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# Rheology of different hydrocolloids-rice starch blends. Effect of successive heating-cooling cycles

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#### ABSTRACT

Hydrocolloids are frequently used for modifying starch functionality. In the present study the possible interaction of three different hydrocolloids – guar gum, hydroxypropylmethylcellulose (HPMC) and xanthan gum – with rice starch was explored by determining the pasting, viscoelastic and swelling properties of the rice starch–hydrocolloids mixtures. The impact of successive heating–cooling cycles on the pasting, viscoelasticity and swelling was also determined. Hydrocolloids tested in the range 0.2–0.8% (w/w) significantly modified the pasting, viscoelastic and swelling properties of rice starch–hydrocolloid pastes (8%, w/w) and the extent of the effect was dependent on hydrocolloid concentration. Guar and xanthan gum mixtures with rice starch had the greatest effect on the pasting properties, whereas HPMC mixtures only changed the viscosity during cooling. The starch–hydrocolloids pastes formed weaker gels compared to those of the starch alone. Rheological results suggested the formation of composite network structures with high frequency dependence. Successive multiple–heating cycles allowed the gel to rearrange resulting in altered gel viscoelasticity and release of water soluble compounds that favour phase separation at the highest hydrocolloid level tested.

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#### 1. Introduction

Starches and hydrocolloids are biopolymers commonly used in food processing to provide proper texture, control moisture and water mobility, improve the overall quality and stability of the products, reduce cost and facilitate processing. The use of starch alone is sometimes hampered due to their tendency to syneresis, retrogradation and breakdown when subjected to cooking, shear stress and cooling, which can lead to increased hardness and undesirable gels (Bárcenas & Rosell, 2005; Ribotta & Rosell, 2010). Numerous studies have been conducted on the effect of hydrocolloids (cellulose derivatives, alginates, carragenaans, xanthan gum, guar gum and so on) on wheat starch that have shown that the effect is greatly dependent on the hydrocolloid structure and concentration (Alloncle, Lefebvere, Llamas, & Doublier, 1989; Christianson, Hodge, Osborne, & Detroy, 1981; Rojas, Rosell, & Benedito, 1999). In general, hydrocolloids lowered the pasting temperature of the starches without affecting the gelatinization temperature of the starch (Liu & Eskin, 1998) and modified the pasting behaviour

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and viscoelastic properties of the starch. However, the interaction is also dependent on the starch origin because of differences in granule size and crystalline microstructure (Techawipharat, Suphantharika, & BeMiller, 2008). Hydrocolloid structure also affect starch interaction and some attempts have been made to explain these differences by the net charge of the hydrocolloids (Shi & BeMiller, 2002).

Rice starch is also used in many food applications for its desirable rheological properties (Rosell & Gómez, 2006). Nevetheless, sometimes the use of hydrocolloids becomes necessary to control or modify the gel or dough properties, like occurred when developing gluten free products (Gujral, Guardiola, Carbonell, & Rosell, 2003; Marco & Rosell, 2008). However, very few fundamental studies have been conducted on the effect of different hydrocolloids on the pasting and rheological properties of rices starches. Liu, Eskin, and Cui (2003) investigated the effect of yellow mustard addition showing that the mucilage significantly modified the texture of the rice gel and increased gel viscosity. A rheological study of rice starch-xanthan gum mixtures in the range of 25–70 °C found that xanthan caused weak gel behaviour, which was strongly dependent on the temperature and gum concentration (Kim & Yoo, 2006). Techawipharat et al. (2008) studied the effect of cellulose derivatives and carrageenans on the pasting, rheological and textural properties of rice starch. These authors reported that those hydrocolloids increased the pasting temperature, and peak

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and final viscosities and led to less structured and less solid-like pastes.

Previous studies conducted with different starches and hydrocolloids indicate that starch-hydrocolloid blends exhibited a phase-separated microstructure in which amylose and amylopectin rich domains were dispersed in a hydrocolloid-rich continuous phase (Alloncle & Doublier, 1991; Techawipharat et al., 2008). In the absence of hydrocolloids, starch formed micellar networks through the association of segments of amylose or amylopectin molecules, which control the swelling process during heating. In the gelatinization process starch dispersions consists of a continuous phase formed by leached amylose and low molecular weight amylopectin and a dispersed phase integrated by swollen granules (Alloncle et al., 1989). When hydrocolloids are mixed with starch, leached amylose and low molecular weight amylopectins can interact with hydrocolloids during gelatinization and form different network structures that result in altered pasting and rheological properties depending on the hydrocolloid and its concentration (Shi & BeMiller, 2002).

The aim of the present study was to provide some insight about the interactions of rice starch with three different hydrocolloids: guar gum, a galactomannan; hydroxypropylmethylcellulose (HPMC), a cellulose derivative; and xanthan gum, an anionic hydrocolloid. The pasting, viscoelasticity and swelling properties during gelatinization of the rice starch-hydrocolloids mixtures were determined. The structure of cooked hydrocolloid-starch mixtures were explored by measurements of viscoelasticity and pasting characteristics under low shear conditions to preserve network structure. In addition, the effect of repeated heating-cooling cycles on the pasting, viscoelasticity and swelling was explored to determine the network stability of the rice starch-hydrocolloids mixtures.

#### 2. Materials and methods

Rice starch was purchased from Sigma (St. Louis, MO). HPMC (Methocel K4M) was generously donated by Dow Chemical Company (Midland, MI, USA). This cellulose derivative was substituted with 22.7% methyl groups and 11.2% hydroxypropyl groups and a 2% solution in water had a viscosity of 4664 mPa s at 20°C. Guar gum was purchased from Sigma (St. Louis, MO). All the chemical reagents were of analytical grade. Xanthan gum was from Bob's Red Mill Natural Foods Inc (Milwaukie, OR, USA).

