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Rheological properties of rice–locust bean gum gels from different rice varieties

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ABSTRACT

Pasting and gelatinization behavior of rice gels from *Japonica* (Ariete, Euro), *Indica* (Gladio, Suriname) and *waxy* (Glutinous) varieties were analyzed. These varieties differ widely in amylose contents and differential scanning calorimetry (DSC) gelatinization temperatures. Besides, the effect of locust bean gum (LBG) addition and the impact of successive viscoanalyser multiple-heating–cooling and freezing–thawing cycles on the gels pasting viscosities (peak-η_{peak}, trough-η_{min}, final-η_{final}), viscoelasticity by oscillatory rheometry and syneresis were evaluated.

Flours from different rice varieties exhibited distinct viscoanalyser curves and viscoelastic behaviors as well as different degree of syneresis. Euro and Ariete showed lower setback from peak (η_{final}–η_{peak}) and syneresis, whereas Waxy had η_{peak} superior to η_{final} (negative setback) and did not exhibit syneresis.

The addition of LBG (0.5%, 1%, 2% w/w) significantly modified the pasting viscosities in single and multiple profiles, viscoelastic and syneresis properties of rice gels and the extent of the effect was dependent of rice varieties. In general, the addition of LBG caused an increase in peak, final and minimum viscosities but only rice gel from Ariete variety exhibited reduction of setback. Reduction of syneresis seems evident for 0.5% LBG addition on rice gels from Suriname and Ariete varieties, but 1% was needed for Gladio variety.

Successive multiple-heating–cooling cycles led to a progressive decrease on viscosity after a second cycle for Japonica and Waxy varieties, in Indica varieties these peak viscosities were maintained or decreased in a lesser degree, syneresis was higher than in single cycles and is largely reduced in the presence of LBG.

This study provides knowledge of different rheological behavior of rice varieties that would be relevant for utilization of rice gels on food applications.

1. Introduction

Rice (*Oryza sativa*) is one of the major cereal crops worldwide and it is consumed principally as a grain obtained from specific varieties. The understanding of their rheological behavior is very important for optimizing industrial applications and allowing consumer to select appropriate types for different culinary recipes.

Rices are commercially classified according to grain morphology into three types: short or round (up to 5.2 mm long), medium (up to 6 mm long) and long (more than 6 mm long). Short or medium grain rices that are more known in Europe are from subspecie *Japonica* varieties Arborio, Carnaroli, Vialone Nano from Italy or Bahia, Senia, Bomba from Spain and long grains are Ariete and EuroSis, grown in France and Portugal. These grains are capable of absorbing a great amount of water without excessive softening. On the other hand, long grains from *Indica* subspecie varieties like Thaibonnet, Gladio and Suriname have different cooking behavior (Rosell, Brites, Pérez, & Gularte, 2007). These varieties may differ in chemical and rheological properties and depend largely of starch composition, a major component of rice grain.

Rice starch represents about 90% of grain matter (Iturriaga, López de Mishima, & Añón, 2006) and it is composed of two major types of molecules – amylose and amylopectin that exhibit important structural differences. Amylose is a linear chain of D-glucopyranose units linked by α (1-4) bonds and with few branches, whereas amylopectin is a highly branched molecule consisting of α (1- 4) linked D-glucopyranose chains that are connected by α (1- 6) branch linkages (Jane, 2004, chap. 7).

Starches develop viscosity when cooked or processed. This functional property is based on the characteristic thermal

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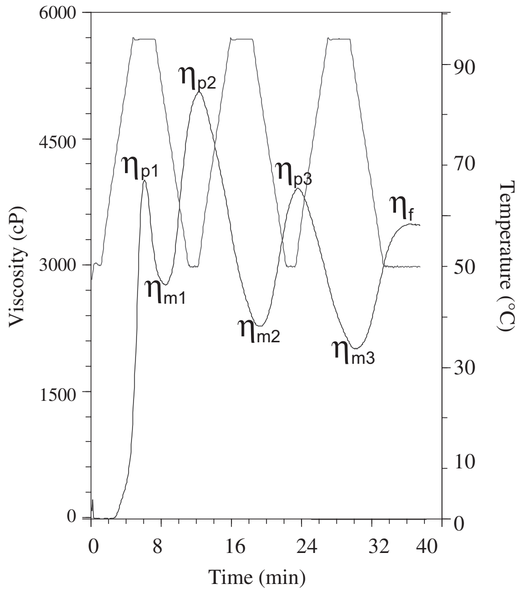

Fig. 1. Rapid viscoanalyser temperature profile for multiple heat–hold–cool cycles and typical curve response showing the parameters determined: peak viscosities in the first cycle when heating (η_{p1}) and cooling (η_{p2}), maximum viscosity during second cycle (obtained at cooling) (η_{p3}), final viscosity after the three cycles application (η_f) and minimum viscosities or troughs (η_{m1}, η_{m2}, η_{m3}).

transition of starch, gelatinization, which involves the lost of the native crystalline organization of granule when it is heated above a particular temperature in an aqueous medium. After cooling, starch can gel due to hydrogen bonding. When these gels are stored, amylose and amylopectin develop a double helical crystalline structure with less water binding capacity. Amylose linear molecules render double-helical crystallites faster than amylopectin, whose rate of retrogradation depends on branch-chain length; the longer the branch chains, the faster it crystallizes (Lai, Lu, & Lii, 2000). These structural characteristics, along with the proportion of amylose/amylopectin in starch granule, are dependent of rice variety.

Different cultivars of waxy and non-waxy rices are usually classified according to their amylose content and gelatinization properties of the extracted starches. Yu, Maa, and Sun (2009) found that in cooked rice, amylose content correlated with starch retrogradation and also with the hardness increase during storage. In rice starch gels, the amylose/amylopectin ratio was found to affect hardness (Hibi, 1998) and retrogradation rate after storage (Mariotti, Sinelli, Catenacci, Pagani, & Lucisano, 2009). Tran, Okadome, Murata, Homma, and Ohtsubo (2001) have reported that in rice, amylose mainly influences texture and stickiness and amylopectin is more associated to gelatinization temperature, pasting and cooking properties.

