 mL of distilled and deionized water or sodium caseinate

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**Table 1.** Composition of Starch Samples Used in the Experiments

starch	pH	% dry basis					
		amylose	ash	fat	N	total dietary fiber	starch
potato	6.42	17.2	0.32	0.27	0.08	0.25	96.69
cassava	5.67	15.6	0.16	0.18	0.14	0.24	96.66
waxy corn	5.93	1.2	0.05	0.18	0.22	0.13	97.93
corn	5.83	22.0	0.07	0.73	0.43	0.27	95.66
wheat	5.74	23.7	0.21	0.77	0.42	0.49	92.59
rice	6.36	15.2	0.23	1.00	0.76	0.47	95.88

solution. The caseinate/starch ratio used was 1:1 (w/w) for all starch concentrations. Samples were placed in an oil bath at 90 °C for 90 min, under gentle agitation.

The rheological measurements were performed using a Parr Physica UDS 200 Universal Dynamic spectrometer (Physica, Stuttgart, Germany), at 70 °C. The flow behavior and viscoelastic modulus curves were obtained using the cone–plate geometry (cone, 75 mm; angle, 2°). The viscoelastic modulus was measured at 1% amplitude over a frequency sweep from 0.01 to 10 Hz. The flow behavior was measured at shear rates of  $10^0$ – $10^3$  and  $10^3$ – $10^6$  s<sup>-1</sup>.

**Pasting Profile.** The starch pasting viscosity and the pasting and final temperatures were measured with a Rapid Visco Analyzer (RVA) (Newport Scientific, Warriewood, Australia). Starch samples (2.0 or 2.5 g, dry basis) were dispersed in 28 g of distilled and deionized water or sodium caseinate solution. The samples were homogenized at 960 rpm. The temperature profile started with holding for 1 min at 50 °C, heating to 95 °C over 4 min, holding at 95 °C for 3 min, and cooling to 50 °C over 4 min. All measurements were performed in triplicate.

**Thermal Properties.** Differential scanning calorimetry (DSC) measurements of the starch samples were performed with a Pyris-1 Thermal Analytical System (Perkin-Elmer, Norwalk, CT). Samples were weighed in steel pans, and distilled water or sodium caseinate solution was added (10 mg of starch, dry basis, to 20  $\mu$ L of water or sodium caseinate solution) before sealing. The sealed pans were equilibrated overnight at 4 °C and then heated from 25 to 180 °C at a heating rate of 3 °C/min. Indium was used for calibration, and an empty pan was used as a reference. Enthalpy changes ( $\Delta H$ ), the gelatinization onset temperature ( $T_{onset}$ ), the gelatinization range ( $T_2 - T_1$ ), and the peak temperature ( $T_{peak}$ ) were calculated automatically.

Statistical analyses of RVA and DSC data were assessed considering starch, sodium caseinate, and their interactions. The RVA data were analyzed for peak viscosity, final viscosity, and peak temperature. The DSC data were analyzed for enthalpy, temperature of gelatinization, peak temperature, peak start temperature, and peak end temperature. All statistical analyses were performed using the Statistical Analysis System (v. 8.1, SAS Institute, Cary, NC).

**Microscopy.** Starch gels at 10% (w/w) were prepared by suspending starch samples in 10 mL of distilled and deionized water or 10% sodium caseinate solution. Samples were placed in an oil bath at 90 °C for 90 min, under gentle agitation.

After cooling at room temperature, slices of gels (~1 mm) were placed in glass slides and observed using an Olympus light microscope, model BX60 (Olympus Optical Co. Ltd., Nagano, Japan). Final images were obtained with a 40 $\times$  objective and were recorded with a camera Spot, RT Slider, model 2.3.0 (Diagnostic Institute, Sterling Heights, MN) connected to the computer.

## RESULTS

**Sample Composition.** As expected, the protein contents were higher in the cereal starches (Table 1) and were not significant in the potato, cassava, and waxy corn starches. Corn and wheat starches presented the highest amylose content values (Table 1).