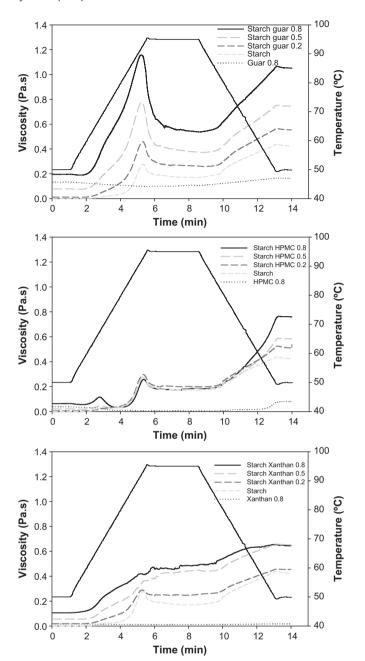
#### 2.1. Molecular weight determination of the hydrocolloids

Molecular weight determination was performed by size-exclusion chromatography and laser light scattering detection on a HPLC (Hewlett Packard Series 1050) equipped with two aqueous SEC columns (Ultrahydrogel 250 and 1000; Waters Co., Milford, MA, USA). The HPSEC system consisted of an HP 1050 pump and auto-injector (Hewlett Packard, Valley Forge, PA, USA) fitted with a 100 ml injection loop. The system also employed a MALLS detector (Dawn DSP-F, Wyatt Tech., Santa Barbara, CA, USA) with a He-Ne laser source ( $\lambda$  = 632.8 nm), a K-5 flow cell, and a differential refractometer detector (RI) (model ERC-7512, ERMA Inc., Tokyo, Japan).

Xanthan and guar gum (0.2%, w/w) and HPMC (0.1%, w/w) were dissolved in 0.1 M NaNO $_3$  containing 0.02% sodium azide. Samples were filtered with 0.45  $\mu$ m nylon filter before injection. Samples were eluted at 0.5 ml/min at 45 °C.

## 2.2. Measurement of starch pasting properties by using a rotational controlled stress rheometer

The pasting properties of the rice starch were determined in triplicate on a constant stress rheometer (Rheolyst AR 1000N, TA



**Fig. 1.** Pasting curves of rice starch–hydrocolloids dispersions (8%, w/w) and hydrocolloid viscosity measured in a rotational rheometer. The number in the legends described the hydrocolloid concentration (%, w/w) in the starch–hydrocolloid blends.

instrument, New Castle, DE, USA). Cone and plate fixtures were used on the rheometer for the measurements. The bottom plate was a Peltier plate. The polysulfone plastic cone had a 4° angle and diameter of 40 mm. The plastic cone had the benefit of being less heating conducting than metal fixtures, and provided a more consistent temperature across the gap as only the bottom surface was heated. The plastic fixture was also transparent, which allowed for a visual check for the absence of air bubbles within the sample. The starch slurry (8.0%, w/w) was prepared by dispersing weighed amounts of starch (dry basis) in deionized water. Hydrocolloids solutions (0.2, 0.5, 0.8%, w/w) were prepared by dispersing the powder in deionized water. The starch–hydrocolloid slurries (8.0%, w/w) were prepared by mixing starch with the previously prepared hydrocolloids solutions. Starch slurries with lower concentration (7.8,

**Table 1**Effect of hydrocolloids on the starch pasting parameters obtained by using a rotational rheometer. The total concentration of the starch–hydrocolloid mixtures was kept at 8.0% (w/w).

Sample	Level (%)	Initial viscosity (Pa·s)	Onset temperature (°C)	Peak pasting temperature (°C)	Peak viscosity (Pa·s)	Through viscosity (Pa·s)	Breakdown (Pa·s)	Final viscosity (Pa·s)	Final viscosity-through viscosity (Pa·s)
Control	0	0.002 ± 0.000a	62.5 ± 0.1e	92.8 ± 0.1bc	0.277 ± 0.012a	0.166 ± 0.002a	0.111 ± 0.010b	0.424 ± 0.013a	0.258 ± 0.011ab
Guar gum	0.2	$0.001 \pm 0.000a$	$59.3 \pm 0.0b$	$92.7 \pm 0.0b$	$0.472 \pm 0.015b$	$0.267 \pm 0.009 d$	$0.206 \pm 0.007c$	$0.563 \pm 0.010b$	$0.296 \pm 0.004$ bc
Guar gum	0.5	$0.082 \pm 0.004e$	$58.5 \pm 0.1a$	$92.1 \pm 0.2a$	$0.819 \pm 0.046c$	$0.387 \pm 0.020e$	$0.432 \pm 0.027 d$	$0.775 \pm 0.039d$	$0.387 \pm 0.018d$
Guar gum	0.8	$0.196 \pm 0.002g$	$58.7 \pm 0.1b$	$91.7 \pm 0.2a$	$1.151 \pm 0.018d$	$0.534 \pm 0.005 f$	$0.617 \pm 0.013e$	$1.042 \pm 0.012e$	$0.508 \pm 0.007$
HPMC	0.2	$0.007 \pm 0.000a$	$62.7 \pm 0.0e$	$93.0 \pm 0.1bc$	$0.297 \pm 0.002a$	$0.194 \pm 0.000b$	$0.104 \pm 0.002b$	$0.527 \pm 0.018b$	$0.333 \pm 0.018c$
HPMC	0.5	$0.021 \pm 0.000b$	$59.9 \pm 0.3d$	$93.0 \pm 0.4bc$	$0.280 \pm 0.014a$	$0.173 \pm 0.011$ ab	$0.106 \pm 0.003b$	$0.577 \pm 0.007b$	$0.404 \pm 0.012d$
HPMC	0.8	$0.063 \pm 0.001d$	$57.9 \pm 0.0a$	$93.1 \pm 0.3c$	$0.261 \pm 0.008a$	$0.176\pm0.010ab$	$0.084 \pm 0.002$ ab	$0.766 \pm 0.034d$	$0.590 \pm 0.024 f$
Xanthan	0.2	$0.018 \pm 0.000b$	$59.6 \pm 0.1$ cd	$92.6 \pm 0.2bc$	$0.290 \pm 0.004a$	$0.237 \pm 0.007c$	$0.053 \pm 0.008a$	$0.454 \pm 0.007a$	$0.217 \pm 0.011a$
Xanthan	0.5	$0.056 \pm 0.005c$	$58.7 \pm 0.1b$	$95.0 \pm 0.0d$	$0.438 \pm 0.010b$	n.d.	n.d.	$0.651 \pm 0.014c$	n.d.
Xanthan	8.0	$0.106\pm0.001f$	$57.9\pm0.1a$	$95.0\pm0.0d$	$0.476\pm0.002b$	n.d.	n.d.	$0.645\pm0.004c$	n.d.

Mean  $\pm$  standard deviation values followed by different letters within a column denote significantly different levels (p < 0.05) (n = 3), n.d.: not detected.

7.5 and 7.2%) were also tested to determine the effect of starch dilution. Hydrocolloids solutions were also tested to assess their viscosity contribution. The dispersions were degassed by agitation for 30 min under vacuum. A pipette was used to transfer 1.1 ml of the dispersion between the cone and plate. The rim of the sample was coated with a thin layer of Silicon Oil (Fisher Sci., NJ, USA) to prevent evaporation during measurements at high temperatures.