Processing and marketing of rice based ready to eat foods has increased considerably in recent years, generating a growing need to study their rheological behavior in cycles of heating, freezing and thawing. Native starches do not generally have ideal properties for

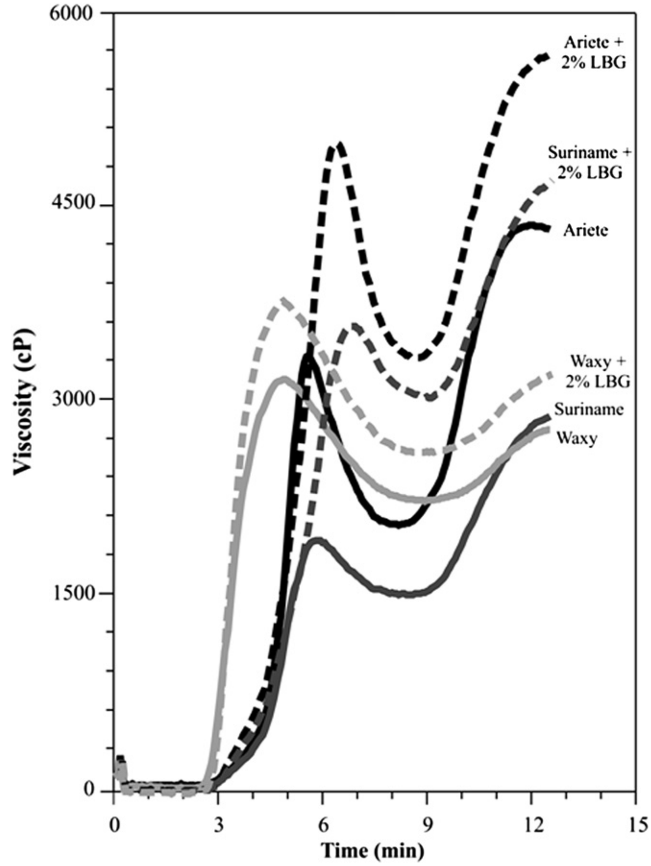

Fig. 2. Rapid viscoanalyser pasting curves of rice flours from Ariete, Suriname and waxy varieties (solid line) and effect of adding 2% LBG (dash line).

the preparation of ready to eat foods due to their tendency to syneresis and retrogradation. They exhibit breakdown and produce weakbodied, cohesive, rubbery pastes, and undesirable gels. All these undesirable phenomena depend on starch composition characteristics (particularly amylose:amylopectin ratio), fat and protein contents, starch:water ratio, processing temperature (Jacobson, Obanni, & Bemiller, 1997) and is further exacerbated after freezing and thawing with detrimental effects in the texture, and acceptability of starch-containing foods.

Therefore, in order to prevent the syneresis and other changes in physical properties of starch gels induced by freezing and thawing, hydrocolloids are frequently used as additives to control the texture and stability of frozen foods (Ferrero, Martino, & Zaritzky, 1993a, 1993b).

Synergistic interactions between rice starches and hydrocolloids have been demonstrated, such as increases in RVA peak and final viscosities and decreases on the enthalpy of gelatinization and on the long-term retrogradation (Banchathanakij & Suphantharika, 2009; Hongsprabhas, Israkarn, & Rattanawattanaprakit, 2007; Satrapai & Suphantharika, 2007; Techawipharat, Suphantharika, & BeMiller, 2008). However, concerning the network formation and

Table 1
Amylose content and thermal properties of rice flours expressed as DSC (means ± standard deviation) onset – T_o, peak – T_p and final – T_f temperatures (°C), enthalpy (ΔH, J/g), range (T_f–T_o) and PHI ($\Delta H/T_p - T_o$).

Varieties	Amylose (%)	T_o (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	Range (°C)	PHI
Ariete	18.5	59.3 ± 2.0	69.9 ± 0.8	81.7 ± 1.7	7.9 ± 0.5	22.4 ± 3.7	0.8 ± 0.3
Euro	15.4	59.3 ± 0.9	68.3 ± 0.4	81.9 ± 2.0	5.9 ± 0.6	22.6 ± 1.0	0.7 ± 0.1
Gladio	24.5	61.9 ± 0.5	73.9 ± 0.6	83.5 ± 0.4	8.5 ± 0.6	21.6 ± 0.4	0.7 ± 0.1
Suriname	26.5	60.7 ± 0.5	70.8 ± 0.1	84.2 ± 0.3	8.7 ± 1.5	23.6 ± 0.7	0.9 ± 0.2
Waxy	1.3	60.1 ± 0.6	68.4 ± 0.4	83.6 ± 1.0	11.5 ± 0.5	23.5 ± 1.1	1.4 ± 0.2

the viscous nature of gels through G′ and G″ measurements, opposite effect have been observed in different studies (Kim, Lee, & Yoo, 2006; Kulicke, Eidam, Kath, Kix, & Kull, 1996; Yoo, Kim, & Yoo, 2005). Different pastes and gel characteristics were obtained with different specific rice starch–hydrocolloid combinations, methods of preparation, and conditions during measurement, in some cases increasing network formation and in other cases decreasing or weakening the network formed.

Within hydrocolloids, locust bean gum (LBG) is the gum obtained from the seeds of the carob tree (*Ceratonia siliqua* L.). World carob pod production is approximately 315,000 t per year; the main producing countries are Spain (42% of total production), Italy (16%), Portugal (10%), Morocco (8%), Greece (6.5%), Cyprus (5.5%) and Turkey (4.8%) (FAO, 1995, chap. 3; Fletcher, 1999). This data suggest the importance of carob derivatives and particularly LBG as food ingredients. LBG is a galactomannan polysaccharide that mainly consists of a linear chain of mannose linked by β (1→4) bonds and galactose units as side chains with α (1→6) linkages (Wielinga & Maehall, 2000, chap. 8). This polysaccharide is widely used in food industry as a thickener agent because of its capability of binding water, increasing viscosity of water suspensions (Garcia Ochoa & Casas, 1992) and freeze–thaw resistance of gels (Lo & Ramsden, 2000).

Most of existing studies that evaluate the effect of hydrocolloids on pasting and freeze/thaw stability have been carried out in rice starch and water systems. However, systems that contain whole grain flour in a gel matrix, such as desserts, sweet and sour sauces are more representative of rice based ready to eat foods and should be studied.

