

Studies on interactions of corn starch with casein and casein hydrolysates

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Abstract

Incorporation of non-starchy substances into starch pastes modify their viscosity and rheological profile. Protein hydrolysates blended with starch have been used in the formulation of hypoallergenic weaning and specialised adult nutritional formulas. In the present work, an attempt has been made to study the interaction of corn starch (5% w/v) with casein and its hydrolysates with respect to changes in the paste viscosity and the gelatinization temperature when heated in a Brabender amylogram. The pastes resulting on heating blends of starch and the casein/casein hydrolysates were also studied for their rheological profile on a Haake viscometer to confirm the effect under varying shear rates. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Corn starch; Casein; Casein hydrolysates; Interaction

1. Introduction

Starch contributes greatly to the texture properties of many foods and is widely used in food and industrial applications as a thickener, colloidal stabilizer, gelling agent, bulking agent, water retention agent and adhesive. These functions of starch are brought about by its gelatinization and retrogradation behavior (Lisa and Jezof, 1992; Madeka and Kokini, 1992; Hamaker and Griffin, 1993). However, the recent increase in demand for functionality and application has made the characteristics of starch insufficient when considered from the viewpoint of material science. It has been considered that the conjugation of non-starchy substances with starch would be important and effective for achieving a wider range of applications and also for improved functionality. Among the likely substances, proteins and their hydrolysates are considered, since these are charged polymer (Hattori et al., 1995).

Food starches are usually used in protein hydrolysate-based nutritional products such as hypoallergenic infant formulas, mainly as emulsion stabilizers and to a lesser extent as sources of calories. In such heated food systems, starch undergoes gelatinization during processing and contributes to product emulsion stability

through increase in viscosity of the aqueous phase (Mahmoud, 1994). Entrapment of the alkyl side chains in the proteins and protein hydrolysates by the helical amylose of starch cannot be ruled out. These helices have been shown to form complexes with a wide assortment of molecules such as aliphatic alcohols, lower aliphatic ketones, fatty acids, aromatic aldehydes, alkyl halides, cyclic alcohols, phenols, benzene, cyclic and aliphatic hydrocarbons, carbon tetrachloride, iodine, nitroethane, pyridine, dyes, pesticides, and many others (Godshall and Solms, 1992), some of which are present in the alkyl side chains of proteins and their hydrolysates.

Interactions between the protein hydrolysates and starch during processing can markedly influence starch gel network structure and the rheological profile. Such interactions between protein hydrolysates and starch have not been extensively studied (Mahmoud, 1994). This aspect needs to be looked into for food product formulations and for the developments therein. The superior nutritional quality of milk protein is the main basis of utilizing its hydrolysates in hypoallergenic infant formulas (Likimani et al., 1990) and specialized adult nutritional formulas in various countries (Cordano and Cook, 1985). The present work aims to study the physicochemical characteristics and rheological profile of corn starch, blended and substituted with casein and three of its hydrolysates.

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2. Materials and methods

2.1. Materials

Food grade corn starch was procured from M/S Wander Ltd., Bombay. Casein and casein hydrolysates (designated as CH₁, CH₂ and CH₃) were obtained from M/S Himedia Laboratories, Bombay.

2.2. Methods

2.2.1. Determination of total and α -amino nitrogen

Casein and the hydrolysates were analyzed for total nitrogen by the Kjeldahl method (ISI, 1984) and for α -amino nitrogen by formol titration (Kuehler and Stine, 1974; Mahmoud et al., 1992). CH₁ and CH₂ were prepared enzymically, while CH₃ was prepared by partial acid and partial enzyme hydrolysis.

2.2.2. Determination of paste viscosity and gelatinization temperature

In a total volume of 450 ml water, addition and substitution of casein and its three hydrolysates (11.1–44.4% w/w of starch) was done with 5% corn starch (containing ~9–10% moisture). The mixtures were heated in a Brabender amylograph (Model PT 100), from 35–95°C, at a heating rate of 1.5°C min⁻¹, at a bowl speed of 75 rpm, held at 95°C for 30 min and then cooled back to 40°C at same rate of 1.5°C min⁻¹. A 350 cmg sensitivity cartridge was used. The results were interpreted with respect to gelatinization (or pasting) temperature, peak viscosity, viscosity at 95°C, viscosity after holding for 30 min at 95°C, and cold paste viscosity at 40°C.