The mineral content analysis showed that potato starch, followed by wheat starch, had the highest phosphorus content. The phosphorus content in the defatted potato starch was close to that in the unfatted sample, whereas the phosphorus content decreased in the defatted samples for the corn, wheat, and rice

**Table 2.** Mineral Composition of Starch Samples

starch	mg/kg of starch, dry basis				
	P	Ca	K	Mg	Na
potato	866	98	925	40	38
defatted potato	808	93	861	39	0
cassava	111	422	372	86	54
defatted cassava	93	410	181	55	0
waxy corn	33	30	59	39	113
defatted waxy corn	29	29	63	37	94
corn	209	27	62	33	87
defatted corn	53	32	57	31	71
wheat	686	77	174	42	379
defatted wheat	119	75	66	29	94
rice	483	52	136	70	746
defatted rice	144	28	94	70	463
caseinate	7086	179	ND <sup>a</sup>	28	12733

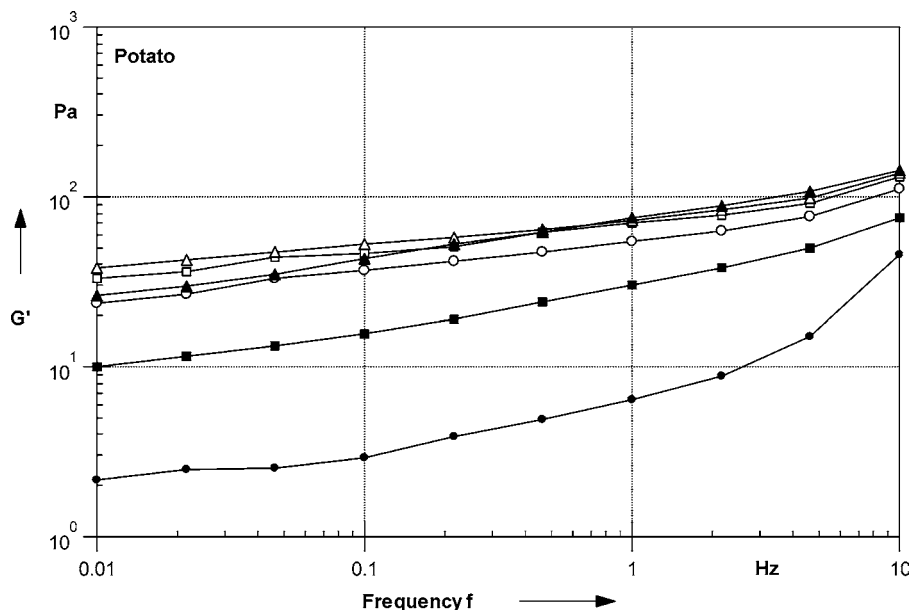
<sup>a</sup> Not detectable.

starches (Table 2). This is in agreement with evidence that the phosphorus in cereal starches is associated with the lipids (11). Potato starch has the highest potassium contents, and the corn and waxy corn starches had the lowest ones. The potassium contents of the wheat and rice starches were also lower for the defatted samples, suggesting that, in these starches, potassium, like phosphorus, might be associated with the lipids. Cassava starch had the highest calcium content.

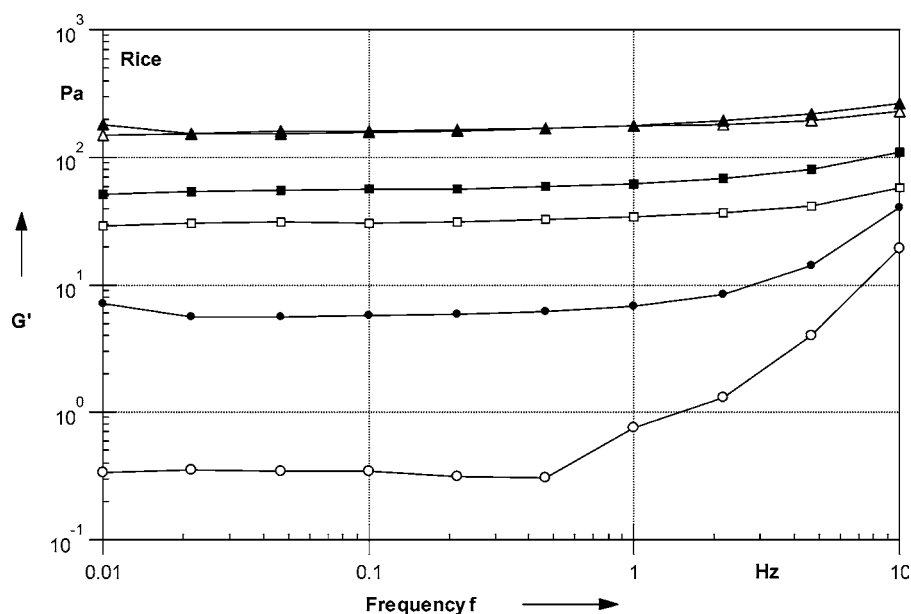
**Viscosity and Viscoelastic Properties.** The results of viscosity and viscoelastic behavior are interpreted, with an exploratory approach, as a general trend of starch samples used in these experiments. The results suggest that, with the exception of potato starch (Figure 1), the storage modulus ( $G'$ ) of samples shows a trend to increase when sodium caseinate is present in the gel composition. This effect seems to be clear, mainly for rice (Figure 2) and wheat starches, at the lower starch concentrations. This would suggest that, for these samples, the viscoelastic properties of the sodium caseinate are more important in the systems with low starch concentrations. Figure 3 shows the ratio of  $G'$  of sodium caseinate–starch to  $G'$  of starch, at a frequency of 1 Hz (values close to 1 suggest no or small changes on viscoelastic modulus). These results suggest that the effect of sodium caseinate on viscoelastic behavior is not the same in all starches. It seems that rice and wheat starches show similar behaviors (Figure 3), suggesting an increase of the storage modulus in the presence of sodium caseinate at lower concentrations. This trend was not very clear at starch concentrations of 7 and 9%.

