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New insights on the thermal analysis of low moisture composite foods

Gaëlle Roudaut[a,*], Joël Wallecan[b]

[a] Food Processing and Physicochemistry Department, UMRA PAM, Agrosup Dijon-Université de Bourgogne, 1 Esplanade Erasme, 21000 Dijon, France
[b] Cargill Global FIS Research, Havenstraat 84, Vilvoorde, Belgium

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ABSTRACT

Low moisture baked products were investigated with a view to characterising the effect of both formulation and humidity on their physical stability. At the end of the baking process, the samples were in the amorphous state as a result of starch gelatinization and sugar melting. Their thermal properties were analyzed with differential scanning calorimetry and their glass transitions were studied. The DSC thermograms were thoroughly studied through a Gaussian deconvolution of the first derivative of their heat flow. This approach evidenced a multiple phase behavior with different glass transitions in composite systems. They were associated with either a polymer-rich phase and/or a plasticizer (sugar)-rich phase whose behavior depended on the sample water content.

This novel approach of thermal properties suggested new insights: considering the phase behavior of complex systems and thus the properties of their individual phases could contribute to a better understanding of the physical stability of the products.

1. Introduction

Material polymer science approaches have been applied to food systems for several decades (White & Cakebread, 1966; Slade & Levine, 1991, 1995) particularly with a view to investigate the phenomena controlling their physicochemical stability. Water relationships are particularly relevant for amorphous food systems. Such products are numerous as many processes (baking, dissolution/drying) lead to a loss of crystallinity, resulting in many foods having polymeric material below or close to their T_g in storage conditions. Water-structure relationships have been particularly studied in low moisture biopolymer-based systems, with a particular insight into the study of the glass transition temperature of these systems whose key role in physical stability has been discussed for several years since its first application (White & Cakebread, 1966; Slade & Levine, 1991, 1995; Champion, Le Meste, & Simatos, 2000; Le Meste, Champion, Roudaut, Blond & Simatos, 2002). Among the key parameters of low moisture food quality, chemical and structural stability (e.g., respectively oxidative reactions or mechanical properties changes), are more critical than microbiological stability ensured by low water activity (Poirier-Brulez, Roudaut, Champion, Tanguy & Simatos, 2006). As an example, the texture of baked products is of critical importance in their acceptability. Factors such as crispiness, snap and hardness are critical. Increasing levels of moisture or aging over time have been described to lead to a loss of crispness, snap and hardness in thin, low moisture products with long shelf-life like crisps, breakfast cereals, ice cream cones (Shogren, Swanson, & Thompson, 1992; Martınez-Navarrete, Moraga, Talens, & Chiralt, 2004). This is particularly relevant since these attributes are key for this type of products. Understanding the physical mechanisms behind these mechanical properties is of primary importance to fully understand and thus adequately control the changes occurring as a material is being stored.

Most studies have been performed on model systems simplified to facilitate the interpretation of the data and facilitate the correlation of a phenomenon to a given polymeric component (Poirier-Brulez et al., 2006; Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, & Lillford; Borde, Bizot, Vigier, & Buleon, 2002). However, baked products of even simple formulation (less than 5 ingredients) are often composed of several biopolymers e.g., polysaccharides (typically both amylose and amylopectin) and proteins, as well as solutes of smaller molecular weight (sugars and amino acids) interacting with their homologues and/or the other components.

Following early work on the effect of hydration on the texture of low moisture baked products (Sauvageot & Blond, 1991) quite a few publications have been dedicated to T_g measurement of these products by dynamic rheology (Le Meste, Huang, Panama, Anderson, & Lentz, 1992; Nikolaidis & Labuza, 1996; Hallberg & Chinachoti, 1992) and later by Differential Scanning Calorimetry

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* Corresponding author. Tel.: +0033 3 80774058; fax: +0033 3 80774047.
E-mail address: gaelle.roudaut@agrosupdijon.fr (G. Roudaut).

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(DSC) (Le Meste et al., 2002) when the sensitivity of the instruments enabled the detection of these phenomena. Generally a unique glass transition was measured from the C_p change by DSC or the maximum in mechanical loss factor (tanδ). The occurrence of unique or multiple glass transitions is generally discussed in terms of compatibility between the polymers (Bikiaris, Prinos, Botev, Betchev, & Panayiotou, 2004). A compatible mix will exhibit a unique relaxation whereas an incompatible mix of amorphous materials will show multiple transition patterns. Today most research on low moisture biopolymer based-systems is more and more focusing on their properties in the glassy state: i.e., structural relaxation (Gonzalez et al., 2010; Haque, Whittaker, Gidley, Deeth, & Fibrianto, 2012), free volume (Townrow, Roussenova, Giardiello, Alarm, & Ubbink, 2010; Sharma, Zaydouri, Roudaut, & Duplâtre, 2011). However, it is important to investigate the contribution of the different components. Combining the individual behaviors enables a deeper understanding of the mechanical properties of the composite structure. This was performed in the present work using an approach that was not previously applied on food composites.