The objective of this work was to study the pasting and gelatinization behavior of five rice varieties differing widely in amylose contents and differential scanning calorimetry (DSC) gelatinization temperatures. The effect of LBG addition and the impact of successive viscoanalyser multiple-heating–cooling and freezing–

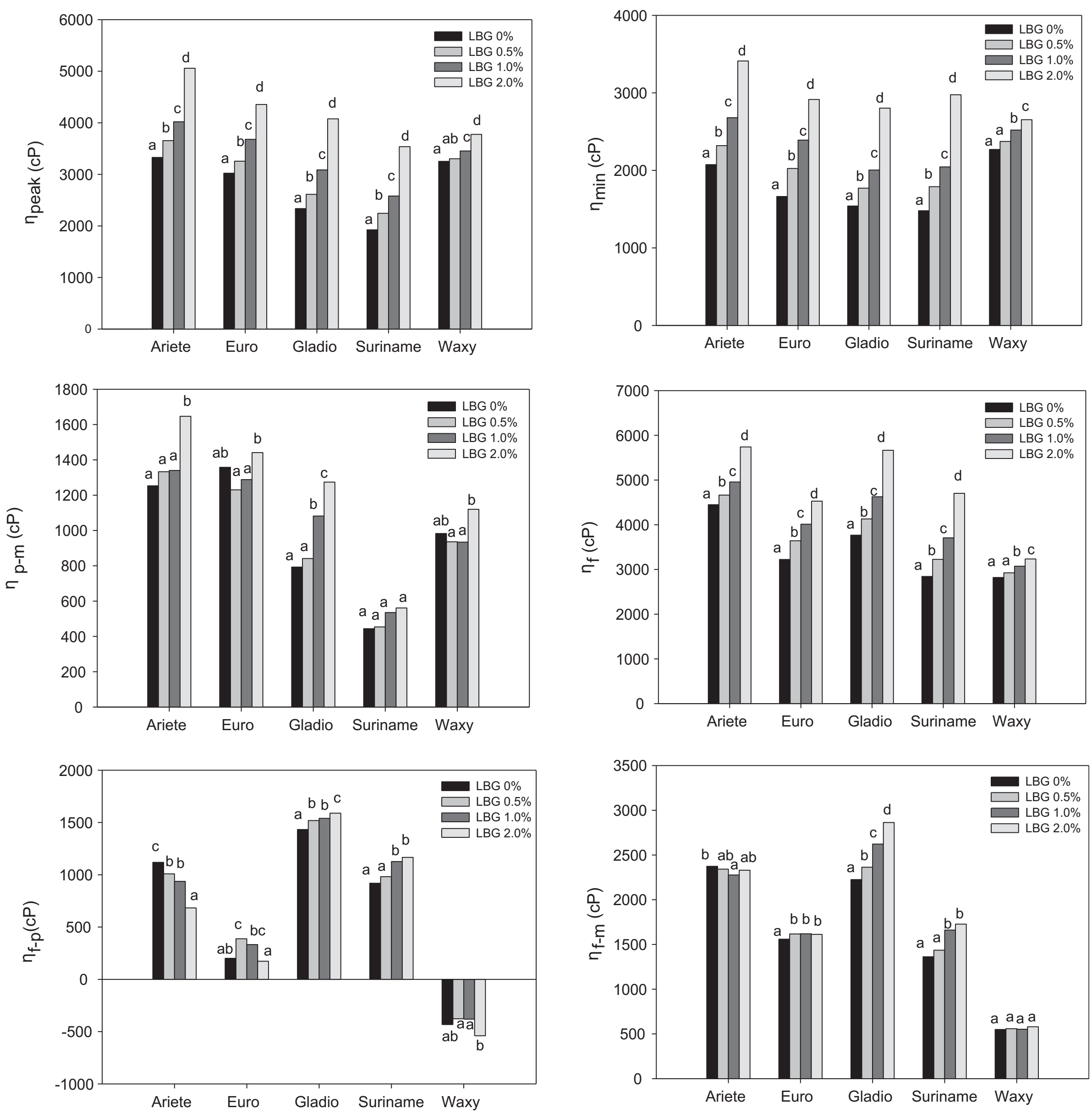

Fig. 3. Rapid viscoanalyser pasting parameters of rice flours varieties and effect of increasing levels of LBG. η_{peak}: peak viscosity, η_{min}: minimum viscosity or trough, η_{final}: final viscosity, $\eta_{p\text{-}m}$: breakdown or difference between peak and minimum viscosity, $\eta_{f\text{-}p}$: setback from peak or the difference between final and peak viscosity, $\eta_{f\text{-}m}$: setback from the minimum viscosity or the difference between final and minimum viscosity. Different letters indicate significant differences within each variety ($P < 0.05$).

thawing cycles on the gels pasting viscosities, viscoelasticity by oscillatory rheometry and syneresis were also evaluated.

2. Materials and methods

2.1. Materials

Five long-grain rice varieties were analyzed; Ariete and Euro (*Japonica*), Gladio (*Indica*) obtained from COTARROZ (Portugal) that had been harvested in 2007, Suriname (*Indica*) and a Glutinous (*Waxy*) obtained from the local grocery store. Rice grains were milled in a Brabender Quadrumat Junior mill to obtain flour. Amylose content was determined according ISO 6647-2:2007 and a differential scanning calorimetry (DSC Q100 TA Instruments, USA) was used to characterize thermal properties of the five rice flours. DSC onset temperature (T_o), peak temperature (T_p), final temperature (T_f), and enthalpy of gelatinization (ΔH) expressed on dry weight basis were calculated by the equipment software (Universal Analysis 2000, TA Instruments, USA). Gelatinization range (R) as (T_f–T_o) and peak height index (PHI) by the ratio $\Delta H/T_p - T_o$ were calculated as described by Krueger, Knutson, Inglett, and Walker (1987). Samples for DSC assays were prepared in the following proportions: rice flour 3 g and water 25 g.

Locust bean gum (LBG) was provided by Industrial Farense LDA (Portugal) and is composed of galactomannans (min. 75%), protein (max. 7%) and ash (max. 1.2%).

2.2. Methods

2.2.1. Pasting properties of rice flour–LBG systems

A viscoanalyser (RVA-4 Newport Scientific Pty.LTD., Warriewood, Australia) was used to study the pasting properties of rice flours and rice–locust bean mixtures. The assays were performed according to the AACC 61-02.01 method (AACC International, 1999). Samples were prepared with 3 g rice flour (12% moisture), 25 g water and LBG at 0% (control), 0.5%, 1.0% and 2.0% levels (rice flour basis). Each sample was maintained during 1 min at 50 °C, then heated from 50 °C to 95 °C in 3 min 45 s, held at 95 °C during 2 min 30 s, cooled from 95 °C to 50 °C in 3 min 51 s and held at 50 °C for 1 min 24 s. The paddle speed was 960 rpm for the first 10 s and then 160 rpm for the rest of the cycle.

