Carbohydrate Polymers 76 (2009) 528–534

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Glass transition temperatures of a ready to eat breakfast cereal formulation and its main components determined by DSC and DMTA

Aleida J. Sandoval [a,*], Martin Nuñez [a,b], Alejandro J. Müller [b], Guy Della Valle [c], Denis Lourdin [c]

[a] Universidad Simón Bolívar, Departamento de Tecnología de Procesos Biológicos y Bioquímicos, Apartado 89000, Caracas 1080-A, Venezuela
[b] Grupo de Polímeros USB, Universidad Simón Bolívar, Departamento de Ciencia de los Materiales, Apartado 89000, Caracas 1080-A, Venezuela
[c] INRA, Unité de Recherches sur les Biopolymères, leurs Interactions & Assemblages (BIA), 44316 NANTES Cedex, France

ARTICLE INFO

Article history:
Received 24 June 2008
Received in revised form 30 October 2008
Accepted 12 November 2008
Available online 21 November 2008

Keywords:
DMTA
DSC
Starch
Oat flour
Rice flour
RTE breakfast formulation

ABSTRACT

The effect of water content on the glass transition temperatures of a ready to eat cereal formulation was determined, as well as for its major components, oat flour, rice flour and an oat–rice flour blend, in the same ratio as they are present in the formulation. All samples were compression moulded at high temperature and were moisture conditioned in a 10–22% interval (dry basis). Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) and the main mechanical relaxation temperatures (T_α), measured by dynamic mechanical thermal analysis (DMTA). The relaxation temperatures taken at tan δ peaks, were found 20–30 °C larger than T_g. Besides the plasticizing effect of water adequately described by the Gordon–Taylor equation, no differences of T_g (and T_α) values between the major components were obtained at a constant moisture content. The T_g and T_α values of the RTE formulation were found to be about 30 °C lower than its components, a result which was attributed to the plasticizing effect of the minor components in the formulation (sugar and malt extract).

1. Introduction

The glass transition temperature (T_g) is an important physical property in food science as it can help explain important physico-chemical behaviours of food systems. At present, different techniques to determine this temperature range in food biopolymers are readily available. They are based on the various ways to measure the changes taking place during the glass–rubber transition, and include calorimetric techniques (DSC), molecular mobility (e.g., dielectric and nuclear magnetic relaxation techniques), mechanical methods and dynamic mechanical methods (i.e., dynamic mechanical thermal analysis, DMTA). Other methods include measurements of volume and spectroscopic techniques, such as, infrared, electron spin resonance and dielectric spectroscopies (Blanshard, 1995). From these, DMTA, DSC and NMR are commonly used to determine the glass transition temperature of food materials (Brent, Mulvaney, Cohen, & Bartsch, 1997; Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, & Lillford, 1992; Ross, Campanella, & Okos, 2002).

Data obtained from DSC and DMTA techniques yield different values and they should be interpreted differently (Champion, Le Meste, & Simatos, 2000; Le Meste, Champion, Roudaut, Blond, & Simatos, 2002; Rahman, 2006). In the case of DSC, the measured temperature at the glassy–rubbery transition, normally determined by the mid point in the heat capacity change, is referred to as the glass transition temperature (T_g). In mechanical spectroscopy, methods such as DMTA, the change at the glassy–rubbery transition determined by the drop in the storage modulus (E' or G'), maximum of the loss modulus (E'' or G'') or loss factor (tan δ) peak is normally interpreted as the temperature associated to the glass transition, i.e., T_α, where long range cooperative relaxation of the material amorphous chains is taking place. Although these methods are not strictly equivalent, as they investigate molecular mobility at different levels, correspondence between the peak in the loss shear modulus (G'') determined at a frequency of 1 Hz and a heating rate of 5 °C/min, and the endpoint glass transition temperature measured on glutenin with moisture content between 4% and 14%, by DSC (at 5 °C/min) has been reported by Cocero and Kokini (1991). Meanwhile, work carried out on different single food biopolymers evidenced approximately the same T_g for that obtained from the peak in E'' (at 1 Hz and 2 °C/min heating), and that determined at 10 °C/min by DSC (Kalichevsky & Blanshard, 1993; Kalichevsky, Blanshard, & Tokarczuk, 1993; Kalichevsky, Jaroszkiewicz, & Blanshard, 1992). Furthermore, these last authors also found that these temperature values fall between those corresponding to the peak in tan δ and to the drop in the elastic modulus (E'). In the particular case of starchy food products, DSC has not shown to be sensitive enough for precise glass transition determinations (Brent et al., 1997; Kalichevsky & Blanshard, 1993). Furthermore, the interest of DMTA was underlined, as it is more sensitive than DSC to the glass transition, and because mechanical properties are of great practical interest.

---

* Corresponding author. Tel.: +58 212 9063976; fax: +58 212 9063971.
E-mail address: asandova@usb.ve (A.J. Sandoval).