For the pasting and rheological measurements of starch dispersions, a continuous program was set up as previously reported (Zhong, Ibanez, Oh, McKenzie, & Shoemaker, 2009). Briefly, the program included: equilibration at 50 °C for 1 min at a shear rate of 200 s<sup>-1</sup>, a linear temperature increase to 95 °C at 10 °C/min, holding at 95 °C for 3 min, a cooling step with a linear temperature decrease to 50 °C at the same speed and holding at 50 °C for 1 min. The shear rate was maintained at  $200 \,\mathrm{s}^{-1}$  during the entire period. When multiple heating-cooling cycles were investigated samples were prepared as above described and the heating-cooling cycle was repeated three times. The onset temperature (the temperature where viscosity first increased, °C), peak pasting temperature (the temperature at which peak viscosity occurred, °C), peak viscosity (the maximum hot paste viscosity, Pas), holding strength or through viscosity (the through at the minimum hot paste viscosity, Pas), breakdown (peak viscosity-through viscosity, Pas), final viscosity (the viscosity at the end of 50 °C, Pas) and the difference between final and through viscosities (related to amylose recrystallization) were calculated from the pasting curve.

After the completion of the pasting program, the temperature was raised to 65 °C and equilibrated for 1 min, before measuring the viscoelastic properties. An oscillatory stress sweep was made at a constant frequency of 1 Hz over an oscillatory stress range of 0.1–10 Pa with 5 steps per log cycle. The storage modulus (G'), loss modulus (G'') and loss tangent ( $\tan \delta = G''/G'$ ) were determined from measurements within the linear viscoelastic range of each paste. Frequency sweep test was performed from 0.01 to 10 Hz at a constant stress (0.5 Pa) within the linear viscoelastic range at 65 °C.

#### 2.3. Starch gel hydration and iodine binding values

The physical properties of the starch–hydrocolloid mixtures, swelling capacity or water holding capacity, and swelling power, were determined. A total concentration of starch and hydrocolloid at 2% (w/w) was maintained for the dispersions by varying the amounts of starch and hydrocolloids. Swelling power defined as the ratio of the wet weight of the sedimented gel to its dry weight (Leach, McCowen, & Schoch, 1959) was determined modifying the method of Techawipharat et al. (2008). Briefly, starch or starch–hydrocolloid dispersions (15 g) were prepared by suspending the starch in the hydrocolloid solutions (0.050, 0.125, 0.200%, w/w) to obtain final dispersion concentration of 2.0% (w/w). Sus-

pensions were placed into 50 ml centrifuge tubes with coated screw caps, heated in a boiling water bath for 10 min and cooled in an ice water bath for 10 min. The effect of multiple heat–cool cycles was studied by three successive heating and cooling cycles as described. The cooled tubes were centrifuged at  $7000 \times g$  for 15 min. Supernatants were dried at  $105\,^{\circ}\text{C}$  to constant weight. Three replicates were made for each sample. Residues  $(W_r)$  and dried supernatants  $(W_s)$  were weighed and swelling power and solubility index were calculated as follows:

Solubility index (SI) (%) = 
$$\left(\frac{W_s}{W_i}\right)$$
  
×100 (Techawipharat et al., 2008)

Swelling power 
$$(g/g) = \frac{W_r}{W_i}(100 - SI)$$
 (Leach et al., 1959)

where  $W_i$  was the sample weight (g, db).

Swelling capacity was the ratio of the wet weight of sedimented gel to the dry weight of starch (Toyokawa, Rubenthaler, Powers, & Schanus, 1989). Iodine binding values are indicative of amylose complex formation. The iodine binding value was determined in the soluble supernatant after gelatinising and centrifuging the samples as described above. The soluble supernatant (100  $\mu$ l) was diluted with deionized water (400  $\mu$ l). The mixture was vortexed vigorously and 50  $\mu$ l were mixed with 1 ml of an aqueous solution of 0.2% KI and 0.65% I2. The absorbance at 690 nm was measured. Four replicates were run for each determination.

#### 2.4. Statistical analysis

Experimental data were statistically analyzed for analysis of variance (ANOVA) using Statgraphics V.7.1 (Bitstream, Cambridge, MN). When analysis of variance indicated significant *F* values, multiple sample comparisons were also performed by Fisher's least significant differences (LSD) test to differentiate means with 95% confidence. The correlation matrix was also performed using Statgraphics V.7.1 software.

#### 3. Results and discussion

#### 3.1. Pasting properties

The effects of the hydrocolloids on the pasting properties of rice starch are shown in Fig. 1 and Table 1. The molecular weight of guar gum, HPMC and xanthan gum were  $2.67 \times 10^7$ ,  $4.22 \times 10^5$  and  $3.61 \times 10^6$  Da, respectively. Different levels of hydrocolloids were studied but the total concentration of starch and hydrocolloid was maintained at a constant level in order to allow comparison

**Table 2**Dynamic rheological properties of rice starch and various hydrocolloids dispersions measured at a frequency of 1 Hz, oscillatory stress of 0.5 Pa and 65 °C.

Sample	Level (%)	<i>G'</i> (Pa)	<i>G</i> " (Pa)	G* (Pa)	Loss tangent $\tan{(\delta)}$	$\eta^*$ (Pas)
Control	0	45.0 ± 1.2a	8.7 ± 0.1a	45.8 ± 1.2a	$0.193 \pm 0.002$ a	7.3 ± 0.2a
Guar gum	0.2	$53.5 \pm 0.1b$	$12.2\pm0.1b$	$54.9 \pm 0.2b$	$0.228 \pm 0.001b$	$8.7 \pm 0.0b$
Guar gum	0.5	$71.3 \pm 0.9d$	$18.3 \pm 0.0d$	$73.6 \pm 0.9d$	$0.257 \pm 0.003c$	$11.7 \pm 0.1e$
Guar gum	0.8	$111.4 \pm 2.0f$	$28.8 \pm 0.5g$	$115.1 \pm 2.1f$	$0.258 \pm 0.000c$	$18.3 \pm 0.3g$
HPMC	0.2	$66.3 \pm 2.8c$	$12.4 \pm 0.3b$	$67.4 \pm 2.8c$	$0.187 \pm 0.003a$	$10.7 \pm 0.4c$
HPMC	0.5	$54.6 \pm 0.4b$	$14.6 \pm 0.1c$	$56.6 \pm 0.4b$	$0.267 \pm 0.000d$	$9.0\pm0.1b$
HPMC	0.8	$62.2 \pm 1.6c$	$19.5 \pm 0.4e$	$65.2 \pm 1.7c$	$0.313 \pm 0.002f$	$10.4 \pm 0.3c$
Xanthan	0.2	$41.0 \pm 0.9a$	$13.8 \pm 0.2c$	$43.2\pm0.9a$	$0.337 \pm 0.005h$	$6.9\pm0.1a$
Xanthan	0.5	$79.7 \pm 3.5e$	$25.7\pm0.9f$	$83.7 \pm 3.6e$	$0.323 \pm 0.002g$	$13.3\pm0.6f$
Xanthan	0.8	$122.1\pm0.8g$	$36.7\pm0.3h$	$127.5\pm0.9g$	$0.301 \pm 0.000e$	$20.3\pm0.1h$