2.3. Rheological study of starch—casein and casein hydrolysates combinations

Addition and substitution of casein and casein hydrolysates (11.1–44.4% w/w of starch) was done with 5% corn starch in 100 ml of distilled water. Each of the above mixtures was stirred well and heated to 95°C for 10 min and then cooled to room temperature (30 ± 2°C). Rheological behavior of the pastes as prepared above was studied using a Haake viscometer (Model RV 3) in the shear rate range of 25–1000 S⁻¹. The flow behavior index 'n' and consistency index 'K' were calculated using a log–log plot of shear rate vs shear stress (Holdsworth, 1971).

3. Results and discussion

Table 1 shows the α -amino nitrogen, total nitrogen and degree of hydrolysis (DH) defined as the ratio of α -amino nitrogen to total nitrogen of the commercially obtained casein and its hydrolysates used in the present

Table 1

^a α -Amino nitrogen, total nitrogen and degree of hydrolysis of casein and casein hydrolysates used in the study

Sample	α -Amino nitrogen (%)	Total nitrogen (%)	DH = α -amino N/total N
Casein (parent protein)	1.32 ± 0.004	12.1 ± 0.08	0.11 ± 0.002
CH ₁ (FE)	4.12 ± 0.006	10.3 ± 0.06	0.40 ± 0.004
CH ₂ (FE)	2.91 ± 0.005	7.5 ± 0.06	0.39 ± 0.003
CH ₃ (PE and PA)	3.58 ± 0.006	10.3 ± 0.05	0.35 ± 0.001

FE, fully enzymic hydrolysis; PE, partially enzymic hydrolysis; PA, partially acidic hydrolysis.

^a Values are mean of three determinations.

study. It can be seen that the three hydrolysates varied in their α -amino nitrogen in the order CH₃ > CH₁ > CH₂. The total nitrogen of CH₁ and CH₃ were almost identical at 10.2%, while that of CH₂ was lower at a value of 7.52%. The DH of the samples under study was in the order CH₁ > CH₂ > CH₃ > casein.

Table 2 shows the cold paste viscosity and gelatinization temperature of 5% corn starch and the changes resulting therein on addition of casein and casein hydrolysates (11.1–44.4% w/w of starch). It is observed that, as the concentration of casein increases in the blend, the gelatinization temperature decreases and the cold paste viscosity increases. For instance, peak viscosity increases from 144 BU for corn starch alone to 222 BU for its combination with 44.4% casein. The corresponding values of cold paste viscosity for corn starch alone and its combination with 44.4% casein are 295 and 365 BU, respectively. Diverse effects have been observed with the Brabender amylogram characteristics of starches extended by proteins and no particular trend has been observed (Yagi and Okamoto, 1976). Heated aqueous dispersions of casein or caseinate and starch do not possess the stickiness or gumminess of starch alone; they can be prepared at various viscosities and find applications in emulsion stabilization (Hermansson, 1979).

Starch pastes are described as suspensions of swollen particles dispersed in a macromolecular medium. It can be considered that proteins are located within the continuous phase, and thus the volume of the phase accessible to the proteins is reduced; this causes an increase in concentration in the continuous medium, thereby resulting in a high viscosity. The swollen particles are mainly composed of amylopectin, while the continuous medium consists of amylose. It is probably the amylose interaction with protein and protein hydrolysates which is dominating in the system. For instance, peak viscosity increases from 144 BU for corn starch alone to 205 BU for its combination with 44.4% CH₃. The corresponding values of cold paste viscosity for corn starch alone and its combination with 44.4% CH₃ are 295 and 430 BU, respectively.