2. Materials and methods

2.1. Preparation of the samples

The exact formulations are given in Table 1.

The dry ingredients, oil and lecithin were pre-mixed in a planetary mixer in order to ensure a good homogeneity before water addition. Water was then added and the whole system was mixed for 1 min at low speed followed by 2 min at high speed. The obtained doughs were then left for equilibration at room temperature for 20 min prior baking. A Silex GTT532 waffle iron was used for the preparation of both sucrose (+) and sucrose (−) samples. Baking conditions for the sucrose (−) were 90 s at 170 °C, while 210 °C for 2.5 min was applied for the sucrose (+) samples.

2.2. Equilibration at controlled relative humidity

The samples were ground to a powder using a household grinder. The samples were equilibrated in air tight containers over P2O5 or various saturated salt solutions between 0 and 75% RH (Greenspan, 1977). They were considered at equilibrium once their weight was constant (after 2 to 3 weeks).

2.3. Differential scanning calorimetry analysis

The instrument (Thermal Analysis Q20) was calibrated at 10 °C/min for temperature and energy with azobenzol and indium. Samples (approximately 10–15 mg) were sealed in aluminium pans and scanned at 10 °C/min (for both cooling and heating) in the range (−20–170 °C) while an empty pan was used as a reference. The samples were submitted to two heating scans: the first one to characterize their thermal behavior history (and the possible overshoot associated with enthalpy relaxation) and the second one to analyze the reversible contribution of the phase transition. The glass transition temperature (T_g) was determined from the midpoint of the observed heat capacity change.

2.4. Peak resolution technique

The first derivative of the heat flow versus temperature was calculated for the different DSC thermograms in the second heating scan to avoid overlap from the endothermic signal. The presence of different phases (i) with their respective glass transitions (T_{gi}) was then evaluated from the dH/dT signal using a peak resolution technique based on Gaussian functions (Hourston, Song, Pollock, & Hammiche, 1997; Song, Hourston, Pollock, Schafer, & Hammiche, 1997; Hourston, Song, Schafer, Pollock, & Hammiche, 1999).

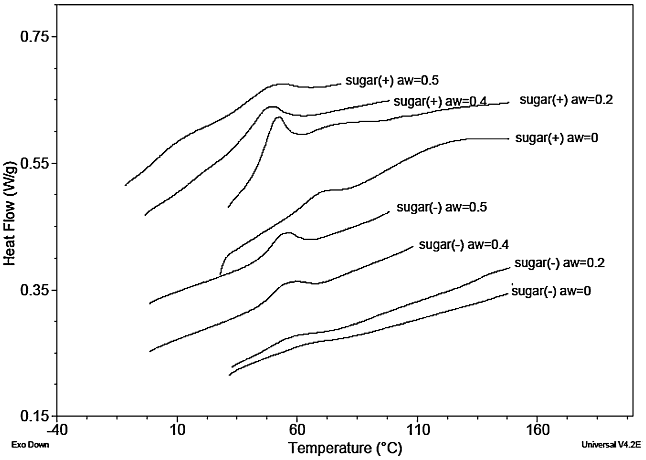

Fig. 1. Effect of water activity on the DSC thermograms (1st heating scan at 10°/min) of sugar (+) and (−) samples.

$$G_i = \frac{\Delta C_{p,i}}{\Delta T_{g,i}\left(\pi/2\right)^{1/2}} \exp\left(-\frac{2\left(T - T_{g,i}\right)^2}{\left(\Delta T_{g,i}\right)^2}\right)$$

Note that ΔT_{gi} obtained in this way corresponds to the width of the Gaussian peak at half height. This method is based on the notion that the dH/dT versus temperature signal of a pure polymer or polymer fraction can be described by one Gaussian function at the glass transition (Hourston et al., 1997). The fitting of the dH/dT signal by means of Gaussian functions was done in excel.

3. Results and discussion

3.1. Sorption data

The sorption isotherms were determined at 25 °C, the sucrose content did not affect the water sorption properties of the samples: for both recipes, the water content ranged between 1.5% and 15% (wb). In literature, sucrose and plasticizers in general have been shown to increase the water sorption properties of starch (Poirier-Brulez et al., 2006; Chinachoti & Steinberg, 1984). In the present work the samples differed not only by their sucrose content but also by their NaCl and vegetable fat content. Their processing conditions were also slightly different. Moreover the model wafers had a more complex formulation than the samples generally studied in literature, which might have affected the sorption properties to a different extent.

3.2. Thermal properties of the samples

The degree of gelatinization of the supplied samples was verified with a heating scan in DSC in excess water (not shown); no endothermic peak assignable to residual crystallinity or incomplete gelatinization was observed in either type of sample. No melting peak from crystalline sugar could be observed either. The supplied samples were therefore considered to be fully gelatinized thus fully amorphous for both recipes although prepared with somewhat different processing conditions. Fig. 1 shows the DSC thermograms (1st scan) obtained at different water activities and for both sugar levels.

Regarding the general pattern of the thermograms 2 main events were observed.