Food Chemistry 111 (2008) 1–10

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Starch–cassia gum interactions: A microstructure – Rheology study

Lovedeep Kaur [a,*], Jaspreet Singh [a], Harjinder Singh [a], Owen J. McCarthy [b]

[a] Riddet Institute, Massey University, Palmerston North, New Zealand
[b] Institute of Food, Nutrition and Human Health, Massey University, Palmerston North, New Zealand

ARTICLE INFO

Article history:
Received 5 October 2007
Received in revised form 17 January 2008
Accepted 5 March 2008

Keywords:
Starch
Cassia gum
Microstructure
Rheology
Pasting
Characterization

ABSTRACT

We present for the first time the interactions of starch and cassia gum – a novel galactomannan recently approved for use in food processing. Viscoelastic, pasting and microstructural characterization of various starches (waxy; high amylose; normal; cross-linked waxy corn starch; potato starch) containing different levels of the cassia gum was carried out. Significant changes were observed in the morphology of granule remnants formed during gelatinization in the starch pastes prepared with and without the addition of cassia gum. The freeze-dried starch–cassia gum pastes presented a shrunken and tight arrangement of the starch granule remnants, when studied by scanning electron microscopy. A significant reduction in the granule remnant size was also calculated using laser diffraction particle size analysis. The extent of interaction with cassia gum differed significantly among the various starch types. All the unmodified corn starches recorded an increase in peak viscosity at all levels of the cassia gum addition. An increase in the final viscosity of these starches was also observed by the addition of cassia gum, with high amylose and normal corn starch showing the maximum. Similarly, the extent of breakdown and setback viscosity also differed among the different starch types. Ranges of dynamic rheological measurements (temperature, time and frequency sweeps) were performed within the viscoelastic zones. Rheological parameters, such as storage modulus (G'), loss modulus (G'') and the gelatinization temperature (T_{gel}), of the corn starches during the heating cycle were observed to increase, when cassia gum was present at lower levels. The starch–gum systems also exhibited higher $\tan\delta$ values during both the heating and the cooling cycles, indicating the dominance of the viscous modulus. The G' and G'' of all the corn starch gels containing cassia gum showed higher values throughout the frequency sweep range. However, the increase in G' and G'' of different starches was not always consistent with the increase in cassia gum levels. The changes in rheological behaviour during storage of the starch gels, aged on the plate of the rheometer and then studied through time sweeps at 5 °C and frequency sweeps at 25 °C, suggested that the starch gels containing cassia gum had less pronounced changes in the rheological parameters than had their control counterparts.

1. Introduction

Plant-derived polysaccharides (gums) are excellent stabilizing and thickening agents, and are used in many food systems (Hallagan, La Du, Pariza, Putnam, & Borzelleca, 1997). The use of common food gums, such as locust bean, guar and xanthan gum, and their interactions with other food materials are well known. Cassia gum, isolated from the purified endosperm of seeds of *Cassia tora* L., may be a new and interesting thickener for many food applications. Recently, the European Food Safety Authority (EFSA) stated that the use of cassia gum, complying with newly defined specifications as an additive for food use, is not a safety concern (EFSA, 2006). Cassia, a member of the family *Leguminosae*, is a potential source of galactomannan, which may be used for different food applications, such as baked and canned goods, soups, jams, jellies, dairy products and frozen foods (Kuhn, 1995). Cassia gum is related to locust bean gum and guar gum in terms of structure and chemical properties (Hallagan et al., 1997). Compared with both of these galactomannans, cassia galactomannan is less well known and less exploited on the industrial scale. Cassia galactomannan consists of a linear chain of 1,4-β-D-mannopyranose units with 1,6-linked-α-D-galactopyranose units (Hallagan et al., 1997). It has mannose and galactose residues in a ratio of 5:1, and a molecular weight ranging from 200,000–300,000 Da, providing a high water-binding capacity (Denkler, 1997). Cassia gum has been reported to form high-viscosity aqueous dispersions after it is boiled in water, but it results in the formation of a gel, when it is used in combination with other gelling or thickening agents, such as carrageen or xanthan gum, in aqueous solution (Hallagan et al., 1997). The nutritional benefits of galactomannans as dietary fibre have been well documented (Ali, Azad Khan, & Hassan, 1995; Gupta,

* Corresponding author. Tel.: +64 6 3505799x5861.
E-mail addresses: L.Kaur@massey.ac.nz, Lovedeep_gill@yahoo.com (L. Kaur).

0308-8146/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2008.03.027

Gupta, & Lal, 2001; Nurnberg & Bleimuller, 1981; Sharma & Raghuram, 1990; Sharma, Raghuram, & Sudhakar, 1990; Trowell et al., 1976). Starch based foods are staples in the diet. They can increase appetite by stimulating the secretion of saliva, and facilitate food intake by assisting stomach peristalsis. Knowledge of the rheological and textural properties of starchy foods, during and after processing, is valuable for process and quality control purposes. Composition, temperature and shear rate are important factors determining the viscosity of a food (Rha, 1975). The relationship between viscosity, shear rate and time can be used to classify foods as Newtonian or non-Newtonian (pseudoplastic, dilatant, thixotropic, rheopectic, viscoelastic). Such classification is known to be useful in processing, quality control, sensory evaluation and structural analysis (Rao & Anantheswaran, 1982). Galactomannans from the ground endosperm of seeds can provide viscous solutions, even at low concentrations. The addition of hydrocolloids, such as galactomannans, to starch-based food systems is widely used to modify rheological properties and to regulate and optimize both the process and the sensory properties of products. The effects of various galactomannans on the rheological properties of different starches (normal, waxy) have been previously reported (Alloncle, Lafebvre, Llamas, & Doublier, 1989; Funami et al., 2005a, 2005b; Sajjan & Rao, 1987; Yoo, Kim, & Yoo, 2005). However, no reports are available on the rheological behaviour of starch and cassia gum mixed systems. The measurement of dynamic rheological and microstructural characteristics can provide insights into the behaviour of starch–gum systems. Therefore, the objectives of the present study were to investigate starch–cassia gum interactions by measuring dynamic rheological properties and pasting properties, and observing structural characteristics by microscopy. Also, the study may provide information indicating potential applications of cassia gum as an ingredient in the development of functional foods.

2. Materials and methods

2.1. Materials

Three types of unmodified corn starches with different amylose contents were used in this study: a high amylose corn starch (HYLON VII, National Starch and Chemical NZ Ltd., Green Mount, Auckland, New Zealand), a waxy corn starch (National Starch and Chemical NZ Ltd., Green Mount, Auckland, New Zealand) and a normal corn starch (Penford New Zealand Ltd., Auckland, New Zealand). In addition, a cross-linked waxy commercial corn starch was obtained from National Starch & Chemical NZ Ltd. (Green Mount, Auckland, New Zealand), and potato starch was isolated from tubers of the cultivar Nadine, obtained from a local supermarket. Cassia gum was obtained from Premcem Gums Pvt Ltd., Mumbai, India.

2.2. Moisture content

The moisture contents of the starches and the cassia gum in dry powder form were calculated from the weight loss upon overnight heating at 105 °C in an oven (AACC method 44-15 A, 1995).

2.3. Sample preparation

Five powdered formulations, with five different levels of starch replacement by cassia gum, were prepared for each type of starch: 0% gum (control), 1% gum, 2% gum and 5% gum (dry

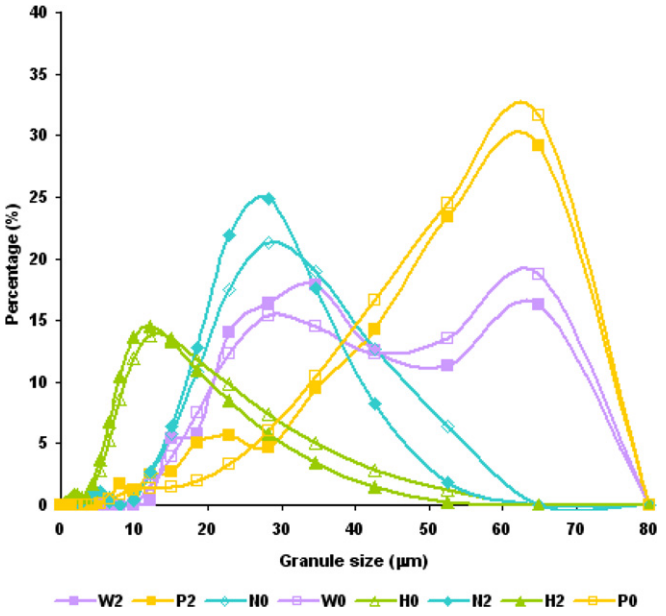

Fig. 1. Effect of cassia gum (0% and 2%) on the particle size distribution of normal (N), waxy (W), high amylose corn (H) and normal potato (P) starch pastes.

