

# Effects of yellow mustard mucilage on functional and rheological properties of buckwheat and pea starches

Huijun Liu <sup>a</sup>, N.A. Michael Eskin <sup>a,\*</sup>, Steve W. Cui <sup>b</sup>

<sup>a</sup> Department of Human Nutritional Science, University of Manitoba, Winnipeg, Man., Canada R3T 2N2

<sup>b</sup> Food Research Programme, Agri-Food and Agriculture Canada, 93 Stone Road West, Guelph, Ont., Canada N1G 5C9

Received 15 October 2003; received in revised form 13 December 2004; accepted 13 December 2004

## Abstract

The effects of yellow mustard mucilage (YMM) on the functional and rheological properties of buckwheat and pea starch were studied. Addition of YMM resulted in a marked increase of peak viscosity for both buckwheat and pea starches. Dynamic oscillation measurements showed that the storage modulus ( $G'$ ), loss modulus ( $G''$ ) and dynamic viscosity ( $\eta^*$ ) of buckwheat and pea starches were increased but tangent  $\delta$  was decreased by addition of YMM. The gel textures of both starches were markedly changed by the presence of YMM, which resulted in an increase of hardness, adhesiveness and chewiness but a decrease of resilience. Differential scanning calorimetry showed that the presence of YMM slightly increased melting enthalpy ( $\Delta H$ ) and the phase transition temperature range ( $T_c-T_o$ ) of buckwheat starch but these did not change much for pea starch. Addition of YMM–locust bean gum mixture (9:1) similarly increased the viscosity of buckwheat and pea starches but decreased gel hardness. The swelling powers of both starches and solubility of buckwheat starch were slightly decreased in the presence of YMM. Addition of YMM slowed the syneresis of buckwheat and pea starch gels.

© 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Mustard gum; Plant starches; Buckwheat; Pea; Yellow mustard

## 1. Introduction

Starch is a major food component and widely used in the food and non-food industries. However, the physical properties of starches (e.g. unstable gel texture, retrogradation and syneresis) limit their usefulness in many commercial applications. It should be possible to increase the amounts of native starch used as thickeners, texturizers and gelling agents if some undesired properties of the native starches could be suppressed. Although chemical modification can improve the gelatinization and retrogradation properties of starches (Liu, Ramsden, & Corke, 1999, 1997), increased concern by consumers

about any chemical modification of components used in food systems has led to alternative ways of modifying native starches. Increased attention has been drawn to utilizing hydrocolloids in starch-based products because of their unique stabilizing properties. These include canned and frozen filling, where hydrocolloids are used to replace a small amount of starch, low caloric salad dressing, where the ingredients are subjected to mechanical shear and acidic foods (Sudhakar, Singhal, & Kulkarni, 1992). The gelatinization and retrogradation properties of starches can be modified by addition of a small amount of hydrocolloids (Alloncle, Lefebvre, Llamas, & Doublier, 1989; Biliaderis, Arvanitoyannis, Izydorczyk, & Prokopowich, 1997; Christianson, Hodge, Osborne, & Detroy, 1981; Ferrero, Martino, & Zaritzky, 1994; Sudhakar, Singhal, & Kulkarni, 1996; Yoshimura, Takaya, & Nishinari, 1999), resulting in an increase of

\* Corresponding author. Tel.: +1 204 474 8078; fax: +1 204 474 7593.  
E-mail address: [eskin@ms.umanitoba.ca](mailto:eskin@ms.umanitoba.ca) (N.A. Michael Eskin).

peak viscosity, improvement of syneresis and freeze–thaw stability (Sudhakar et al., 1992; Yoshimura, Takaya, & Nishinari, 1998, 1999), a change of phase transition temperature range and melting enthalpy of starch crystallites (Biliaderis et al., 1997), and increase of dynamic modulus ( $G'$ ) (Liu & Lelievre, 1992). A mechanism of the interaction of starches with hydrocolloids has been suggested. The co-operative mechanism (Christianson et al., 1981; Sajjan & Rao, 1987) involves the formation of soluble starch–gum associations, contributing to the increased viscosity. In contrast, the exclusion mechanism (Alloncle & Doublier, 1991; Annable, Fitton, Harris, Phillips, & Williama, 1994; Biliaderis et al., 1997; Morris, 1990; Sasaki, Yasui, & Matsuki, 2000) involves phase separation of biopolymer mixtures in aqueous solutions, which is a common phenomenon due to incompatibility between unlike polymers, amylose and hydrocolloids. That results in an increase of effective concentration of each component in its microdomain, causing a substantial enhancement in the viscosity of the mixed system with enhanced firmness of the mixture gel. Christianson, 1982; Christianson et al., 1981 suggested that the presence of gum in the starch media also influences the physical properties of starch granules such as shape, granule integrity, and amount of exudates from starch granules, resulting in an earlier onset viscosity in amylograms compared with starch control. Shi and BeMiller (2002) stated that interactions between certain leached molecules, primarily amyloses, and certain gums, were responsible for the viscosity increase occurring before starch pasting.

Yellow mustard mucilage (YMM) exhibited unique rheological properties with considerable potential as a food thickener and stabilizer (Cui, Eskin, & Billaderis, 1993, 1994, 1995). YMM was shown to be composed of both neutral sugars and uronic acids (Cui et al., 1993). The monosaccharides identified were primarily glucose, arabinose, xylose, rhamnose, galactose and mannose (Cui et al., 1993; Siddiqui, Yiu, Yiu, Jones, & Kalab, 1986; Theander, Aman, Miksche, & Yasuda, 1977; Vose, 1974). Significant synergistic interactions between YMM and locust bean gum (LBG) were observed by small strain oscillatory rheological measurement, resulting in a marked increase in viscosity (Cui, Eskin, Billaderis, & Mazza, 1995). The optimum ratio for synergism was 9:1 for YMM:LBG systems. There is very little information available on the interaction of YMM with starches except for the report by Liu and Eskin (1998) that showed significant interaction of YMM with pea starch. Knowledge about how YMM influences the functional properties of starches is highly important if yellow mustard mucilage is going to be used as a food gum.

The objective of this study was to investigate the effects of YMM on the functional and rheological properties of buckwheat and pea starches, including pasting

and thermal properties, swelling and solubility, rheological properties, gel structure and syneresis.