The following parameters were determined using the Thermocicline software for Windows (version 2.4 b 31) provided with the instrument: peak viscosity (η_{peak}), minimum viscosity or trough (η_{min}), final viscosity (η_{final}), breakdown or difference between peak and minimum viscosity ($\eta_{p\text{-}m}$), setback from peak or the difference between final and peak viscosity ($\eta_{f\text{-}p}$) and setback from trough or the difference between final and minimum viscosity ($\eta_{f\text{-}m}$). Each assay was performed by triplicate.

The effect of a multiple heat–hold–cool profile on pasting properties of rice flour–LBG systems was also analyzed. In this assay, samples were subjected three times to the standard heat–hold–cool profile as it is shown in Fig. 1. The parameters determined were: peak viscosities in the first cycle when heating (η_{p1}) and cooling (η_{p2}), maximum viscosity during second cycle (obtained at cooling) (η_{p3}) and final viscosity after the three cycles application (η_f). Minimum viscosities or troughs (η_{m1}, η_{m2}, η_{m3}) in each cycle were also obtained.

2.2.2. Freezing, thawing and syneresis of rice flour–LBG systems

The gels obtained from a standard heat–hold–cool assay and after three heat–hold–cool cycles as described in 2.2.1 were stored at −5 °C for 17 h and then thawed at room temperature for 3 h. After freeze–thaw cycling, the gels were centrifuged at 7000 rpm for 10 min (Centrifuge Sigma 200), the supernatant layer was removed and the water loss was determined by drying the supernatant in an oven at 130 °C for 2 h. The gel moisture was also determined to calculate the amount of water provided by the gel fragments that were present in the supernatant. The percentage of syneresis was calculated as the amount of water released per 100 g of rice gel and each assay was performed by triplicate.

2.2.3. Viscoelasticity properties of rice flour–LBG gels

Rice flour, distilled water and locust bean gum (0.0% and 2.0%) were used to prepare gels according to 2.2.2. Ingredients were heated for 5 min at 95 °C and subjected to stirring for gel preparation; the temperature was raised to 25 °C, before measuring the viscoelastic properties.

Viscoelastic behavior of gels was evaluated by dynamic oscillatory tests in a Haake RS600 controlled stress rheometer (Haake, Germany). A serrated plate–plate sensor system with a 1.5 mm gap between parallel plates was used. The assay was performed at 25 ± 0.1 °C and semisolid Vaseline oil was used to avoid gel dehydration during the test. Samples were allowed to rest 15 min before measurements to allow their relaxation. In order to determine the linear viscoelastic range, deformation sweeps were performed at a constant frequency (1 Hz). Frequency sweeps were performed at a constant stress value within the linear viscoelastic range. The G' (elastic or storage modulus), G'' (viscous or loss modulus) moduli and the complex viscosity (η^*) were analyzed. The assays were performed in duplicate.

2.2.4. Statistical analysis

Analysis of variance to evaluate the effects and the significance of differences among the varieties and LBG levels were,

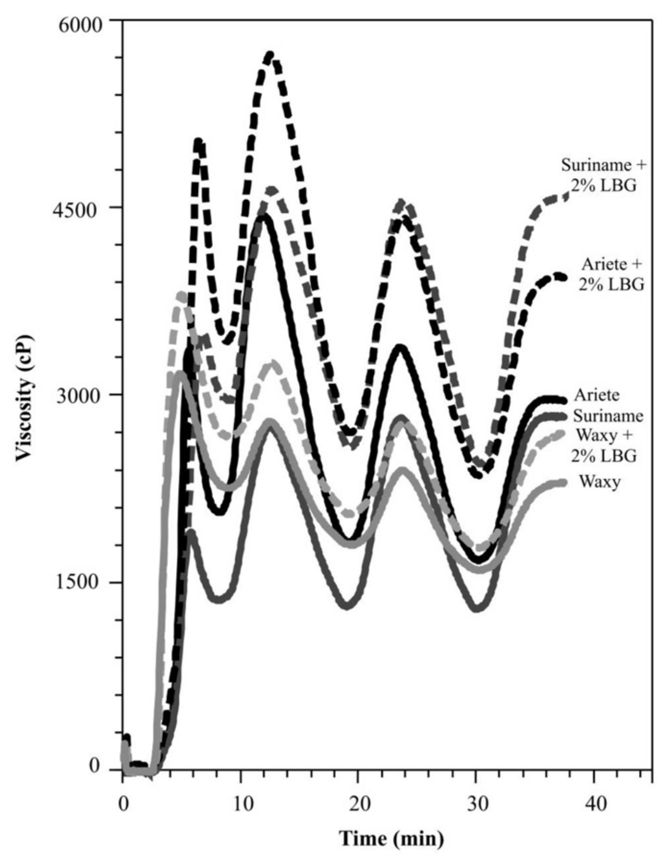

Fig. 4. Rapid viscoanalyser curves at three heat–hold–cool cycles of rice flours from Ariete, Suriname and waxy varieties (solid line) and effect of adding 2% LBG (dash line).

respectively, analyzed with the ANOVA procedure and Duncan's multiple range tests ($P < 0.05$) of the SAS/STAT® software (SAS Institute Inc., Cary, NC).

3. Results and discussion

3.1. Composition and thermal properties of rice flours

The amylose contents of rice varieties were found in a range from 1.3% to 26.5% (Table 1) and could be classified according to the amylose content as waxy (1.3%, Glutinous), intermediate (15.4%, Euro; 18.5%, Ariete) and high (24.5%, Gladio; 26.5%, Suriname). As expected, the flours from Indica type (Gladio, Suriname) had higher amylose contents than those from Japonica varieties (Ariete, Euro).

The rice flours gelatinization temperature (T_p) varied significantly (68.4–73.9 °C) and increased with higher amylose content, although no significant differences between different varieties in initial (T_o) and final (T_f) gelatinization temperatures were found. The presence of short chains (DP < 10) in amylopectin probably causes a decrease in the stability of the double helix, which could induce lower gelatinization temperatures on waxy and Japonica varieties (Gidley & Bulpin, 1987).

Waxy gelatinization enthalpy (11.5 J/g) was significantly higher than enthalpies for Japonica varieties (5.9–7.9 J/g) but no significant differences were found among Japonica and Indica varieties, despite the different amylose content.

The amylopectin molecular structure is related to crystalline structure of starch granules and this fact determines that more energy is needed for gelatinization in absence of amylose amorphous regions in waxy starches (Krueger et al., 1987).