Table 1
Particle size distribution data for starch and starch–cassia gum pastes

Starch source	Small particles (%) (1–10 μm)	Medium size particles (%) (11–30 μm)	Large particles (%) (>30 μm)	*D* [*v*, 0.5] (μm)
High amylose corn starch	y	y	w	w
H0 (with 0% cassia gum)	34.63[a]	56.30[b]	9.07[b]	15.41[b]
H2 (with 2% cassia gum)	41.59[b]	53.20[a]	5.21[a]	13.76[a]
Normal corn starch	x	y	x	x
N0 (with 0% cassia gum)	3.98[a]	57.95[a]	38.07[b]	30.91[b]
N2 (with 2% cassia gum)	3.73[a]	68.65[b]	27.62[a]	28.74[a]
Waxy corn starch	–	x	y	y
W0 (with 0% cassia gum)	–	40.88[a]	59.12[a]	40.79[a]
W2 (with 2% cassia gum)	–	41.98[a]	58.02[a]	39.39[a]
Cross-linked waxy corn starch	w	x	y	y
C0 (with 0% cassia gum)	1.55[b]	39.21[a]	59.24[b]	39.92[a]
C2 (with 2% cassia gum)	0.78[a]	43.49[b]	55.73[a]	39.01[a]
Normal potato starch	x	w	z	z
P0 (with 0% cassia gum)	2.63[a]	14.13[a]	83.24[b]	59.88[b]
P2 (with 2% cassia gum)	3.21[a]	20.55[b]	76.24[a]	55.92[a]

Values with the same superscripts (a, b, c, d; within each starch type) in a column did not differ significantly ($p < 0.05$).
Values with the same letters (w, x, y, z) in a column, among the different starch types, did not differ significantly ($p < 0.05$).

starch basis). For rapid viscosity analysis measurements, an aqueous suspension of starch or starch/cassia gum was prepared by gradually adding 2.5 g of the dry ingredient(s) to 25 g of water, and stirring with the Rapid Visco Analyser (RVA-4, Newport Scientific Pty Ltd., Warriewood, Australia) paddle to break up any lumps. The dry ingredients were well blended prior to slurrying in water. The abbreviations used in the following text for the different starch samples are: H, W, N, P, and C for high amylose corn starch, waxy corn starch, normal corn starch, potato starch and cross-linked waxy corn starch, respectively. Levels of gum addition are identified by 0, 1, 2, and 5, e.g., potato starch samples with 0%, 1%, 2%, and 5% cassia gum are represented as P0, P1, P2, and P5.

2.4. Particle size analysis and scanning electron microscopy

The particle size distribution of pastes (starch-only control, and starch with 2% cassia gum) was determined at room temperature with a laser diffraction particle size analyzer (Malvern Mastersizer, Malvern Instruments Limited, UK). The starch or starch–gum slurry (4%, w/v) was cooked in a boiling water bath (at 100 ± 1 °C) for 20 min and immediately ≈5 g paste was mixed with 25 ml of hot distilled water. Some portion of the resulting suspension was then loaded into the small volume sample presentation unit of the Mastersizer to obtain an obscuration level of ~20%. Refractive indices of 1.530 and 1.330 were used for the starch and liquid phases, respectively, while the starch granule absorption was set at 0.1 (Nayouf, Loisel, & Doublier, 2003).

The remaining starch paste was cooled to room temperature, freeze-dried, packaged and stored at 4 °C until used for scanning electron microscopy (SEM). The freeze-dried pastes were fractured with the help of forceps. The fractured surface of the pastes was examined and photographed using a scanning electron microscope (Stereoscan 250 Mk3, Cambridge Instruments Limited, Cambridge, UK) at different magnifications. An accelerating potential of 20 kV was used during micrography.

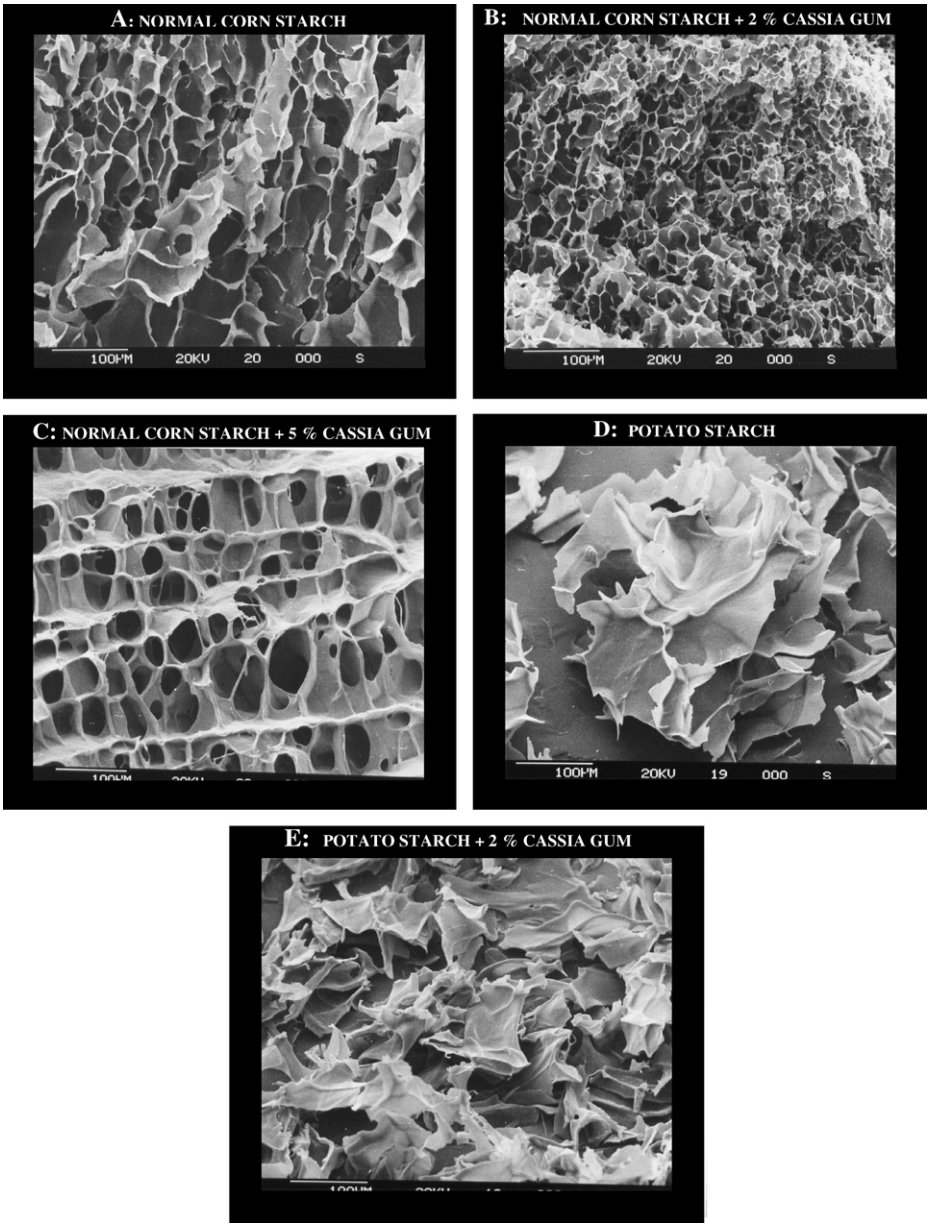

Fig. 2. Scanning electron micrographs (SEM) of freeze-dried starch and starch–cassia gum pastes (at 200×). As artifacts produced by freeze-drying are present, these micrographs do not necessarily represent the structures of the gels prior to freeze-drying.