## 2. Materials and methods

### 2.1. Materials

Pea starch was purchased from Parrheim Foods (Portage la Priori, MB, Canada) (amylose content was 35%). Yellow mustard mucilage was extracted from yellow mustard seed bran following the method of Cui, Eskin, Han, Duan, and Zhang (2001), dried by a freeze dryer and stored in a desiccator prior to use. Buckwheat starch was traditionally extracted: whole buckwheat grain (10 g) was ground with (coffee grinder) for 1 min before the sample was soaked in 10 ml 0.02 N HCl at 4 °C overnight. After the pH was adjusted to seven, the sample was centrifuged and the supernatant was discarded. The grist was ground for 5 min before 30 ml Tris–HCl buffer (pH 7), 30  $\mu$ l xylanase (Mehazyme, Lot 70502, 4000 U/ml) and 5 mg proteinase K (Sigma, P 8044) were added. The sample was incubated in a waterbath at 35 °C overnight before it was sieved through a 75  $\mu$ m stainless sieve. The resultant slurries were centrifuged and the sediment was washed with 70% cesium chloride (once) and distilled water three times. The pure starch was dried in an oven at 35 °C after centrifuging. The amylose content was 26.5%, according to the method by Chrastil (1987).

### 2.2. Pasting property

A rapid Visco-analyzer model 3D (RVA) (Newport scientific Pty. Ltd., Narrabeen, Australia) was employed to test the viscosity of starch. A starch suspension (8%, w/w), with or without YMM gum (0.2%, 0.5%, 0.8%, w/w), was placed in the aluminium RVA sample canister. A programmed heating and cooling cycle was used, where the sample was held at 50 °C for 1 min, heated to 95 °C in 3 min 42 s, held at 95 °C for 2 min 30 s, cooled to 50 °C in 3 min 48 s, then held at 50 °C for a further 2 min. Parameters recorded were peak viscosity, trough (=viscosity at the end of 95 °C), breakdown (=peak viscosity – trough), final viscosity (=viscosity at 50 °C at the end of 13 min cycle), and setback (=final viscosity – trough).

### 2.3. Dynamic viscoelastic measurement

Small amplitude oscillatory rheological test was conducted using an AR 1000 Rheometer (TA Instruments Ltd., Surrey, England) with 4 cm cone plate (1°) geometry at 25 °C. A starch dispersion (6%, w/w) in YMM medium (0.2%, 0.5%, 0.8%, w/v) or in YMM–LBG mixture (9:1, 0.5%, w/v) was placed in a sealed stainless con-

tainer and heated in boiling water for 10 min and subsequently cooled in a waterbath at 25 °C for 15 min. Immediately after cooling, the gel was transferred onto the plate of rheometer. The upper plate was lowered onto the gel to a gap of 1.0 mm and excess material was trimmed from the periphery. After the sample was equilibrated at 25 °C on the plate for 2 min, a small strain oscillatory testing was carried out at 25 °C. The sample was subjected to oscillatory sweep at a frequency range from 0.1 to 20 Hz. The oscillatory stress was 0.02%. The modulus  $G'$ , loss modulus  $G''$ , dynamic viscosity  $\eta^*$  and loss tangent were examined.

#### 2.4. Gel texture

The gels of starches, with or without YMM were prepared using RVA with the same programmed heating and cooling cycle as in pasting property testing. Immediately after the heating and cooling cycle, the starch paste in the sample canister was covered and kept at 5 °C in refrigerator for 24 h. Gel texture was determined using a TA-XT2 Texture Analyzer (Stable Micro systems, Godalming, Surrey, England). Two cycles of the compression–withdrawal programme were conducted at the same speed. The gel was compressed at a speed of 1.0 mm/s to a distance of 10 mm with a cylindrical flattened probe of 6 mm diameter. The hardness value is the peak force of the first compression of the sample. The negative area from the curve during the first retraction of probe was termed adhesiveness. The chewiness = hardness \* (the area of work during the second compression divided by area of work during the first compression) \* (the distance of the detected height of the sample on the second compression divided by the original compression distance). Resilience = area during the withdrawal of the first compression divided by the area of first compression.

#### 2.5. Thermal property

DSC measurements of granular starch dispersions were carried out using a DuPont thermal analyzer (9900; Wilmington, DE) equipped with a DSC cell (DuPont 910). Starch (30%, w/w) was dissolved in the previously prepared gum solutions (0.2%, 0.5%, 0.8%, w/v), and aliquots of starch dispersions (10.0 mg) were pipetted into DSC pans and hermetically sealed. The starch suspensions were heated from 20 to 120 °C (10 °C/min) to gelatinize the granules. The onset temperature, peak temperature, conclusion temperature and transition enthalpy ( $\Delta H$ ) were recorded.

#### 2.6. Swelling power and solubility

Swelling power was determined according to the method by Sasaki et al. (2000) with a small modification.

Starch–gum dispersions (1.25% starch and 0.031%, 0.078%, 0.125% gum) were put into tubes with coated screw-caps and heated in a boiling water bath for 10 min. A starch–water mixture, similarly heated, served as a control. After cooling in ice for 5 min, the samples were centrifuged at 11,200g at 5 °C for 15 min and the supernatant was removed to determine solubilized starch and amylose contents. Swelling power was determined as ratio by weight, of wet sediment to initial dry starch. The method of Gibson, Solah, and McCleary (1997) was used to determine the total carbohydrates in the recovered supernatant; meanwhile, the amylose content in the supernatant was determined according to the method by Chrastil (1987).

#### 2.7. Syneresis

The extent of syneresis was measured on starch suspension (4%, w/w) in water or YMM (0.2%, 0.5%, 0.8%, w/w) heated in the boiling water bath for 10 min. Following cooling, samples were stored at 5 °C for 15 days. Syneresis was estimated by the weight of water separated and expressed as the ratio, by weight, of separated water to starch gel.

### 3. Results and discussion

#### 3.1. Viscoamylography

The viscosity profiles of buckwheat and pea starches, with or without YMM, tested by RVA, are shown in Figs. 1 and 2 and Table 1. Both YMM (0.8%, w/w) and YMM–LBG mixture (9:1, 0.5% w/w) showed negligible viscosity using the amylograph. Addition of the hydrocolloid decreased the pasting temperature of buckwheat starch compared to the starch control, but did not change that of pea starch. The magnitude of the onset temperature, in the amylogram, decrease for buckwheat starch depended on the concentration of the hydrocolloid. Addition of YMM caused a marked increase in peak and cool paste viscosity for both buckwheat and pea starches (Figs. 1 and 2). For example, the viscosities were 22.67, 57.34 and 81.75 RVU higher than the starch control for buckwheat and 13.83, 45.17 and 64.17 RVU higher for pea starch in the presence of 0.2%, 0.5% and 0.8% YMM, respectively. The breakdowns of buckwheat and pea starches were slightly decreased by addition of YMM, indicating that the cross-linking structures of the starch pastes were strengthened by the interaction of YMM with the starches. Addition of YMM–LBG mixture (9:1, 0.5%, w/v) resulted in further increase of viscosity (84.09 RVU higher for buckwheat starch and 73.25 RVU higher for pea starch than the corresponding starch control). However, starch in YMM–LBG mixture (9:1, 0.5%, w/v) showed higher