Mean  $\pm$  standard deviation values followed by different letters within a column denote significantly different levels (p < 0.05) (n = 3).

of the network structures at different hydrocolloid concentrations (Kulicke, Eidam, Kath, Kix, & Kull, 1996). Starch suspensions having the same starch concentration of the starch–hydrocolloid mixtures were also tested to assess the effect of starch dilution. Pasting properties were evaluated using a rotational rheometer that provided similar plots to those of the rapid viscoanalyzer (Newport Scientific, Warriewood NSW, Australia) (Zhong et al., 2009) in order to preserve the network structure by using only low deformation amplitude (Kulicke et al., 1996).

Guar and xanthan gums induced an increase of the viscosity of the rice starch during the heating and cooling cycle, and that increase was dependent on the hydrocolloid concentration. Only the paste viscosity during cooling was raised by HPMC. The enhancement of viscosity in the hydrocolloid-starch pastes has been attributed to the increase of viscosity of the continuous phase occupied by the hydrocolloid during starch swelling. By this explanation the overall viscosity of the system would be the result from the additive effect of the increased viscosity of the hydrocolloid that is more concentrated as the volume of the available water decreases and the viscosity of the swollen starch granules, and the hydrocolloid dominates the overall viscosity (Techawipharat et al., 2008). In the present study the individual effect of the hydrocolloids was also tested to determine if the change of viscosity was either additive or synergistic. Individual hydrocolloids gave solutions of very low viscosity, which barely decreased when the temperature was increased, only HPMC showed an increase of viscosity during cooling (Fig. 1). Moreover, the viscosity increase of the guar or xanthan-rice starch mixtures begins much earlier than the starch alone. At these earlier times the uptake of water is small and therefore the concentration of the hydrocolloids should be similar to the initial concentration. However, the viscosity increase is several times higher than the sum of the hydrocolloid and starch. Therefore, these patterns suggest the synergistic effect of these hydrocolloids on rice starch gelatinization. At a molecular level they may be due to entrapment of water by starch granule aggregates bound by hydrocolloid molecules. In addition, a shoulder in the gelatinization peak of the starch was detected in the presence of guar and xanthan gums, and its size augmented with the hydrocolloid concentration. It has been previously described that starch gelatinization consists in two stages, the first one corresponding to swelling process is not detected with the viscograph (Liu & Eskin, 1998) but it can be detected with the oscillatory rheometer, and the second one is observed as large change in viscosity in the starch dispersions. The first stage viscosity increase has been explained by interactions between specific gums and amylose that leaches out of the granules below the gelatinization temperature (Shi & BeMiller, 2002), thus it seems that these hydrocolloids are prone to interact with leached amylose favouring its diffusion to the solution instead of being located at the granule surface or near the periphery of the granules (Shi & BeMiller, 2002). In the case of HPMC an earlier peak was detected before starch swelling became evident, and the magnitude of the peak increases with the hydrocolloid concentration. HPMC is known to form gels at temperatures above  $50\,^{\circ}$ C. The peak observed in the viscoamylographs might correspond to the HPMC hydrocolloid gelation, which transitions from pregel to gel and has been detected previously by dynamical oscillatory studies from 50 to  $65\,^{\circ}$ C (Rosell & Foegeding, 2007).

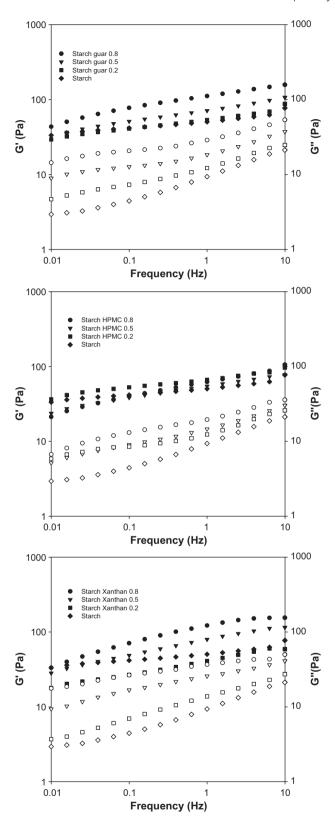
Starch–hydrocolloids dispersions showed higher initial viscosity than that of the individual starch (Table 1), although in the case of guar gum and HPMC, a level higher than 0.2% was necessary to increase the viscosity. With the exception of HPMC at 0.2%, hydrocolloids significantly decreased the onset temperature during pasting. It must be pointed out that HPMC gelation might partially mask the onset temperature, and most likely this temperature will correspond to the hydrocolloid gelation.

To ensure that the observed effects were not due to starch dilution, starch suspensions with the same starch concentration contained in the starch-hydrocolloid mixtures were tested (results not showed). No significant effect on the onset temperature was observed when the starch concentration varied from 7.2% to 8.0%. Therefore, hydrocolloids are responsible for the earlier starch swelling that occurred at lower temperature, probably by inducing the disruption of starch granule integrity (Liu et al., 2003) or interacting with leached amylose as occurred with corn starch-carboxymethylcellulose pastes (Shi & BeMiller, 2002).

The peak viscosity of the guar and xanthan gum (concentration higher than 0.2%) starch dispersions increased, whereas HPMC did not modify this parameter at any of the level tested. Starch dilution in the starch–hydrocolloid mixtures may result in a viscosity decrease. In fact, when starch dispersions with concentrations ranged from 7.2% to 8.0% were analyzed, viscosities along the pasting curve showed a significant decrease with dilution (results not showed). Therefore, the increase in peak viscosity observed with the lower starch levels and higher hydrocolloid levels must be attributed to the starch–hydrocolloid interactions.