Table 2

^aComparative effect of addition of casein and casein hydrolysates on the viscosity and gelatinization temperature of corn starch

Ingredients	Gelatinization temperature (°C)	Peak viscosity (BU)	Viscosity at 95°C (BU)	Viscosity after 30 min at 95°C (BU)	Cold paste viscosity at 40°C
CS	85.0±0.5	144±2	142±2	134±2	295±5
CS+A1	84.0±0.5	195±2	178±2	195±2	335±5
CS+A2	83.5±0.5	204±2	192±2	212±2	350±5
CS+A3	81.5±0.5	212±4	196±2	215±2	360±5
CS+A4	81.0±0.5	222±4	200±4	225±4	365±5
CS+A'1	85.0±0.5	160±2	155±2	190±2	365±5
CS+A'2	86.0±0.5	165±2	165±2	195±2	385±5
CS+A'3	86.0±0.5	168±2	168±2	200±2	395±5
CS+A'4	86.0±0.5	172±2	172±2	204±2	400±5
CS+A''1	86.0±0.5	155±2	155±2	195±2	375±5
CS+A''2	86.0±0.5	170±2	165±2	202±2	295±5
CS+A''3	85.0±0.5	175±2	172±2	205±2	400±5
CS+A''4	85.5±0.5	185±2	185±2	210±2	420±5
CS+A'''1	84.0±0.5	175±2	170±2	195±2	370±5
CS+A'''2	83.0±0.5	180±2	175±2	200±2	405±5
CS+A'''3	83.0±0.5	205±2	195±2	215±2	420±5
CS+A'''4	83.0±0.5	205±2	195±2	220±2	430±5

CS, 5% w/v corn starch; A1, casein, 11.11% of starch w/w; A2, casein, 22.22% of starch w/w; A3, casein, 33.33% of starch w/w; A4, casein, 44.44% of starch w/w; A'1, CH₁, 11.11% of starch w/w; A'2, CH₁, 22.22% of starch w/w; A'3, CH₁, 33.33% of starch w/w; A'4, CH₁, 44.44% of starch w/w; A''1, CH₂, 11.11% of starch w/w; A''2, CH₂, 22.22% of starch w/w; A''3, CH₂, 33.33% of starch w/w; A''4, CH₂, 44.44% of starch w/w; A'''1, CH₃, 11.11% of starch w/w; A'''2, CH₃, 22.22% of starch w/w; A'''3, CH₃, 33.33% of starch w/w; A'''4, CH₃, 44.44% of starch w/w.

^a Values are mean of three determinations.

Sugar, at high concentration, is known to increase cold paste viscosity of starch pastes, which is attributed to the crosslinking or sugar bridges (Spies and Hosney, 1982). Proteins contain many hydrophilic groups such as –OH, –NH₂, –COOH and –SH in the alkyl side chains, all of which are capable of forming crosslinks with starch. It is possible that such crosslinks may be present in starch–casein and starch–casein hydrolysate blends, which may be responsible for their higher cold paste viscosity as compared to starch alone. The differences in individual protein and protein hydrolysates could be attributed to differences in their ability to crosslink with starch. This is possible, since proteins subjected to different mode and degree of hydrolysis would have different surface characteristics. In a system containing whey proteins and corn starch, it has been postulated that it is the entanglement of the protein rather than the swelling of starch which causes differences in the viscosity of the system (Ling, 1984).

Table 2 shows that casein hydrolysates did not influence the swelling or gelatinization temperature of corn starch. However, with casein a steady decrease in gelatinization temperature was observed. These observations can be explained on the basis of electrical double-layer theory (Oosten, 1983). According to this theory, an electrical double layer of cations surrounding the starch exists which excludes the anions; hence the anions cannot penetrate and cause gelatinization. From studies on

effects of salts on gelatinization behavior of starch, it has been found that anions are the gelatinizing agents (Oosten, 1990). Proteins being amphoteric in nature will contain both positive and negative charges. It can be conceived that the collective negative charge on the protein may be working in a fashion similar to the anion in the salt and facilitating the gelatinization of starch with casein. This type of an arrangement may not be happening with casein hydrolysates and hence the observation of an almost constant gelatinization temperature.

Table 3 shows the effect of substitution of corn starch (11.1–44.4% w/w of starch) with casein and casein hydrolysates. A decrease in peak viscosity, viscosity at 95°C, viscosity at 95°C after holding for 30 min and cold paste viscosity, was observed in all cases. For instance, peak viscosity decreases from 144 BU for corn starch alone to 28 BU when substituted with 44.4% casein. The corresponding values of cold paste viscosity for corn starch alone and its substitution with 44.4% casein are 295 and 68 BU, respectively. This decrease in viscosity is simply attributed to the dilution of starch. The same is true for an increase in gelatinization temperature. In dilute solutions, there is a decrease in the electrical double-layer by which the penetration of anions facilitated and hence gelatinization can occur (Oosten, 1983).