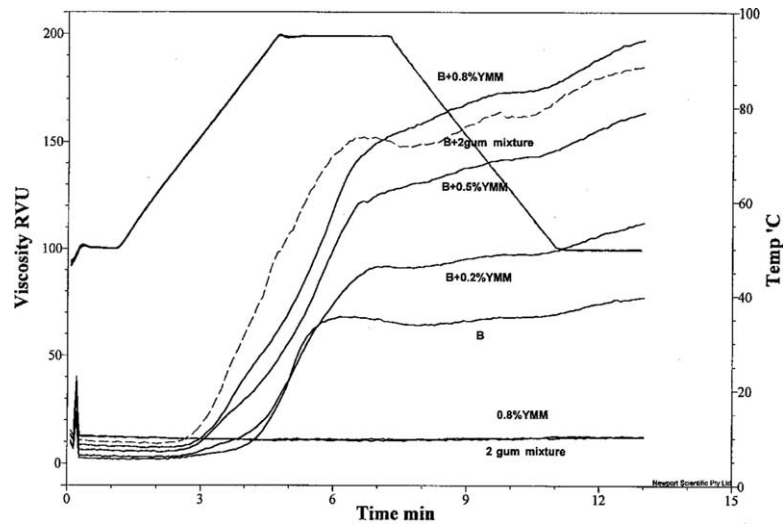


Fig. 1. Effect of yellow mustard mucilage (YMM) on the amylogram of buckwheat starch. Starch concentration: 8%, w/w; YMM concentration: 0.2%, 0.5%, 0.8%, w/w; 2 gum mixture: YMM:LBM = 9:1, 0.5%, w/w.

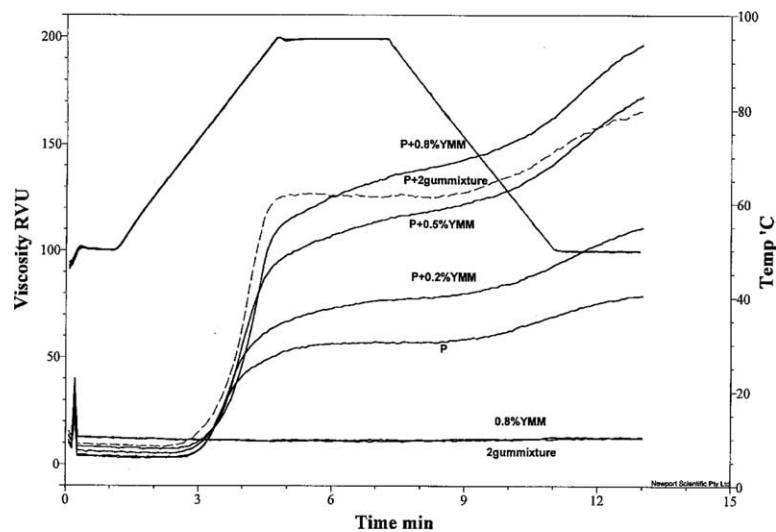


Fig. 2. Effect of yellow mustard mucilage (YMM) on the amylogram of pea starch. Starch concentration: 8%, w/w; YMM concentration: 0.2%, 0.5%, 0.8%, w/w; 2 gum mixture: YMM:LBM = 9:1, 0.5%, w/w.

Table 1  
Effects of yellow mustard mucilage (YMM) on the pasting properties of buckwheat and pea starches

Starch <sup>a</sup>	Peak viscosity (RVU)	Trough (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)
Buckwheat	68.33	64.43	3.92	77.58	13.17
Buckwheat + 0.2%YMM	91.92	91.17	0.75	112.67	21.50
Buckwheat + 0.5%YMM	125.67	127.50	-1.83	163.92	36.42
Buckwheat + 0.8%YMM	150.08	153.08	-3.00	197.33	44.25
Buckwheat + 2 gum mixture <sup>b</sup>	152.42	147.75	4.67	185.25	37.50
Pea	53.00	56.58	-3.58	79.17	22.58
Pea + 0.2%YMM	66.83	76.92	-10.08	111.00	34.08
Pea + 0.5%YMM	98.17	115.08	-16.92	172.42	57.33
Pea + 0.8%YMM	114.17	134.92	-20.75	196.42	61.50
Pea + 2 gum mixture	126.25	125.17	1.08	165.42	40.25

<sup>a</sup> Starch concentration: 8%.

<sup>b</sup> 2 Gum mixture: YMM:LBM = 9:1, 0.5%, w/v.



breakdown for both starches and lower cool viscosity for pea starch than for the starch–YMM mixture (0.5%).

A decrease in the onset temperature of amylograms, by adding hydrocolloids (CMC, xanthan gum, guar gum or LBG), was also reported by other authors (Alloncle et al., 1989; Christianson et al., 1981; Crossland & Favor, 1948). Shi and BeMiller examined the normal zaize–CMC mixture on the hot stage of a microscope and found no change in gelatinization temperature compared with normal maize–water mixture, indicating that the first-stage viscosity increase was not due to a lowering of the gelatinization temperature of starch granules, but due to an interaction between gum molecules and leached starch molecules. Christianson et al. (1981) attributed the earlier developed viscosity to the changing of the starch granule structure by the gum medium. Bean and Yamazaki (1978) found a rapid increase in granule swelling between 58 and 70 °C corresponding to the onset of viscosity produced in the wheat starch–CMC amylograph curve. In this study, however, addition of YMM slightly inhibited the swelling of buckwheat and pea starches (Table 4). The decrease in the onset temperature of amylograms by YMM (Figs. 1 and 2) should be due to the interaction of YMM with the small amount of amylose released by the limited swelling of the starch granules. The onset temperature for pea starch did not change by addition of YMM which could be attributed to the higher amylose content of pea starch (35%), which made a tighter molecular structure of the starch granule leading lower amount of amylose released to the continue phase, consequently making the interaction (amylose–YMM) undetectable. Compared to YMM (0.5% w/w), addition of the YMM–LBG mixture (0.5%, YMM: LBG = 9:1) to buckwheat starch further hastened the onset of initial paste viscosity.

