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Thermal and physicochemical characterization of seven argentine rice flours and starches

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Abstract

Differential scanning calorimetry (DSC) was used to evaluate phase transitions of rice flours and starches from seven new argentine genotypes in systems with different water content. Flours of high, medium and low T_G (gelatinization temperature) were detected; ΔH_G (total gelatinization enthalpy) showed two homogenous groups (8.1–9.2 and 10.1–10.4 mJ/mg). Amylose–lipid complex melting endotherm in waxy rice flours was observed despite the low amylose content. It is suggested that this complex could be originated in the longest amylopectin branches and extra granular complexing lipids. Differential behaviour in waxy genotypes was found with decrease of water content, probably due to the highest water absorption capacity of the AP (amylopectin). Genotypes with high (26.8–28.6 g/100 starch), medium (19.6–20.7 g/100 g starch) and low total amylose (TAM) content was found (1.3–2.1g/100 g starch). In using X-ray diffraction, the relative crystallinity in waxy genotypes was found to be higher (48%) than that corresponding to the non-waxy ones (37–40%). A linear correlation between gelatinization process cooperativity and TAM was found to exist but no between ΔH_G and T_G with crystallinity and TAM.

Glass transitions (T_g) of gelatinized starch–water systems were also determined by DSC. Results indicated higher values (−5.0 to 6.3 °C) for flours than for starches (−10 °C).

Keywords: Rice; Starch; Gelatinization; Starch–lipid complex; Glass transitions

1. Introduction

Because of starch is a structure-maker hydrocolloid in foods, it is of particular interest to investigate its molecular design, phase transitions, interactions with other components, and how they affect its functional properties. In order to understand some features of the gelatinization at the molecular level and to characterize starches from different sources, this process has been investigated by using DSC, X-ray diffraction, birrefringence and other methods (Biliaderis, Maurice, & Vose, 1980; Donovan, 1979; Lai, Shen, Yeh, Juliano, & Lii, 2001; Liu, Lelievre, & Ayoung-chee, 1991; Nakazawa, Noguchi, Takahashi, & Takada, 1984b; Nara, Mori, & Komiya, 1978; Zobel, 1984).

In recent times much attention has been paid to the study of starch using physicochemical properties of synthetic polymers (Biliaderis, 1992; Slade & Levine, 1987). Since starch granule is a natural polymer and has amorphous, intercrystalline and crystalline regions, studies were performed on its amorphous fraction by glass transition (T_g) measurements. It must be pointed out that those determinations on native starch by DSC were not successful due to the fact that the amorphous zones are not independent and are interspread between the crystalline zones, thereby producing small Cp changes and making difficult measurements by DSC (Zeleznak & Hoseney, 1987). However, T_g and T'_g in water–gelatinized starch systems closely related to the retrogradation phenomenon were found to be appropriate

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even for technological purposes (Levine & Slade, 1986; Roos & Karel, 1991).

Rice, a cereal mainly consumed as whole grain (Kohlwey, Kendall, & Mohindra, 1995), shows marked differences in texture, which is closely related to starch gelatinization properties (approximately 90% grain dry weight) (Juliano & Betchel, 1985), and amylose content (Juliano, 1985, 1998; Juliano et al., 1981). In consequence, there would be a relationship between cooked rice qualities and the physicochemical properties of its starch.

Argentina is the main producer of rice of the MERCOSUR after Brazil. It satisfies its internal demand and export 80% of its production. In Argentina new cultivars are being developed to cover the new consumer preferences and there exist a potential market for waxy genotypes (Livore, 1998). Traditionally, physical parameters have been used as quality indicator such as grain length, length: width ratio, grain density, grain weight, and physicochemical parameters such as gelatinization temperature and amylose content, although they are not typified.

At this moment, there are few studies dealing with the physicochemical properties of the argentine varieties. The purpose of the present paper was to provide additional data on the physicochemical properties of rice flours and starches of new seven argentine genotypes and further knowledge of the starch properties.

2. Materials and methods

2.1. Samples

Rice grains from seven new argentine genotypes were used: El Paso 144, San Miguel, H-144-7, Palmar, Rico, W4109 and W4111; all of them from the Estación Experimental Concepción del Uruguay (INTA), province of Entre Ríos, Argentina. The flours from the same genotypes were provided by the Instituto de Tecnología de Alimentos, Facultad de Ingeniería, Universidad Nacional del Litoral, Santa Fé, Argentina.