Table 4 shows apparent viscosities of corn starch on addition of (11.1–44.4% w/w of starch) casein and

Table 3

^aComparative effect of substitution of casein and casein hydrolysates on the viscosity and gelatinization temperature of corn starch

Ingredients	Gelatinization temperature (°C)	Peak viscosity (BU)	Viscosity at 95°C (BU)	Viscosity after 30 min at 95°C (BU)	Cold paste viscosity at 40°C
CS	85.0±0.5	144±2	142±2	134±2	295±5
CS+A1	85.5±0.5	124±2	124±2	152±2	245±5
CS+A2	86.0±0.5	85±2	85±2	112±2	160±2
CS+A3	87.5±0.5	48±2	48±2	80±2	105±2
CS+A4	88.0±0.5	28±2	28±2	46±2	68±2
CS+A'1	86.0±0.5	110±2	110±2	140±2	270±5
CS+A'2	87.0±0.5	75±2	75±2	100±2	200±5
CS+A'3	89.0±0.5	45±2	45±2	75±2	145±2
CS+A'4	90.5±0.5	28±2	28±2	55±2	85±2
CS+A''1	86.0±0.5	100±2	100±2	140±2	265±5
CS+A''2	87.5±0.5	65±2	65±2	110±2	220±2
CS+A''3	89.0±0.5	45±2	45±2	80±2	160±2
CS+A''4	90.0±0.5	30±2	30±2	50±2	100±2
CS+A'''1	85.0±0.5	120±2	120±2	144±2	232±5
CS+A'''2	85.5±0.5	65±2	62±2	80±2	144±2
CS+A'''3	85.0±0.5	55±2	55±2	68±2	106±2
CS+A'''4	85.0±0.5	32±2	32±2	52±2	76±2

CS, 5% w/v corn starch; A1, casein, 11.11% of starch w/w; A2, casein, 22.22% of starch w/w; A3, casein, 33.33% of starch w/w; A4, casein, 44.44% of starch w/w; A'1, CH₁, 11.11% of starch w/w; A'2, CH₁, 22.22% of starch w/w; A'3, CH₁, 33.33% of starch w/w; A'4, CH₁, 44.44% of starch w/w; A''1, CH₂, 11.11% of starch w/w; A''2, CH₂, 22.22% of starch w/w; A''3, CH₂, 33.33% of starch w/w; A''4, CH₂, 44.44% of starch w/w; A'''1, CH₃, 11.11% of starch w/w; A'''2, CH₃, 22.22% of starch w/w; A'''3, CH₃, 33.33% of starch w/w; A'''4, CH₃, 44.44% of starch w/w.

^a Values are mean of three determinations.

Table 4

^aEffect of addition of casein and casein hydrolysates on the apparent viscosities of corn starch