The breakdown was only significantly (p < 0.05) affected by guar gum, which increased this parameter and thus reduced the stability of the rice starch paste during cooking. Guar gum was the hydrocolloid that mostly affected the pasting properties during heating, likely indicating strong interaction between the galactomannan structure and the starch molecules. HPMC showed the least interaction with starch, despite its similar neutral structure to guar gum. Presumably, limited thermodynamic compatibility between HPMC and starch as has been observed with protein polymers (Rosell & Foegeding, 2007) might explain this behaviour. No decrease in the paste viscosity during holding at 95 °C was detected in the mixtures of rice starch–xanthan gum. This hydrocolloid, due to its anionic character, modifies the starch gelatinization process by stabilizing the integrity of the starch granule during heating and retarding amylose leaching (Shi & BeMiller, 2002).

Starch–hydrocolloid mixtures had significantly (p < 0.05) higher final viscosities or viscosities at 50 °C than the starch paste, with the



**Fig. 2.** Dynamic mechanical spectra of different pastes containing rice starch and various hydrocolloids measured at oscillatory stress of 0.5 Pa and 65 °C. Closed symbols referred to storage modulus (G') and open symbols designated loss modulus (G''). The number in the legends described the hydrocolloid concentration (%, w/w) in the starch–hydrocolloid blends.

exception of 0.2% xanthan gum. Bárcenas, De la O'Keller, and Rosell (2009) reported that HPMC did not affect the pasting properties of wheat starch during heating, but increased the final viscosity during cooling. The same findings have been described for rice starch (Techawipharat et al., 2008). Peak viscosity, breakdown and final viscosity of guar and xanthan gums with tapioca starch increased but the setback viscosity decreased with guar gum and increased with xanthan (Chaisawang & Suphantharika, 2006).

#### 3.2. Hydrocolloid-starch gel viscoelasticity

The viscoelastic parameters were determined for the rice starch and hydrocolloid mixtures with a constant total concentration of 8% (Fig. 2 and Table 2). Measurements were carried out at 65°C to limit the degree of retrogradation after pasting (Zhong et al., 2009). The magnitude of the viscoelastic moduli for rice starch paste agrees with previously reported values (Zhong et al., 2009). The starch pastes behaved as a gel (G' > G'') and the same behaviour was observed in the presence of the different hydrocolloids tested (Fig. 2). The viscoelastic behaviour of starch pastes within concentration range of 7.2-8.0% was determined to assess the magnitude of the effect of starch dilution (results not showed). A decrease in the starch concentration slightly decreased the storage and loss moduli, but the loss tangent was not significantly modified. Therefore, in the range of starch concentration studied with the hydrocolloid mixtures, starch only gels had similar rheological characteristics. Therefore, changes in the viscoelastic parameters observed in the presence of hydrocolloids must be ascribed mainly to the gums effect on the gel structure.

The viscoelastic moduli of the hydrocolloid-starch gels as a function of the frequency were determined (Fig. 2). The rice starch paste had typical biopolymer gel behaviour where G' was higher than G'' along the frequency sweep and both moduli were frequency-dependent. The hydrocolloids tested modified the dynamic mechanical spectra of the rice starch, although different trends were observed. The G" mechanical spectrum was affected to a greater extent than that of G'. All the hydrocolloids increased G" and that enhancement was dependent on hydrocolloid concentration. Guar gum induced a progressive increase of G', whereas xanthan gum produced that effect when pastes contained more than 0.2% gum, and resulting pastes had higher frequency dependence. Xanthan gum at 0.2% resulted in a decrease of G' at low frequencies. HPMC had the smallest effect on G' and only at levels of 0.5 and 0.8% reduced G' at low frequency and the opposite effect was induced at high frequencies. The trend change observed when increasing xanthan gum or HPMC can be ascribed to phase separation process as has been observed with waxy corn starch and xanthan gum blends (Achayuthakana & Suphantharika,

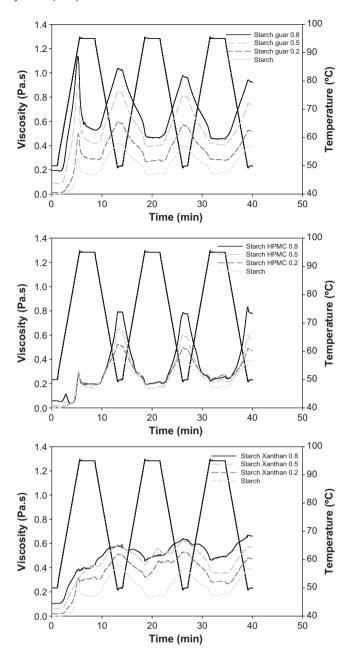
Increasing levels of xanthan and guar gum resulted in a significant (p < 0.05) increase in the magnitudes of G' and G' (Table 2), which agrees with previous observations (Kim & Yoo, 2006). HPMC also induced a significant (p < 0.05) increase of both moduli, but no tendency with the hydrocolloid level was observed in G'. The loss tangent,  $\tan \delta$ , significantly (p < 0.05) increased in the presence of hydrocolloids, with the exception of 0.2% HPMC. Therefore, these hydrocolloids led to weaker structures with less gel-like character than the rice starch alone. Similar findings have been obtained with waxy rice starch and guar gum indicating that the starch network shifted from an elastic-like nature to a more viscous-like (Kulicke et al., 1996). HPMC at 0.8% had the greatest increase in tan  $\delta$ , which has been partially related to its ability for reducing or preventing amylose retrogradation (Techawipharat et al., 2008). Xanthan gum was the most effective at increasing the magnitude of tan  $\delta$  even at the lowest level tested (0.2%), and further concentration increases resulted in a significant reduction in the loss tangent. This unique effect could be ascribed to xanthan's rod-like conformation which is more responsive to shear thinning (Kim & Yoo, 2006). Rice starch led to more structured and more solid like (lower  $\tan \delta$ ) gels than those obtained with hydrocolloid mixtures (Techawipharat et al., 2008).