Conversely, for cassava starch, the effect of sodium caseinate on the viscoelastic properties of gels seems to be stronger at high concentrations (Figure 3). This could have been due to the lower natural viscosity and viscoelastic modulus of cassava starches, which were at the threshold of detection at the lower concentration. However, it is not clear if there are differences in the storage modulus after the addition of sodium caseinate on normal corn and waxy corn starches. For potato starch, opposite to the behavior of the other starches, the results suggest a decreasing storage modulus in the presence of sodium caseinate, mainly at low starch concentrations.

**Flow Behavior.** As for the viscoelastic properties, the results (Figure 4) suggest some differences in flow behavior between starch gels and sodium caseinate–starch gels. Gels with sodium caseinate seem to show an increasing viscosity on wheat and rice starches. The results suggest that the effect of sodium caseinate on the gel viscosity for wheat and rice starch gels was greatest at lower concentrations (5%), particularly at low shear rates (10 s<sup>-1</sup>). At high shear rates (100 s<sup>-1</sup>), it seems the



**Figure 1.** Storage modulus during frequency sweep in samples at 70 °C of potato starch and sodium caseinate–potato starch at different concentrations:  $\Delta$ , potato starch gel at 7%;  $\blacktriangle$ , sodium caseinate–potato starch gel at 7%;  $\square$ , potato starch gel at 5%;  $\blacksquare$ , sodium caseinate–potato starch gel at 5%;  $\circ$ , potato starch gel at 3%;  $\bullet$ , sodium caseinate–potato starch gel at 3%.



**Figure 2.** Storage modulus during frequency sweep in samples at 70 °C of rice starch and sodium caseinate–rice starch at different concentrations:  $\Delta$ , rice starch gel at 9%;  $\blacktriangle$ , sodium caseinate–rice starch gel at 9%;  $\square$ , rice starch gel at 7%;  $\blacksquare$ , sodium caseinate–rice starch gel at 7%;  $\circ$ , rice starch gel at 5%;  $\bullet$ , sodium caseinate–rice starch gel at 5%.

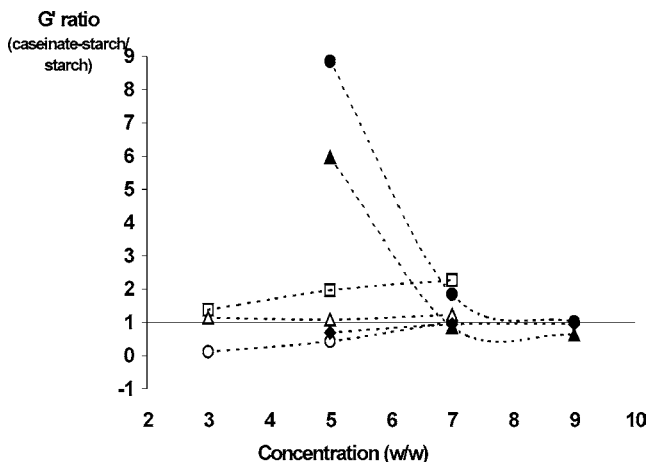
effect of sodium caseinate on the viscosity was lower (data not shown). This suggests that sodium caseinate contributed to improve the gel strength but that this structure was easily broken (the gel was more brittle) with an increase with shear (**Figure 5**). Conversely, in gels at high starch concentrations (9%), the contribution of sodium caseinate to the gel viscosity was greater at high shear rate ( $100 \text{ s}^{-1}$ ). These results suggest an interaction between concentration and shear rate that plays an important role in the rheological properties of sodium caseinate–starch gels.