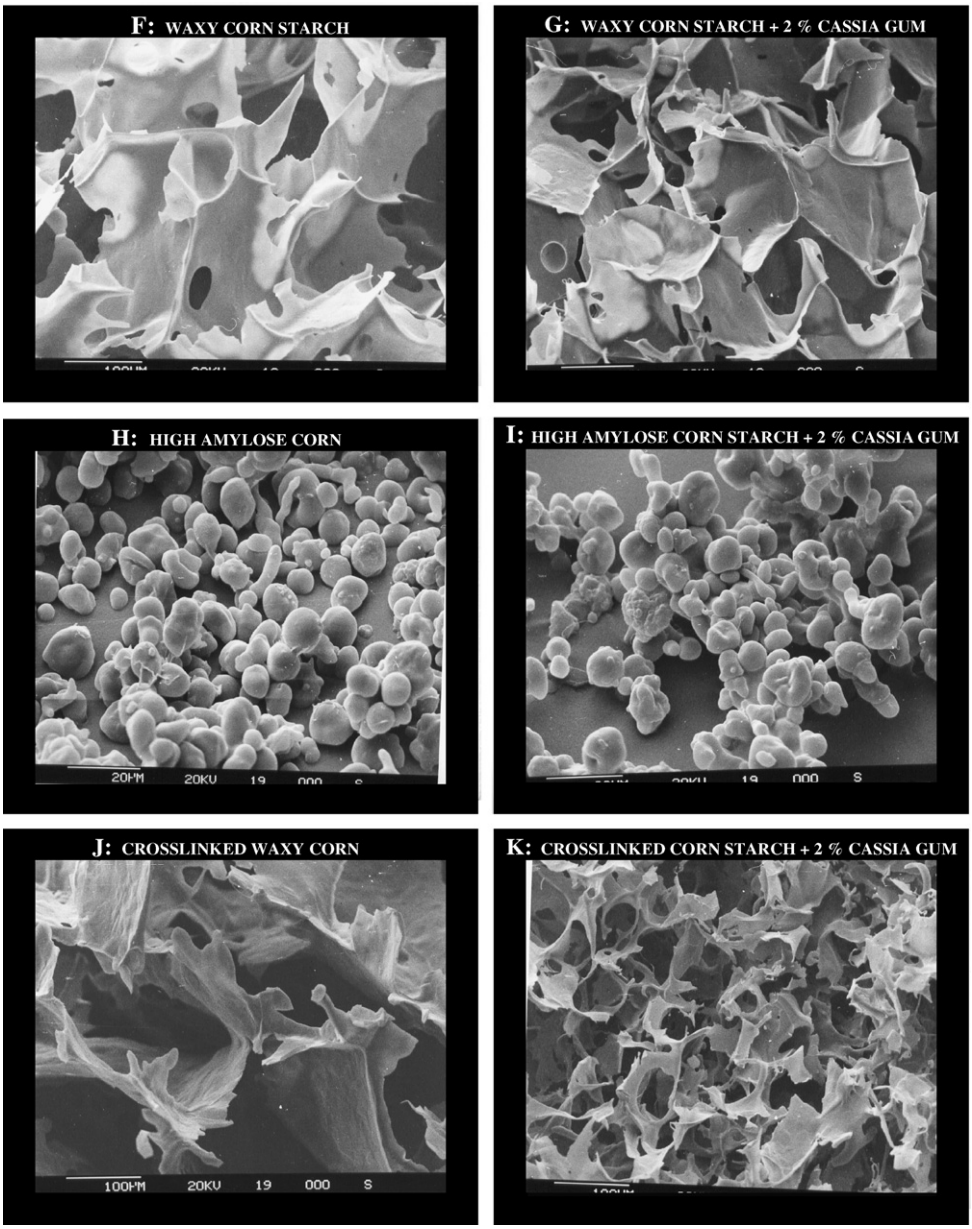

Fig. 2 (*continued*)

2.5. Pasting properties

The pasting properties of the starch–cassia gum mixtures were determined using RVA. Aqueous dispersions of starch–gum systems (9.1%, w/w) were prepared as described in Section 2.3. Dispersions were equilibrated at 50 °C for 1 min, heated at the rate of 6 °C/min to 95 °C, held at 95 °C for 5 min, cooled to 50 °C at a rate of 5.5 °C/min and, lastly, held at 50 °C for 2 min. A constant paddle rotational speed (160 rpm) was used throughout the entire analysis, except for rapid stirring at 960 rpm for the first 2 min to disperse the sample. The pasted system obtained was immediately subjected to dynamic rheological measurements.

2.6. Dynamic rheometry

2.6.1. General

Small amplitude oscillatory rheological measurements were made on the starch–gum suspensions and pastes with a dynamic rheometer (Physica MCR 301, Anton Paar GmbH, Germany) equipped with a parallel plate system (4 cm diameter). Starch–gum suspensions were prepared by adding 88 g of water gradually with continuous stirring to 12 g of dry ingredients (starch–gum mixture), to obtain a 12% by mass final concentration. The resulting slurry was stirred for 10 min with a magnetic stirrer at very low speed prior to rheological measurements. For measurements on pastes, the starch or starch–gum mixture was pasted in the RVA as described in Section 2.3.

2.6.2. Starch–gum suspensions (temperature sweep)

Small amplitude oscillatory two-step rheological measurements (temperature sweeps during heating and during cooling) were made on starch or starch–cassia gum slurries for each starch type. The gap size was set at 1.0 mm. Before starting an experiment, the sample was loaded on to the lower plate of the rheometer (preheated to 40 °C); the upper plate was lowered, and the edges of the sample were covered with a thin layer of low-density

silicone oil (to minimize evaporation losses). For temperature sweeps, strain and frequency were set at 1.0% and 1.0 Hz, respectively. The sample was heated from 40 to 90 °C and cooled from 90 to 25 °C at a rate of 3 °C/min and then held at 25 °C for 5 min.

2.6.3. Ageing (time and frequency sweep)

To study the effect of storage at 5 °C on the mechanical spectrum, starch pastes (0% and 2% gum) from the RVA were loaded onto the rheometer at 50 °C, immediately cooled to 5 °C and held for 14 h at that temperature at a constant strain of 1% and a frequency of 1 Hz, respectively. Thereafter, the starch gels were heated from 5 °C to 25 °C in 30 min and then subjected to frequency sweep using the same conditions as given above for the fresh pastes. Dynamic rheological parameters such as storage modulus (G'), loss modulus (G'') and loss tangent ($\tan\delta$) were determined for each sample as a function of frequency.

2.7. Statistical analysis

The data reported are all averages of triplicate observations. The data were subjected to statistical analysis using Minitab Release 14 Statistical Software (Minitab Inc., State College, PA). Results were analyzed using analysis of variance (ANOVA) and Tukey's HSD significance test.

3. Results and discussion

3.1. Particle size analysis and scanning electron microscopy

Particle size distributions of selected cooked starch pastes containing different levels of cassia gum are shown in Fig. 1, and the distributions of all pastes in terms of percentages of small, medium size and large particles in Table 1. There was significant variation in particle size among the different cooked pastes. Among the pure starch pastes, P0, C0, and W0 contained fairly high percentages (83.24%, 59.24% and 59.12%, respectively) of large particles (>30 μm), whereas N0 and H0 had the lowest (38.07% and 9.07%, respectively). The percentage of large particles was observed to be lower in the starch pastes containing cassia gum. The percentages of small (1–10 μm) and medium size (11–30 μm) particles also varied to a significant extent among the different starch–cassia gum pastes. The median diameter, $D[v, 0.5]$ (the size at which 50% of particles by volume are smaller and 50% are larger) was observed to be highest for pastes containing potato starches (56–60), followed by those containing waxy, cross-linked and normal corn starches (29–41), whereas it was significantly lower for those containing high amylose starches (14–15). The medium particle size of the control starch pastes was lower than that of the counterpart starch–cassia gum pastes, except in the case of high amylose starch. The variation in the particle size distribution of pure starch pastes may be attributed to differences in the swelling patterns of the starches. Potato starch granules, which have a very high swelling power, produced large granule remnants in potato starch paste, whereas high amylose maize starch, with a very low swelling power, resulted in pastes with very few, small granule remnants (Singh, McCarthy, & Singh, 2006; Singh, Kaur, and McCarthy, 2007; Singh, McCarthy, Singh, Moughan, & Kaur, 2007; Tester & Karkalas, 2002). The presence of cassia gum may have affected the swelling and gelatinization patterns of the different starches resulting in remnants with a lower particle size distribution.