An increase in starch peak viscosity, by addition of a hydrocolloid, has been reported by other authors (Alloncle et al., 1989; Liu & Eskin, 1998; Sasaki et al., 2000). The cause of the synergistic effect of hydrocolloids on starch paste viscosity has been attributed to various factors. Alloncle et al. (1989) suggested that, when starch gelatinized in a gum medium, the volume of the continuous phase accessible to the gum was reduced, yielding an increase in gum concentration within the continuous phase that resulted in a dramatic increase in viscosity. Yoshimura, Takaya, and Nishinari (1996) reported that addition of hydrocolloids also increased the effective starch concentration by immobilizing water molecules. However, some authors attributed the increase in viscosity to the interaction between exudates from the starch granule (solubilized amylose and low molecular weight amylopectin) and gum (Christianson et al., 1981). The change of the physical properties of starch granules, such as shape, granule integrity and amount of exudates from starch granules, has also been

speculated to be the reason for the increased paste viscosity (Lai & Liao, 2002). The marked increase in viscosity following addition of YMM could be explained on a similar basis. Addition of YMM to starch suspension increased the effective concentration for both YMM and starch in the continuous phase. Meanwhile, the amylose leached out (and perhaps the low molecular weight amylopectin) could also form a strong entanglement with YMM. Both of these effects could result in the increased viscosity of the starch paste.

### 3.2. Dynamic rheological properties

Because RVA performs a high shearing and large deformation measurement that easily disrupts the network of starch gels (Lai & Liao, 2002), the rheological properties of starch–YMM mixture were also examined using a small deformation rheometer. The mechanical spectra of buckwheat and pea starch, with or without YMM, are shown in Figs. 3 and 4. Both YMM (0.8%, w/w) and YMM–LBG mixture (9:1, 0.5%) showed negligible  $G'$  and  $G''$ , tested under the same conditions. Addition of YMM caused an increase of modulus ( $G'$ ) and loss modulus ( $G''$ ) for both buckwheat (Fig. 3) and pea starch (Fig. 4). The magnitudes of the  $G'$  and  $G''$  increases depending on the concentration of the hydrocolloid. For example, the higher the concentration of YMM, the more were  $G'$  and  $G''$  increased. The tangents (ratio of  $G''$  to  $G'$ ) of buckwheat and pea starches in the presence of YMM were decreased by addition of YMM. The dynamic viscosity ( $\eta^*$ ) of buckwheat and pea starches, with or without YMM, decreased with increasing frequency – showing pseudoplastic behavior. Addition of YMM resulted in an increased of  $\eta^*$  for both buckwheat and pea starches. In the presence of YMM–LBG mixture (9:1, 0.5%), buckwheat and pea starches showed lower  $G'$ ,  $G''$  and  $\eta^*$ , but higher tangent than the starch dissolved in YMM (0.5%).

It has been suggested by Hansen, Hosoney, and Faubion (1991) that the rheological characteristics of starch pastes and gels depend on the concentration of granules, amount of amylase and amylopectin leached from the granules during heating, shape of the granules, swelling power of the granules, entanglement between the amylose and amylopectin, and granule–granule, amylose–granule, and amylopectin–granule interactions. The large increase in  $G'$  by addition of YMM indicated that the elastic structure (junction zones) of starch gel could be strengthened by the interaction of YMM with the starches to form a cross-linking network throughout the system. This also could be proved by the result of loss tangent ( $G''/G'$ ) (Figs. 3 and 4). The ratio of  $G''$  to  $G'$  (loss tangent or tangent) compares the energy lost with the energy stored during each oscillation of the probe (Hansen et al., 1991). As the cross-linking structure of the starch–hydrocolloid mixture was reinforced

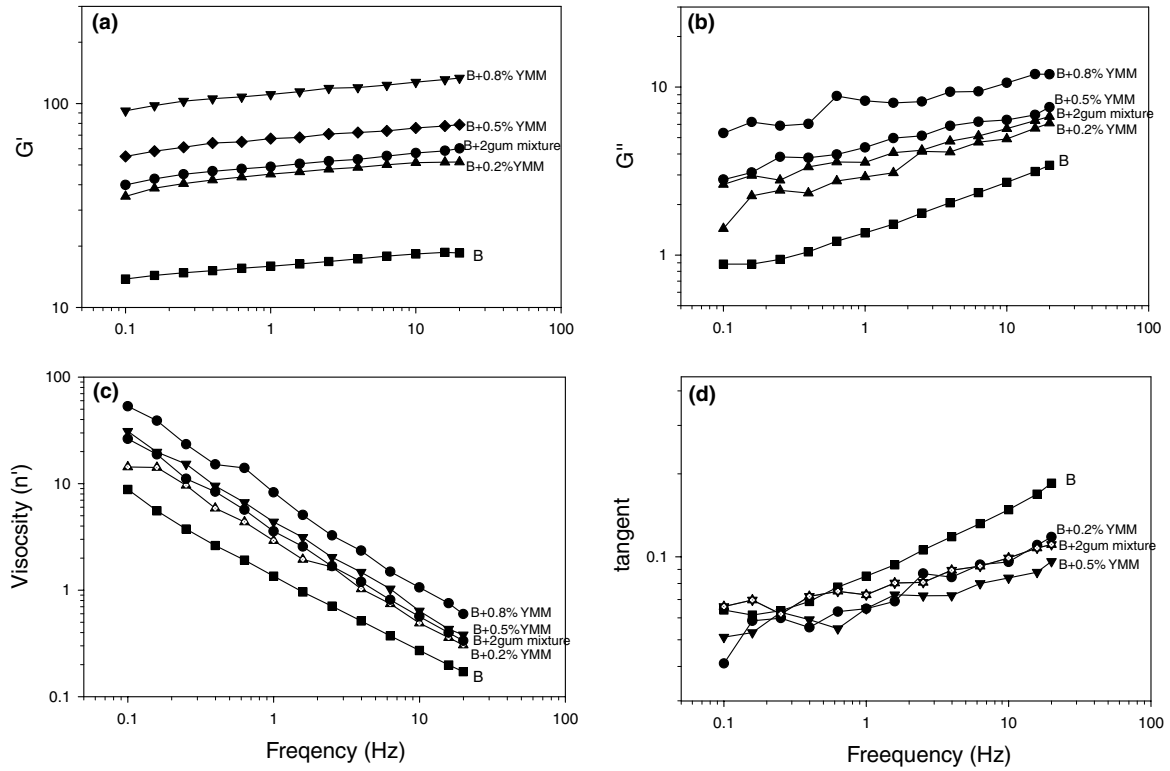


Fig. 3. Effect of yellow mustard mucilage (YMM) on the mechanical spectra of buckweat starch. Starch concentration 6%. Testing temperature: 25 °C. Oscillatory stress: 0.02%.