Cassava, normal corn, and waxy corn starch curves suggest that the viscosity increased in the sodium caseinate–starch systems, especially at higher concentrations (**Figure 4**). The effect of caseinate on the viscosity of cassava starch gels seems to be accentuated at low shear rate. In contrast to the rice and wheat starches, the addition of sodium caseinate to the cassava,

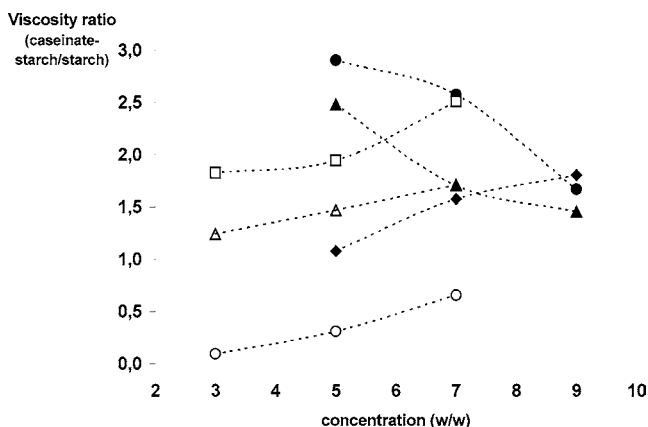
corn, and waxy corn starches at different concentrations seems to have the same effect at shear rates of 10 and  $100 \text{ s}^{-1}$ .

Potato starch results suggest a different trend of viscoelastic behavior from the other starches. The results suggest that the viscosity decreased when sodium caseinate was added to the system, and this effect seems to be strongest at lower concentrations (**Figure 4**).

**RVA Results.** The RVA results showed significant differences between samples with and without sodium caseinate and, as expected, between the starches (**Table 3**). The peak viscosity can be interpreted as the maximum apparent viscosity of a starch solution during the gelatinization process. Starches with low lipid contents, such as starches from roots and tubers, are expected to have faster solubilization and higher swelling potential.



**Figure 3.** Effect of sodium caseinate on the storage modulus of gels with different starches at several concentrations, measured at a frequency of 1 Hz: ●, rice starch; ▲, wheat starch; □, cassava starch; △, waxy corn starch; ◆, corn starch; ○, potato starch.



**Figure 4.** Effect of sodium caseinate on the viscosity of gels with different starches at several concentrations at a shear rate of  $10 \text{ s}^{-1}$ : ●, rice starch; ▲, wheat starch; □, cassava starch; △, waxy corn starch; ◆, corn starch; ○, potato starch.

Caseinate addition promoted a significant increase in the peak viscosity for all starches, with the exception of potato starch, which had a decrease in peak viscosity (Table 3). That the viscosity increased in the samples with sodium caseinate addition supports the idea that suggests that limitation of water as a result of soluble nonstarch polysaccharide hydration can restrict starch gelatinization (12).

The increases in peak viscosity for the samples with sodium caseinate addition were markedly greater for the waxy corn and cassava starches, followed by corn starch, whereas the viscosity increases were smaller for the rice and wheat starches. These results might suggest that the presence of sodium caseinate in the solution not only interferes in the starch swelling but also causes a reduction in leached amylose. It has been observed that, in waxy corn starch, more  $\alpha$ -glucan is leached in the presence of nonstarch polysaccharides than in water systems (12). This could explain the greater effect of sodium caseinate addition on the peak viscosity of the cassava and waxy corn starches, compared with the corn, wheat, and rice starches.