Scanning electron micrographs of the starch pastes with 2% and without cassia gum are shown in Fig. 2. The morphologies of granule remnants differed considerably between pure starch and starch–cassia gum pastes. The pure starch pastes generally showed a less uniform network of disrupted starch granule fragments than did those containing gum; the starch–cassia gum pastes presented a shrunken and tight arrangement of the granule remnants. Among the pure starch pastes, potato, waxy corn and cross-linked waxy corn starch pastes had larger granule remnants. High amylose corn starch showed smaller granule remnants and many granules that were not completely ruptured. These microscopical observations are consistent with the particle size distribution results. Compared with the pure starch pastes, the extent of granule disruption was seen to be considerably higher for starch–cassia gum pastes. Upon increasing the gum concentration to 5%, the granule remnants were observed to form a close network, with the cassia gum–amylose thickened matrix filling the space between the remnants, resulting in a honeycomb-like structure (Fig. 2C).

3.2. Pasting properties

The different pure starches displayed considerable variation in their pasting behaviour (Table 2). P0 exhibited highest peak viscosity and breakdown, followed by C0, W0 and N0. The peak starch paste viscosity has been reported to be influenced by the extent of amylose leaching, amylose–lipid complex formation, friction between swollen granules, granule swelling, and competition for free water between leached amylose and remaining ungelatinized granules (Liu, Ramsden, & Corke, 1997; Olkku & Rha, 1978). Final viscosity and setback of the pure starch pastes decreased in the order C0 > P0 > W0 > N0. As expected, the high amylose starch showed significantly lower peak and final viscosities, and did not show any breakdown in viscosity.

The pasting profiles of the starches were altered to a significant extent by the addition of cassia gum. Peak viscosity of all the starches started to increase with cassia gum addition (up to 2% levels) except for potato starch, which showed a significant decrease,

Table 2
RVA pasting properties of starches and starch–cassia gum mixtures

Sample	Peak viscosity (cP)	Breakdown (cP)	Final viscosity (cP)	Setback (cP)
High amylose corn starch[A]	v		v	
H0 (with 0% cassia gum)	21^{a}	–	21^{a}	–
H1 (with 1% cassia gum)	28^{a}	–	37^{a}	–
H2 (with 2% cassia gum)	50^{b}	–	64^{b}	–
H5 (with 5% cassia gum)	158^{c}	–	232^{c}	–
Normal corn starch	w	v	w	v
N0 (with 0% cassia gum)	1791^{a}	771^{b}	1692^{a}	672^{b}
N1 (with 1% cassia gum)	2030^{b}	686^{a}	1958^{b}	614^{a}
N2 (with 2% cassia gum)	2117^{b}	691^{a}	2134^{c}	708^{bc}
N5 (with 5% cassia gum)	2634^{c}	951^{c}	2423^{d}	740^{c}
Waxy corn starch	x	w	x	v
W0 (with 0% cassia gum)	3134^{a}	1278^{d}	2688^{a}	832^{c}
W1 (with 1% cassia gum)	3272^{b}	1074^{c}	2848^{b}	650^{b}
W2 (with 2% cassia gum)	3332^{c}	961^{b}	2926^{c}	555^{a}
W5 (with 5% cassia gum)	3170^{a}	773^{a}	2920^{c}	523^{a}
Cross-linked waxy corn starch	y	x	z	w
C0 (with 0% cassia gum)	4926^{a}	1536^{a}	4882^{c}	1492^{b}
C1 (with 1% cassia gum)	5015^{b}	1688^{b}	4828^{c}	1501^{b}
C2 (with 2% cassia gum)	5607^{d}	2017^{c}	4631^{a}	1041^{a}
C5 (with 5% cassia gum)	5430^{c}	2534^{d}	4726^{b}	1830^{c}
Normal potato starch	z	y	y	vw
P0 (with 0% cassia gum)	6925^{c}	4455^{d}	3168^{a}	698^{a}
P1 (with 1% cassia gum)	6264^{b}	3710^{c}	3320^{b}	766^{b}
P2 (with 2% cassia gum)	5653^{a}	3085^{b}	3309^{b}	741^{b}
P5 (with 5% cassia gum)	5489^{a}	2456^{a}	3743^{c}	710^{a}

Values with the same superscripts (a, b, c, d; within each starch type) in a column did not differ significantly ($p < 0.05$).
Values with the same letters (v, w, x, y, z) in a column among the different starch types did not differ significantly ($p < 0.05$).
[A] High amylose corn starch mixtures showed no breakdown/setback in viscosity.

even at 1% cassia gum addition. The increase in the peak viscosities of the corn starches could be explained by intermolecular associations between leached amylose and galactomannan molecules in the continuous phase (Shi & BeMiller, 2002). An increase in the viscosity of native rice starch upon addition of gellan or gellan-locust bean gum has already been reported in the literature (Liu & Lelievre, 1992).

All the starches (except cross-linked waxy corn starch) showed a significant increase in final viscosity with an increase in gum level. The thermal and shear resistant amylopectin molecules of modified waxy corn starch have been reported to have lower swelling and solubility in starch–gum systems and therefore contribute to a lesser extent to the concentration of the continuous phase (Tecante & Doublier, 1999), thus resulting in lower final viscosity. The starch pastes displayed a general decrease in breakdown values with the addition of cassia gum; however, the breakdown increased for the modified corn starch paste. A significant decrease in breakdown viscosity of potato starch with increasing gum level may have been due to less swelling of the potato starch granules in the presence of gum, while the leached out amylose and cassia gum concentrated phase in the gelatinized paste may have raised the final viscosity (Fig. 3a). The decrease in the peak viscosity of potato starch with the addition of cassia gum reflects the restrictions imposed on the swelling of the large potato starch granules by the concentrated aqueous phase containing the gum and leached out amylose molecules (Fig. 3a and b). Song, Kwon, Choi, Kim, and Shin (2006) reported that the addition of hydrocolloids results in reduced swelling of starch granules because of the osmotic pressure generated within the continuous hydrocolloid phase.

3.3. Viscoelastic properties

3.3.1. Temperature sweep of starch/gum suspensions

The structural transitions associated with phase change in the starch systems are reflected by changes in the rheological profiles and are described by parameters such as G', G'' and $\tan\delta$. The G' and G'' of control starch dispersions increased to maxima during initial heating ($G' > G''$) (Fig. 4a) and then dropped with further heating, which is in agreement with the previous findings on starch (Hsu, Lu, & Huang, 2000). For the control starch suspensions, at early stages of heating, amylose molecules would have dissolved from the starch granules and the suspension would have become a