0144-8617/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2008.11.019

Glass transition or main relaxation temperatures of individual food biopolymers such as amylopectin, amylose, malto-oligosaccharides, gluten, glutenin, as well as the effect of water and other low molecular weight plasticizers such as sugars has been widely discussed in the literature (Cocero & Kokini, 1991; Kalichevsky, Blanshard, &Tokarczuk, 1993; Kalichevsky et al.,1992; Kalichevsky, Jaroszkiewicz, & Blanshard, 1993; Orford, Parker, Ring, & Smith, 1989). However, using these data to extrapolate the behaviour of more complex systems such as flours could be misleading, because interactions among components cannot be neglected. Additionally, thermal transitions of individual biopolymers may be affected by the treatments used in their isolation processes (Kaletunç & Breslauer, 2003). In this way, more complex products, such as wheat flour (Georget & Smith, 1996), durum wheat semolina (Cuq & Icard-Vernière, 2001), oat and corn meal (Brent et al., 1997), rice flour (Chen & Yeh,2000, 2001) and corn flour (Chanvrier, Colonna, Della Valle, & Lourdin, 2005; Chanvrier, Della Valle, & Lourdin, 2006), have been investigated, and different behaviour of the complex system in comparison to that of their individual main components have been found. On one hand, values of the glass transition temperatures of the complex product has been found to be in between those of the main single components, as for example the T_g of durum wheat gluten with moisture content between 6% and 27%, was reported to fall between those of the starch and wheat gluten (Cuq & Icard-Vernière, 2001). Conversely, Brent et al. (1997) found that the glass transition region of cornmeal with moisture content greater than 20% was located above the one reported for amylopectin. Meanwhile, values of T_g for dry extruded rice pellet were slightly higher than the literature value reported for anhydrous amylopectin of 227 °C (Chen & Yeh, 2001). Similar values of mechanical relaxation temperatures, determined by the peak of tan δ, were found for mixtures of starch/zein (85/15) and corn flour at 12% of moisture content (Chanvrier et al., 2005). Although a single relaxation process is often seen around T_g in these mixtures of biopolymers, it may be the result of superimposed multiple independent glass transitions occurring within a narrow temperature range (Kaletunç & Breslauer, 2003). Even though knowledge of the thermal transition of single food biopolymers is well established in the literature, further work is needed to understand different interactions and their subsequent contribution to the glass transition in complex food systems like those normally used in the food industry.

Cereals and starchy based products are the main source of ingredients in ready to eat breakfast formulations, obtained by extrusion processes. Structural features of the product, and hence, its texture, are established during the expansion phenomena, which finishes when the cooling material crosses the glass transition temperature range (Della Valle, Vergnes, Colonna, & Patria, 1997; Fan, Mitchell, & Blanshard, 1994, 1996; Moraru & Kokini, 2003). Although the texture creation by extrusion is still complex, the role of glass transition is of importance and more knowledge about its temperature values would help to control the process and the final product properties in the same way as suggested for breadmaking (Cuq, Abecassis, & Guilbert, 2003). Consequently, the aim of this study was to determine glass transition and mechanical relaxation temperatures of a complex food system formulation and their main components, as measured by DSC and DMTA. Special attention was dedicated to the effect of water on the location of these temperatures.

2. Materials and methods

2.1. Raw material: description and composition

The ready to eat (RTE) breakfast cereal formulation, called RTE blend, was mainly composed of oat flour (70%, dry ingredient) and rice flour (13%, dry ingredient). Other minor components included sucrose and malt extract (in a proportion 1:0.7), salt and vitamin blend (<1%). All the ingredients were donated by Alfonzo Rivas & Cía. (Caracas, Venezuela). Major components of this formulation, i.e., oat flour and rice flour were analysed separately. Additionally, oat–rice flour blend was also investigated in the same proportion that it is present in the RTE blend. Both oat–rice flour and RTE blends, were prepared by mixing the dry ingredients in the proportions indicated above in a food powder mixer (Bolafix®) for approximately 30 min.

Sample proximate composition (moisture, protein, fat, ash and carbohydrate contents) was determined on the oat flour, rice flour, oat–rice flour blend and RTE blend. Moisture content was assessed by the Chopin method, for which an approximate amount of 2 g of sample was placed in an atmospheric oven at 130 °C for 4 h. Standard procedures from AOAC (1975) were followed for the following analyses: Protein content (Kjeldahl method No. 14.063) with a conversion factor of 6.25, fat content (Soxhlet method No. 14.062), total ashes (method No. 14.006). Carbohydrate content was obtained by difference. A direct acid hydrolysis method (No. 8.017) was followed to determine the starch content of the samples considered.

2.2. Sample preparation

Initial preparation of all samples involved their complete transformation by compression moulding at high temperatures, so that amorphous materials could be obtained. To do this, Native samples were moistened up to 30% (wet base, w.b.), by slowly adding water while continuously stirring. These powders were compression moulded employing a plate mould ($22 \times 10 \times 0.5$ mm^3) within a two heating plate moulding press (Pinette, France) at 200 bar and 160 °C for 15 min. Each sample was cooled under pressure in order to avoid water bubble forming inside the materials. Moisture loss during this treatment was hence negligible. Complete transformation of the samples by using this procedure was further confirmed by the absence of residual gelatinization enthalpy, determined by DSC experiments in excess of water, as referred elsewhere (Chanvrier et al., 2005). Strip samples were divided into two groups for subsequent analysis by DSC and DMTA measurements.

For DSC experiments, strip samples were grinded in a cryogrinder (SPEX Freezer/Mill, Spex Industries, Inc., Metuchen NJ 08840 USA) for 2 min, into a very fine powder (<100 μm), and stored in different controlled relative humidity atmospheres for 3 weeks at 25 °C so as to reach equilibrium at different moisture contents. These environments were obtained with the saturated salt solutions NaBr (0.576), $CuCl_2$ (0.684), NaCl (0.753), KCl (0.843), $BaCl_2$ (0.902) (the number in parenthesis shows water activity at equilibrium, Greenspan, 1977). For the DMTA measurements, strip samples were directly stored in similar controlled ambient conditions. In both cases, at water activity greater than 0.8, crystalline thymol was placed inside the desiccators to prevent the microbial spoilage of the samples.

2.3. Sorption characteristics

As the moisture content of samples immediately after compression moulding was about 30%, the equilibrium was reached by desorption. Isotherms at 25 °C for all the material considered in this work, for powder and strip samples, were obtained by representing the moisture content against their respective water activity, a_w, values. After storage of the samples conditioned in the different relative humidity atmospheres (powder and strips), their moisture content was determined as detailed before.

2.4. Differential scanning calorimetry (DSC)

Calorimetric measurements were done on the powder samples using a DSC Q100 differential scanning calorimeter (TA Instrument), previously calibrated with Indium. This equipment utilizes nitrogen as purge gas with a flow rate of 50 mL/min, and it was provided with a TA Instruments intracooler (−90 °C). An amount of 20 ± 1 mg of each sample with the adjusted moisture content considered in this work was weighed in stainless steel pans (100 μL; 30 bar). Each sample was heated from −50 to 150 °C using an empty pan as a reference. After a first scan performed to delete any thermal event due to ageing phenomena taking place during the storage, samples were rapidly cooled to −50 °C (60 °C/min). The glass transition temperature of the specimens was determined from the midpoint of the heat capacity change observed on the second scan, at a heating rate of 3 °C/min (see an example in Fig. 2). Three to five samples of each material were measured and the T_g values obtained from the scans were averaged.