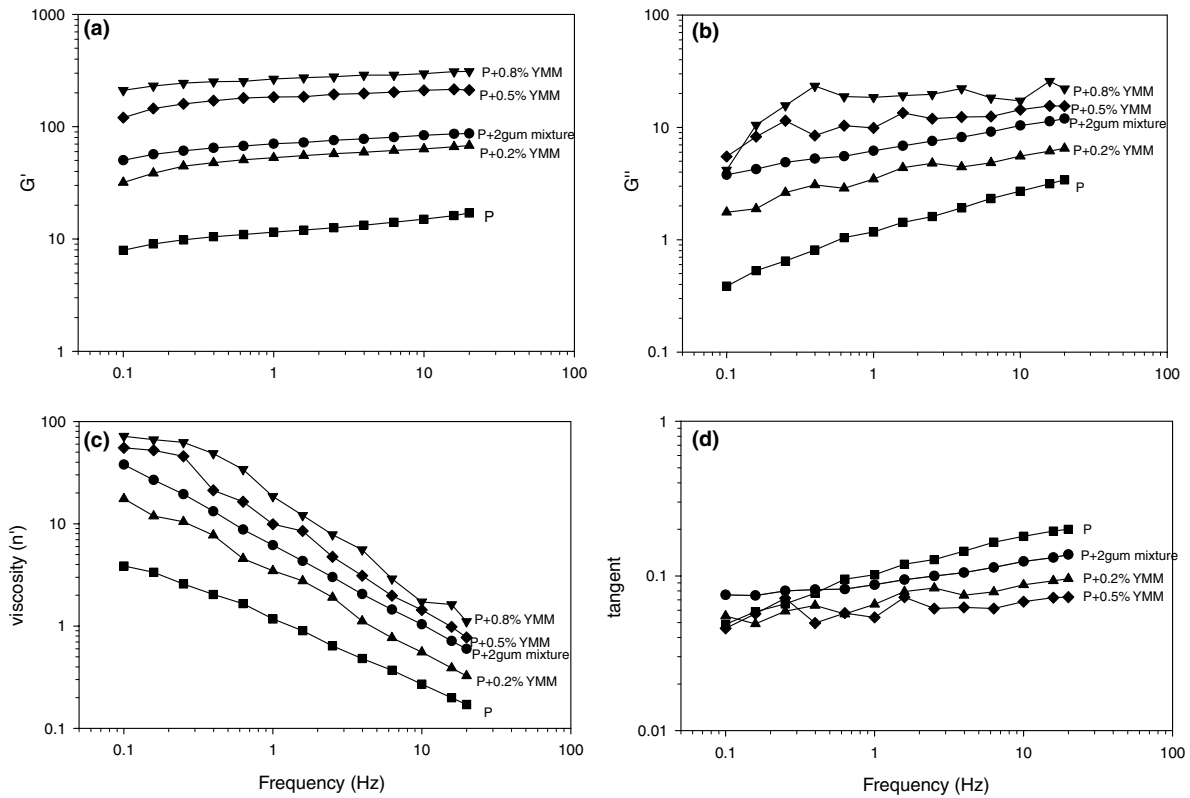


Fig. 4. Effect of yellow mustard mucilage (YMM) on the mechanical spectra of pea starch. Starch concentration 6%. Testing temperature: 25 °C. Oscillatory stress: 0.02%.

by addition of YMM, the energy stored increased, while the energy lost decreased. Consequently, the tangent decreased. The lower  $G'$  and higher tangent of both starches dissolved in YMM–LBG (9:1, 0.5%, w/v) than when dissolved in YMM (0.5%, w/v) reflected the difference of interaction between starch with YMM and starch with LBG.

### 3.3. Gel texture

Gel texture measurements for buckwheat and pea starches, with or without YMM, are summarized in Table 2. Native pea starch gel showed higher hardness, adhesiveness and chewiness than buckwheat starch gel. This can be attributed to the higher amylose content of pea starch, which formed strong associations between amylose chain increasing junction zones, leading to the formation of a harder gel. Addition of YMM resulted in an increase in hardness, adhesiveness and chewiness but a decrease of resilience for both buckwheat and pea starch gels. The gel texture of buckwheat and pea starches in the presence of YMM–LBG (0.5%, 9:1) was totally different from the gel made with 0.5% YMM, characterized by decrease in gel hardness, adhesiveness, chewiness and resilience.

When starches are heated to their gelatinization temperatures in the presence of hydrocolloids, the hydrocolloid may form hydrogen bonds with the soluble starch and the swollen granule. This could reinforce the entanglement structure of the starch–hydrocolloid mixture, making the starch gel more elastic, and consequently increasing hardness, adhesiveness and chewiness. Another explanation is that when different polymers are mixed they tend to become incompatible for thermodynamic reasons, resulting in phase separation (Morris, 1990). Such phase separation could affect gel structure. Yoshimura et al. (1996) reported that, when starch is gelatinized in a hydrocolloid medium, the hydrocolloid

could increase the effective starch concentration by immobilizing water molecules. Moreover, the hydrocolloid concentration within the continuous phase around the swollen starch granules also increases when starch swells during gelatinization (Sasaki et al., 2000). Either of these effects could contribute to increasing gel hardness. A change in gel textures of buckwheat and pea starches by addition of YMM could be the consequence of either the association between YMM and the amylose and amylopectin, to form cross-linking structure or incompatibility between starch and YMM, resulting in effective concentration of both starch and YMM being increased. However, when starches were gelatinized in the presence of YMM–LBG (9:1, 0.5%, w/v) mixture, the gel structure was totally different. The reason for this was not clear.