Sodium caseinate did not change the temperature of the peak pasting viscosity for the cereal starches. Conversely, for the cassava and waxy corn starches, an increase of  $3 \text{ }^\circ\text{C}$  in the peak temperature was observed in systems with sodium caseinate. For potato starch, the presence of sodium caseinate increased the peak pasting temperature by  $23 \text{ }^\circ\text{C}$  (Table 3). This suggests

**Table 3.** Average of Rapid Visco Analyzer Parameters for Starches with and without Sodium Caseinate and Their Significance Levels for the Starch, Caseinate, and Their Interactions

starch/treatment	peak viscosity	final viscosity		peak temp		
	(RVU) <sup>a</sup>	(RVU) <sup>a</sup>	(RVU) <sup>a</sup>	( $^\circ\text{C}$ )		
	$\Delta\text{PV}^b$	$\Delta\text{FV}^b$	$\Delta\text{FV}^b$	$\Delta\text{PT}^b$		
waxy corn	244		115	80		
waxy corn caseinate	393	149	208	93	83	3
potato	760		261	72		
potato caseinate	389	-371	362	101	95	23
cassava	281		168		88	
cassava caseinate	403	122	287	119	91	3
wheat	122		131		95	
wheat caseinate	148	26	269	138	95	0
corn	141		140		95	
corn caseinate	206	65	328	188	95	0
rice	96		159		95	
rice caseinate	123	27	251	92	95	0
	<i>P</i> levels <sup>c</sup>					
starch	<0.001		<0.001		<0.001	
caseinate	0.0308		<0.001		<0.001	
starch $\times$ caseinate	<0.001		<0.001		<0.001	

<sup>a</sup> Rapid Visco Analyzer units. <sup>b</sup>  $\Delta\text{PV}$ ,  $\Delta\text{FV}$ , and  $\Delta\text{PT}$  indicate differences between sodium caseinate–starch and starch systems for peak viscosity, final viscosity, and peak temperature, respectively. <sup>c</sup> Significance levels ( $P > F$  values) in RVA means for different starches, samples with and without sodium caseinate and their interactions.

that sodium caseinate plays a major role in the speed of starch granules swelling and that this effect is observed mainly in starches with high amylopectin and low lipid contents.

Sodium caseinate also increased the final paste viscosity, suggesting a reduction in syneresis during retrogradation and cooling. These changes in final viscosity were greatest in corn starch, followed by wheat starch and cassava starch.

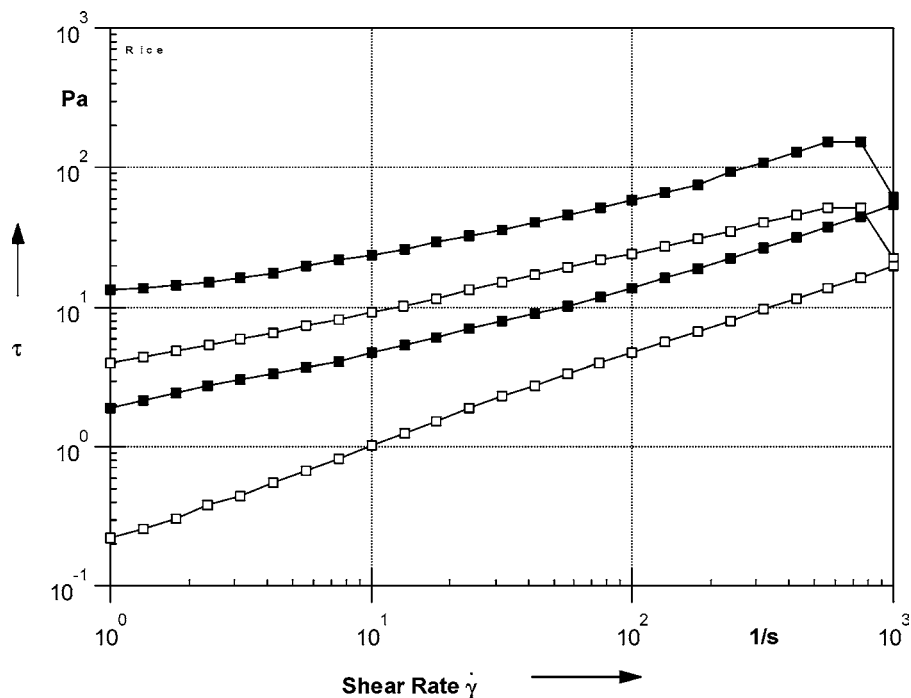
**Thermal Properties.** In DSC analysis, the samples containing sodium caseinate showed a decrease in the enthalpy of gelatinization. Statistical analysis from DSC data showed that there is no significant interaction between starch and sodium caseinate addition, suggesting that sodium caseinate addition had the same effect in decreasing the enthalpy for all starches (Table 4).

Significant interactions between starch and sodium caseinate were observed for the gelatinization onset temperature, the peak temperature, and the end temperature (Table 4). In samples with sodium caseinate addition, a shift in the gelatinization peak was observed, with increases in the onset temperature, the peak gelatinization temperature, and the end temperature, in agreement with the results obtained by Erdogdu et al. (13) for casein–wheat starch samples.