2.5. Dynamical mechanical thermal analysis (DMTA)

Thermomechanical measurements were carried out in a Rheometric Scientific dynamic mechanical thermal analyser (MKIV). Strip samples were placed in a dual cantilever geometry, and oscillated at a frequency of 1 Hz. In all cases, the heating rate was 3 °C/min and the heating range applied to the samples depended on their moisture content. The strain amplitude was maintained at 0.1% in order to remain within the linear viscoelastic range. Strip sample dimensions of $22 \times 10 \times 0.5$ mm^3 were used and the specimens were coated with teflon grease (Super Lube brand) to limit dehydration at high temperatures (approximately 1% of weight loss at 70 °C, as confirmed by thermogravimetric analysis). The temperature at which the slope in E' changed was determined by the extrapolated onset analysis tool of the software RSI Orchestrator (V6.5.3) and by the peak in tan δ. Between four and six samples of each material were measured and the values of T_α were averaged.

3. Results and discussion

3.1. Sample composition

Results from the proximate analysis of the materials considered in this work are shown in Table 1. Starch contents of oat flour, rice flour, oat–rice flour blend and the RTE formulation were (expressed as g/100 g): 64.01 ± 0.75, 75.93 ± 0.96, 65.87 ± 0.84, and 65.21 ± 0.25, respectively. These starch values are close to the carbohydrate contents determined by difference in the proximate analysis (Table 1), particularly for rice flour. The larger difference obtained for the oat flour, oat-flour blend might be attributed to the fiber content of the oat flour, which has made it to be recognized as a source of dietary fiber and a value of around 10% has been reported (Eliasson & Larsson, 1993; Zhou, Robards, Glennie-Holmes, & Helliwell, 1999). In case of the RTE blend such a difference is additionally due to the sucrose and malt extract present in this formulation. Other differences in the proximate composition of the flours analysed in this work are fat and protein contents. Eliasson and Larsson (1993) reported values of 5.8% and 11.3% for oat flour, and 1.2% and 8.1% for rice flour, respectively, which are very close to those reported in Table 1 (they differ in only 3% or less).

Table 1
Proximate analysis of the oat flour, rice flour, oat–rice flour blend and the RTE blend (g/100 g total wet weight).

Parameter	Flour or blend			
	Oat	Rice	Oat–rice	RTE
Moisture	10.35 ± 0.08	14.39 ± 0.09	11.10 ± 0.19	9.42 ± 0.14
Protein	13.98 ± 0.09	8.64 ± 0.21	13.21 ± 0.19	11.39 ± 0.61
Fat	5.74 ± 0.02	0.31 ± 0.00	4.91 ± 0.07	4.05 ± 0.06
Ashes	1.83 ± 0.02	0.92 ± 0.02	1.67 ± 0.05	1.60 ± 0.36
Carbohydrate	68.10 ± 0.17	75.74 ± 0.15	69.11 ± 0.30	73.57 ± 0.46

3.2. Sorption behaviour of the RTE blend and its different components

The sorption behaviour of the samples is illustrated by the desorption isotherms of these materials presented in Fig. 1a and b, for the powder and strip forms, respectively. In most cases, the moisture contents of the powder was slightly higher than the corresponding strips (although sometimes within the experimental errors involved in the measurements), which may be attributed to the larger exposed surface area of powder, in agreement with the results presented by Chen and Yeh (2000, 2001) for rice flour and extruded pellets. In both powder and strip form cases, for water activity values lower than 0.75 (corresponding to a moisture content of around 16 g/100 g of dry solids or% d.b., as it will be referred to in the rest of the paper), the RTE blend exhibited lower equilibrium moisture content than the other materials, while the opposite behaviour occurred at a_w values greater than 0.75. The greater equilibrium moisture content exhibited by the RTE blend at $a_w > 0.75$ can be attributed to the high sorption capacity of sugars, which are present in the formulation in high proportion (around 17%). In our case, these sugar components were in the amorphous form, which has been reported to be very hygroscopic (Aguilera, de Valle, & Karel, 1995). Additionally, as it will be shown

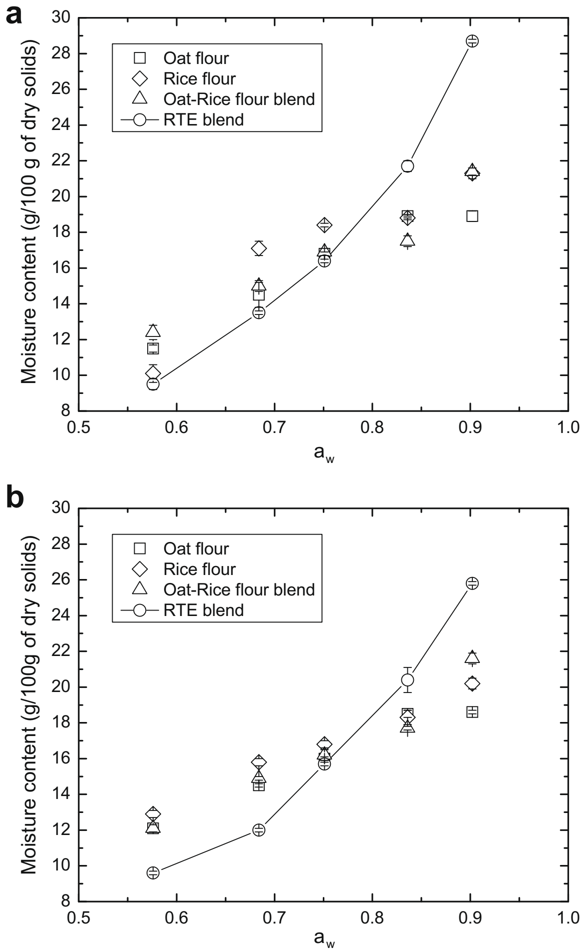

Fig. 1. Sorption characteristics for the oat flour, rice flour, oat–rice flour blend and the RTE blend in powder (a) and strip (b) forms at 25 °C.

later for the RTE blend, samples with moisture contents greater than 13% (d.b.), both in powder and compact form, were in the rubbery state, which promotes molecular mobility and consequent exposure of more active sites for the sorption mechanism.