2.2. Starch extraction

Starch was extracted from flours by enzyme proteolysis, after that a portion was defatted using water-saturated-butanol (Morrison & Laignelet, 1983).

2.3. Determination of total amylose (TAM) and apparent amylose content (ApAM)

The colorimetric method of Juliano et al. (1981) was used. Potato amylose (Sigma Type III) and defatted starch W4111 were used as standards to prevent amylopectin interference. Absorbance was measured at 620 nm in a Unicam UV/Vis 310 spectrophotometer. TAM was determined with deffated starches and ApAM in native starches.

2.4. Relative crystallinity determination

Crystallinity degree (CD) was measured using the method described by Priestley (1975). $CaCO_3$ was used as internal standard (100% crystallinity). Mixtures of starch and $CaCO_3$, 5% w/w, were homogenized in a mortar for around 30 min. The analysis was performed in a powder diffractometer (Philips PW 1710), equipped with crystalline graphite monochromator, radiation Kα of Cu, 40 KV voltage and 20 mA, 2θ/min run velocity from 8° to 32°, and 10 mm/2θ paper velocity. The CD was calculated as the percent ratio between the height of the peak corresponding to $CaCO_3$ (3.04 Å peak) and that of the most clearly defined peak in the X-ray spectrum of starch (3.8 Å peak) (Fig. 1). Unit cell size d (Å) was estimated using the Bragg law.

2.5. Phase transitions

Phase transitions were assessed by differential scanning calorimetry, using a Polymer Laboratories calorimeter controlled by PL-V5.41 software. Hermetic aluminium pans (Dupont) were used in which 15 mg samples with different water contents: 70:30, 50:50, 40:60, 30:70, 20:80 (water:flour or starch, w:w) were prepared. Samples were homogenized and kept at rest for at least 2 h before run. Temperature scanning from 25 to 150 °C at a rate of $\beta = 10$ °C/min was used. An empty pan (air) and indium were used as a reference and calibration standard, respectively. Thermal curves resulting from scanning were characterized by T_o and T_G (onset and gelatinization temperatures); by ΔH_G (gelatinization total enthalpy); by T_{p1}, T_{p2} and ΔH_f (peak temperatures and fusion enthalpy of the amylose–lipid complex). Temperatures were expressed in °C and

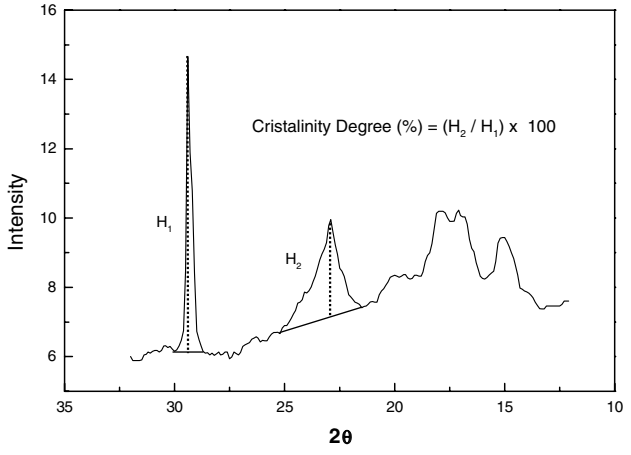

Fig. 1. X-ray diffraction patterns corresponding to blend of Rico starch and $CaCO_3$.

enthalpies in mJ/mg dry sample, and evaluated as the area below the curve. The gelatinization process cooperativity was obtained by measuring the width peak at half height ($\Delta T_{1/2}$) in those thermograms with high water content (70:30; water:flour). The dissociation process of the amylose–lipid complex in flours as well as in starches was studied by means of a second scanning performed just after the first one (annealing process). Samples were cooled from approximately 150 to 30 °C, under nitrogen stream at 5 °C/min, then heated to 70 °C, and kept at this temperature for 5 min. Finally, they were heated again up to 150 °C at a rate of 10 °C/min.

2.6. Determination of glass transition (T_g)

The glass transition (T_g) phenomenon was studied in rice flour and starch gels by DSC. 8 mg samples of pastes, containing 50:50 w:w (water:flour) were prepared and run in a differential calorimeter (Dupont 910 DSC) as follows: (a) heating from room temperature up to 150 °C at 15 °C/min; (b) immediate cooling to −40 °C using a mechanical device; (c) re-heating from −40 to 30 °C at a 2 °C/min. T_g was recorded on the thermogram corresponding to the second heating scanning by measuring the midpoint variation over the baseline.