The mechanical spectra of logarithmic plot of G' or G" versus frequency of the blended gels were evaluated by linear curve fitting (Table 3). The intercept corresponds to the magnitude of G' or G'' and the slope will give information about the frequency dependence of the sample (Hayta & Schofield, 2004; Rosell & Gómez, 2006). Threedimensional polymer networks should have zero slope, whereas low values would indicate an intermediate network structure containing highly crosslinked material mixed with some uncrosslinked one (Kokini, Cocero, Madeka, & de Graaf, 1994). An increase of the hydrocolloid level resulted in a steady increase of the slope and intercept of G', with the exception of HPMC that did not change intercept values and 0.2% xanthan gum that decreased the intercept. Kim and Yoo (2006) also described a less stabilized starch network with rice starch-xanthan gum mixtures of 0.2% gum. Guar gum and xanthan gum resulted in gels with decreased elasticity and lower resistance to deformation. In the case of xanthan gum, an increase in the intercept with increasing gum level has been attributed to the thickening properties of xanthan gum in the continuous phase (Kim & Yoo, 2006). The incorporation of HPMC resulted in a more elastic network, but with low resistance to deformation. Generally, the linear fitting curve show that rice starch-hydrocolloids mixtures result in a weak network structure where crosslinked zones alternate with ordered chain segments that do not allow crosslinking. Guar gum and xanthan decreased the frequency dependence on G'' as indicated by the decreased slope and increased intercept (Table 3). No trend with HPMC concentration was observed in the slope of G''. Similar effects on G''were obtained with tapioca starch added to guar gum or xanthan gum solutions but with less frequency dependence (Chaisawang & Suphantharika, 2006). The increase in the intercepts and the slopes confirmed the hypothesis that the number of junction zones in helically structured starch polysaccharides decrease and result in an intermediate network structure with a different viscoelastic behaviour that will depend on the ratio of starch to hydrocolloid (Kulicke et al., 1996).

#### 3.3. Multiple heating-cooling cycles

Hydrocolloid-starch pastes were successively heated and cooled in order to determine if thermal treatments could either intensify or weaken the network structure (Fig. 3). After gelatinization, traces with high viscosities during cooling and low viscosities during heating were observed that indicated the reversibility of the gels. During heating a viscosity shoulder was repeatedly observed in the starch pastes and the magnitude of this peak did not change in the presence of the hydrocolloids. On cooling, the dispersed starch molecules form a gel, which retrogrades gradually with the formation of new semi-crystalline regions that differs greatly from the crystalline structure of the native granule (Copeland, Blazek, Salman, & Tang, 2009). Likely, the presence of the observed stable shoulders are indicative of those semi-crystalline order structures, which were more stable than the original crystalline structures since they occur at higher temperatures and since no variation was detected when successive heating-cooling cycles were applied.

Higher final viscosity is related to the formation of gels with looser molecular structure and widely spaced junction zones (Salman & Copeland, 2010), therefore a progressive decrease in the maximum viscosity along successive cooling cycles, might indicate the formation of tighter gels due to the alignment of the starch chains favoured by the temperature increase and the shear



**Fig. 3.** Pasting curves of rice starch–hydrocolloids dispersions (8%, w/w) measured in a rotational rheometer when subjected to multiple heating–cooling. The number in the legends described the hydrocolloid concentration (%, w/w) in the starch–hydrocolloid blends.

stress. In the presence of HPMC, a reproducible second viscosity peak was observed when the temperature was held at 95 °C. The same observation was described by Shi and BeMiller (2002) when phosphorylated maize starch was heat in  $\lambda$ -carrageenan solution, although in the present study it could not be explained by charge interaction. A plausible explanation could be the formation of gel aggregates whose association was aided by the successive formation and melting of the gels, similarly to the observation when lipids aggregated because exceeding its solubility in starch pastes (Salman & Copeland, 2010).

The evaluation of the mechanical spectra of the gels subjected to successive heating cooling cycles showed profound changes in the viscoelastic behaviour, and in consequence in the network structure. Intercepts and slopes obtained from fitting the

**Table 3**Slope and intercept value obtained from the regression lines of viscoelastic moduli versus frequency for different rice starch–hydrocolloids blends.

Sample	Level (%)	One cycle		Multiple cycles									
		G'			<i>G</i> "			G'			G"		
		Intercept	Slope	$R^2$	Intercept	Slope	$R^2$	Intercept	Slope	$R^2$	Intercept	Slope	$R^2$
Control	0	1.73	0.105	0.94	0.99	0.305	0.98	1.65	0.070	0.91	0.93	0.302	0.99
Guar gum	0.2	1.75	0.141	0.97	1.12	0.241	0.98	1.68	0.150	0.98	1.10	0.283	0.99
Guar gum	0.5	1.86	0.162	1.00	1.31	0.197	0.95	1.89	0.151	0.99	1.31	0.217	0.96
Guar gum	0.8	2.04	0.175	0.99	1.50	0.178	0.96	2.05	0.163	0.95	1.52	0.199	0.96
HPMC	0.2	1.84	0.124	0.98	1.15	0.206	0.95	1.65	0.137	0.97	1.10	0.293	0.99
HPMC	0.5	1.74	0.162	1.00	1.20	0.243	0.99	1.66	0.174	1.00	1.18	0.316	0.98
HPMC	0.8	1.80	0.213	0.99	1.32	0.224	0.99	1.86	0.169	0.99	1.33	0.247	0.99
Xanthan	0.2	1.61	0.177	1.00	1.14	0.293	1.00	1.64	0.178	0.99	1.06	0.269	1.00
Xanthan	0.5	1.89	0.203	0.99	1.41	0.206	0.99	1.76	0.245	0.98	1.35	0.209	0.99
Xanthan	0.8	2.04	0.220	0.96	1.55	0.146	0.99	2.03	0.209	0.98	1.52	0.144	0.99

Slope of  $\log G'$  or G'' vs.  $\log$  frequency.

logarithmic plot of G' and G'' versus frequency changed after multiple heating-cooling cycles (Table 3). Starch gel showed a decrease in the slope of G' and G'', which would be indicative of a more ordered structure consistent with greater alignment of starch chains during repeated cycles. The gels obtained in the presence of hydrocolloids showed diverse behaviour depending on the hydrocolloid concentration. After repeating cycles, gels containing low hydrocolloid concentration (0.2% or 0.5%) showed higher G' slope that would correspond to composite network structures with less number of junction zones among the biopolymers. Conversely, lower G' slope was observed in the gels containing the highest hydrocolloid level tested (0.8%), which might be attributed to improved network structure. In the case of guar gum, a slope reduction was also obtained with 0.5% gum level. These results could be ascribed to phase separation process that increase the hydrocolloid concentration in certain micro-domains (Alloncle & Doublier, 1991), which will favour the formation of a network structure with less gel-forming junction zones with the starch and more entanglements between the hydrocolloids chains as was observed with rice starch-galactomannans mixtures (Kulicke et al., 1996). Regarding loss modulus, higher slopes were obtained with guar gum and HPMC, whereas diverse effect was observed with xanthan gum depending on its concentration.