No significant differences were found among gelatinization range nor PHI, but waxy rice showed a tendency to higher values of PHI due to the higher gelatinization enthalpy.

3.2. Pasting properties of rice flour–LBG systems

Pasting behavior curves of rice varieties analyzed using RVA are summarized in Fig. 2.

Peak viscosity (η_{peak}), trough (η_{min}), breakdown ($\eta_{p\text{-}m}$), final viscosity (η_{final}), setback from peak ($\eta_{f\text{-}p}$) and setback from trough ($\eta_{f\text{-}m}$) ranged from 1925 to 3328 cP, 1541 to 2270 cP, 444 to 1358 cP, 2820 to 4448 cP, −432 to 1432 cP and 550 to 2373 cP, respectively (Fig. 3), for the five rice flours. Japonica varieties, Ariete and Euro presented similar pasting profiles, with a higher η_{peak} and pronounced breakdown ($\eta_{p\text{-}m}$). In contrast, Gladio and Suriname (Indica varieties) exhibited a lower η_{peak}, less marked breakdown and highest setbacks. Peak viscosity is a parameter related to water binding capacity and to starch granule fragility (Copeland, Blazek, Salman, & Tang, 2009). These results would suggest that granules from Japonica varieties are more easily disrupted. This is confirmed by the higher values for breakdown or structural rupture due to heating ($\eta_{p\text{-}m}$) obtained for these samples. The lowest breakdowns ($\eta_{p\text{-}m}$) found for Indica varieties indicate that their starch granules were less susceptible to heating at 95 °C.

The most different profile was observed for the Waxy rice, whose composition consisted of amylopectin, with an absence of amylose. In this case, the starch granule swelled rapidly (lower gelatinization temperature) and to a great extent (higher η_{peak}).

Chung, Liu, Lee, and Wei (2011) studied rice starches from different sources and found an increase in setback and in final

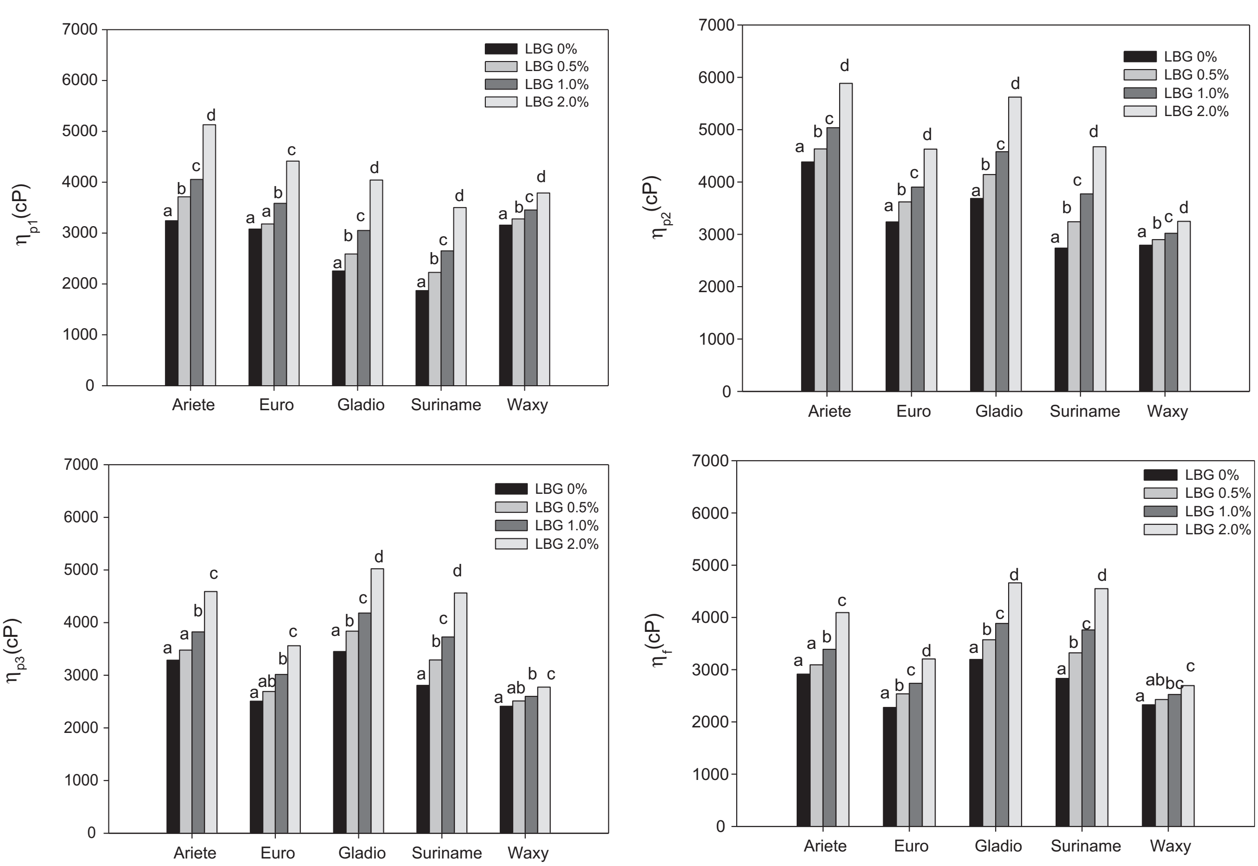

Fig. 5. Rapid viscoanalyser peak viscosities (η_{p1}, η_{p2}, η_{p3}) and final viscosities (η_f) at three heat–hold–cool cycles from rice pastes and effect of increasing levels of LBG. Different letters indicate significant differences within each variety ($P < 0.05$).

viscosity for varieties with higher amylose contents whereas the peak viscosity and breakdown showed negative correlations with amylose content. During the cooling of starch paste, leached amylose molecules rapidly aggregate and the formation of amylose junction zones is responsible for a setback and final viscosity (Jane et al., 1999). With no or less amylose present in waxy rice, setback and final viscosity were substantially low, whereas the highest setback and final viscosity were observed in Indica varieties with the highest amylose content, findings in agreement with Chung et al. (2011).

The effects of LBG addition on peak viscosity (η_{peak}), minimum viscosity (η_{min}), final viscosity (η_{final}), breakdown ($\eta_{p\text{-}m}$), setback from peak ($\eta_{f\text{-}p}$) and setback from the minimum viscosity ($\eta_{f\text{-}m}$) of the five rice gels are showed on Figs. 2 and 3.