Changes in the gelatinization onset and peak temperatures appeared to be higher in cereal starches, even if the changes did not always follow this trend. In contrast to the wheat and rice starch samples, the endothermic peak at  $100 \text{ }^\circ\text{C}$  (relative to the complex amylose–lipid in the cereal starch samples) was not observed in the sodium caseinate–starch samples. However, it is not clear whether these results were not, at least in part, caused by a dilution effect (13). It has been reported that the changes in the thermal behavior of starch caused by the addition of nonstarch polysaccharide solution to the starch is markedly high at starch/solvent ratios of 1:10 (or above) and that the end temperature increases as the nonstarch polysaccharide concentration increases in the system (12).

**Microscopy.** Microscopy of the starch and sodium caseinate–starch gels showed different results for cereal starches and waxy corn, cassava, and potato starches.





**Figure 5.** Shear of rice starch gels during a shear rate sweep at 70 °C (from  $10^0$  to  $10^3$   $s^{-1}$  and from  $10^3$  to  $10^0$   $s^{-1}$ ) □, rice starch gel at 7%; ■, sodium caseinate–rice starch gel at 7%.

**Table 4.** Average of DSC Parameters for Starches with and without Sodium Caseinate and Their Significance Levels for the Starch, Caseinate, and Their Interactions

starch/treatment	$\Delta H^a$ (J/g)	$T_{onset}^a$ (°C)	$T_{peak}^a$ (°C)	$T_1^a$ (°C)	$T_2^a$ (°C)	$T_2 - T_1^a$ (°C)
waxy corn	16.65	62.7	67.0	50.5	85.5	35.0
waxy corn caseinate	12.85	66.6	71.4	57.0	85.1	28.2
potato	18.37	58.1	61.7	50.0	76.5	26.5
potato caseinate	13.54	60.4	64.3	53.4	74.6	21.1
cassava	15.60	61.4	66.4	52.1	85.8	33.7
cassava caseinate	11.62	65.1	70.5	58.8	89.1	30.3
wheat	10.94	54.8	59.5	45.7	74.6	28.9
wheat caseinate	5.85	59.2	63.3	51.6	80.5	28.9
corn	14.67	64.1	67.4	55.7	83.1	27.5
corn caseinate	9.58	67.5	71.9	62.9	84.2	21.3
rice	10.98	57.0	64.0	49.5	82.1	32.7
rice caseinate	8.12	62.6	68.3	53.9	86.5	32.7
			<i>P</i> levels <sup>b</sup>			
starch	<0.001	<0.001	<0.001			<0.001
caseinate	<0.001	<0.001	<0.001			<0.001
starch × caseinate	ns <sup>c</sup>	0.0042	0.0013			<0.001

<sup>a</sup>  $\Delta H$  = enthalpy change,  $T_{onset}$  = gelatinization onset temperature,  $T_{peak}$  = peak temperature,  $T_1$  = peak start temperature,  $T_2$  = peak end temperature,  $T_2 - T_1$  = gelatinization range. <sup>b</sup> Significance levels ( $P > F$  values) in DSC value means for different starches; samples with and without sodium caseinate and their interactions. <sup>c</sup> Not significant.

Homogeneous matrices were observed in the gels from potato, cassava, and waxy corn starches, with no apparent differences from the gels with sodium caseinate addition (Figure 6A–F).

The matrix was not as homogeneous in the gels from corn, rice, and wheat starches (Figure 6G,I,K) as in the gels from cassava, waxy corn, and potato starches (Figure 6A,C,E). For those samples, the addition of sodium caseinate promoted the formation of a homogeneous matrix (Figure 6H,J,L).