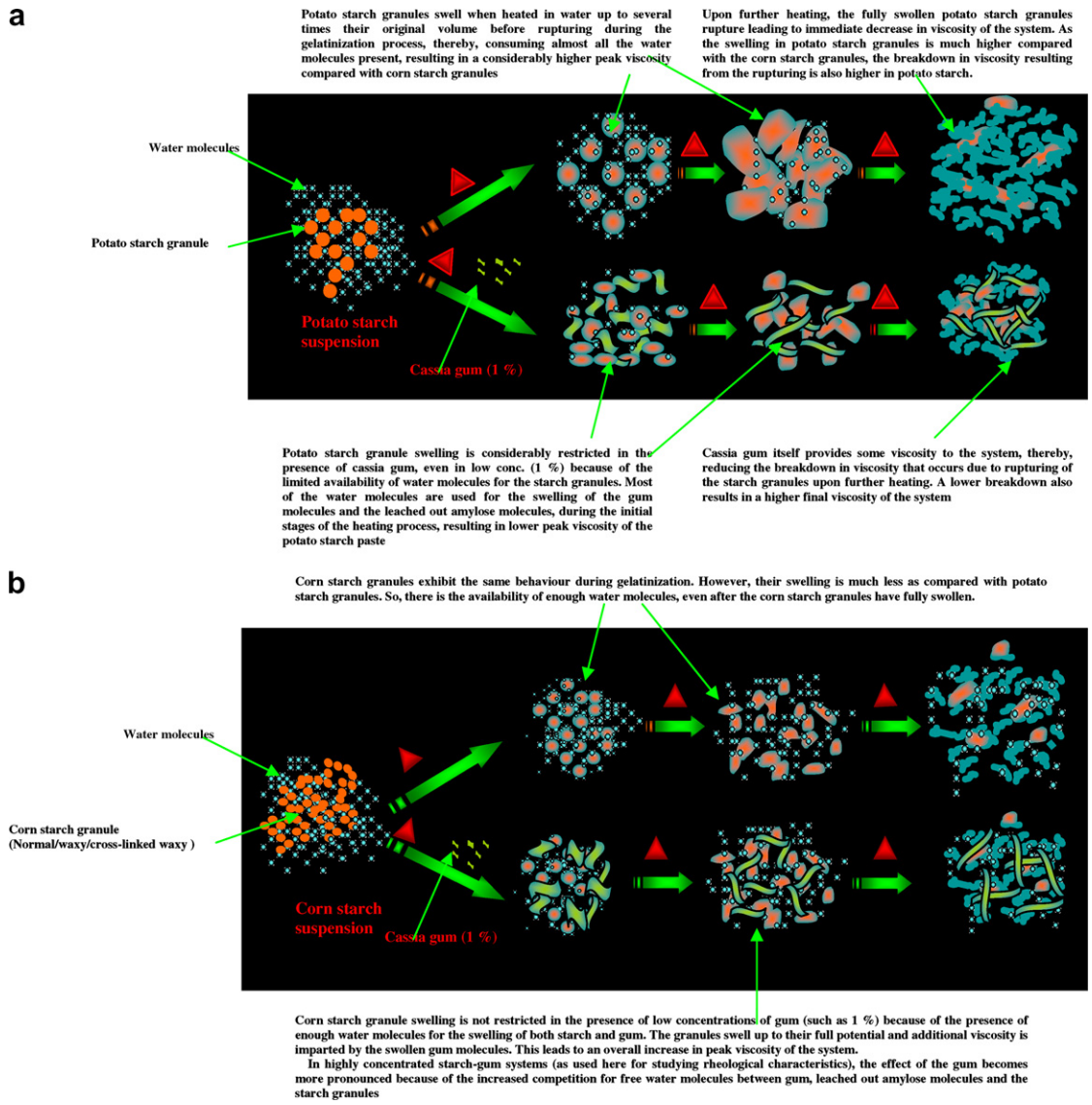

Fig. 3. Starch swelling.

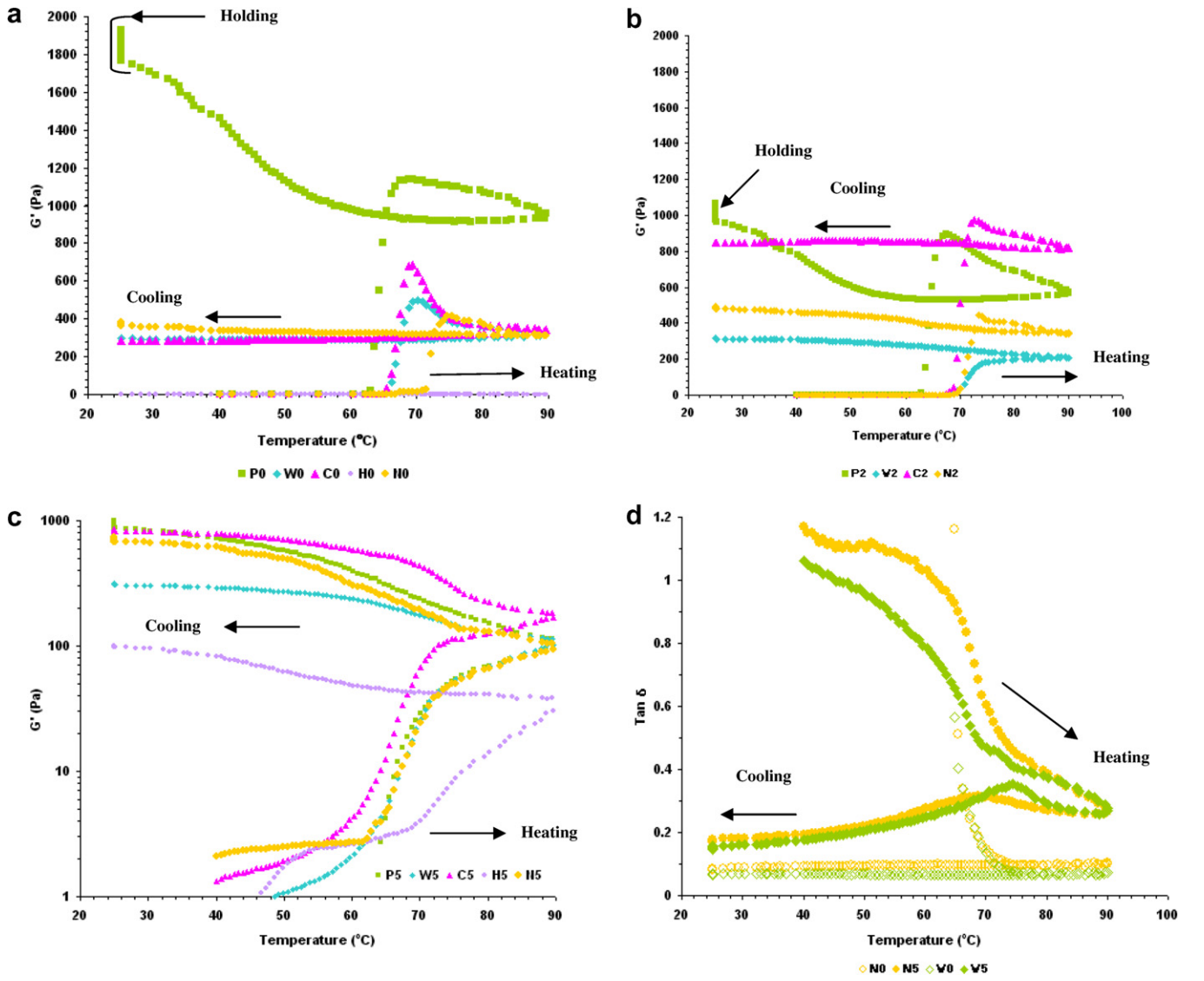

Fig. 4. Effect of the addition of cassia gum on the storage modulus (G') and loss tangent ($\tan\delta$) of starch suspensions during temperature sweeps (heating from 40 to 90 °C, cooling from 90 °C to 25 °C and then holding at 25 °C for 5 min).

sol; thus increases in G' and G'' were relatively small. With further increase in temperature, G' and G'' increased more steeply and reached maxima, owing to the formation of a network of swollen starch granules (gelatinization) (Fig. 4a). Decrease in G' and G'' with further increase in temperature indicates the destruction of this gel structure with prolonged heating (Hsu et al., 2000).

Among the control starch pastes, peak G' and G'' values were observed to decrease in the order P0 > C0 > W0 > N0 > H0 (Table 3); for H0, there was in fact no change in G' during heating and cooling. The temperature at which G' was maximal (T_{gel}) also showed a considerable variation among the different pure starches (data not shown). Potato starch paste had a lower T_{gel} than had waxy, normal and cross-linked waxy corn starch pastes. As expected, $\tan\delta$ decreased with continuous heating of the starch suspensions, indicating gel formation except for high amylose corn starches. In pure high amylose starches, the lower degree of swelling, resulting from the high amylose content, retards gelatinization, thus inhibiting the formation of a gel network (Kaur, Singh, & Singh, 2005; Singh, Kaur, & Singh, 2004; Singh, Kaur, et al., 2007).

Upon addition of cassia gum, peak G' values for all the corn starch pastes were observed initially to increase and then to decrease with increasing gum level (Fig. 4b and c). G' and G'' were both maximal at 1% cassia gum and both minimal at 5% cassia gum for all starches except potato and high amylose corn starch (Fig. 5). The extent of the increase to maximal values itself increased in the order N0 > C0 > W0. The G' and G'' of high amylose corn starch increased with increasing gum level. Potato starch showed a decrease in peak G' and G'' with increasing gum level, which could be explained on the basis of its granule structure and swelling patterns (Fig. 3a). The high amylose corn starch and all the starches with the higher cassia gum levels (2% and/or 5%) showed a continuous increase in G' throughout the heating cycle (Fig. 4c) and did not exhibit a T_{gel}. T_{gel} was observed to increase with an increase in gum level for potato, normal corn and modified waxy corn starches but, for waxy corn starch, T_{gel} was unaffected by the presence of cassia gum. For the high amylose starch studied here, $\tan\delta$ was observed to decrease from 5000 (for pure high amylose starch) to 0.43 at 1% cassia gum concentration and then increased with increasing gum level to 5%.

