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New insights on the thermal analysis of low moisture composite foods

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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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(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).

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

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.

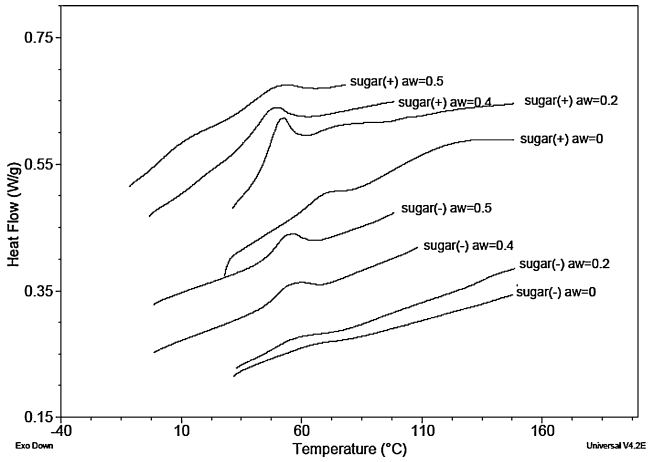

Fig. 1. Effect of water activity on the DSC thermograms (1st heating scan at 10°/min) of sugar (+) and (−) samples.

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.

Table 1
Recipes of the studied systems.

Ingredients	(Sucrose +)		(Sucrose −)	
	(g in dough)	% on db	(g in dough)	% on db
Wheat flour albatros (8.4% protein)	500	64	500	98.3
Sucrose	215	27	/	/
Liquid lecithin	10	1.3	1.6	0.3
Regular sunflower oil	45	5.8	5	1
Salt	15	1.9	/	/
Water (20 °C)	500	/	660	/
Sodium bicarbonate	2	0.3	2	0.4
Total	1287		1168.6	

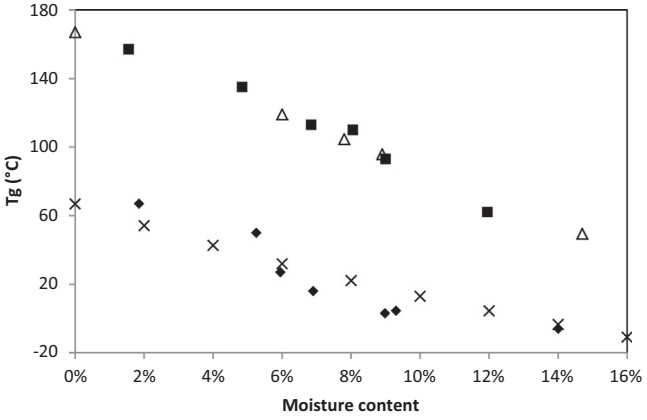

Fig. 2. Glass transition temperature (midpoint DSC) versus moisture content for samples with (♦) and without sucrose (■), compared with wheat flour samples (△) (Kaletunç & Beslauer, 1996) and sucrose (×) (Roos & Karel, 1991).

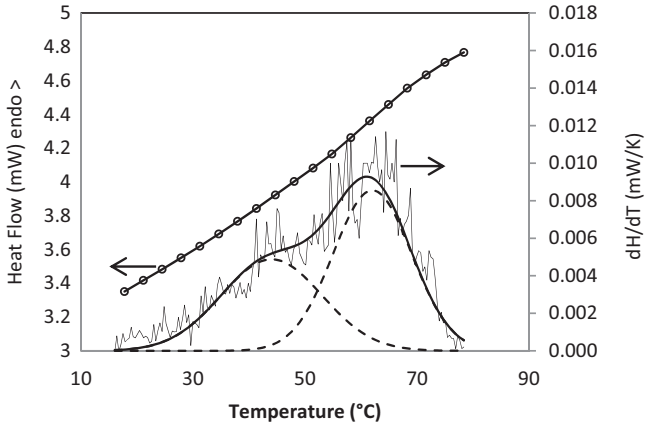

Fig. 3. Deconvolution of the DSC thermogram of sugar (−) system equilibrated at A_w = 0.6. Heat flow: -◯- (left *Y* axis); first derivative of the heat flow: --- (right *Y* axis); ---- Gaussian functions fitting the signal; --- sum of Gaussian functions.