2.7. Statistical analysis

All the tests were done in triplicate and Statgraphics software program was used for statistical assessment. Data were performed using the one-way variance analysis (ANOVA). Tukey's test was used to compare mean values when variance was found to be significant. Significant values $p < 0.05$ were considered.

3. Results and discussion

3.1. Total and apparent amylose contents

The data obtained for TAM using defatted starches (Table 1) showed the highest content in El Paso 144, H-144-7 and San Miguel; W4109 and W4111 (waxy cultivars) showed the lowest content; the remaining genotypes had an intermediate content. This pattern is consistent with that reported by Juliano (1985). Variability ranged from 4% to 12% for the non-waxy genotypes and 40–50% for the waxy ones. These were minor variations when compared with those reported by Juliano et al. (1981) who found values as high as 23% for non-waxy samples.

Table 1
TAM, ApAM, and ΔAM contents of rice starches from seven argentine genotypes

Variety	TAM g/100 g of starch[n]	ApAM g/100 g of starch[n]	ΔAM*
El Paso 144	28.6[a]	25.9[a]	2.7
Palmar	20.7[b]	16.2[b]	4.5
Rico	19.6[b]	20.3[c]	−0.7
H-144-7	26.8[a]	27.5[a]	−0.7
San Miguel	28.1[a]	22.8[d]	5.3
W4109	2.1[c]	0.5[e]	1.6
W4111	1.3[c]	1.0[e]	0.3

[n] The mean value of triplicates. Values followed by the same letter in the same column are not significantly different ($p < 0.05$).

[*] ΔAM was calculated as the difference between TAM and ApAM.

Results from ApAM, measured in no defatted starches (Table 1) showed lower values than those of TAM, as evidenced by ΔAM values. Undoubtedly, this difference was positive for all the genotypes excepting Rico and H-144-7 for which it was negative. No significant differences between the TAM and ApAM of these two genotypes were detected ($p < 0.05$). This might be the consequence of an experimental error associated with the differential effect of lipids on the maximum wavelength value in the bluish amylose–iodine complex (Morrison & Laignelet, 1983).

3.2. Relative crystallinity

Densitograms corresponding to the X-ray diffraction spectra of starch from the seven genotypes showed a type A pattern typical of cereal starches with peaks at 5.8, 3.8 Å and two overlapped peaks at 5.2 and 4.9 Å (Fig. 2).

While waxy starches, W4109 and W4111, evidenced the greatest CD (48%) the other varieties showed lower values (37–40%). This result is consistent since it is widely accepted that the amylopectin is the predominant crystalline component in granules, with the short branched chains forming local organizations compatible with cluster models (French, 1984; Imberty, Buléon, Tran, & Perez, 1991). However, no significant differences were found among the non-waxy varieties crystallinity ($p < 0.05$) despite their different amylose: amylopectin ratios.

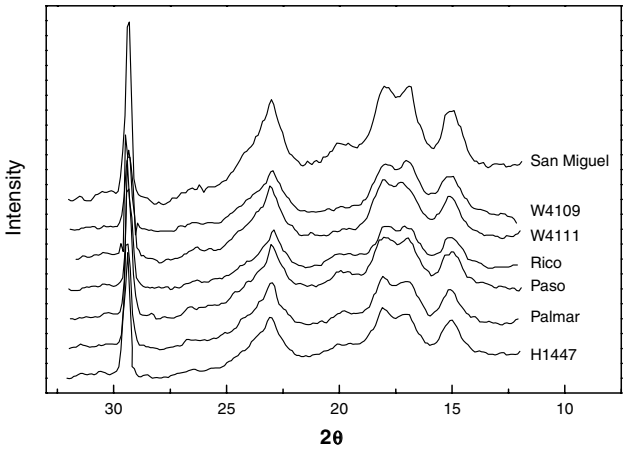

Fig. 2. X-ray densitograms corresponding to blends of rice starches and pure $CaCO_3$.

Ong and Blanshard (1995) reported similar relative crystallinities for 11 non-waxy rice starch varieties whereas Nara et al. (1978) and Cooke and Gidley (1992) supported the same findings for maize, wheat, and potato and rice starches. Much remains to be learnt about how amylose and amylopectin are tightly packed in the starch granules.