Ingredients	Apparent viscosities (Pa s) at shear rates (s ⁻¹) of							
	27.05	44.9	75.19	125.5	245	349.4	583.1	971.6
CS	288±4	231±2	177±2	133±2	97.1±1	80.6±0.8	62.5±0.6	50.6±0.5
CS+A1	625±5	463±3	308±2	190±2	118±1	96.3±0.7	71.5±0.5	56.5±0.5
CS+A2	700±6	505±4	323±2	205±2	137±1	107±1.0	79.0±0.8	59.2±0.4
CS+A3	790±6	535±4	342±2	225±2	150±1	116±1.0	90.4±0.7	68.9±0.6
CS+A4	856±6	612±4	435±2	262±2	188±1	141±1.0	103±0.8	77.2±0.7
CS+A'1	234±4	192±2	140±2	114±2	81.7±0.8	62.7±0.8	54.4±0.7	42.2±0.7
CS+A'2	319±5	206±2	182±2	131±2	95.4±0.6	80.7±0.8	62.9±0.6	49.5±0.5
CS+A'3	328±5	233±3	195±2	137±2	99.2±0.8	83.3±0.7	64.3±0.6	51.2±0.4
CS+A'4	362±5	277±3	238±2	153±2	106±1.0	88.7±0.8	70.7±0.7	55.1±0.5
CS+A''1	270±5	212±3	165±2	132±2	93.8±1.0	77.5±1.0	61.1±0.8	46.4±0.6
CS+A''2	248±4	207±2	153±2	125±2	87.0±0.8	73.1±0.9	57.7±0.8	44.9±0.6
CS+A''3	245±4	205±2	160±2	119±2	84.9±0.6	70.4±0.6	54.5±0.5	43.7±0.5
CS+A''4	228±3	155±2	140±2	111±2	78.7±0.8	66.3±0.7	50.4±0.6	40.2±0.5
CS+A'''1	437±5	325±3	254±2	158±2	101±1	80.8±0.7	59.5±0.5	47.6±0.4
CS+A'''2	760±5	363±3	281±2	191±2	109±1	87.6±0.9	66.5±0.5	50.8±0.5
CS+A'''3	811±6	631±4	402±2	218±2	123±1	96.9±1.0	69.8±0.7	52.3±0.5
CS+A'''4	971±8	693±4	478±3	295±2	165±1.5	122±1.0	83.9±0.8	60.9±0.6

CS, 5% w/v corn starch; A1, casein, 11.11% of starch w/w; A2, casein, 22.22% of starch w/w; A3, casein, 33.33% of starch w/w; A4, casein, 44.44% of starch w/w; A'1, CH₁, 11.11% of starch w/w; A'2, CH₁, 22.22% of starch w/w; A'3, CH₁, 33.33% of starch w/w; A'4, CH₁, 44.44% of starch w/w; A''1, CH₂, 11.11% of starch w/w; A''2, CH₂, 22.22% of starch w/w; A''3, CH₂, 33.33% of starch w/w; A''4, CH₂, 44.44% of starch w/w; A'''1, CH₃, 11.11% of starch w/w; A'''2, CH₃, 22.22% of starch w/w; A'''3, CH₃, 33.33% of starch w/w; A'''4, CH₃, 44.44% of starch w/w.

^a Values are mean of three determinations.

Table 5

^aEffect of substitution of casein and casein hydrolysates on the apparent viscosities of corn starch

Ingredients	Apparent viscosities (Pa s) at shear rates (s ⁻¹) of							
	27.05	44.9	75.19	125.5	245	349.4	583.1	971.6
CS	288 ± 4	231 ± 2	177 ± 2	133 ± 2	97.1 ±	80.6 ± 0.8	62.5 ± 0.6	50.6 ± 0.5
CS + A1	691 ± 7	435 ± 5	265 ± 3	154 ± 2	98.6 ± 1	82.0 ± 0.7	63.1 ± 0.6	51.1 ± 0.4
CS + A2	433 ± 5	354 ± 4	239 ± 3	150 ± 2	85.7 ± 1	66.0 ± 0.8	47.4 ± 0.5	37.3 ± 0.4
CS + A3	421 ± 5	268 ± 4	211 ± 2	142 ± 1.5	82.7 ± 1	58.5 ± 0.6	44.1 ± 0.5	30.9 ± 0.3
CS + A4	288 ± 4	219 ± 4	189 ± 2	126 ± 1.0	70.2 ± 0.7	46.2 ± 0.5	28.9 ± 0.3	22.3 ± 0.3
CS + A'1	169 ± 3	143 ± 3	122 ± 2	91.1 ± 0.9	65.2 ± 0.6	54.2 ± 0.5	44.3 ± 0.4	34.5 ± 0.3
CS + A'2	149 ± 3	87.2 ± 2	72.7 ± 1.5	60.6 ± 0.7	44.2 ± 0.6	36.8 ± 0.5	28.2 ± 0.3	24.6 ± 0.2
CS + A'3	43.4 ± 2	31.5 ± 1	26.9 ± 0.7	22.9 ± 0.6	19.7 ± 0.5	17.5 ± 0.3	15.7 ± 0.2	12.7 ± 0.2
CS + A'4	23.5 ± 1	19.8 ± 0.8	18.7 ± 0.7	17.3 ± 0.5	15.2 ± 0.5	14.3 ± 0.3	12.9 ± 0.2	10.7 ± 0.2
CS + A''1	207 ± 2	158 ± 2	126 ± 1	105 ± 1	76.9 ± 0.7	65.2 ± 0.6	50.5 ± 0.5	42.1 ± 0.4
CS + A''2	110 ± 1	100.3 ± 1	73.8 ± 0.7	66.6 ± 0.6	47.3 ± 0.5	41.0 ± 0.4	32.9 ± 0.3	27.1 ± 0.3
CS + A''3	76.4 ± 1	56.2 ± 0.8	47.5 ± 0.7	44.4 ± 0.5	33.1 ± 0.4	28.5 ± 0.3	22.0 ± 0.2	19.5 ± 0.2
CS + A''4	47.5 ± 1	40.2 ± 0.8	29.4 ± 0.6	25.3 ± 0.5	20.6 ± 0.4	18.4 ± 0.3	16.1 ± 0.2	13.4 ± 0.2
CS + A'''1	645 ± 6	474 ± 4	197 ± 2	136 ± 1	91.8 ± 0.9	75.3 ± 0.7	56.5 ± 0.5	45.9 ± 0.3
CS + A'''2	497 ± 5	364 ± 4	242 ± 2	131 ± 1	63.2 ± 0.7	42.8 ± 0.5	31.8 ± 0.3	25.8 ± 0.2
CS + A'''3	441 ± 4	333 ± 3	198 ± 2	106 ± 1	53.0 ± 0.7	38.2 ± 0.5	26.7 ± 0.3	19.0 ± 0.2
CS + A'''4	395 ± 4	296 ± 3	176 ± 2	88.4 ± 0.8	38.3 ± 0.6	21.2 ± 0.3	15.6 ± 0.2	13.7 ± 0.2