3.3. Glass transition temperatures of the RTE blend and its different components: effect of moisture content

3.3.1. Differential scanning calorimetry (T_g)

Estimation of glass transition temperatures (T_g) from DSC experiments was carried out from the midpoint of the typical heat capacity change at the transition observed in the second run, as shown in Fig. 2, for typical DSC scans obtained for these materials with a moisture content of around 12% (d.b.). In most cases, good repeatability was obtained for the glass transition temperatures (T_g), since these DSC experiments yielded results with a variation coefficient of less than 10%.

Fig. 2 shows that similar glass transition temperatures are exhibited by rice flour, oat flour and oat–rice flour blend (in the range 63–68 °C) while a lower glass transition temperature was observed for the RTE blend (28 °C). The lower glass transition temperature exhibited by the RTE blend can be attributed to the presence of lower molecular weight materials in it, such as sugar and those found in malt extract, confirming the plasticizing effect of small molecules on starchy products already reported in the literature (Chen & Yeh, 2000; Georget & Smith, 1996; Huang, Chang, Chang, & Lii, 1994; Kalichevsky & Blanshard, 1993; Kalichevsky, Jaroszkiewicz, et al., 1993). Salt was present in such a low proportion in the RTE blend (<0.5%, dry ingredient), that its effect on T_g can be considered negligible, as reported by Huang et al. (1994) on rice starch and flour gels, and in wheat dough by Laaksonen and Labuza (2001).

Results obtained at different moisture contents for the glass transition temperature as measured by DSC experiments are shown in Fig. 3. As expected, the T_g values of all materials decreased as moisture content increased, confirming the plasticizing effect of water, widely recognized in the literature. T_g values changed (see Fig. 3) from 70 to 25 °C for oat flour, rice flour and oat–rice flour blend when the moisture content increased from 10% to 22% (d.b.) and from 40 to 6 °C for the RTE blend when moisture content increased from 9% to 16% (d.b.). T_g values obtained at 5 °C/min in rice flour have been reported to vary between 105 and 25 °C for moisture contents ranging between 10 and 21% (Chen & Yeh, 2000), although these authors did not establish whether the moisture content was expressed in wet or dry basis. In case the reference basis for moisture contents were dry basis, according to the results on sorption isotherms, presented in the same paper, our results for rice flour would be in good agreement with the values reported by Chen and Yeh, for the highest moisture content (i.e., 27 °C for 21% (d.b.) of moisture content, in this work). For the lower moisture contents, there would be a larger difference with the values obtained here (i.e., 68 °C for 10% moisture content (d.b.)), which could be attributed to the large plasticizing effect of water on biopolymers: as the moisture content shifted to lower values, small variations on moisture contents greatly affect the T_g value in that region.

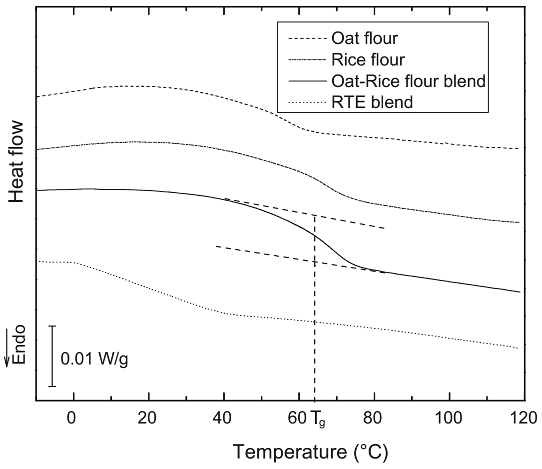

Fig. 2. Typical DSC curves, as a function of temperature for oat flour (MC = 11.5 g/100 g of dry solids), rice flour (MC = 10.2 g/100 g of dry solids), oat–rice flour blend (MC = 12.4 g/100 g of dry solids) and RTE blend (MC = 13.6 g/100 g of dry solids).

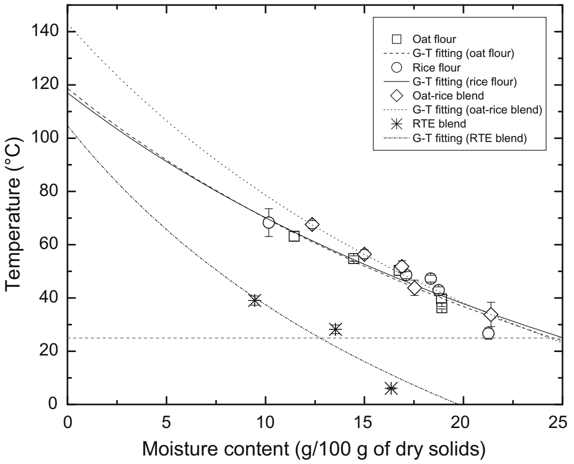

Fig. 3. Glass transition temperature of oat flour, rice flour, oat–rice flour blend and RTE blend, as function of moisture content, measured by DSC.

The Gordon–Taylor equation (Eq. (1)) was applied to the DSC data of the materials studied, so as to predict the effect of water on the glass transition temperature of the materials considered here. Even though this equation was originally deduced for binary polymer mixtures, its use has been extended to more complex mixtures such as starchy flours, by assuming water as solvent and the remaining components as solids or solutes (Chen & Yeh, 2001; Cuq & Icard-Vernière, 2001).

$$T_g = \frac{W_1 T_{g_1} + K W_2 T_{g_2}}{W_1 + K W_2} \tag{1}$$

where W_1 and W_2 are the mass fractions of the flour or blend and of water, T_{g_1} and T_{g_2} their T_g values, respectively, and K a constant. The fitting to the Gordon–Taylor equation were performed employing absolute temperatures (i.e., Kelvin degrees or K). However, for the sake of consistency all temperatures throughout the text are expressed in °C.