### 3.4. Differential scanning calorimetry

The DSC results for starches, with and without added hydrocolloids, are summarized in Table 3. Buckwheat starch showed lower gelatinization temperature ( $T_p$ ) but higher enthalpy ( $\Delta H$ ) than pea starch. Addition of YMM did not influence the peak gelatinization temperature ( $T_p$ ) of either buckwheat or pea starches. However, the enthalpy ( $\Delta H$ ) and gelatinization temperature range ( $T_c-T_o$ ) of buckwheat starch were slightly increased, while pea starch did not show much change. The effect of hydrocolloids on thermal properties of starches has been studied previously. Gudmundsson, Eliasson, Bengtsson, and Aman (1991) found that the addition of rye arabinoxylan increased  $\Delta H$  of wheat starch, slightly decreased  $\Delta H$  of maize and potato starches, but had no effect on  $\Delta H$  of waxy maize starch. An increase of phase transition temperature range ( $T_c-T_o$ ) and melting enthalpy ( $\Delta H$ ) of waxy maize and wheat starches, by addition of polysaccharides (xanthan,  $\beta$ -glucan, arabinoxylan and guar gum), has been reported

Table 2  
Effect of yellow mustard mucilage (YMM) on the gel texture of buckwheat and pea starches

Starch <sup>a</sup>	Hardness (g)	Adhesiveness (gs)	Chewiness	Resilience
Buckwheat	25.34	30.46	9.77	0.092
Buckwheat + 0.2%YMM	29.67	51.99	11.03	0.059
Buckwheat + 0.5%YMM	30.99	62.91	11.41	0.053
Buckwheat + 0.8%YMM	32.86	73.08	11.82	0.056
Buckwheat + 2 gum mixture <sup>b</sup>	12.97	28.32	5.85	0.049
Pea	72.90	153.79	24.75	0.083
Pea + 0.2%YMM	87.16	183.57	29.09	0.073
Pea + 0.5%YMM	94.72	226.41	33.34	0.068
Pea + 0.8%YMM	96.58	224.25	34.72	0.057
Pea + 2 gum mixture	52.60	84.52	20.34	0.062

<sup>a</sup> Starch concentration: 8%.

<sup>b</sup> 2 Gum mixture: YMM:LBG = 9:1, 0.5%, w/v.

Table 3  
Effect of yellow mustard mucilage (YMM) on the thermal properties of buckwheat and pea starches

Starch <sup>a</sup>	$T_p$ (°C)	$\Delta H$ (J/g)	$T_c - T_o$ (°C)
Buckwheat	64.06 ± 0.21 <sup>b</sup>	10.15 ± 0.20	25.7 ± 0.85
Buckwheat + 0.2%YMM	64.65 ± 0.35	10.87 ± 0.16	30.8 ± 1.31
Buckwheat + 0.5%YMM	64.99 ± 0.16	11.45 ± 0.31	30.0 ± 1.26
Buckwheat + 0.8%YMM	64.39 ± 0.32	11.84 ± 0.35	29.8 ± 0.48
Buckwheat + 2 gum mixture <sup>c</sup>	64.73 ± 0.08	11.14 ± 0.19	30.5 ± 0.75
Pea	66.25 ± 0.28	9.04 ± 0.33	27.1 ± 1.45
Pea + 0.2%YMM	66.20 ± 0.23	9.05 ± 0.06	27.5 ± 0.35
Pea + 0.5%YMM	66.16 ± 0.15	8.73 ± 0.28	27.9 ± 0.93
Pea + 0.8%YMM	66.56 ± 0.35	8.59 ± 0.22	28.4 ± 1.14
Pea + 2 gum mixture	66.57 ± 0.17	8.62 ± 0.38	27.5 ± 1.02

<sup>a</sup> Starch concentration: 30%.

<sup>b</sup> Standard deviation of duplicate.

<sup>c</sup> 2 Gum mixture: YMM:LBG = 9:1, 0.5%, w/v.

(Biliaderis et al., 1997). Sugars and polyhydroxy compounds have been shown to increase the gelatinization temperature of starch (Kim & Walker, 1992; Spies & Hosene, 1982). The stabilizing effect of polyhydroxy compounds on starch molecular structure has been attributed to either competition for water between starch and sugar (D'Appolonia, 1972) or to an interaction between sugar and starch, forming a cross-linking structure involving hydrogen bonds (Spies & Hosene, 1982). The slight increase in the phase transition temperature range and melting enthalpy of buckwheat starches by YMM (Table 2) may be due to either interaction between YMM and starch or competition with starch for water. This could result in a greater requirement for energy to gelatinize the starch granule. The difference between buckwheat starch and pea starch by addition of YMM during the gelatinization may result for the different crystalline structures. The X-ray diffraction pattern of buckwheat starch showed a typical cereal "A" pattern (Lorenz & Dilsaver, 1982), whereas pea starch showed a "C" pattern (Hoover & Ratnayake, 2002).

### 3.5. Swelling power and solubility

The swelling power and solubility of buckwheat and pea starches, with or without hydrocolloid, are summarized in Table 4. Addition of YMM resulted in a slight decrease of swelling power for both buckwheat and pea starches. The amount of solubilized amylose and starch did not show much change except that the amount of solubilized starch (of buckwheat) showed a slight decrease compared to the starch control. The swelling power and solubility of both starches dissolved in YMM–LBG (9:1, 0.5%) mixture did not show big difference compared with the starch dissolved in YMM (0.5%). The morphological changes during the heating of starch granules in the presence of hydrocolloids have been studied by Christianson (1982). He found that, when starch was heated in the presence of different hydrocolloids (xanthan, guar, CMC), the shapes of the starch granules and the amounts of soluble amylose were different. He speculated that, during heating, the submicropores of starch granule may be enlarged,

Table 4  
Effects of yellow mustard mucilage (YMM) on the swelling power, solubilized starch and amylose contents of buckwheat and pea starches<sup>a</sup>

Starch <sup>a</sup>	Swelling power (g/g)	Solubilized starch(%)	Solubilized amylose (%)
Buckwheat	14.1 ± 0.25 <sup>b</sup>	12.47 ± 0.23	7.99 ± 0.08
Buckwheat + 0.2%YMM	12.53 ± 0.14	11.56 ± 0.11	8.15 ± 0.23
Buckwheat + 0.5%YMM	12.21 ± 0.35	11.23 ± 0.38	8.35 ± 0.37
Buckwheat + 0.8%YMM	12.0 ± 0.28	11.18 ± 0.32	8.33 ± 0.23
Buckwheat + 2 gum mixture <sup>c</sup>	12.89 ± 0.21	11.63 ± 0.21	8.29 ± 0.16
Pea	11.64 ± 0.14	12.98 ± 0.37	8.64 ± 0.22
Pea + 0.2%YMM	10.80 ± 0.28	12.90 ± 0.40	8.46 ± 0.39
Pea + 0.5%YMM	10.43 ± 0.08	12.84 ± 0.33	8.33 ± 0.11
Pea + 0.8%YMM	10.02 ± 0.37	12.14 ± 0.09	8.42 ± 0.09
Pea + 2 gum mixture	9.91 ± 0.22	12.75 ± 0.11	8.39 ± 0.08

<sup>a</sup> Starch concentration: 1.25%.

<sup>b</sup> Standard deviation of duplicate.