The thermograms recorded from the first heating scan exhibited an endothermic endotherm between 35 °C and 70 °C, its amplitude was variable depending on the sample. Second, an event assignable to a glass transition was observed in a temperature range sensitive to both water and sucrose content. It is worth mentioning that a clear reversible C_p change was presence in both heating and cooling scans (data not shown). The endothermic peak measured between 40 °C and 60 °C, has previously been described for many biopolymers whether amorphous (Shogren et al., 1992; Kalichevsky et al., 1992; Appelqvist, Cooke, Gidley, & Lane, 1993; Gidley, Cooke, & Ward-Smith, 1993; Le Meste, Roudaut, & Davidou, 1996) or fully ordered such as dried agar gels (Cooke, Gidley, & Hedges, 1996), It has generally been attributed to a structural relaxation associated with storage in sub-T_g conditions. In the present study (Fig. 1), it can be observed that the temperature of this endothermic peak is slightly affected by A_w but not by the sucrose content of the samples. When both water and sucrose contents increased, the glass transition was shifted for the samples with an A_w above 0.25 to temperature values below the endothermic peak.

It is particularly visible for sucrose (+) sample equilibrated at A_w = 0.5, it exhibited a glass transition midpoint around 0 °C, whereas the peak temperature of the endothermic peak was situated around 50 °C. This data suggest that the endothermic peak may not relate to the species causing the observed glass transition, since structural relaxation is unlikely to occur in a species already above its glass transition.

Fig. 2 gathers the DSC-measured T_g midpoints of the samples with and without sugar as a function of water content. A clear plasticizing effect of both water and sugar could be observed.

The plasticizing effect of water was comparable to previously published values on similar systems (Martınez-Navarrete et al., 2004). Moreover, these values were comparable to those reported in literature for wheat flour (Kaletunç & Beslauer, 1996).

However, the drop in T_g when adding sugar to the composite was much larger than has been described in literature (Poirier-Brulez et al., 2006) (for similar hydration ranges and sucrose levels). The measured glass transition temperatures were very similar to the ones reported for sucrose (Roos & Karel, 1991).

This clearly indicated that the observed glass transitions did not originate from the same components in the sugar (−) and sugar (+) samples. In absence of sugar, it seemed that the detected transition was coming from flour while for the sucrose (+) samples the dominant relaxation appeared to originate from the sucrose. This seemed peculiar at first, as the sucrose (+) systems still contained about 64% of flour on dry basis. However, the 'disappearance' of the flour signal might be explained by the differences in ΔC_p between sucrose (0.76 kJ/kg K Kalichevsky et al., 1992), gluten (0.22 kJ/kg K, Kalichevsky et al., 1992) and starch (0.47 kJ/kg K, (Orford, Parker, Ring, & Smith, 1989). In addition to the lower C_p values, the composition heterogeneities of the flour (versus sucrose) may cause a widening of the signal contributing to the disappearance or total attenuation of the signal.

These data suggested that in the case of composite samples, the dominant relaxation observed in DSC depends on the product composition. Moreover, the enthalpy relaxation peak was actually observed between the two glass transition temperatures, which meant that it would then only be associated with the structural relaxation of the highest T_g phase.

The first derivative the heat flow (dH/dT) was therefore calculated as a tool to investigate the possible occurrence of multiple transitions. This was first performed on the second scan of the sucrose (−) samples which consisted of almost pure flour (Fig. 3). The dominant glass transition in the heat flow signal was observed

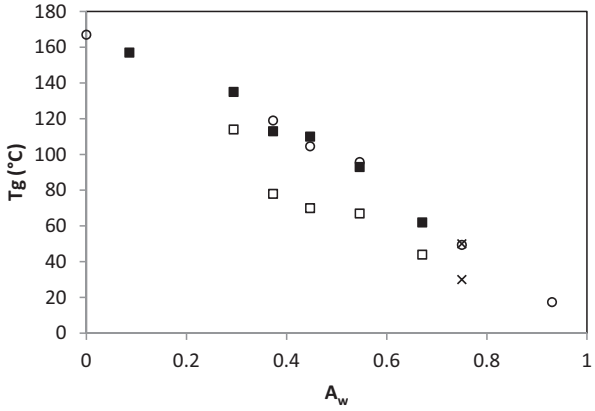

Fig. 4. Evolution of glass transition temperatures versus A_w for sucrose (−) samples. (□) T_{g1}, (■) T_{g2}, (o) literature values for flour (Kaletunç & Beslauer, 1996). (×) T_{g1} and T_{g2} of a 90/10 wheat starch/gluten mixed system equilibrated at an A_w of 0.75.