### 3.4. Swelling behaviour of rice starch in the presence of hydrocolloids

The impact of hydrocolloids on starch pasting properties may be due to interactions between specific gums and starch molecules. namely amylose that leaches out during swelling. The effect of different levels of guar gum, HPMC and xanthan gum on the swelling power, swelling capacity and solubility index was studied (Table 4). Hydrocolloids significantly affected the amount of solids leached out from the starch. It should be expected that the SI increases in the presence of hydrocolloids since hydrocolloids themselves are soluble in water. However, different trends were observed depending on the hydrocolloid tested. SI was significantly (p < 0.05) decreased by 0.05 and 0.125% guar gum but SI increased with increasing hydrocolloid concentration, and SI was the same as the control with 0.2% guar gum. Possibly guar gum and the amylose leached during swelling interact and remain associated with the starch granules yielding lower amount of water solubles, but when excessive guar gum was present in the continuous phase the viscosity increases the osmotic pressure favouring the amylose leaching and granule swelling. Iodine values used to quantify leached amylose also increase with increasing guar gum concentration (Table 4). Liu et al. (2003) suggested that lower solubility and swelling could be inter-

**Table 4**Effect of different hydrocolloids on the solubility index (SI), swelling power (SP), swelling capacity, and iodine binding absorbance of rice starch after one heating–cooling cycle or after three successive heating and cooling cycles. Iodine binding is expressed in absorbance at 690 nm.

Sample	Level (%)	SI (%)	SP(g/g)	Swelling capacity (g/g)	Abs <sub>690nm</sub>
One cycle					
Control		$17.7 \pm 0.4c$	$18.5 \pm 0.2$ de	$15.2 \pm 0.2c$	$0.373 \pm 0.022bc$
Guar gum	0.050	$6.7 \pm 0.2a$	$10.3 \pm 0.4a$	$10.0 \pm 0.4a$	$0.257 \pm 0.016a$
Guar gum	0.125	$12.8 \pm 0.5b$	$13.7 \pm 0.3b$	$13.2 \pm 0.2b$	$0.326 \pm 0.028$ ab
Guar gum	0.200	$16.7 \pm 0.6c$	$17.0 \pm 0.4c$	$16.7 \pm 0.4d$	$0.405 \pm 0.054 bcd$
HPMC	0.050	$18.5 \pm 0.0$ cd	$18.6 \pm 0.3$ de	$15.7 \pm 0.2c$	$0.655 \pm 0.016f$
HPMC	0.125	$24.3 \pm 0.1ef$	$17.8 \pm 1.1$ cd	$15.9 \pm 0.1$ cd	$0.484 \pm 0.089$ de
HPMC	0.200	$20.5 \pm 2.3d$	$19.6 \pm 0.6e$	$18.3 \pm 0.5e$	$0.304 \pm 0.045 ab$
Xanthan	0.050	$26.7 \pm 0.5f$	$24.5 \pm 0.3 f$	$18.7 \pm 0.2e$	$0.534 \pm 0.035e$
Xanthan	0.125	$24.0 \pm 0.6e$	$25.7 \pm 0.5 f$	$21.5 \pm 0.3f$	$0.384 \pm 0.008bcd$
Xanthan	0.200	$25.5\pm1.2ef$	$27.6\pm0.6g$	$24.2\pm0.5\mathrm{g}$	$0.441\pm0.036cde$
Multiple cycles					
Control		$21.5 \pm 0.2d$	$21.4 \pm 0.1e$	$16.8 \pm 0.1$ cd	$0.444 \pm 0.044$ abcd
Guar gum	0.050	$10.7 \pm 0.2a$	$11.3 \pm 0.4a$	$10.6 \pm 0.3a$	$0.348 \pm 0.019a$
Guar gum	0.125	$14.0 \pm 0.2b$	$14.5 \pm 0.4b$	$13.7 \pm 0.4b$	$0.365 \pm 0.025 ab$
Guar gum	0.200	$19.8 \pm 0.4c$	$18.3 \pm 0.3c$	$17.3 \pm 0.3d$	$0.419 \pm 0.019$ abc
HPMC	0.050	$24.8 \pm 0.3e$	$21.1 \pm 0.6e$	$16.5 \pm 0.5c$	$0.533 \pm 0.112cd$
HPMC	0.125	$21.8 \pm 0.2d$	$19.7 \pm 0.2d$	$17.0 \pm 0.2$ cd	$0.573 \pm 0.027d$
HPMC	0.200	$20.7\pm1.1cd$	$20.8 \pm 0.3$ de	$19.7 \pm 0.1f$	$0.448\pm0.074 abcd$
Xanthan	0.050	$26.8\pm0.4f$	$24.6\pm0.5f$	$18.6 \pm 0.4e$	$0.490 \pm 0.014$ bcd
Xanthan	0.125	$25.5\pm0.7ef$	$25.6\pm0.5 g$	$21.1\pm0.3g$	$0.457\pm0.022abcd$
Xanthan	0.200	$25.3 \pm 0.9ef$	$28.3 \pm 0.4h$	$24.9 \pm 0.2h$	$0.477\pm0.022 abcd$

 $Mean \pm standard\ deviation\ (\textit{n} = 4).\ Different\ letters\ within\ a\ column\ and\ treatment\ denote\ significantly\ different\ levels\ (\textit{p} < 0.05).$ 

 Table 5

 Correlation matrix between swelling, pasting and viscoelastic parameters of rice starch-hydrocolloids mixtures.

	SP (g/g)	Swelling capac- ity (g/g)	Abs <sub>690nm</sub>	G' (Pa)	<i>G</i> " (Pa)	Loss tangent tan $(\delta)$	Initial viscosity (Pa·s)	Onset temperature (°C)	Peak pasting temperature (°C)	Peak viscosity (Pa·s)	Through viscosity (Pa·s)	Breakdown (Pa·s)	Final viscosity (Pa·s)	Final viscosity- through viscosity (Pa·s)
SI (%) SP (g/g) Swelling capacity (g/g)	0.932***	0.824*** 0.903*** 0.518**	0.635*** 0.589** 0.058	-0.197 -0.276 0.273	0.004 -0.080 0.538**	0.442* 0.405* 0.230	-0.052 -0.108 -0.099	0.087 0.177 0.099	0.222 0.235 -0.166	-0.353 -0.421* -0.108	-0.279 -0.346 -0.202	-0.396* -0.464* 0.104	-0.161 -0.265 0.281	0.006 -0.102
Abs $_{690nm}$ $G'$ (Pa) $G''$ (Pa) Loss tangent $\tan (\delta)$				0.121	0.097 0.911***	0.101 0.136 0.525** 0.342	0.049 0.940*** 0.956*** -0.789***	0.234 -0.497** -0.761*** -0.091	0.048 -0.642*** -0.578** 0.118	-0.072 0.889*** 0.808*** 0.234	-0.016 0.873*** 0.834*** 0.039	-0.109 0.886*** 0.778*** 0.374*	-0.030 0.933*** 0.964*** 0.395*	-0.035 0.700*** 0.791***
Initial viscosity (Pas)								-0.607***	-0.708***	0.892***	0.891***	0.879***	0.942***	0.696***
Onset temperature (°C)									0.330	-0.509**	-0.567**	$-0.462^{*}$	-0.728***	-0.659***
Peak pasting temperature										-0.836***	-0.840***	-0.820***	-0.588**	-0.153
(°C) Peak viscosity (Pas)											0.986***	0.994***	0.846***	0.441*
Through viscosity (Pas)												0.960***	0.841***	0.419*
Breakdown (Pas)													0.836***	0.449*
Final viscosity (Pas)														0.844***

Correlations indicated by  $R^2$  values.