3.3. Thermal analysis

3.3.1. Thermal behaviour of starch in high water content systems

Typical thermograms corresponding to flour and starch of two rice genotypes, El Paso 144 and W4109, with high water content (70:30) are depicted in Fig. 3. Flour thermograms (Figs. 3(a) and (c)) clearly show a marked peak, which corresponds to the gelatinization process (G), and three minor peaks corresponding to the dissociation of the amylose–lipid complex (M_1, M_2 and M_3) evenly in the waxy varieties. Similar thermograms were obtained for starch samples (Figs. 3(b) and (d)). These results agree with those reported by Biliaderis (1990).

3.3.1.1. Gelatinization process. Table 2 shows the T_o and T_G for flours and starches in presence of excess of water (70:30; water:sample). Both parameters were found to be higher in flours than in starches, which may be attributed to the presence of proteins, sugar and salts. Water is absorbed by these compounds, which inhibit the gelatinization (Chungcharoen & Lund, 1987; Eliasson, 1992).

Three T_G statistical homogenous groups were found in flours and starches. They were identified as high T_G: H-144-7 and San Miguel; low T_G: El Paso 144, and intermediate T_G for the remaining genotypes.

The highest ΔH_G values were detected in the genotypes W4109, W4111, San Miguel and H-144-7 whereas minor values were found in the others (Table 2). Likewise that observed in temperatures, the ΔH_G values were lower in flours than in starches where there is more available water for gelatinization (Eliasson, 1992; Huang, Chang, Chang, & Lii, 1994). These results were similar to those reported by other authors who found values of $\Delta H_G = 8.0$–25 mJ/mg for starch from different sources and high water content (Donovan, 1979; Tester & Morrison, 1990a, 1990b).

The correlation between the properties already mentioned is very useful for establishing rice cooking quality predicting parameters and has been deeply studied by many researchers. No correlation has been detected between ΔH_G and T_G for the genotypes studied in this work. Fujita, Morita, and Fujiyama (1993) reported a positive correlation between ΔH_G and T_G for starches from rice and other cereals. Biliaderis, Page, Maurice, and Juliano (1986a) and Biliaderis, Page, and Maurice (1986b) considered differences among the DSC transitions of high water content rice starches as obvious and showed dispersions in the results alike those in this work.

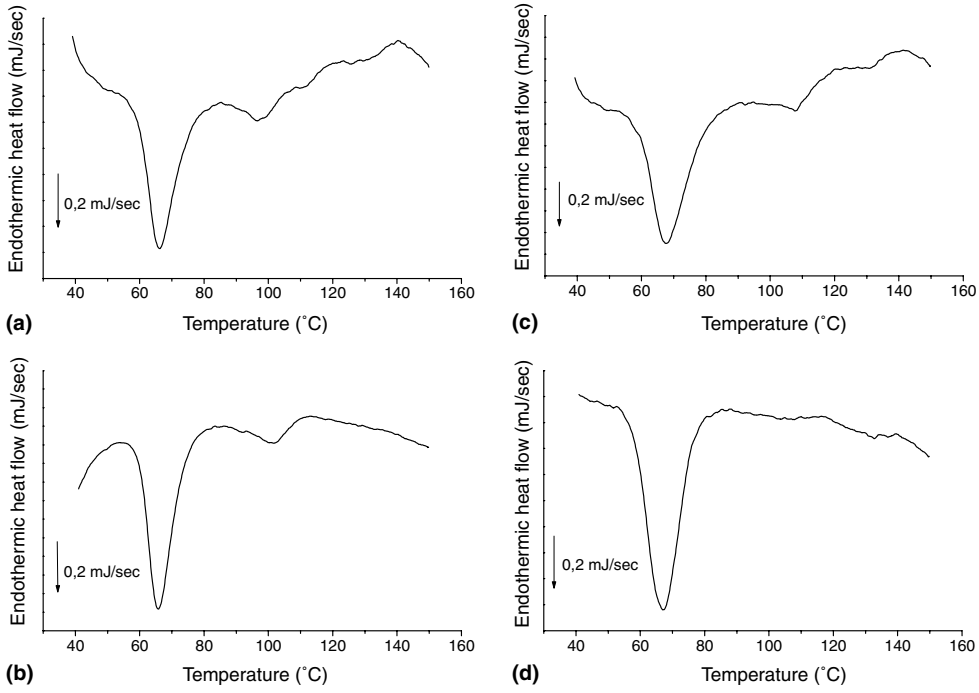

Fig. 3. Differential scanning calorimetry thermograms corresponding to: (a) flour El Paso 144, (b) starch El Paso 144, (c) flour W4109 and (d) starch W4109.