The linearised form of Eq. (1) was represented for the data collected for each sample, considering their T_g's and their respective moisture content (Fig. 3). A value of −139 °C was used for the glass transition of amorphous water (T_{g_2} in Eq. (1)), as suggested by Orford et al. (1989). Data from the RTE blend used in the linear regression were those corresponding to moisture contents lower than 20% (d.b.). DSC scans obtained for samples with greater values of moisture content, showed that the glass transition region was masked by the fusion temperature range of ice.

The fits to Eq. (1) for each material considered are shown in Fig. 3. This figure shows that in spite of R^2 values not very high, the Gordon–Taylor equation describes fairly the plasticizing effect of water in the flours and blends employed here. The regression parameters (i.e., K and glass transition temperature values for the dry amorphous flours and blends (T_{g_1} in Eq. (1)) are shown in Table 2. The K values varied in the range of 2.2–3.8. Values of K presented

Table 2
Gordon–Taylor constants (K, T_{g_1}) obtained from linear regression to evaluate the plasticizing effect of water on the glass transition of oat flour, rice flour, oat–rice flour blend and RTE blend.

Flour or Blend	Gordon–Taylor constants		
	K	T_{g_1} (°C)	R^2
Oat	2.3	119	0.873
Rice	2.2	117	0.778
Oat–rice	3.0	143	0.944
RTE	3.8	105	0.708

in the literature for binary systems of biopolymer–water, have been reported to vary between 1.3 and 7.7 for sodium caseinate (Kalichevsky, Blanshard, & Tokarczuk, 1993) and matodextrins (Roos & Karel, 1991a), respectively. Additionally, for more complex systems, values such as 3.4–5.5 have been reported for wheat durum semolina (Cuq & Icard-Vernière, 2001) and 4.2 for rice flour (Chen & Yeh, 2001). These reported K values are in the same order of magnitude than those obtained here (Table 2).

The T_g values of the dry amorphous oat flour, rice flour and RTE blend were in the range 105–120 °C (Table 2). As shown in this table, T_g values of the dry amorphous oat–rice flour blend were found higher than those obtained for their components analysed separately. This result is due to the irregular decrease of experimental T_g values with moisture content, an effect that was more marked for the oat flour and rice flour. In all cases, glass transition temperatures for the dry amorphous materials were considerably lower than those reported for pure starch materials. For example, glass transition temperatures for dry starch individual components i.e., amylose and amylopectin have been reported to be the same, and in the order of 227 °C (Orford et al., 1989). Meanwhile, in amorphous dry starch materials such as potato and waxy maize starch, the T_g values reported have been in the range 285–316 °C (Bizot et al., 1997). In the same way, they were also lower than other dry amorphous materials, such as 229 °C for gelatin (Mousia, Farhat, Blachot, & Mitchell, 2000), 162 °C for gluten (Kalichevsky et al., 1992), 144 °C for casein, and 162–225 °C for wheat durum semolina (Cuq & Icard-Vernière, 2001). Large differences between the values reported here and those found in the literature, are partly due to the complex composition and structure heterogeneity of food systems such as cereal products, a fact that underlines the need of determining these parameters in other complex systems extensively used in the food industry. Another factor affecting the differences in value is the fact that errors involved in the extrapolation must also be present.

Fig. 3 also depicts a dash horizontal line representing the sample conditioning temperature (i.e., 25 °C). It can be seen in this figure that, in case of the RTE blend, samples with moisture contents greater than 13% (d.b.) were in the rubbery state at 25 °C, while oat flour and rice flour, as well as their blend were in the glassy state during conditioning.

3.3.2. *Dynamic mechanical thermal analysis (T_α)*

The temperature of main mechanical relaxation T_α, which is normally associated with the glass transition temperature of the material T_g, was determined from the drop in the storage modulus E' and from the peak in tan δ. The extrapolation procedure employed to determine T_g from E' is illustrated in a typical DMTA curve for rice flour with 16.8% (d.b.) (Fig. 4). In most cases, the T_α relaxation temperatures obtained by DMTA for all samples were well reproducible with a variation coefficient of less than 7%.

Results for the variation of the main relaxation temperatures associated to the glass transition (T_α), as measured by DMTA, with moisture contents for all the materials employed here, are shown in Fig. 5a–d. Gordon–Taylor fits taken from Fig. 3 are also drawn for comparison purposes. For the same moisture content as in DSC measurements, i.e., around 12% (d.b.), T_α obtained for oat flour and rice flour as well as for their blend, exhibited similar trends, in the order of 65 and 90 °C, within experimental error, as indicated by the drop in E' and the peak in tan δ, respectively (Fig. 5a–c). The RTE blend, on the other hand, exhibited lower T_α temperatures, i.e., 48 °C obtained by E' and 65 °C by tan δ (Fig. 5d). DMTA results are therefore consistent with the DSC results presented above, since they yield similar T_α values for the major components (oat flour, rice flour and oat–rice flour blend) and considerably lower values for the RTE blend. Like the T_g values determined by DSC and as expected, T_α values decreased as moisture content increased.

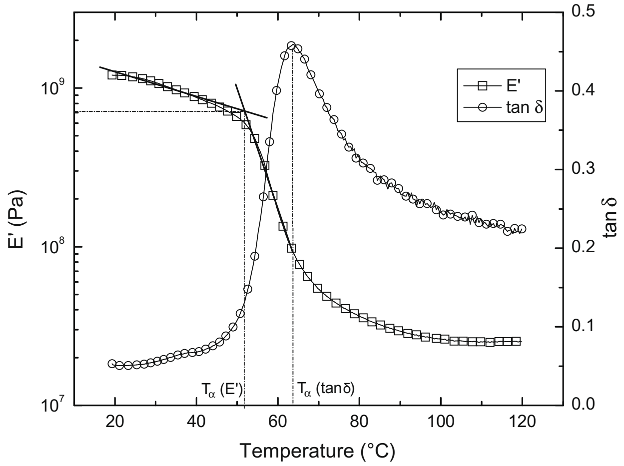

Fig. 4. Typical DMTA curves (E' and tan δ) as a function of temperature for rice flour with moisture content of 16.8 g/100 g of dry solids.