Addition of LBG resulted in a marked increase in η_{peak}, η_{min} and η_{final} for all the non waxy rice varieties. In the case of waxy rice increase viscosity parameters were obtained only with LBG $\geq$1%.

An increase in rice starch peak viscosity in the presence of a hydrocolloid was previously reported by other authors (Banchathanakij & Suphantharika, 2009; Hongsprabhas et al., 2007; Rosell, Yokoyama, & Shoemaker, 2011; Satrapai & Suphantharika, 2007; Techawipharat et al., 2008). One of the possible causes for this behavior could be the interaction between the exudate from the starch granule (solubilized amylose and low-molecular weight amylopectin) and the hydrocolloid (Christianson, Hodge, Osborne, & Detroy, 1981). However, in galactomannan–rice starch systems another mechanism has been proposed by Kim et al. (2006). These authors found that viscoelastic moduli G' and G'' increased with the increase in gum concentration in the range of 0.2–0.8% and moduli of rice starch–LBG mixtures were in general higher than those of rice starch–guar gum mixtures. These findings would suggest that molecular structure of LBG, with a lesser degree of substitution (leading to more extended non-hairy regions) than guar, could favor a thermodinamically incompatible network structure in which interactions between polymers of the same type are favored. Besides, LBG could self-associate, driven by these segregative interactions with starch. Other authors have suggested that the higher viscosity can be related to a combination of the increased effective starch concentration and entanglements between hydrocolloid and amylose released from the granule (Liu, Eskin, & Cui, 2003). These mechanisms of action of LBG could explain the increase in viscosity observed in the present work.

The absence of solubilized amylose in waxy rice would explain that the viscosity increase was not as pronounced for this variety.

Concerning LBG effect on breakdown and setback from peak, differences in varieties behavior were observed. No effect of LBG on breakdown of Suriname, Euro and Waxy was found. Significant differences respect to control were detected only for LBG $\geq$1% for Gladio and LBG at 2% for Ariete. The breakdown is indicative of the extent of disruption of the swollen granules.

The setback from peak ($\eta_{f\text{-}p}$) is the increase in viscosity that occurs on cooling a pasted starch and is an indirect measurement of retrogradation of starches. It was observed that this value significantly decreased with increasing LBG level for Ariete. This fact indicates that final viscosity due to gelation was increased in a lesser extent than peak viscosity when LBG level increased, thus leading to a decrease of the difference between both viscosities. In the case of Euro, setback did not markedly change with LBG addition. Indica varieties exhibited the opposite trend: setback from peak augmented with increasing levels of LBG, indicating final viscosities were more relatively augmented than peak viscosities with LBG.

Waxy variety showed negative setback values with almost no influence of LBG level, indicating that final viscosity is lower than peak one.

The setback from minimum ($\eta_{f\text{-}m}$) a parameter directly related with amylose content (Copeland et al., 2009) only presented a significantly increase in Indica varieties (Gladio and Suriname) in the presence of LBG. These differences can be attributed to the same causes involved in setback from peak. Since Japonica varieties have less amylose than Indica ones, effect of LBG would be less pronounced and thus, after heating and cooling, starch pastes from Japonica rice varieties develop lower setbacks from minimum.

LBG–rice gels were successively heated and cooled (three times) and Fig. 5 shows maximum peak viscosities attained in each cycle and the final viscosity for pastes without and with LBG. When LBG is added, viscosities are increased with increasing hydrocolloid level but differences in behaviors among varieties are maintained. After a second cycle, gradual but pronounced decreases in maximum viscosities (from η_{p2} to η_{p3}) were obtained for Japonica and Waxy varieties (Figs. 4 and 5). In Indica varieties these peak viscosities were maintained or decreased in a lesser degree.

Salman and Copeland (2010) applied multiple heating–cooling cycles to different starch samples and attributed the decline in viscosities to the increasing alignment of starch chains during repeated heating with shear. The increase in viscosity at the cooling stage is due to the formation of junction zones among amylose chains. The more widely spaced are these junction zones, the looser is the formed network and so, more water is entrapped and higher viscosity is obtained. When amylose is inhibited to form extended junction zones (due to previous alignment), the result is a gel with less entrapped water and lower viscosity is obtained.

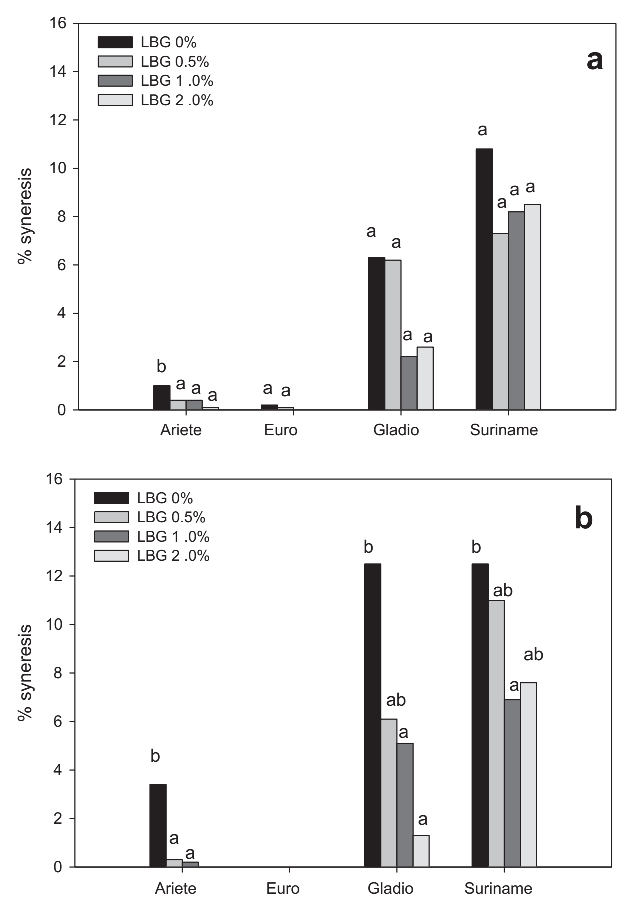

Fig. 6. Syneresis of gels obtained from different rice varieties and effect of increasing levels of LBG. (a) after one heat–hold–cool cycle (b) after three heat–hold–cool cycles. Different letters indicate significant differences within each variety ($P < 0.05$).