Table 2
Temperature, enthalpy and cooperativity of gelatinization process of rice flours and starches of seven genotypes, in high water content systems (70:30)

Genotype	Gelatinization						
	Flours				Starches		
	T_o (°C)[n]	T_G (°C)[n]	ΔH_G (mJ/mg)[n]	Cooperativity (°C)[n]	T_o (°C)[n]	T_G (°C)[n]	ΔH_G (mJ/mg)[n]
El PASO 144	59.0 ± 0.2^a	66.0 ± 0.4^a	8.2 ± 0.4^a	5.2^a	59.1 ± 0.1^a	65.7 ± 0.4^a	10.5 ± 0.1^a
Palmar	59.9 ± 0.4^a	68.5 ± 0.2^b	8.1 ± 1.8^a	5.8^a	60.1 ± 0.1^a	68.1 ± 0.2^b	10.0 ± 0.3^a
Rico	59.8 ± 0.6^a	68.4 ± 0.4^b	8.6 ± 0.6^a	5.5^a	59.2 ± 0.9^a	66.7 ± 0.4^b	10.0 ± 0.4^a
H-144-7	69.2 ± 0.1^b	75.4 ± 0.2^c	10.1 ± 0.8^b	5.2^a	68.1 ± 0.1^b	74.8 ± 0.1^c	13.1 ± 1.0^b
San Miguel	68.3 ± 0.4^b	74.7 ± 0.3^c	9.2 ± 1.3^b	5.3^a	67.6 ± 0.5^b	74.4 ± 0.2^c	12.7 ± 0.1^b
W4109	58.1 ± 0.7^c	67.7 ± 0.6^b	10.4 ± 1.5^b	6.9^b	57.6 ± 0.1^c	66.8 ± 0.2^b	12.0 ± 0.7^b
W4111	57.1 ± 0.5^c	67.2 ± 0.2^b	10.4 ± 1.4^b	6.8^b	57.6 ± 0.1^c	66.7 ± 0.6^b	13.2 ± 0.7^b

[n] The mean value of triplicates. Values followed by the same letter in the same column are not significantly different ($p < 0.05$).

Unlike Slade and Levine (1989) and Huang et al. (1994), no correlation was observed between ΔH_G and CD. According to the theory of synthetic polymers, the higher crystallinity degree the higher the enthalpy of gelatinization, that is, the energy needed to disorganize the starch structure. This partly explains our results, since the genotypes having high crystallinity were those with higher enthalpy. Nevertheless, genotypes H-144-7 and San Miguel showed similar ΔH_G to those of the waxy genotypes and lower crystallinity. This mismatch might be explained in terms of the findings of Fujita et al. (1993) since these genotypes showed high T_Gs.

Nakazawa, Noguchi, Takahashi, and Takada (1984a) reported higher T_G for waxy than for non-waxy rice starches since the former are more crystalline and consequently more resistant to gelatinization. Assuming that the linear fraction of the starch constitutes most of the amorphous zone of the granule, it follows that the higher the amylose content, the lower T_G. Our results did not show such correlation.

From the above it can be concluded that it is very hard to establish a relation between the TAM and the ΔH_G. Gelatinization is a non-equilibrium transition where granule swelling and crystallite melting (highly endothermic event) along with hydration and crystal reorganization (exothermic event) occur, then enthalpy is a net thermodynamic quantity (Biliaderis, 1990). In this process, both fractions play an important role. The amylose acts in the hydration of the amorphous zones and the amylopectin provokes the swelling of the granule (Tester & Morrison, 1990b). In this sense, there was a direct relationship between $\Delta T_{1/2}$ values (cooperativity) and TAM content was found (Fig. 4). This behaviour may be ascribed to the amorphous domains destabilization (rich in amylose) during the gelatinization process. The amorphous zones absorb water and become swollen prior to any change in the small crystallites (rich in amylopectin) facilitating the striping of chains and the melting of the crystallites and thus rendering this process more cooperative (Biliaderis et al., 1986a, 1986b; Morrison & Azudin, 1987).