<sup>c</sup> 2 Gum mixture: YMM:LBG = 9:1, 0.5%, w/v.



resulting in other hydrophilic hydroxylated chains, or even a portion, being absorbed into the amorphous regions. The remaining portion of the longer chain would cover the surface of the granule and extend from the granule into the media. This could affect both swelling and starch solubilization. The present study showed a slight decrease in the swelling power of buckwheat and pea starches and solubility of buckwheat starch by addition of YMM, suggesting that interaction may occur within the starch granule via hydrogen bonds, inhibiting starch swelling and solubility.

### 3.6. Syneresis

The effects of YMM on the syneresis of buckwheat and pea starch gels with storage time at 5 °C is shown in Fig. 5. Pea starch gel showed higher syneresis than buckwheat starch gel and this could be attributed to

the higher amylose content of pea starch, leading to a higher retrogradation tendency. Addition of the hydrocolloid markedly reduced syneresis for both buckwheat and pea starch gels. The degree of syneresis decreased with increase in hydrocolloid concentration. The syneresis of buckwheat starch dissolved in YMM–LBG (9:1, 0.5%) was slightly lower than when dissolved in YMM (0.5%). However, the syneresis of pea starch dissolved in YMM–LBG (9:1, 0.5%) did not show a great difference compared with that dissolved in YMM (0.5%) until after six days, when a slightly lower syneresis could be seen.

Syneresis in starch gels is due to increased molecular association between starch chains at reduced temperature, excluding water from the gel structure (Liu et al., 1999).

Ferrero et al. (1994) speculated that, during starch gelatinization, amylopectin remains mostly inside the

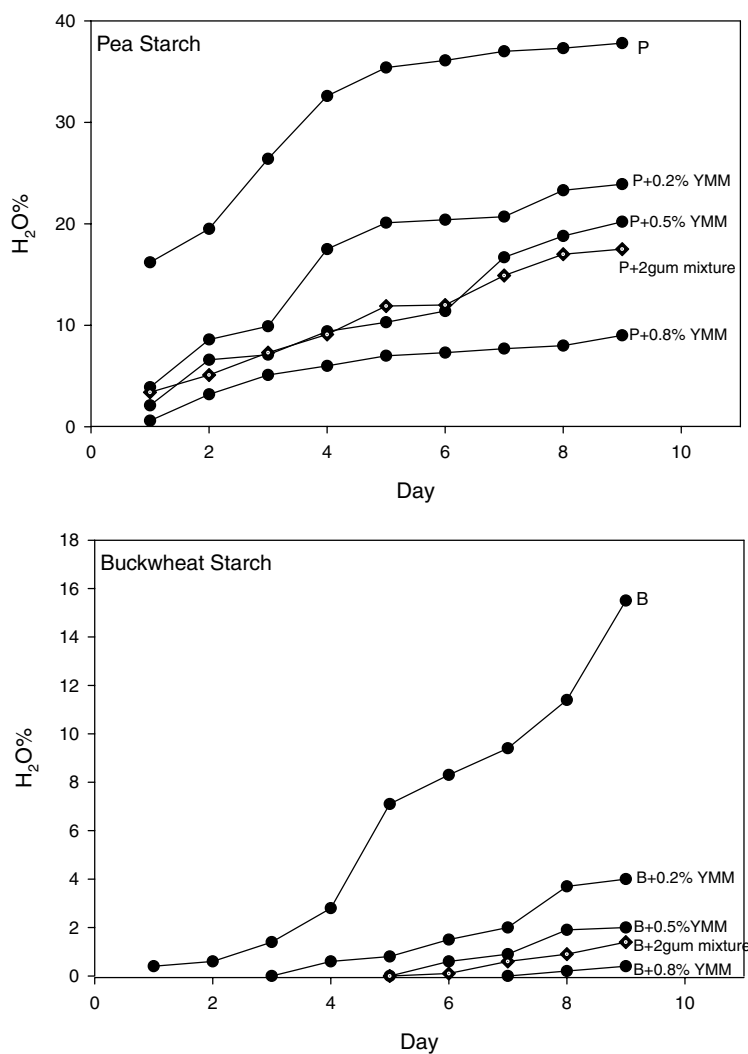


Fig. 5. Effect of yellow mustard mucilage (YMM) on the syneresis of buckwheat and pea starches. Concentration of buckwheat and pea starches: 4%, w/w; storage temperature: 5 °C; syneresis was expressed as H<sub>2</sub>O% separated from starch paste.

starch granules while amylose is released outside. After cooling, amylose forms a gel matrix surrounding the granules. Thus, the amylose, now with greater exposure, has the potential to undergo molecular interaction with other components of the paste. The entanglements of hydrocolloid with amylose may compete with amylose–amylose interactions, resulting in the reduction of retrogradation of starch and thereby lower syneresis. Sudhakar et al. (1996) also reported that improvements in freeze–thaw stability could be due to interaction between the hydrocolloid and amylose, thereby slowing retrogradation. A decrease in syneresis by YMM (Fig. 2) could be attributed to its interaction with amylose.

## Acknowledgement

Financial support by the Natural Sciences and Engineering Council of Canada in enabling this work to be carried out is greatly appreciated.