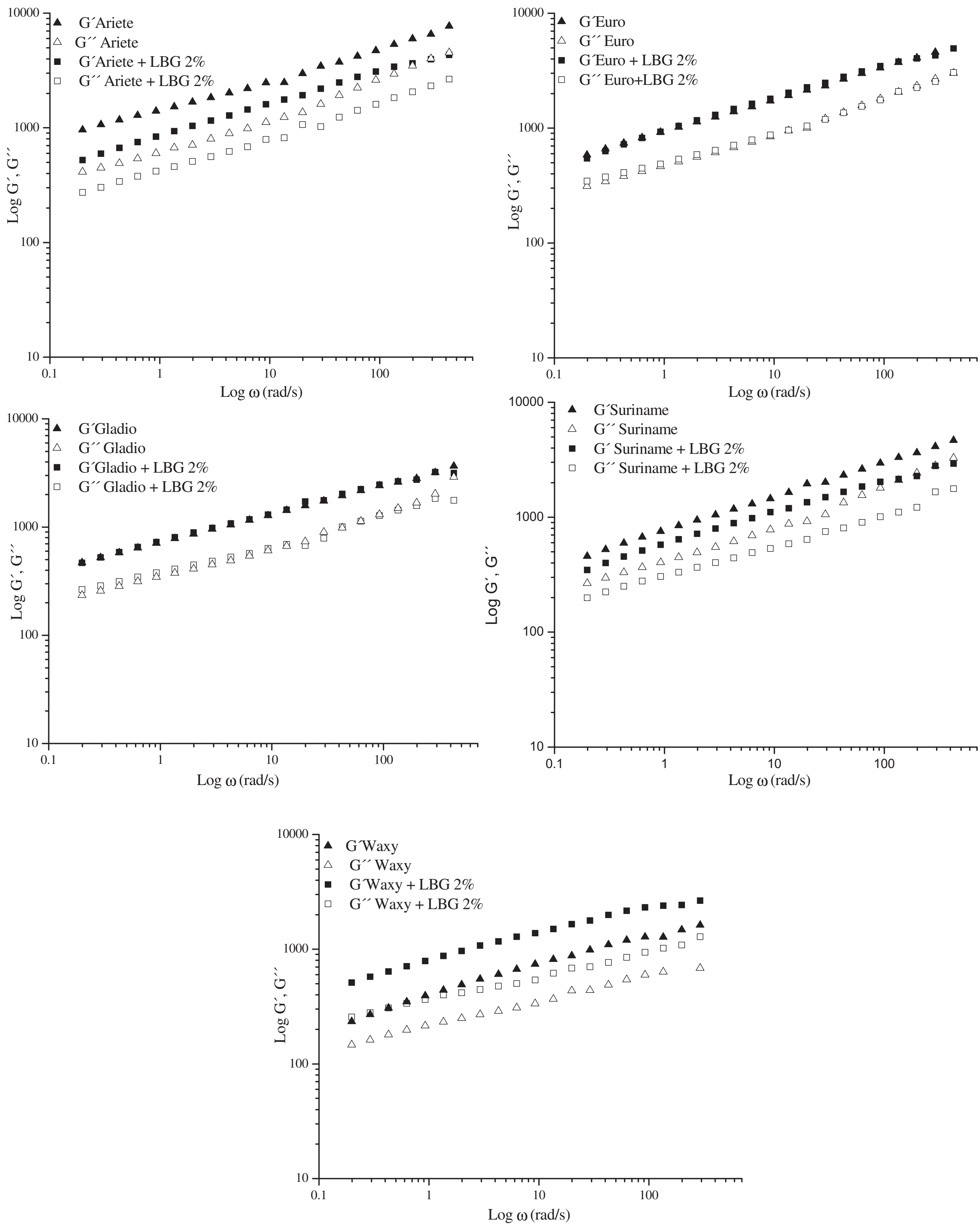

Fig. 7. Typical mechanical spectra for different rice varieties, without and with LBG 2%.

The results obtained in the present work indicate a differential behavior of rice flours submitted to drastic thermal variations. Varieties with more amylose (Indica ones) are more able to maintain gel viscosity when applying multiple cycles, probably due to their higher amylose content and consequent ability to form more junction zones. Indica varieties (Gladio and Suriname) showed lower η_{p1} (maximum peak viscosity when heating at the first cycle) but rendered a highest viscosity at the end (η_f) in comparison with Japonica varieties and waxy, indicating more propensity to retrogradation.

3.3. Syneresis properties of rice flour–LBG gels

The percentage of syneresis was calculated as the amount of water released per 100 g of rice gel (Fig. 6). Since repeatability of these assays was low, no significant differences were found among samples with different LBG levels.

However, differences in varieties behaviors have been detected; those with the highest content of amylose (Gladio and Suriname) presented the highest syneresis. In the case of Euro and Waxy, no syneresis could be determined. For Gladio and Suriname the addition of LBG seems to decrease syneresis (Fig. 6A). In agreement with our results, Charoenrein, Tatirat, and Muadklay (2008) showed that medium-amylose (17.6%) rice flour gels had a significantly lower syneresis after the first freeze–thaw cycle than did high-amylose (32.5%) rice flour gels, confirming that amylose plays an important role in the retrogradation associated with freezing and thawing. In our case, the addition of LBG in Gladio and Suriname varieties, helped reduce exudate from 6.3% to 2.6% (41% of exudate reduction) in Gladio and from 10.8 to 8.5% (21% of reduction) in Suriname.

For Ariete type, syneresis was much lower (1%) but even so, it was reduced to 0.1 (90%) with LBG. In this case the addition of LBG caused a slight decrease in setback from peak (Fig. 3) which would imply a reduction in retrogradation and, consequently, an improvement in freeze/thaw stability. Waxy and Euro varieties did not evidence syneresis, therefore LBG addition would be unnecessary. These results confirmed that the setback from peak values obtained from the pasting curves might be considered indicators of freeze/thaw stability.

The application of thermal stresses as multiple heating–cooling cycles helps to anticipate system response when cold chain is disrupted and the product is subsequently re-cooled. After the third heating–cooling cycle the application of freezing–thawing process (Fig. 6B), significantly increased syneresis; however, it was largely reduced in the presence of the hydrocolloid. LBG at a 1% level was more effective than 2% in reducing syneresis of rice gels both in the case of single as multiple RVA cycles. An excessive segregative effect caused by higher levels of LBG could favor syneresis by an increase of interactions in the starch concentrated phase. Consequently, for an adequate prevention of syneresis, several factors as rice variety, hydrocolloid level and thermal treatment should be taken into account.