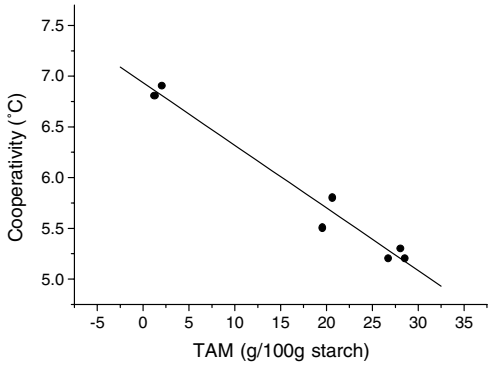

Fig. 4. Correlation between gelatinization process cooperativity and TAM in high water content systems. Correlation factor = 0.98, $p < 0.0001$.

Previous discussion was based mainly on starch crystallinity that partially explains our results as gelatinization is considered a process made up of several events. Starch is a complex semi-crystalline entity, and although great improvement in the knowledge of its structure has been done, the divergences found in this paper can be attributed to the amorphous zone of the granule, which has not been deeply studied.

3.3.1.2. Dissociation process of the amylose–lipid complex. Multiple peaks, also reported by other authors (Biliaderis & Seneviratne, 1990; Bulpin, Welsh, & Morris, 1982), can be observed in Fig. 3. This multiplicity of peaks could account for different kinds of lipids (Bulpin et al., 1982; Raphaedelis & Papavergou, 1991), which could form complexes with different structures (Kowblansky, 1985; Raphaelides & Karkalas, 1988). Two polymorphic structures were reported in rice: form I (melting <100 °C) and form II (melting >100 °C). They are differently arranged and could be interconverted by temperature in association with lipids (Biliaderis & Seneviratne, 1990). On the other hand, these endotherms could be related to macromolecular crystals in meta-stable equilibrium, which could undergo rearrangements during heating (Biliaderis, Page,

Slade, & Sirett, 1985; Biliaderis et al., 1986a, 1986b; Biliaderis & Galloway, 1989). Hence, these peaks at increasing temperatures could be the result of the melting of more ordered and perfected crystals by annealing.

In order to determine the origin of the multiple endotherms present in flour, and considering the reversible nature of the amylose–lipid complex dissociation, a second scanning was carried out. After gelatinization, samples were subjected to annealing treatment as described in Materials and Methods. A single homogeneous peak appeared after the second scanning, corresponding to the non-waxy genotypes: El Paso 144, H-144-7 and Palmar (Fig. 5), where $\Delta H_D = 3.1$–3.5 mJ/mg and $T_p = 101.2$–101.6 °C within the range of M_1 and M_2 (first scanning) were obtained.

This single peak clearly evidenced the rearrangement in these varieties during the first heating. Besides, the formation of two different crystals, depending on the type of lipid was not observed. The occurrence of the endotherm in the complex area of waxy genotypes must be highlighted, although the low amylose content was more significant in flours than in starches (Fig. 3). This may indicate that the complex would be built up not only by the starch linear fraction but also by some amylopectin branches. The polymerization degree (15–20) of the C short chains of AP inhibits it from forming complexes, however this kind of transitions has been found in waxy maize (Evans, 1986). Moreover, it has been demonstrated that amylopectin from waxy rice and palmitic acid at 80 °C, can form complexes in which its branched chains could also be involved (Juliano, 1982). Unlike other cereals, rice contains complexing lipids (phospholipids, mono- and diacylglycerols, free fatty acids); in certain non-waxy varieties such lipids were found to be present either inside or outside the granules. In waxy varieties they were only found outside the granule, which in turn contains negligible amounts of intragranular lipids (Azudin & Morrison, 1986; Maniñgat & Juliano, 1980). Then it may be suggested that extra granular lipids and the longest branched chains of amylopectin could give rise to the complex found in the waxy genotypes.

3.3.2. Gelatinization and melting process; its relationship with water content

The plastizant effect of water on T_o, T_G and ΔH_G for all genotypes is shown in Fig. 6. At water contents higher than 50:50, the non-waxy genotypes tended to a T_G constant values. On the other hand, the waxy genotypes evidenced a fall of T_G over the range of water content analysed, though tending to reach a constant value. This behaviour could be explained by the great capacity of water absorption derived from the high AP content (Tester & Morrison, 1990b). Increase of water led to an increase of T_o up to a constant value (Fig. 6(b)), especially in the H-144-7, W4109 and W4111 genotypes. In some cases, T_o showed an irregular be-