## References

- Alloncle, M., & Doublier, J. L. (1991). Viscoelastic properties of maize starch/hydrocolloid pastes and gels. *Food Hydrocolloid*, *5*, 455–467.
- Alloncle, M., Lefebvre, J., Llamas, G., & Doublier, J. L. (1989). A rheological characterization of cereal starch–galactomannan mixtures. *Cereal Chemistry*, *66*, 90–93.
- Annable, P., Fitton, M. G., Harris, B., Phillips, G. O., & Williams, P. A. (1994). Phase behavior and rheology of mixed polymer systems containing starch. *Food Hydrocolloids*, *8*, 351–359.
- Bean, M. M., & Yamazaki, W. T. (1978). Wheat starch gelatinization in sugar solutions. I. Sucrose: Microscopy and viscosity effects. *Cereal Chemistry*, *55*, 936.
- Biliaderis, C. G., Arvanitoyannis, I., Izydorczyk, M. S., & Prokopoulos, D. J. (1997). Effect of hydrocolloids on gelatinization and structure formation in concentrated waxy maize and wheat starch gels. *Starch/Stärke*, *49*, 278–283.
- Chrastil, J. (1987). Improved colorimetric determination of amylose in starches or flours. *Carbohydrate Research*, *159*, 154–158.
- Christianson, D. D. (1982). Food Carbohydrates. In D. R. Lineback & G. E. Inglett (Eds.), *Hydrocolloid interactions with starches* (pp. 399–419). AVI Publ. Comp. Inc..
- Christianson, D. D., Hodge, J. E., Osborne, D., & Detroy, R. W. (1981). Gelatinization of wheat starch as modified by xanthan gum, guar gum, and cellulose gum. *Cereal Chemistry*, *58*, 513–517.
- Crossland, L. B., & Favor, H. H. (1948). Starch gelatinization studies. II. A method for showing the stages in swelling of starch during heating in the amylograph. *Cereal Chemistry*, *25*, 213–220.
- Cui, W., Eskin, N. A. M., & Billaderis, C. G. (1993). Chemical and physical properties of yellow mustard (*Sinapis alba* L.) mucilage. *Food Chemistry*, *46*, 169–176.
- Cui, W., Eskin, N. A. M., & Billaderis, C. G. (1994). Yellow mustard mucilage: chemical structure and rheological properties. *Food Hydrocolloids*, *8*, 203–214.
- Cui, W., Eskin, N. A. M., Billaderis, C. G., & Mazza, G. (1995). Synergistic interaction between yellow mustard polysaccharides and galactomannans. *Carbohydrate Polymer*, *27*, 127–133.
- Cui, W., Eskin, N. A. M., Han, N. F., Duan, Z. Z. & Zhang, X.Y. (2001). Extraction process and use of yellow mustard gum. *US Patent No. 6,194,016B1*.
- D'Appolonia, B. L. (1972). Effect of bread ingredients on starch gelatinization properties as measured in the amylograph. *Cereal Chemistry*, *49*, 532–543.
- Ferrero, C., Martino, M. N., & Zaritzky, N. E. (1994). Corn starch–xanthan gum interaction and its effect on the stability during storage of frozen gelatinized suspensions. *Starch/Stärke*, *46*, 300–308.
- Gibson, T. S., Solah, V. A., & McCleary, B. V. (1997). A Procedure to measure amylose in cereal starches and flours with concanavalin A. *Journal of Cereal Science*, *25*, 111–119.
- Gudmundsson, M., Eliasson, A.-C., Bengtsson, S., & Aman, P. (1991). The effects of water soluble arabinoxylan on gelatinization and retrogradation of starch. *Starch/Stärke*, *43*, 5–10.
- Hansen, L. M., Hosney, R. C., & Faubion, J. M. (1991). Oscillatory rheometry of starch–water system: effect of starch concentration and temperature. *Cereal Chemistry*, *68*, 347–351.
- Hoover, R., & Ratnayake, W. S. (2002). Starch characteristic of black bean, chick pea, lentil, navy bean and pinto bean cultivars grown in Canada. *Food Chemistry*, *78*, 489–498.
- Kim, C. S., & Walker, C. E. (1992). Effects of sugars and emulsifiers on starch gelatinization evaluated by differential scanning calorimetry. *Cereal Chemistry*, *69*, 212–217.
- Lai, L. S., & Liao, C. L. (2002). Steady and dynamic shear rheological properties of starch and decolorized hsian-tso leaf gum composite systems. *Cereal Chemistry*, *79*, 58–63.
- Liu, H., & Eskin, N. A. M. (1998). Interactions of native and acetylated pea starch with yellow mustard mucilage, locust bean gum and gelatin. *Food Hydrocolloids*, *12*, 37–41.
- Liu, H., & Lelievre, J. (1992). Differential scanning calorimetric and rheological study of the gelatinization of starch granules embedded in a gel matrix. *Cereal Chemistry*, *69*, 597–599.
- Liu, H., Ramsden, L., & Corke, H. (1999). Physical properties of cross-linked and acetylated normal and waxy rice starch. *Starch/Stärke*, *51*, 249–252.
- Liu, H., Ramsden, L., & Corke, H. (1997). Physical properties and enzymatic digestibility of acetylated *ae*, *wx*, and normal maize starch. *Carbohydrate Polymers*, *34*, 283–289.
- Lorenz, K., & Dilsaver, W. (1982). Buckwheat (*Fagopyrum esculentum*) starch physico-chemical properties and functional characteristics. *Starch/Stärke*, *34*, 217–220.
- Morris, E. R. (1990). In P. Harris (Ed.), *Food gels* (pp. 291). London: Elsevier.
- Sajjan, S. U., & Rao, M. R. R. (1987). Effect of hydrocolloids on the rheological properties of wheat starch. *Carbohydrate Polymer*, *7*, 395–402.
- Sasaki, T., Yasui, T., & Matsuki, J. (2000). Influence of non-starch polysaccharides isolated from wheat flour on the gelatinization and gelation of wheat starches. *Food Hydrocolloids*, *14*, 295–303.
- Shi, X., & BeMiller, J. N. (2002). Effects of food gums on viscosities of starch suspensions during pasting. *Carbohydrate Polymers*, *50*, 7–18.
- Siddiqui, I. R., Yiu, S. H., Yiu, J. D., Jones, J. D., & Kalab, M. (1986). Mucilage in yellow mustard (*Brassica hirta*) seeds. *Food Microstructure*, *5*, 157–162.
- Spies, R. D., & Hosney, R. C. (1982). Effect of sugars on starch gelatinization. *Cereal Chemistry*, *59*, 128–131.
- Sudhakar, V., Singhal, R. S., & Kulkarni, P. R. (1992). Starch–gum interactions: formulations and functionality using amaranth/corn starch and CMC. *Starch/Stärke*, *44*, 369–374.
- Sudhakar, V., Singhal, R. S., & Kulkarni, P. R. (1996). Starch–galactomannan interaction: functionality and rheological aspects. *Food Chemistry*, *55*, 259–264.
- Theander, O., Aman, P., Miksche, G. E., & Yasuda, S. (1977). Carbohydrates, polyphenols and lignin in seed hulls of different colors from turnip rapeseed. *Journal of Agriculture and Food Chemistry*, *25*, 270–273.

- Vose, J. R. (1974). Chemical and physical studies of mustard and rapeseed coats. *Cereal Chemistry*, *51*, 658–665.
- Yoshimura, M., Takaya, T., & Nishinari, K. (1996). Effects of konjac-glucomannan on the gelatinization and retrogradation of corn starch as determined by rheology and differential scanning calorimetry. *Journal of Agriculture and Food Chemistry*, *44*, 2970–2976.
- Yoshimura, M., Takaya, T., & Nishinari, K. (1998). Rheological studies on mixtures of corn starch and konjac-glucomannan. *Carbohydrate Polymer*, *35*, 71–79.
- Yoshimura, M., Takaya, T., & Nishinari, K. (1999). Effects of xyloglucan on the gelatinization and retrogradation of corn starch as studied by rheology and differential scanning calorimetry. *Food Hydrocolloids*, *13*, 101–111.