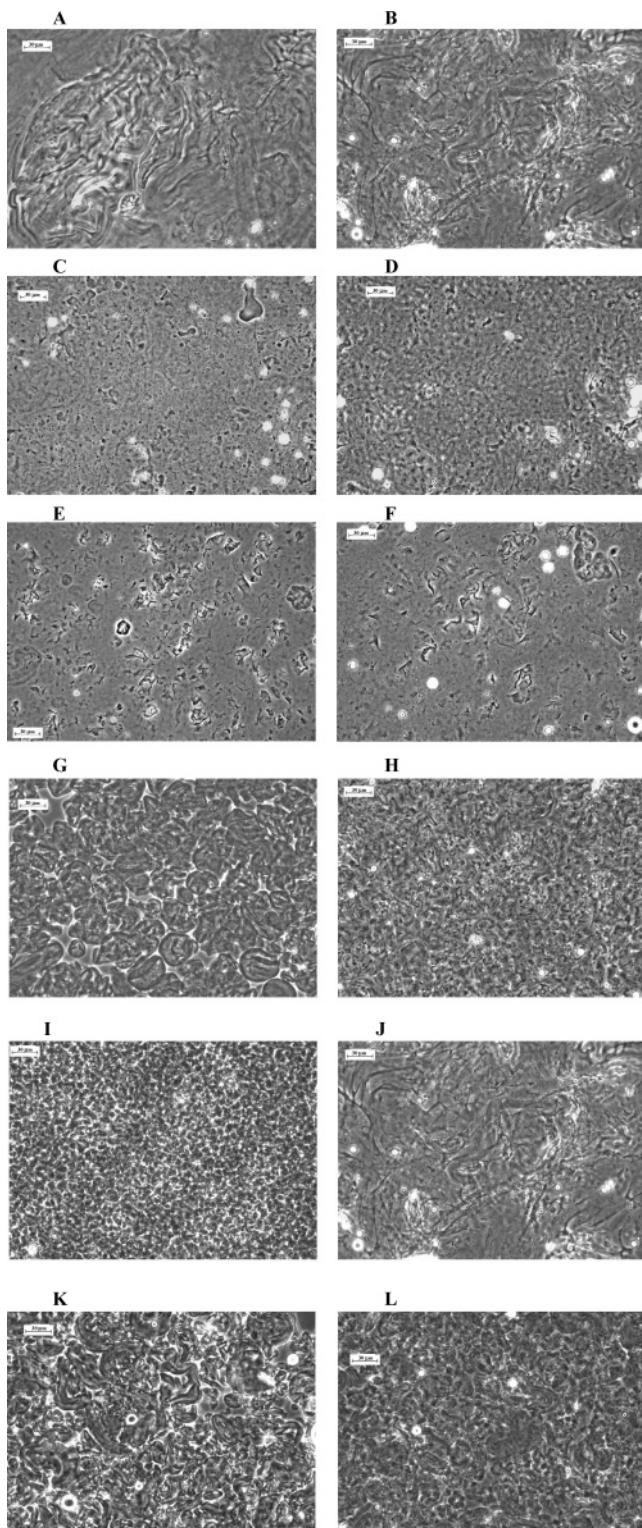
The nonhomogeneous matrix could have been due to an incomplete gelatinization in the cereal starches, as a consequence of the limitation of swelling and the high gelatinization temperature because of the presence of lipids. Microscopic observations during starch gelatinization/melting at low moisture contents (400 g/kg) have shown that corn starch results in a non homogeneous matrix with faster dehydration when compared with cassava starch (14). The faster swelling of cassava

starch and its lower gelatinization temperature would result in a homogeneous matrix (14).

In gels of cereal starches, the presence of sodium caseinate appeared to contribute to the formation of a homogeneous matrix, even if the gelatinization temperature increased when sodium caseinate was present in the system.

## DISCUSSION

In this work, the rheological behavior of sodium caseinate–starch systems was related to the contribution from the starch. This has been previously shown for systems formed from modified starch, caseinate, and calcium (15) and in systems with casein and starch (4). In fact, in complex systems, such as béchamel sauces, the rheological properties exhibited are markedly similar to those of starch–water systems and the



**Figure 6.** Light microscope images of starch and sodium caseinate–starch gels: **A**, potato starch gel; **B**, sodium caseinate–potato starch gel; **C**, cassava starch gel; **D**, sodium caseinate–cassava starch gel; **E**, waxy corn starch gel; **F**, sodium caseinate–waxy corn starch gel; **G**, corn starch gel; **H**, sodium caseinate–corn starch gel; **I**, rice starch gel; **J**, sodium caseinate–rice starch gel; **K**, wheat starch gel; **L**, sodium caseinate–wheat starch gel.

viscoelastic moduli change according to the starch used in the formulation (16).

A decrease in the storage modulus of water–starch–casein systems (16, 17) and a decrease in both the storage and the loss moduli in water-modified starch–sodium caseinate systems

(15) have been reported. Water–wheat starch–sodium caseinate systems presented viscoelastic behavior similar to that of the water–wheat starch system, but had lower elasticity (18). Conversely, it has been reported that the viscosities of waxy corn starch and corn starch increase with sodium caseinate addition (3).