<sup>\*\*\*</sup> p-value < 0.001.

<sup>\*\*</sup> p-value < 0.01.

<sup>\*</sup> *p*-value < 0.05.

actions within the starch granule via hydrogen bonds induced by the gum presence.

The presence of HPMC or xanthan gum increased SI, but no tendency could be observed with the hydrocolloid concentration. In addition, the iodine values increased when low levels of these hydrocolloids were present, likely indicating that more amylose leached out of the starch granule.

The impact of hydrocolloids on starch swelling is shown in Table 4. Guar gum significantly (p < 0.05) decreased SP and swelling capacity compared to control, but SP and swelling capacity increased with the hydrocolloid concentration. HPMC did not affect the starch swelling, which agrees with the behaviour observed in the pasting studies. In opposition, increasing levels of xanthan gum induced steady increase of the SP and swelling capacity. The addition of hydrocolloids forces the leaching of amylose at temperatures above the gelatinization, likely due to the shear forces exerted by the hydrocolloids onto the surface of the swollen starch granule (Christianson et al., 1981) or the osmotic pressure exerted by the continuous hydrocolloid phase onto the starch phase (Song, Kwon, Choi, Kim, & Shin, 2006). As a consequence of the shear forces or pressure on the starch granule increases the water uptake and the material exuded into the continuous phase (Techawipharat et al., 2008). It has also been suggested that the effect on swelling by gelling hydrocolloids may be an artefact. The high viscosity of the continuous phase may impede the settling of the swollen granules during centrifugation (Song et al., 2006). Likely, both effects must be considered for explaining the effects exerted by hydrocolloids on starch swelling. In the case of guar gum shear forces exerted on the granule are responsible for the swelling decrease, whereas high xanthan gum viscosity caused the increase in swelling, likely the different structure of both hydrocolloids might be responsible of that behaviour.

When starch-hydrocolloids blends were subjected to multiple heating-cooling cycles, results showed the same tendency observed with one heating-cooling cycle, but in general increased values were obtained for all the parameters. Likely, successive heating-cooling cycles increased the amount of released soluble compounds present in the continuous phase due to the better network arrangement as supported the viscoelastic and pasting observations.

### 3.5. Relationships between pasting, rheological and swelling characteristics

The effect of hydrocolloids on starch functionality has been commonly studied by following the pasting, the viscoelastic characteristics of the gels and the swelling properties. Those studies provided valuable information for understanding the possible interaction between the hydrocolloid chains and the starch biopolymer. Swelling, pasting and viscoelastic properties might be related among them, since those properties are somewhat interconnected and all of them are reflecting the possible network structure.

Experimental data from pasting, small deformation rheology and swelling were submitted to multivariate analysis to obtain information on the possible significant correlations within those parameters. A range of correlation coefficients was obtained by using Pearson correlation analysis (Table 5). Swelling parameters (SI, SP, swelling capacity) were highly and positively correlated, and the lowest correlation coefficients were obtained with the iodine binding. It has been previously reported when studying different starches that SI showed a non-linear relationship with SP, showing a linear positive relationship for low SI, but there is a limiting SI value after which SP decreases due to the amount of leached solids (Li & Yeh, 2001). Swelling power had a negative relationship with peak viscosity and breakdown, that effect might be related with the

stability of the granule to keep its integrity. Wheat starch paste peak viscosity is highly correlated with starch swelling power (Crosbie, 1991), thus the negative relationship obtained in the present study might be related to the interference of the high viscosity with the settling down of the swollen granules required for determining the swelling index, as has been previously described that was mainly observed in the rice starch–xanthan gum mixtures.

Regarding viscoelastic properties, loss tangent showed positive relationship with swelling related parameters (SI, SP and swelling capacity). Therefore, more swollen granules would produce less rigid paste, which agree with the effect previously described that hydrocolloids led to weak structures. Similar result was observed when tested different types of starches (Li & Yeh, 2001). Highly significant correlations were found between the viscoelastic moduli and the pasting properties. Viscoelastic moduli showed negative relationship with onset temperature and peak pasting temperature, but the correlation was positive with initial viscosity, peak viscosity, through, breakdown, final viscosity and also with the parameter related to amylose retrogradation (final viscosity-through viscosity). Within the pasting properties, initial viscosity, peak viscosity, through and final viscosities showed many relationships. Therefore, parameters that define the swelling behaviour of the starch-hydrocolloid mixtures were significantly correlated with viscoelastic properties and also pasting properties.

#### 4. Conclusions

The pasting and rheology of the rice starch paste are strongly affected by the particular hydrocolloid added and the level of replacement. Gelling hydrocolloids induced the greatest effect on the rice starch pasting properties, whereas rice starch-HPMC mixtures only differed in the viscosity during cooling. The incorporation of hydrocolloids on the rice starch pastes originated weaker structures with less gel-like character than the starch alone. The viscoelastic behaviour might be derived of the intermediate network structure resulted from the reduced number of junctions zones of the starch combined with hydrocolloids entanglements. When starch-hydrocolloid pastes were subjected to multiple heating-cooling cycles, a progressive reduction of the maximum viscosity during cooling indicate the formation of tighter gels due to the alignment of the starch chains favoured by the temperature increase and the shear stress. In addition, the viscoelastic properties of the resulting gels suggested that while the mixtures with low hydrocolloid concentration kept composite network structures, the gels with high hydrocolloid concentration underwent phase separation due to the chains rearrangement favoured by successive heating-cooling cycles.

Swelling parameters (SI, SP, swelling capacity) were highly and positively correlated, and they also had a significant positive relationship with loss tangent. Highly significant correlations were found between the viscoelastic moduli and the pasting properties. The correlation matrix showed that swelling, pasting and viscoelastic properties were highly correlated.

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