From the above results, it can be seen that, in all cases, the relaxation temperatures measured by E' (Fig. 5a–d), fall approximately 15–20 °C below those measured by the peak position in tan δ. A difference of around 20 °C between the onset of the drop in the elastic modulus and the tan δ peak has been reported before (Kalichevsky, Jaroszkiewicz, Ablett, et al., 1992). As indicated by the Gordon–Taylor fitting curves, glass transition temperatures measured by DSC were lower than those of the main mechanical relaxation determined by DMTA (Fig. 5a–d). This difference is expected in terms of how the structural relaxation of the material responds to thermal and mechanical stimuli. DMTA applies mechanical stress at a frequency of 1 Hz in addition to the superimposed heating rate, as opposed to DSC, where only thermal energy is supplied at similar heating rates. The difference found between T_g and T_α may comfort the hypothesis of extrusion expansion model which considers the cessation of bubble growth at $T_g + 30$ °C (Fan et al., 1994), in similar interval of moisture content. In this way, the much lower values of characteristic temperatures found for RTE blends, confirm the interpretation given by Fan et al. (1996), to explain the lower expansion for sugar containing products: even for lower moisture contents, say 12% (d.b.), the T_α values are lower than 100 °C, and no internal vapour pressure sustains the collapse of the cooling melt (Della Valle et al., 1997).

Values of T_α for moisture content greater than 16% (d.b.) were omitted (Fig. 5d) because under such conditions, the behaviour of the RTE blend was peculiar and displayed a reproducible shoulder on the E' curve at around 45 °C and a subsequent decrease of E' with temperature as illustrated in Fig. 6, for a moisture content of 26% (d.b.). Indeed this thermomechanical behaviour is different from the one observed at lower moisture content (Fig. 3). Fig. 6, also shows that the occurrence of this behaviour coincided with the corresponding peak in tan δ. It was observed that the temper-

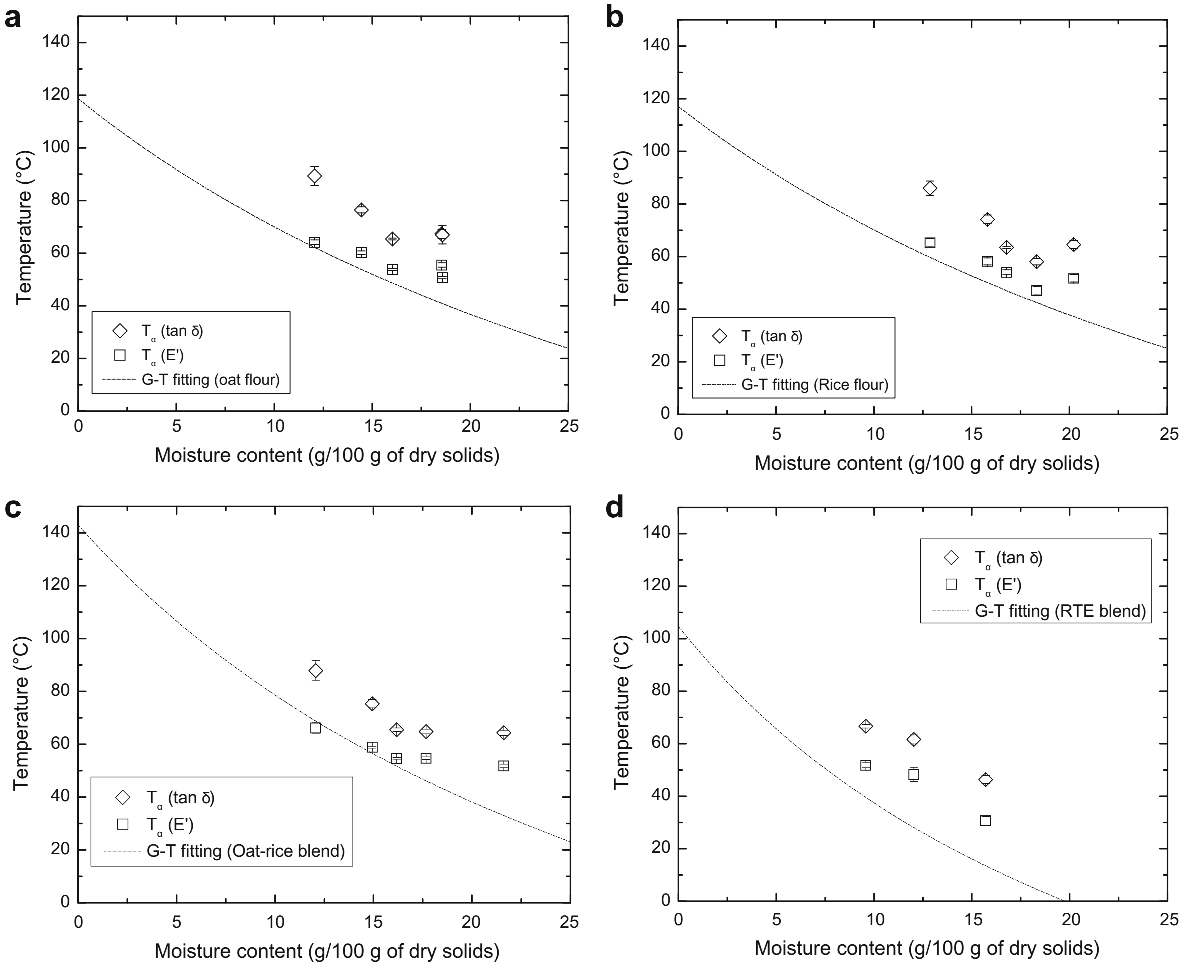

Fig. 5. Mechanical relaxation temperature of (a) oat flour, (b) rice flour, (c) oat–rice flour blend and (d) RTE blend, as function of moisture content, measured by DMTA.

ature at which the E' curve exhibited the shoulder, increased as the moisture content decreased in the range of 20–25% (d.b.).