Despite these conflicting results, it seems clear that changes in the viscoelastic properties of the systems can be attributed to the limitation of starch swelling and gelatinization by sodium caseinate addition (16, 17), as for most nonstarch polysaccharides (12). The effect of sodium caseinate on starch swelling seems to be as marked as the water is restricted in the system (12) and is more evident in starches with high amylose content (18).

A three-phase system (starch, nonstarch polysaccharide, and water) has been proposed by Tester and Sommerville (12), in which a potential dynamic interchange in the water molecules between different polymers would occur rather than a relative exclusion of different polymers from each other. In these systems, at a starch/water ratio of 1:1, the gelatinization is incomplete and the residual order depends on the botanical origin of the starch. The addition of nonstarch polysaccharides to starch–water systems limits the hydration of the starch and, as water has a plasticizing effect in amorphous regions of the starch, the mobility of the plasticizer is also restricted. Thus, the nonstarch polysaccharides might have an “anti-plasticizing” effect (12).

As the swelling behavior of the starches was the main factor that was altered in these systems, it is expected that factors related at the botanical origin of starch responsible for starch swelling, such as amylose/amylopectin ratio, molecular weight of amylose and amylopectin, their distribution on the granule starch, lipid content, minor components (such as minerals and salts), granule size, and affinity of starch for water should play an appreciable role in changes promoted by the sodium caseinate. However, the contribution of sodium caseinate to the rheological properties of starch gels is strongly related to the concentration and the botanical origin of the starch.

Potato starch swells more readily and distinctly than corn, waxy corn, cassava, mung bean, rice, sweet potato, and wheat starches, resulting in high leaching of the amorphous material from the starch granule to the solution (19). This is attributed to the granule size and its amylopectin/amylose ratio, but the phosphorus content is also expected to play an important role in the swelling power of potato starches (22–24). Potato starches are also unique in having a significant concentration of phosphate ester groups that are covalently bound at the C3 and C6 positions to their amylopectin molecules (20). Long-chain units are more substituted than shorter chain units, and it has been suggested that substitution of position C6 is more pronounced in the amorphous region (21). It has also been suggested that extreme starch phosphate contents could result in low peak viscosities because of particle dissociation as a result of significant electrostatic repulsion between monoesterified phosphate groups (21).

It is important to consider the amounts of sodium and phosphorus added into the systems with the addition of sodium caseinate (Table 1). Kelly et al. (25) suggested that the decrease in the viscosity of sodium caseinate–potato starch systems might be attributed to the presence of associated ions. These authors reported that the addition of sodium chloride to the systems resulted in a reduction in the viscosity of potato starch, but had no significant effect on cassava, wheat, maize, sago, and rice starches, in agreement with our results. Changes in the viscosity properties of potato starch have also been correlated to divalent

and monovalent ion contents and to the calcium/magnesium/phosphorus ratio (22, 24, 25). Divalent cations, such as  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , suppress the swelling of potato starch granules by forming complexes between phosphate groups and these cations (22). Nevertheless, it seems that the effect on the viscosity is dependent on the concentration, as well as on the ratio of divalent/monovalent cations. Addition of  $\text{Ca}^{2+}$ , as well as  $\text{Mg}^{2+}$  and  $\text{Na}^+$ , to caseinate–starch systems promotes changes in the viscoelastic properties, resulting in a phase inversion according to the  $\text{Ca}^{2+}$  concentration (15). Despite the idea that this interaction would be specific to the anionic properties of potato starch (25, 26), the nature of the bonds involved in this interaction is not clear. The presence of non-covalent hydrogen interactions (4) or chemical bonds (26) between starch and caseinate has been suggested; these interactions seem to be more stable at a casein/starch ratio of 1:1 (26).

A better understanding of the interactions between starch and milk proteins is essential for the manipulation of food systems, especially dairy product systems. Obviously, the presence of some proteins, such as sodium caseinate, in the systems affects swelling and starch gelatinization. These changes will determine some of the characteristics of the matrix, depending on the botanical origin of the starch, the caseinate/starch ratio, and the minor components. However, further research is necessary to identify the factors involved in interactions between sodium caseinate and starch. With respect to the particular behavior of potato starch in such systems, we consider that attention should be focused on developing knowledge of the roles that phosphorus, calcium, and sodium play in the protein–starch interactions.

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