For all the other starches, $\tan\delta$ values increased with increasing gum levels. This reflects the greater influence of cassia gum on viscous than on elastic properties of the starch–gum system. Fig. 4d presents the effect of cassia gum (5%) on the $\tan\delta$ of normal and waxy corn starch pastes. This increase in $\tan\delta$ values with increase

Table 3
Dynamic rheological properties of starches and starch–cassia gum mixtures measured during temperature sweeps (heating)[A]

Sample	G' (Pa)	G'' (Pa)	tan δ
High amylose corn starch	v	v	x
[B]H0 (with 0% cassia gum)[C]	ND	ND	ND
[B]H1 (with 1% cassia gum)	0.7[a]	0.3[a]	0.43[a]
[B]H2 (with 2% cassia gum)	0.6[a]	0.3[a]	0.50[ab]
[B]H5 (with 5% cassia gum)	34[b]	20[b]	0.59[b]
Normal corn starch	w	w	v
N0 (with 0% cassia gum)	415[b]	61[b]	0.15[a]
N1 (with 1% cassia gum)	668[c]	105[c]	0.16[a]
N2 (with 2% cassia gum)	447[b]	74[b]	0.17[b]
[B]N5 (with 5% cassia gum)	99[a]	27[a]	0.27[c]
Waxy corn starch	w	wx	vw
W0 (with 0% cassia gum)	497[c]	84[b]	0.16[a]
W1 (with 1% cassia gum)	561[d]	97[b]	0.17[a]
[B]W2 (with 2% cassia gum)	206[b]	37[a]	0.18[a]
[B]W5 (with 5% cassia gum)	107[a]	30[a]	0.28[b]
Cross-linked waxy corn starch	x	x	v
C0 (with 0% cassia gum)	735[b]	99[b]	0.13[a]
C1 (with 1% cassia gum)	948[c]	128[c]	0.14[a]
C2 (with 2% cassia gum)	977[c]	135[c]	0.14[a]
[B]C5 (with 5% cassia gum)	175[a]	50[a]	0.28[b]
Normal potato starch	y	y	w
P0 (with 0% cassia gum)	1140[d]	256[d]	0.23[b]
P1 (with 1% cassia gum)	962[c]	212[c]	0.22[b]
P2 (with 2% cassia gum)	894[b]	149[b]	0.17[a]
[B]P5 (with 5% cassia gum)	105[a]	45[a]	0.43[c]

(G') = storage modulus, (G'') = loss modulus, (tan δ) = loss tangent.
ND – not detected.
Values with the same superscripts (a, b, c, d; within each starch type) in a column did not differ significantly ($p < 0.05$).
Values with the same letters (v, w, x, y, z) in a column among the different starch types did not differ significantly ($p < 0.05$).
[A] Rheological parameter values at T_{gel} for mixtures where gelatinization occurred.
[B] Rheological parameter values at 90 °C (for mixtures with no gelatinization temperature).
[C] High amylose starch (0% cassia gum) showed no change in rheological properties in the temperature range studied.

Table 4
Dynamic rheological properties of starches and starch–cassia gum mixtures measured during temperature sweeps (cooling)[A]

Sample	G' (Pa)	G'' (Pa)	tan δ
High amylose corn starch	v	v	x
H0 (with 0% cassia gum)[B]	ND	ND	ND
H1 (with 1% cassia gum)	8[a]	3[a]	0.38[a]
H2 (with 2% cassia gum)	4[a]	2[a]	0.44[b]
H5 (with 5% cassia gum)	99[b]	37[b]	0.37[a]
Normal corn starch	wx	wx	w
N0 (with 0% cassia gum)	392[a]	32[a]	0.08[a]
N1 (with 1% cassia gum)	713[c]	60[b]	0.08[a]
N2 (with 2% cassia gum)	497[b]	46[b]	0.09[a]
N5 (with 5% cassia gum)	735[c]	126[c]	0.17[b]
Waxy corn starch	w	w	v
W0 (with 0% cassia gum)	297[a]	20[a]	0.07[a]
W1 (with 1% cassia gum)	306[a]	28[a]	0.09[a]
W2 (with 2% cassia gum)	319[b]	36 [b]	0.11[ab]
W5 (with 5% cassia gum)	315[ab]	47[b]	0.15[b]
Cross-linked waxy corn starch	x	x	v
C0 (with 0% cassia gum)	285[a]	17[a]	0.06[a]
C1 (with 1% cassia gum)	704[b]	56[b]	0.08[a]
C2 (with 2% cassia gum)	845[c]	69[b]	0.08[a]
C5 (with 5% cassia gum)	857[c]	135[c]	0.16[b]
Normal potato starch	y	y	vw
P0 (with 0% cassia gum)	1930[d]	102[c]	0.05[a]
P1 (with 1% cassia gum)	1530[c]	83.7[ab]	0.06[a]
P2 (with 2% cassia gum)	1070[b]	59[a]	0.06[a]
P5 (with 5% cassia gum)	995[a]	284[d]	0.29[b]

(G') = storage modulus, (G'') = loss modulus, (tan δ) = loss tangent.
ND – not detected.
Values with the same superscripts (a, b, c, d; within each starch type) in a column did not differ significantly ($p < 0.05$).
Values with the same letters (v, w, x, y, z) in a column among the different starch types did not differ significantly ($p < 0.05$).
[A] Rheological property values of the mixtures after cooling from 90 °C to 25 °C and then holding for 5 min at 25 °C.
[B] High amylose starch (0% gum) showed no change in rheological properties in the temperature range studied.

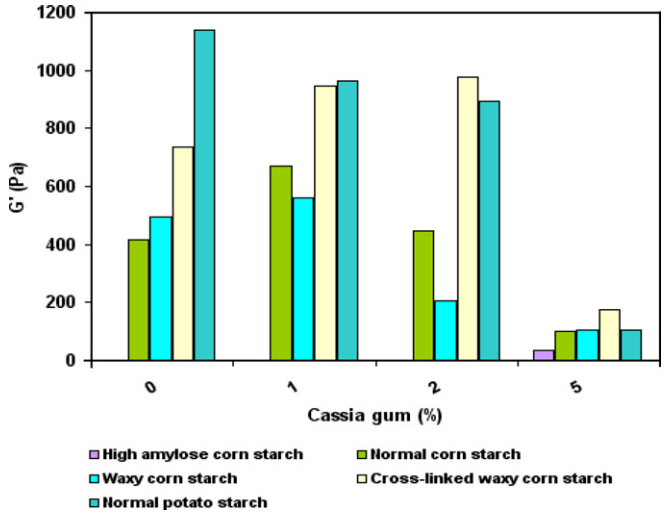

Fig. 5. Effect of the addition of cassia gum on the storage modulus (G') of starch suspensions during heating from 40 to 90 °C.

in gum concentration, which indicates an increase in liquid-like behaviour, is in accordance with the results observed for other starch–galactomannan mixtures (Alloncle & Doublier, 1991; Kim & Yoo, 2006; Kim, Lee, & Yoo, 2006; Korus, Juszczak, Witczak, & Achremowicz, 2004; Kulicke, Eidam, Kath, Kix, & Hamburg, 1996; Yoo et al., 2005). Kim et al. (2006) reported that the characteristics of rice starch (permanent junction zones in the network) and the characteristics of galactomannans (such as temporary entanglements in the network) mainly control the rheological behaviour of starch–galactomannan mixtures. Eidam and Kulicke (1995) reported that the number of junction zones in the starch gel decreases with increasing galactomannan concentration, decreasing the overall elasticity and increasing viscous behaviour. The decrease in the number of junction zones could also be explained by thermodynamic incompatibility between amylose and the galactomannans – chemically dissimilar polysaccharide molecules coexisting in the gel matrix (Alloncle & Doublier, 1991; Kulicke et al., 1996).

During cooling of the starch pastes, both the storage and the loss moduli increased continuously with a decrease in temperature, which reflects retrogradation. Normal corn and potato starches exhibited a higher increase in these rheological parameters during cooling, which was observed to be dependent on their corresponding rheological properties during heating (Table 4, Fig. 4a–c). The extent of increase in the rheological parameters during cooling was observed to be influenced by the type of starch. For cross-linked waxy corn and the unmodified waxy corn starch pastes, there were small increases only. This is in accord with the lower tendency of these starch pastes to retrograde, which in turn is due their very low amylose content (Singh, Kaur, et al., 2007). A decrease in tan δ during cooling of starch pastes has been suggested to be evidence of gel formation (Reddy & Seib, 2000) (Fig. 4d). The decrease might be due to retrogradation of leached components and interaction between molecules remaining inside

the granule, reinforcing the gel structure during cooling (Hsu et al., 2000).