CS, 5% w/v corn starch; A1, casein, 11.11% of starch w/w; A2, casein, 22.22% of starch w/w; A3, casein, 33.33% of starch w/w; A4, casein, 44.44% of starch w/w; A'1, CH₁, 11.11% of starch w/w; A'2, CH₁, 22.22% of starch w/w; A'3, CH₁, 33.33% of starch w/w; A'4, CH₁, 44.44% of starch w/w; A''1, CH₂, 11.11% of starch w/w; A''2, CH₂, 22.22% of starch w/w; A''3, CH₂, 33.33% of starch w/w; A''4, CH₂, 44.44% of starch w/w; A'''1, CH₃, 11.11% of starch w/w; A'''2, CH₃, 22.22% of starch w/w; A'''3, CH₃, 33.33% of starch w/w; A'''4, CH₃, 44.44% of starch w/w.

^a Values are mean of three determinations.

Table 6

^aEffect of addition of casein and casein hydrolysates on the rheological characteristics of corn starch

Addition level to 5% starch	Casein		CH ₁		CH ₂		CH ₃	
	n	K	n	K	n	K	n	K
0%	0.51 ± 0.004	1.59 ± 0.02	0.51 ± 0.004	1.59 ± 0.02	0.51 ± 0.004	1.59 ± 0.02	0.51 ± 0.004	1.59 ± 0.02
11.11%	0.32 ± 0.002	6.43 ± 0.06	0.52 ± 0.006	1.18 ± 0.03	0.50 ± 0.07	1.43 ± 0.02	0.33 ± 0.002	4.42 ± 0.04
22.22%	0.26 ± 0.005	8.08 ± 0.04	0.50 ± 0.002	1.51 ± 0.01	0.50 ± 0.03	1.39 ± 0.01	0.25 ± 0.005	7.38 ± 0.03
33.33%	0.13 ± 0.003	18.59 ± 0.09	0.48 ± 0.001	1.91 ± 0.03	0.49 ± 0.06	1.37 ± 0.03	0.20 ± 0.001	11.07 ± 0.05
44.44%	0.13 ± 0.004	21.38 ± 0.08	0.46 ± 0.005	2.15 ± 0.05	0.53 ± 0.02	1.02 ± 0.02	0.17 ± 0.003	17.13 ± 0.07

n, flow behavior index; K, consistency index (Pa sⁿ). α-Amino nitrogen of casein, CH₁, CH₂ and CH₃ were 1.32, 4.12, 2.91 and 3.58, respectively. CH₁ and CH₂ were enzymically hydrolysed, while CH₃ was partially acidic- and partially enzyme-hydrolysed.