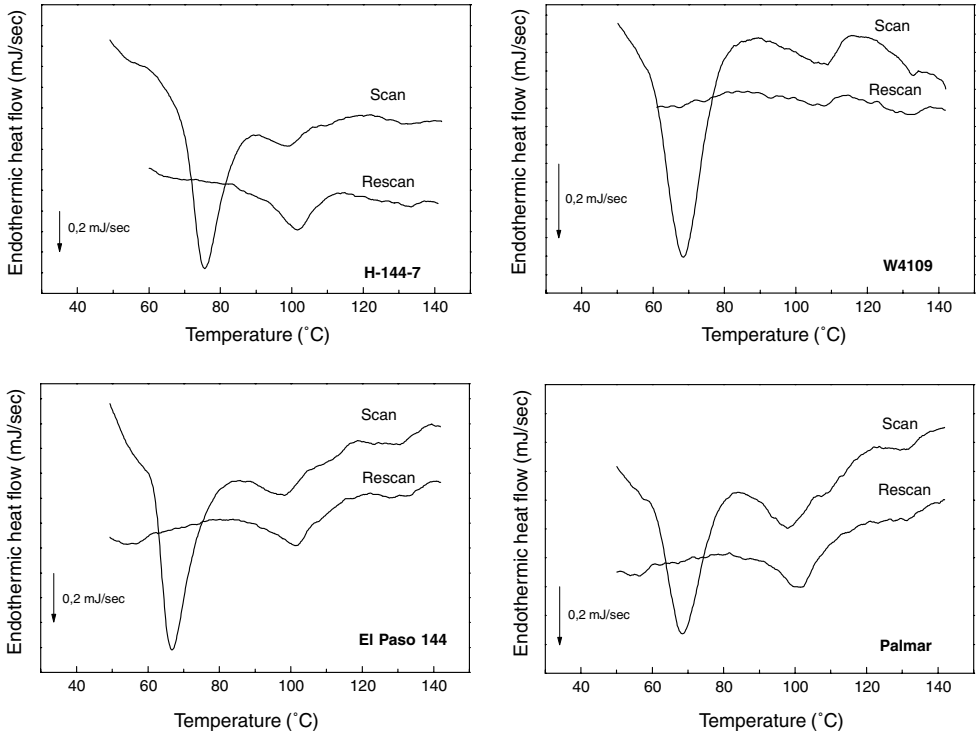

Fig. 5. Thermograms corresponding to scans and rescans of rice flours. The rescans were done after an annealing process.

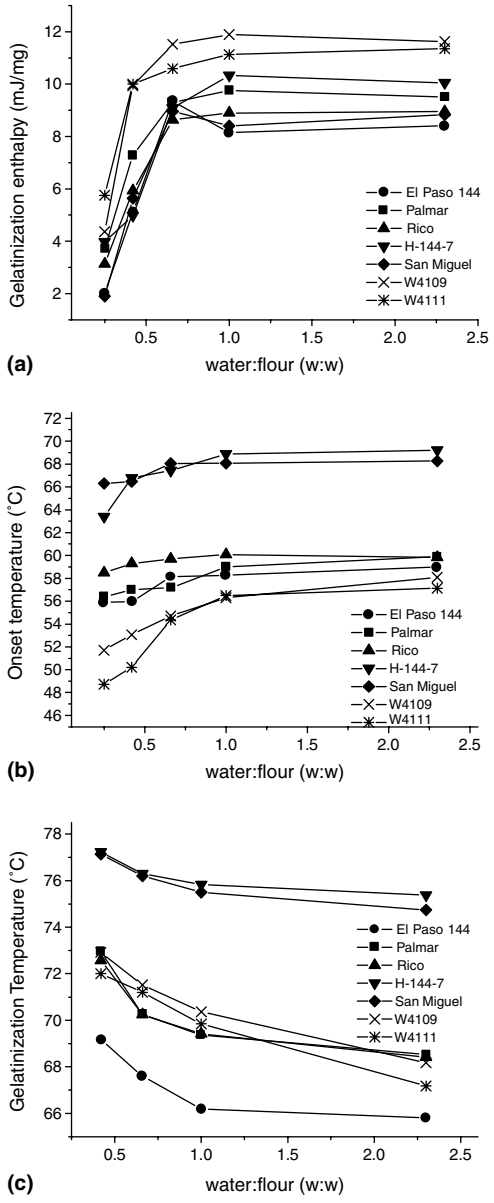

Fig. 6. Gelatinization enthalpy (a), onset gelatinization temperature (b) and peak gelatinization temperature (c) vs. water content.

haviour related to the very low water contents (20:80; water: sample) (data not shown). Those genotypes of high T_G also showed the highest T_o unlike the waxy genotypes that presented intermediate T_G values and a low T_o.