3.3.2. Changes in rheological properties during storage of the starch gels on rheometer

During the early stages of storage of the starch gels, G' and G'' increased (Fig. 6a and b) and $\tan\delta$ decreased, and this effect was more pronounced in high amylose corn, potato and normal corn starch gels. The increase in G' of the starch gels during storage agrees with reported findings (Funami et al., 2005b; Kim et al., 2006). Amylose retrogradation has been reported to occur rapidly during the first few hours of storage, which may be responsible for the rapid increase of the storage and loss modulus of the starch gels, particularly high amylose corn starch. It is noteworthy that the waxy and the modified waxy corn starch gels showed fewer changes in their rheological parameters throughout the storage period, which can be explained on the basis of their lower tendency towards retrogradation. The variation in the retrogradation properties of different starches during storage has been reported to be affected by amylose to amylopectin ratio, size and shape of the granules and presence/absence of lipids. The amylose content has been reported to be one of the influential factors for starch retrogradation (Singh et al., 2007). Being low in amylose, the waxy and modified waxy starches generally show lower syneresis and are more freeze-thaw-stable than are the normal starches.

The high amylose corn, potato and normal corn starch gels with added cassia gum showed less pronounced changes in their rheological parameters during initial hours of storage than did their starch-only controls during storage at 5 °C for 14 h, suggesting that the cassia gum retarded the amylose retrogradation process (Fig. 6a and b). Also, the addition of the cassia gum led to a greater increase in the storage and loss moduli of all the starch gels. However, increase in G'' was greater than in G' for all the starch gels, which may be attributed to the viscous character imparted by the cassia gum. Waxy corn starch gel was the least affected by the addition of cassia gum. The frequency dependence of the G' and G'' can give valuable information about the structure of a gel. Mechanical spectra for selected starch/gum systems before and after storage at 5 °C for 14 h are presented in Fig. 7a and b. A material whose G' and G'' are frequency-independent over a large time scale, with $G' \gg G''$, is generally solid-like; a true gel system is such a material. In contrast, strong frequency dependence suggests a material structure with molecular entanglements. Such a material behaves more like a solid (lower $\tan\delta$) at higher frequencies and more like a liquid (higher $\tan\delta$) at lower frequencies (Ross-Murphy, 1984). Both G' and G'' increased with increasing frequency. All the starch gels, except the H0 gel, showed normal mechanical spectra with G' prevailing over G'' throughout the frequency sweep range. The starch-only gels and their counterpart starch–galacto-

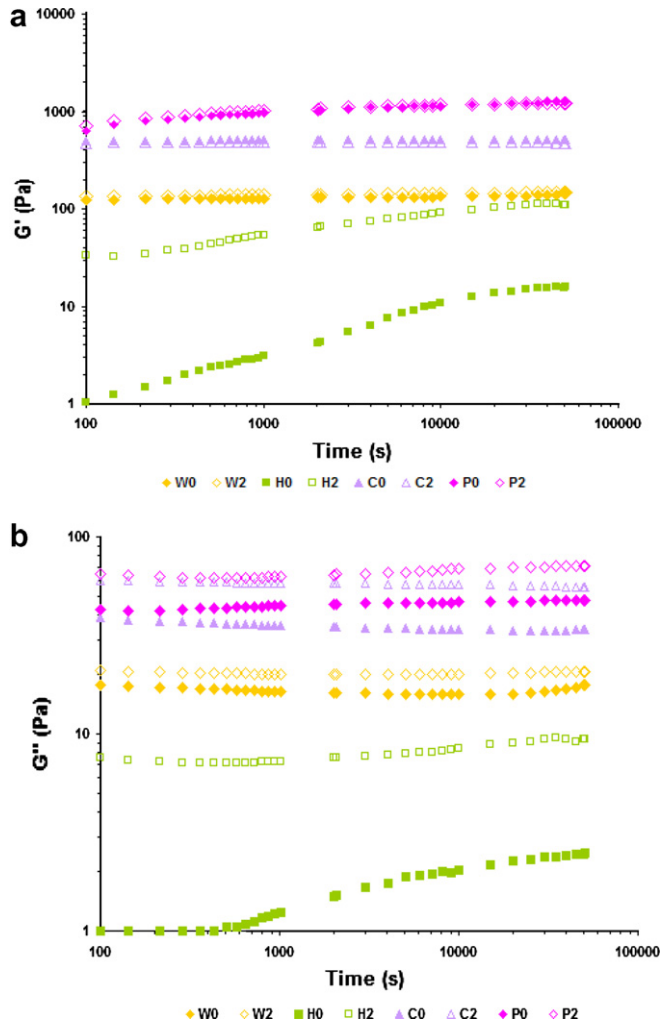

Fig. 6. Changes in dynamic rheological properties of starch and starch–cassia gum gels during storage at 5 °C at 1 Hz.

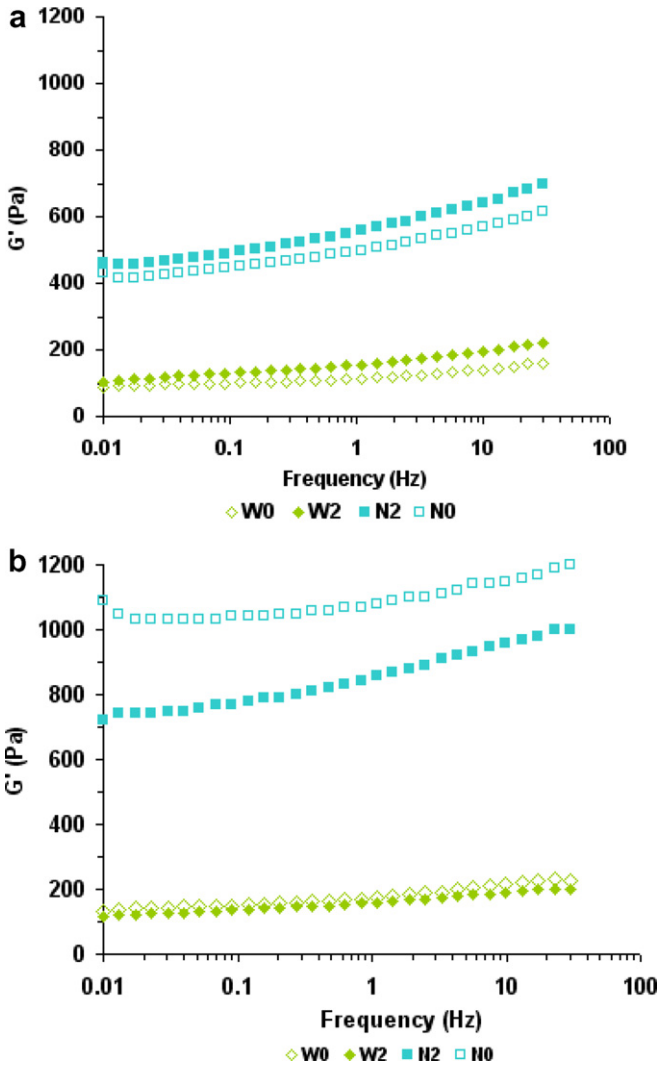

Fig. 7. Effect of the addition of cassia gum on the storage modulus (G') of (a) fresh and (b) stored starch gels, measured during frequency sweeps.

mannan gels behaved in a similar manner, with the latter showing increasing values for G', except for potato starch gels. It is also noteworthy that the increase in G'' was sharper than that observed for G' for the starch gels containing cassia gum. No difference was observed in the frequency dependence of G' between the fresh and stored starch gels. The addition of cassia gum resulted in a higher G' range in freshly prepared and a lower G' range for the starch gels stored on the plate of rheometer, than their counterpart control starch gels (Fig. 7a). Each system responded to cassia gum in a different way, depending on the type of starch. The differences between the rheological parameters of fresh and stored starch gels were observed to decrease with the addition of cassia gum. Normal corn starch, high amylose corn starch and the potato starch pastes showed pronounced effects on the addition of cassia gum, whereas waxy corn and the cross-linked waxy corn starch pastes were affected to a lesser extent during storage at 5 °C.