^a Values are mean of three determinations.

casein hydrolysates in the shear rate range of 25–1000 S⁻¹. In all cases apparent viscosity decreases with an increase in shear rate, suggesting a shear-thinning character in all combinations. A similar trend is observed in Table 5, which shows the apparent viscosities of corn starch alone and when substituted with 11.1–44.4% w/w casein and casein hydrolysates.

Table 6 shows the flow behavior index 'n' and the consistency index 'K' of corn starch and in its blend with 11.1–44.4% w/w casein and casein hydrolysates. It is observed that the flow behavior index of 0.505 for corn starch alone steadily decreased to 0.126 for corn starch blended with 44.4% casein. A similar trend was

observed when corn starch was blended with CH₃. In the case of corn starch blended with CH₁ and CH₂, results were found to be erratic. This could be due to the different mode of preparation of the hydrolysates. CH₁ and CH₂ were prepared by an enzymic route, while CH₃ was obtained by partial acidic and partial enzymic hydrolysis. A lower value of flow behavior index indicates a pseudoplastic nature. Hence it can be concluded that corn starch–casein and casein hydrolysates combinations are more pseudoplastic than starch alone. The higher pseudoplasticity of starch–xanthan combinations, as compared to starch alone, is attributed to the ionic and highly branched structure of xanthan which

Table 7

^aEffect of substitution of casein and casein hydrolysates on the rheological characteristics of corn starch

Substitution level to 5% starch	Casein		CH ₁		CH ₂		CH ₃	
	n	K	n	K	n	K	n	K
0%	0.51 ± 0.004	1.59 ± 0.02	0.51 ± 0.004	1.59 ± 0.02	0.51 ± 0.004	1.59 ± 0.02	0.51 ± 0.004	1.59 ± 0.02
11.11%	0.25 ± 0.001	6.36 ± 0.04	0.50 ± 0.004	1.22 ± 0.03	0.56 ± 0.005	0.88 ± 0.03	0.31 ± 0.002	4.51 ± 0.05
22.22%	0.24 ± 0.002	7.02 ± 0.08	0.62 ± 0.002	0.48 ± 0.01	0.58 ± 0.006	0.47 ± 0.01	0.14 ± 0.003	10.93 ± 0.07
33.33%	0.20 ± 0.003	8.96 ± 0.05	0.77 ± 0.001	0.08 ± 0.02	0.62 ± 0.003	0.26 ± 0.01	0.03 ± 0.001	14.19 ± 0.06
44.44%	0.18 ± 0.002	10.60 ± 0.04	0.80 ± 0.003	0.05 ± 0.01	0.64 ± 0.007	0.15 ± 0.02	-0.04 ± 0.001	16.51 ± 0.08

n: flow behavior index; K, consistency index (Pa sⁿ). α -Amino nitrogen of casein, CH₁, CH₂ and CH₃ were 1.32, 4.12, 2.91 and 3.58, respectively. CH₁ and CH₂ were enzymically hydrolysed, while CH₃ was partially acidic- and partially enzyme-hydrolysed.

^a Values are mean of three determinations.

Table 8

Regression equation giving correlations between addition or substitution of starch with casein and casein hydrolysate (CH₃) with the flow behavior index (n) and the consistency index (K)

Sample	Flow behavior index, n		Consistency index, K	
	Regression equation	R ²	Regression equation	R ²
<i>Effect of addition:</i>				
Casein	$y = -0.0085x + 0.4576$	0.9185	$y = 0.4657x + 0.866$	0.9457
CH ₃	$y = -0.0072x + 0.4508$	0.8907	$y = 0.3396x + 0.772$	0.9713
<i>Effect of substitution:</i>				
Casein	$y = -0.0063x + 0.4152$	0.7068	$y = 0.1856x + 2.782$	0.9156
CH ₃	$y = -0.0123x + 0.4636$	0.9636	$y = 0.3558x + 1.6406$	0.9724

