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

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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 physicochemical 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.

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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),