4. Conclusion

Starch–cassia gum interactions studied through microstructure observation and rheology illuminate the behaviour of different starches in the presence of this unique galactomannan. The restrictions imposed on the swelling of the starch granules by the cassia gum during gelatinization result in the size reduction of starch granule remnants and an alteration in their pasting and viscoelastic characteristics. The rheological characterization carried out at refrigeration temperature suggests greater stability of starch–cassia gum pastes at low temperature and resistance towards retrogradation. Depending on the type of starch, the amylose concentration and granule size distribution are important factors affecting the extent of starch–cassia gum interactions, which may result in varied functional behaviour. Recently approved for food use, cassia gum, like other galactomannans, may find successful applications in the food processing industry.

References

AACC. (1995). *Approved methods of the American Association of Cereal Chemists* (10th ed.). St. Paul, MN.

Ali, L., Azad Khan, A. K., & Hassan, Z. (1995). Characterization of the hypoglycaemic effects of Trigonella foenum graecum seeds. *Planta Medica, 61*, 358–360.

Alloncle, M., & Doublier, J. L. (1991). Viscoelastic properties of maize starch/hydrocolloid pastes and gels. *Food Hydrocolloids, 5*, 455–467.

Alloncle, M., Lafebvre, J., Llamas, G., & Doublier, J. L. (1989). A rheological characterization of cereal starch–galactomannan mixtures. *Cereal Chemistry, 66*, 90–93.

Denkler, M. (1997). Based on US Pat. No. 4743659; Derivatives of cassia. Freedom Chemical Diamalt GmbH. Private communication, 31 January.

Eidam, D., & Kulicke, W. M. (1995). Formation of maize starch gels selectively regulated by the addition of hydrocolloids. *Starch/Starke, 47*, 378–384.

European Food Safety Authority (2006). Opinion of the scientific panel on food additives, flavourings, processing aids and materials in contact with food on a request from the commission related to an application on the use of cassia gum as a food additive. *The ESFA Journal, 389*, 1–16.

Funami, T., Kataoka, Y., Omoto, T., Goto, Y., Asai, I., & Nishinari, K. (2005a). Food hydrocolloids control the gelatinization and retrogradation behavior of starch. 2a. Functions of guar gums with different molecular weights on the gelatinization behavior of corn starch. *Food Hydrocolloids, 19*, 15–24.

Funami, T., Kataoka, Y., Omoto, T., Goto, Y., Asai, I., & Nishinari, K. (2005b). Food hydrocolloids control the gelatinization and retrogradation behavior of starch. 2b. Functions of guar gums with different molecular weights on the retrogradation behavior of corn starch. *Food Hydrocolloids, 19*, 25–36.

Gupta, A., Gupta, R., & Lal, B. (2001). Effect of Trogonella foenum-graecum (fenugreek) seeds on glycaemic control and insulin resistance in Type II diabetes mellitus: A double blind placebo controlled study. *Journal of Association of Physicians of India, 49*, 1057–1061.

Hallagan, J. B., La Du, B. N., Pariza, M. W., Putnam, J. M., & Borzelleca, J. F. (1997). Assessment of cassia gum. *Food and Chemical Toxicology, 35*, 625–632.

Hsu, S., Lu, S., & Huang, C. (2000). Viscoelastic changes of rice starch suspensions during gelatinization. *Journal of Food Science, 65*, 215–220.

Kaur, L., Singh, J., & Singh, N. (2005). Effect of glycerol monostearate on physico-chemical, thermal, rheological and noodle making properties of corn and potato starches. *Food Hydrocolloids, 19*, 839–849.

Kim, C., Lee, S.-P., & Yoo, B. (2006). Dynamic Rheology of rice starch–galactomannan mixtures in the aging process. *Starch/Starke, 58*, 35–43.

Kim, C., & Yoo, B. (2006). Rheological properties of rice starch–xanthan gum mixtures. *Journal of Food Engineering, 75*, 120–128.

Korus, J., Juszczak, L., Witczak, M., & Achremowicz, B. (2004). Influence of selected hydrocolloids on triticale starch rheological properties. *International Journal of Food Science and Technology, 39*, 641–652.

Kuhn, M. (1995). Frredom Chemical Diamalt GmbH. Private communication, 28 September.

Kulicke, W. M., Eidam, D., Kath, F., Kix, M., & Hamburg, A. H. (1996). Hydrocolloids and rheology: Regulation of visco-elastic characteristics of waxy rice starch in mixtures with galactomannans. *Starch/Starke, 48*, 105–114.

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. (1997). Physical properties and enzymatic digestibility of acetylated ae, wx, and normal corn starch. *Carbohydrate Polymers, 34*, 283–289.

Nayouf, M., Loisel, C., & Doublier, J. L. (2003). Effect of thermomechanical treatment on the rheological properties of cross linked waxy corn starch. *Journal of Food Engineering, 59*, 209–219.

Nurnberg, E., & Bleimuller, G. (1981). Development of a galactomannan product for tablets. *Pharmazeutische Industrie, 43*, 1238–1242.

Olkku, J., & Rha, C. K. (1978). Gelatinization of starch and wheat flour starch – A review. *Food Chemistry, 3*, 293–317.

Rao, M. A., & Anantheswaran, R. C. (1982). Rheology of fluid in food processing. *Food Technology, 36*, 116–126.

Reddy, I., & Seib, P. A. (2000). Modified waxy wheat starch compared to modified waxy corn starch. *Journal of Cereal Science, 31*, 25–39.

Rha, C. (1975). *Theory, determination and control of physical properties of food material* (pp. 7–24). Dordrecht, Holland: D. Reidel Publ. Co.

Ross-Murphy, S. B. (1984). Rheological methods. In H. W.-S. Chan (Ed.), *Biophysical Methods in Food Research* (pp. 138–199). Blackwell.

Sajjan, S. U., & Rao, M. R. R. (1987). Effect of hydrocolloids on the rheological properties of wheat starch. *Carbohydrate Polymers, 7*, 395–402.

Sharma, R. D., & Raghuram, T. C. (1990). Hypoglycaemic effect of fenugreek seeds in non-insulin dependent diabetic sunjects. *Nutrition Research, 10*, 731–739.

Sharma, R. D., Raghuram, T. C., & Sudhakar, R. (1990). Effect of fenugreek seeds on blood glucose and serum lipids in Type I diabetics. *European Journal of Clinical Nutrition, 44*, 301–306.

Shi, X., & Bemiller, J. N. (2002). Effects of food gums on viscosities of starch suspensions during pasting. *Carbohydrate Polymers, 50*, 7–18.

Singh, J., Kaur, L., & Singh, N. (2004). Effect of acetylation on some properties of corn and potato starches. *Starch, 56*, 586–601.

Singh, J., McCarthy, O. J., & Singh, H. (2006). Physico-chemical and morphological characteristics of New Zealand Taewa (Maori potato) starches. *Carbohydrate Polymers, 64*, 569–581.

Singh, J., Kaur, L., & McCarthy, O. J. (2007). Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications – A review. *Food Hydrocolloids, 21*, 1–22.

Singh, J., McCarthy, O. J., Singh, H., Moughan, P. J., & Kaur, L. (2007). Morphological, thermal and rheological characterization of starch isolated from New Zealand Kamo Kamo fruit – A novel source. *Carbohydrate Polymers, 67*, 233–244.

Song, J.-Y., Kwon, J.-Y., Choi, J., Kim, Y.-C., & Shin, M. (2006). Pasting properties of non-waxy rice starch–hydrocolloid mixtures. *Starch/Starke, 58*, 223–230.

Tecante, A., & Doublier, J. L. (1999). Steady flow and viscoelastic behavior of crosslinked waxy corn starch-κ-carrageenan pastes and gels. *Carbohydrate Polymers, 40*, 221–231.

Tester, R. F. & Karkalas, J. (2002). Starch. In A. Steinbüchel (series Ed.) & E. J. Vandamme, S. De Baets, & A. Steinbüchel (Vol. Eds.) *Biopolymers Vol. 6, Polysaccharides II: Polysaccharides from Eukaryotes* (pp. 381–438). Weinheim: Wiley-VCH.

Trowell, H., Southgate, D. A. T., Wolever, T. M. S., Leeds, A. R., Gassull, M. A., & Jenkins, D. J. A. (1976). Dietary fibre redefined. *Lancet, I*, 967.

Yoo, D., Kim, C., & Yoo, B. (2005). Steady and dynamic shear rheology of rice starch–galactomannan mixtures. *Starch/Starke, 57*, 310–318.