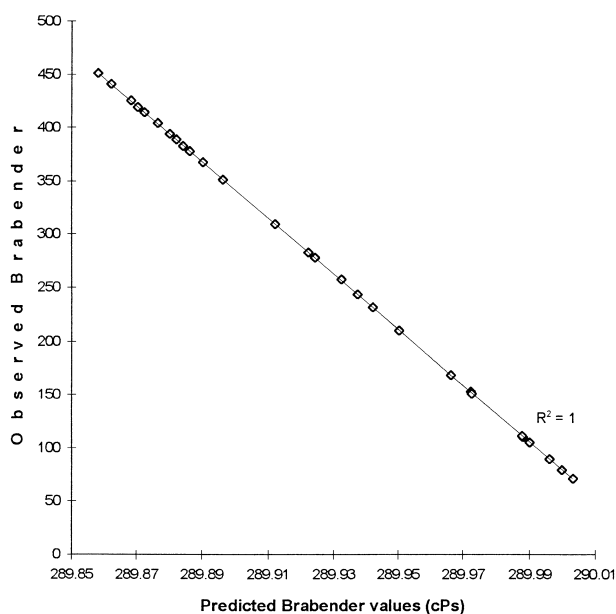


Fig. 1. Correlation between predicted Brabender values and observed Brabender values.

causes the molecules to repel each other and keep them in a highly extended conformation which in turn interacts with the amylose component of starch (Kovacs and Kang, 1977). Being ionic in nature, it is postulated that casein and its hydrolysates may interact readily with

amylose and outer branches of amylopectin through non-covalent hydrogen bonding. This results in an extended conformation of the starch-protein blend systems which in turn may increase the degree of pseudoplasticity. The consistency index 'K' of corn starch blended with casein and CH₃ increased steadily with an increase in the concentration of casein and casein hydrolysates. This is suggestive of a higher viscosity of starch-casein and casein hydrolysate blends as compared to starch alone. This fact has also been observed from Brabender characteristics (Table 2). Corn starch blended with CH₁ and CH₂ again gave erratic results.

Table 7 shows the flow behavior index 'n' and the consistency index 'K' of corn starch substituted with 11.1–44.4% w/w casein and casein hydrolysates. Results with casein and CH₃ showed a similar trend of a decrease in flow behavior index and an increase in consistency index, while CH₁ and CH₂ gave an opposite trend. No suitable explanation can be given for this behavior except the differences in the mode of preparation of the casein hydrolysates. Unlike proteins, the viscosity of hydrolysates is generally unaffected by heating. Hydrolysis of proteins also alters the hydrophobicity, which depends on the site of cleavage on the protein molecule (Mahmoud et al., 1992). All these phenomena may be ultimately responsible for the interactions of casein and casein hydrolysates with starch as manifested in the observed results.

Attempts were made to correlate the level of addition and substitution of casein and CH₃ in the starch blend with the flow behavior index, 'n' and the consistency index, 'K'. CH₁ and CH₂ were omitted for aforementioned reasons. The results are presented in Table 8. A good correlation was observed between the addition and substitution levels of casein and CH₃ with the rheological characteristics, as indicated by the correlation coefficient (R^2). These results point to a direct influence of casein and CH₃ on the rheological properties of the blend systems.

In order to compare the results obtained using the Brabender amylograph, which has a fixed configuration and shear rate (approximately 40 S⁻¹), a plot of Brabender cold paste viscosity vs consistency index of corn starch–casein and casein hydrolysates blends was obtained to yield a regression output. The consistency index was converted to cP (centipoises) by the formula 1 Pa sⁿ = 1000 cP. Similarly, Brabender cold paste viscosity values were also converted into cP units using the relationship 1 BU = 1.05 cP under the experimental conditions of a bowl speed of 75 rpm, heating rate 1.5°C min⁻¹ and a 350 cmg cartridge used (Wood and Goff, 1973). Using the regression equation, predicted Brabender cold paste viscosity was calculated. Fig. 1 shows a plot of predicted vs observed Brabender cold paste viscosity of all the model systems, under study ($R^2 = 1$). The close proximity of the observed Brabender values to the predicted values validates the starch–casein and casein hydrolysate interactions as obtained only from a single point measurement using a Brabender amylograph.

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