This slight increase of the elastic modulus appearing after the glass transition temperature of samples with high moisture content, indicating stiffening of the sample, has been reported by Kalichevsky, Blanshard, and Marsh (1993) to appear in the interval 30–50 °C in amylopectin conditioned at high relative humidities (>92%), and at 45 °C in wheat samples with 24% (d.b.) by Georget and Smith (1996). These increases in E' were attributed to dehydration or to an increase in crystallinity in the case of Kalichevsky et al. (1993). In our case, DSC scans from the first run (not shown here) of amorphous RTE flour blend samples with moisture content greater than 20% (d.b.) exhibited an endothermic peak at temperatures around 67.6 °C (peak temperature), which indicated that samples crystallized during storage. This behaviour was expected in an amorphous sugar-rich system with high moisture content (i.e., the RTE blend), as their T_g values were shifted well below 25 °C (i.e., the conditioning temperature). Indeed, at such humidity conditions, where the system was in the rubbery state, as it was shown in Fig. 3 (dash horizontal line), the sample crystallization time greatly decreases as the ($T-T_g$) temperature difference increases (Roos & Karel, 1991b).

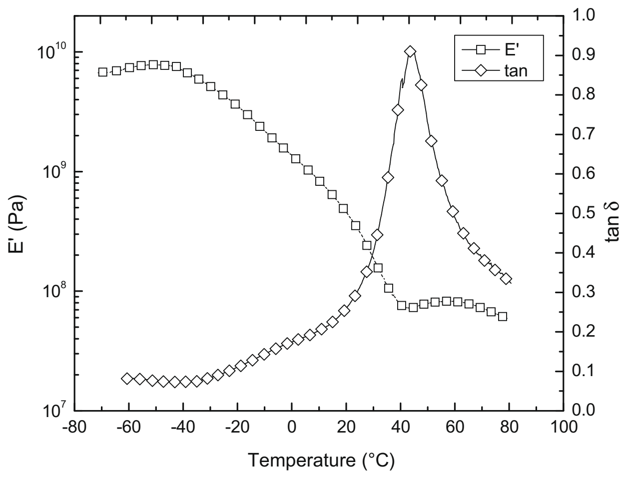

Fig. 6. Typical DMTA curves as a function of temperature for the RTE blend with moisture content of 26 g/100 g of dry solids.

4. Conclusions

This work presents measurements of glass transition temperatures of a complex starchy ready to eat breakfast cereal formulation and its main components. Such data on complex cereal formulations are scarce in the literature.

The glass transition temperature of the RTE cereal formulation and that of its main components (oat flour, rice flour and oat–rice flour blend) decreased as moisture content increased as expected, either determined by DMTA or DSC, in the range of moisture contents commonly employed in extrusion processes. The effect of the moisture content was modeled by the Gordon–Taylor equation, and the fitted K values were in the same order of magnitude as those reported in the literature for similar materials. Differences on glass transition temperatures for the dry solid flour and blends, compared to other food biopolymers were attributed to their complex composition. The T_g values obtained for the main components were found to be similar within the experimental errors of the measurements at any given moisture content. Glass transition temperatures of the starchy RTE formulation were found much lower than the ones of its main components, an effect likely due to the plasticizing effect of the minor components in the formulation (sugar and malt extract). Glass transition temperature values were found about 20 °C lower than the ones of the main mechanical relaxation, measured by the tan δ peak in DMTA.

Acknowledgements

We acknowledge the financial support for this work from the National Funding for Science and Technology *FONACIT* in Venezuela through Grant S1-2002000524 and from the Ministry of Foreign Affairs *MAE* in France and *FONACIT* through the post-graduate program (PCP) “starchy product extrusion”.

References

Aguilera, J. M., de Valle, J. M., & Karel, M. (1995). Caking phenomenon in amorphous food powders. *Trends in Food Science and Technology, 6*(5), 149–155.

AOAC. (1975). Official methods of analysis of AOAC international. Association of Official Analytical Chemists (AOAC). 6th ed. Washington, DC, USA.

Bizot, H., Le Bail, P., Leroux, B., Davy, J., Roger, P., & Buléon, A. (1997). Calorimetric evaluation of the glass transition in hydrated, linear and branched polyanhydroglucose compounds. *Carbohydrate Polymers, 32*(1), 33–50.

Blanshard, J. M. (1995). The glass transition, its nature and significance in food processing. In ST. Beckett (Ed.), *Physico-chemical aspects of food processing (pp. 17–48)*. Glasgow, UK: Chapman & Hall.

Brent, J. L., Mulvaney, S. J., Cohen, C., & Bartsch, J. A. (1997). Thermomechanical glass transition of extruded cereal melts. *Journal of Cereal Science, 26*(3), 301–312.

Champion, D., Le Meste, M., & Simatos, D. (2000). Towards an improved understanding of glass transition and relaxations in foods: molecular mobility in the glass transition range. *Trends in Food Science and Technology, 11*(2), 41–55.

Chanvrier, H., Colonna, P., Della Valle, G., & Lourdin, D. (2005). Structure and mechanical behaviour of corn flour and starch-zein based materials in the glassy state. *Carbohydrate Polymers, 59*(1), 109–119.

Chanvrier, H., Della Valle, G., & Lourdin, D. (2006). Mechanical behaviour of corn flour and starch-zein based materials in the glassy state: A matrix–particle interpretation. *Carbohydrate Polymers, 65*(3), 346–356.

Chen, C. M., & Yeh, A. I. (2000). Expansion of rice pellets: Examination of glass transition and expansion temperature. *Journal of Cereal Science, 32*(2), 137–145.