Conflicting results has been reported regarding T_o trends with water content; data obtained in this work are consistent with the ones reported for rice starches (Biliaderis et al., 1980), and some other species (Tester & Morrison, 1990a). Chungcharoen and Lund (1987) showed increments of T_o with a decrease of water content, while Seow and Teo (1993) could not find any changes within the range of water contents studied (25–50% w/w starch/water).

The ΔH_G also showed a marked dependence on water content. In Fig. 6(c), it can be seen that the increase of total enthalpy of gelatinization parallels the rise in water content to reach a constant value at 50:50; water:sample ratio. The waxy genotypes presented greater values of H_G, even when the water content was much lower, and they are likely to reach a constant value earlier than the others. Then the AP fraction, which is responsible for water absorption capacity, would be the distinguishing feature of waxy and non-waxy genotypes in that makes them distinguishable from each other.

Other studies have reported that waxy genotypes are more crystalline, because of which they require greater gelatinization energy than that required for the non-waxy ones (Huang et al., 1994; Nakazawa et al., 1984b). Our results carried out in high water content systems, were not consistent with this. Fujita et al. (1993) stated that gelatinization enthalpy would be closely related to starch granule density rather than crystallinity.

3.3.3. Glass transitions

When a gelatinized starch–water system is frozen, the amount of crystallized water depends on the thermal history. Depending on the cooling rate, some water would remain in amorphous state, without crystallizing. When the system is heated, and the glass transition temperature (T_g) is reached, relaxing of the amorphous zones occurs, and ice melting is observed. The glass transition temperature is represented by T_g' when the matrix has been maximally cryoconcentrated.

T_g was found to be higher in flour than in starch (Table 3). This is consistent with the fact that water is adsorbed in flour proteins and sugars, so its plastizant effect decreases, indicating an increment of T_g. Slade and Levine (1993) demonstrated that water as a plastizant agent is able to diminish T_g from ~200 °C (anhydrous polymers such as starch, gluten, colloids) up to ~−10 °C that is the characteristic temperature of high molecular weight biopolymers with water contents around or higher than 30% w/w.

Results obtained in this work are also supported by Huang et al. (1994). Ferrero, Martino, and Zaritzky

Table 3
Onset and midpoint temperatures of the glass transition process of rice starches and flours from four genotypes, in intermediate water content systems (50:50)

Genotype	Glass transition temperature			
	Flours		Starches	
	T_o (°C)	T_g (°C)	T_o (°C)	T_g (°C)
El Paso 144	−7.4[a]	−6.3[a]	−11.7[a]	−10.6[a]
H-144-7	−7.4[a]	−6.1[a]	−12.9[a]	−10.9[a]
Palmar	−7.1[a]	−5.9[a]	−11.9[a]	−10.6[a]
W4109	−7.3[a]	−6.1[a]	−13.1[a]	−10.9[a]

(1996) reported T'_g (−6 to −8 °C) for maize starches either with or without hydrocolloids.

4. Conclusions

The results obtained allow us to classify these new argentine varieties of rice according amylose content, T_G and CD. In this sense, El Paso 144 cultivar showed a high TAM, low T_G and CD; Rico and Palmar had intermediate TAM, T_G, and low CD; and waxy cultivars (W4109 and W4111) showed very low TAM, intermediate T_G and high CD.

A direct correlation between the cooperativity of the gelatinization process (in high water content) and TAM was found, probably due to the disestablishing effect of the amorphous zones (rich in amylose) on the crystallites (rich in amylopectin). However, no correlation between the thermal resistance (T_G) and the energy required for the gelatinization process (ΔH_G) with crystallinity and TAM was found for these seven genotypes. The crystallinity is partially related to the thermal properties of the gelatinization since it is one of the events of this process.

The major water absorption capacity of the amylopectin could be the reason for the differential behaviour found on the waxy varieties when the water content was decreased.

There were no differences between genotypes in the amylose–lipid melting range, since in the annealing process only one peak appeared. A relevant finding was the presence of this transition in waxy flours and starches. We suggest that this structure could be formed with the longest amylopectin branches and extragranular complexing lipids natives in starch rice.

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