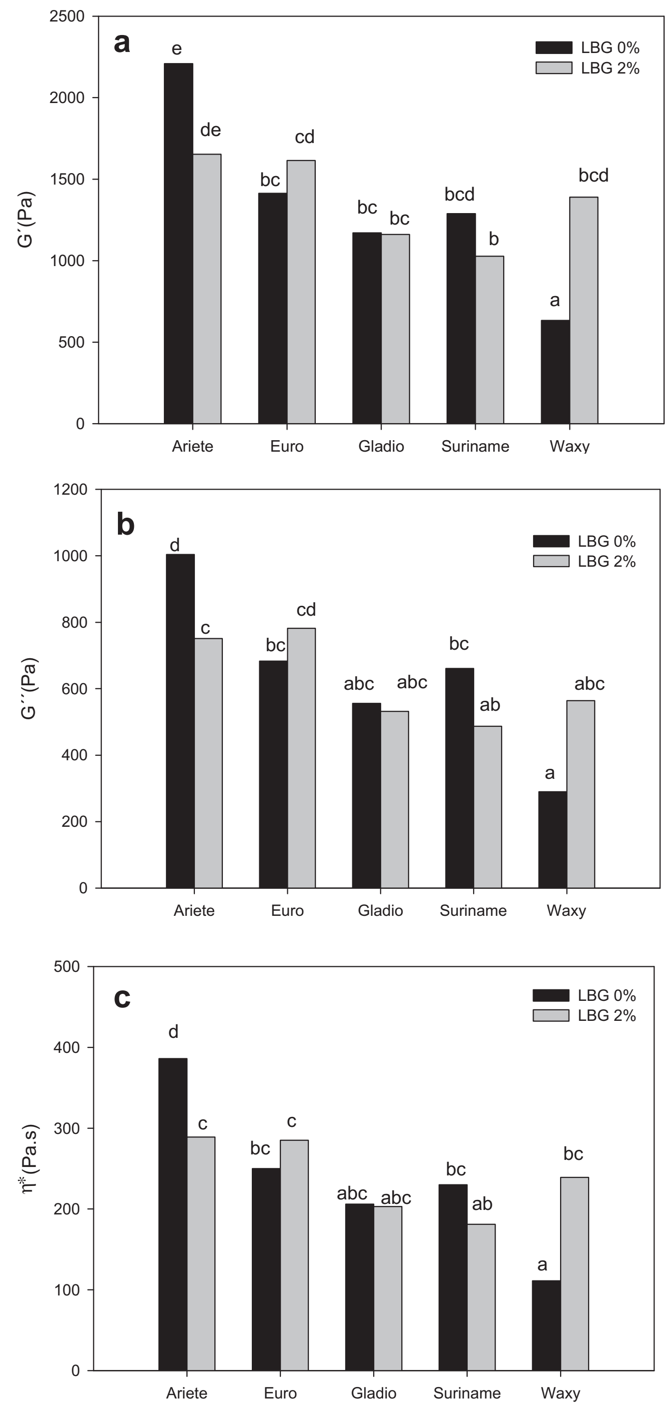

Fig. 8. Viscoelastic parameters of rice gels measured at 1 Hz a) G', storage modulus, b) G'', loss modulus, c) η^*, complex viscosity and effect of adding 2% LBG. Different letters indicate significant differences ($P < 0.05$).

3.4. Viscoelasticity of rice flour–LBG gels

In Fig. 7, typical spectra of rice starch gels without and with LBG (2%) are shown. In all cases, G' results higher than G'' along the tested range and both moduli show a dependence with frequency which is an evidence of a weak gel structure (Kim et al., 2006). Only in the case of Waxy rice samples, an increase in moduli values was observed when LBG was added.

Values of dynamic rheological parameters (G', G'' and η^*) measured at 1 Hz are shown in Fig. 8. Incorporation of LBG did not significantly changed G' and η^* in most cases. Only in the case of Waxy sample a significant increase was observed when LBG 2% was added. Ariete variety showed a pronounced tendency to decreased values of G', G'' and η^* in the presence of LBG. This decrease would evidence a negative effect of the presence of LBG on amylose gel formation as it could be concluded from viscoanalyser results. Waxy rice presented a marked more elastic behavior in LBG presence. In all cases, the viscous modulus, G'' presented a trend similar to G'. Ratio between G'' and G'' (tan δ) reflects the dynamic elastic behavior of gels; it was close to 0.45 for all samples (data not shown). In general, G' and η^* did not reflect the trends observed with viscoanalyser parameters. This different behavior is due to the fact that viscoanalyser parameters are measured during rotational stress application under heating, while dynamic complex viscosity is measured after the gel was equilibrated at 25 °C and new and more molecular bonds are stabilizing the network.

4. Conclusions

The studied rice varieties differing widely in amylose contents and differential scanning calorimetry (DSC) gelatinization temperatures exhibit distinct viscoanalyser and rheometric behavior as well as different degree of syneresis when submitted to freezing and thawing. Japonica varieties like Euro and Ariete, with intermediate amylose contents (15.4–18.5%) exhibited lower setback from peak ($\eta_{final}-\eta_{peak}$) and syneresis than Indica types. Waxy variety (1.3% amylose) had η_{peak} superior to η_{final} (negative setback) and did not exhibit syneresis.

The addition of LBG (0.5%, 1%, 2% w/w) significantly modified the pasting viscosities in single and multiple profiles, viscoelastic and syneresis properties of rice gels and the extent of the effect was dependent of rice varieties. The different behavior among varieties could be related not only to amylose content but also to other molecular characteristics, so it is not possible to establish a clear correlation between viscosity, syneresis and amylose content. In general, the addition of LBG caused an increase in peak, final and minimum viscosities but only rice gel from Ariete variety exhibits reduction of setback. Reduction of syneresis seems evident for 0.5% LBG addition on rice gels from Suriname and Ariete varieties, but 1% is needed for Gladio variety.

Successive multiple-heating–cooling cycles led to a progressive decrease on viscosity after a second cycle for Japonica and waxy varieties. In Indica varieties, these peak viscosities were maintained or decreased in a lesser degree. Though syneresis was higher than with a single cycle, it was largely reduced in the presence of LBG.

LBG was efficient in reducing syneresis of gels from Ariete, Gladio and Suriname varieties even when samples were submitted to drastic conditions of structural damage (three heating–cooling cycles and then freezing). These results show that this hydrocolloid could act as an effective ingredient for stabilizing gel structure under thermal changes but the efficacy and the optimal level of use depends of the rice variety.

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