Chen, C. M., & Yeh, A. I. (2001). Effect of amylose content on expansion of extruded rice pellets. *Cereal Chemistry, 78*(3), 261–266.

Cocero, A. M., & Kokini, J. L. (1991). The study of the glass transition of glutenin using small amplitude oscillatory rheological measurements and differential scanning calorimetry. *Journal of Rheology, 35*(2), 257–270.

Cuq, B., Abecassis, J., & Guilbert, S. (2003). State diagrams to help describe wheat bread processing. *International Journal of Food Science and Technology, 38*(7), 759–766.

Cuq, B., & Icard-Vernière, C. (2001). Characterisation of glass transition of durum wheat semolina using modulated differential scanning calorimetry. *Journal of Cereal Science, 33*(2), 213–221.

Della Valle, G., Vergnes, B., Colonna, P., & Patria, A. (1997). Relations between rheological properties of molten starches and their expansion by extrusion. *Journal of Food Engineering, 31*(3), 277–296.

Eliasson, A. C., & Larsson, K. (1993). *Components in other cereals. In: Cereals in breadmaking. A molecular colloidal approach (pp. 203–240)*. New York, USA: Marcel Dekker, Inc..

Fan, J., Mitchell, J. R., & Blanshard, J. M. (1994). A computer simulation of the dynamics of bubble growth and shrinkage during extrudate expansion. *Journal of Food Engineering, 23*(3), 337–356.

Fan, J., Mitchell, J. R., & Blanshard, J. M. (1996). The effect of sugars on the extrusion of maize grits: I. The role of the glass transition in determining product density and shape. *International Journal of Science and Technology, 31*(1), 55–65.

Georget, D. M., & Smith, A. C. (1996). The effect of sugars on the mechanical properties of processed cereals. *Journal of Thermal Analysis, 47*(5), 1377–1389.

Greenspan, L. (1977). Humidity fixed points of binary saturated aqueous solutions. *Journal of Research of the National Bureau of Standards–A. Physics and Chemistry, 81A*(1), 89–96.

Huang, R. M., Chang, W. H., Chang, Y. H., & Lii, C. Y. (1994). Phase transition of rice starch and flour gels. *Cereal Chemistry, 71*(2), 202–207.

Kaletunç, G., & Breslauer, K. J. (2003). Calorimetry of pre- and post-extruded cereal flours. In G. Kaletunç & K. J. Breslauer (Eds.), *Characterization of cereals and flours. Properties, analysis, and applications (pp. 1–35)*. New York, USA: Marcel Dekker, Inc..

Kalichevsky, M. T., & Blanshard, J. M. (1993). The effect of fructose and water on the glass transition of amylopectin. *Carbohydrate Polymers, 20*(2), 107–113.

Kalichevsky, M. T., Blanshard, J. M., & Marsh, R. D. (1993). Applications of mechanical spectroscopy to the study of glassy biopolymers and related systems. In J. M. Blanshard & P. L. Lillford (Eds.), *The glassy state of foods (pp. 142–144)*. UK: Nottingham University Press. Nottingham.

Kalichevsky, M. T., Blanshard, J. M., & Tokarczuk, P. F. (1993). Effect of water content and sugars on the glass transition of casein and sodium caseinate. *International Journal of Science and Technology, 28*(2), 139–151.

Kalichevsky, M. T., Jaroszkiewicz, E. M., Ablett, S., Blanshard, J. M., & Lillford, P. L. (1992a). The glass transition of amylopectin measured by DSC, DMTA and NMR. *Carbohydrate Polymers, 18*(2), 77–88.

Kalichevsky, M. T., Jaroszkiewicz, E. M., & Blanshard, J. M. (1992b). Glass transition of gluten. 1: Gluten and gluten—sugar mixtures. *International Journal of Biological Macromolecules, 14*(5), 257–266.

Kalichevsky, M. T., Jaroszkiewicz, E. M., & Blanshard, J. M. (1993). A study of the glass transition of amylopectin–sugar mixtures. *Polymer, 34*(2), 346–358.

Laaksonen, T. J., & Labuza, T. P. (2001). Effects of moisture, sucrose, NaCl, and arabinoxylan on relaxation in wheat dough as measured by DMTA. *International Journal of Food Properties, 4*(2), 311–325.

Le Meste, M., Champion, D., Roudaut, G., Blond, G., & Simatos, D. (2002). Glass transition and food technology: A critical appraisal. *Journal of Food Science, 67*(7), 2444–2458.

Moraru, C.I., & Kokini, J.L. (2003). Nucleation and expansion during extrusion and microwave heating of cereal foods. Comprehensive Reviews in Food Science and Food Safety, 2, 120–138. Available from www.ift.org.

Mousia, Z., Farhat, I. A., Blachot, J. F., & Mitchell, J. R. (2000). Effect of water partitioning on the glass-transition behaviour of phase separated amylopectin–gelatin mixtures. *Polymer, 41*(5), 1841–1848.

Orford, P. D., Parker, R., Ring, S. G., & Smith, A. C. (1989). Effect of water as a diluent on the glass transition behaviour of malto-oligosaccharides, amylose and amylopectin. *International Journal of Biological Macromolecules, 11*(2), 91–96.

Rahman, M. S. (2006). State diagram of foods: Its potential use in food processing and product stability. *Trends in Food Science and Technology, 17*(3), 129–141.

Ross, K. A., Campanella, O. H., & Okos, M. R. (2002). The effect of porosity on glass transition measurement. *International Journal of Food Properties, 5*(3), 611–628.

Roos, Y., & Karel, M. (1991). Plasticizing effect of water on thermal behavior and crystallization of amorphous food models. *Journal of Food Science, 56*(1), 38–43.

Roos, Y., & Karel, M. (1991). Water and molecular weight effects on glass transition in amorphous carbohydrates and carbohydrate solutions. *Journal of Food Science, 56*(6), 1676–1681.

Zhou, M., Robards, K., Glennie-Holmes, M., & Helliwell, S. (1999). Oat lipids. *Journal of the American Oil Chemists Society, 76*(2), 159–169.