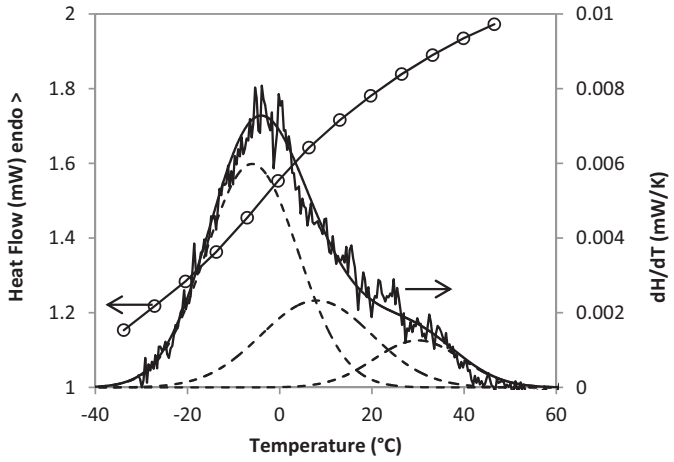

Fig. 5. Deconvolution of the DSC thermogram of sucrose (+) system equilibrated at A_w = 0.75. Heat flow: -o- (left *Y* axis); first derivative of the heat flow: (right *Y* axis); ---- Gaussian functions fitting the signal; ___ sum of Gaussian functions.

in the calculated d*H*/d*T* profile as a clear peak around 65 °C. However a shoulder was also observed in the low temperature end. This pointed toward the presence of another phase with a distinct relaxation behavior. The d*H*/d*T* values only came back to 0 below 15 °C or above 80 °C, clearly indicating that the transition region was broader than initially expected.

Gaussian curves fitting showed that the signal could be very well described by a sum of 2 Gaussian functions suggesting that 2 glass transitions were present in flour. This is of particular interest, as gelatinized flour is a complex system containing starch and gluten that was until now always described as having a single glass transition (Martınez-Navarrete et al., 2004; Kaletunç & Beslauer, 1996; Brent, Mulvaney, Cohen & Bartsch, 1997; Pereira & Oliveira, 2000).

Fig. 4 shows the evolution of both transitions (T_{g1} in the low end, T_{g2} in the high end) versus A_w for sucrose (−) samples compared with flour samples data (Kaletunç & Beslauer, 1996). Due to the fact that 2 phases were detected, it was judged more appropriate to use the A_w value instead of moisture content, as the distribution of the moisture between the two phases might be different. The highest glass transition temperature corresponded well with the one reported for flour. A low temperature event remained detectable over the almost entire A_w range. It is hypothesized that the lower glass transition is coming from the gluten-rich fraction, while the higher transition from the starch-rich one. To confirm this, a mixed system comprising 90% of wheat starch and 10% of wheat gluten was made. Both components were mixed in excess of water prior heating up to 120 °C in a Rapid Visco Analyser (RVA) instrument, in order to fully gelatinize the starch. The obtained slurry was then quench cooled and freeze-dried. The resulting powder was subsequently stored at an A_w of 0.75 over 2 weeks in order to reach equilibrium. Three independent samples were measured in DSC and the obtained signals were deconvoluted. Two glass transitions were found in all cases with average values of 30 °C ± 1.2 °C and 50 °C ± 0.5 °C, which confirmed the present of two events. The latter T_g corresponded well with the data found in literature (see Fig. 4). Their origin and composition will be further examined in the future.

A similar approach was then taken for the sucrose containing samples. Fig. 5 presents the deconvolution results of the sucrose containing system at A_w = 0.75. In this case (and for all sucrose containing samples), a sum of 3 Gaussian functions fitted the data well: pointing toward 3 thermal transitions on the thermogram. The lowest T_g (noted T_{g1}) determined with the deconvolution corresponded to the most visible transition on the raw heat flow signal (noted initial T_g) and corresponded quite well with the glass transition values reported for sucrose (Fig. 4). It suggested that this relaxation could be attributed to a sucrose-rich fraction of the system.

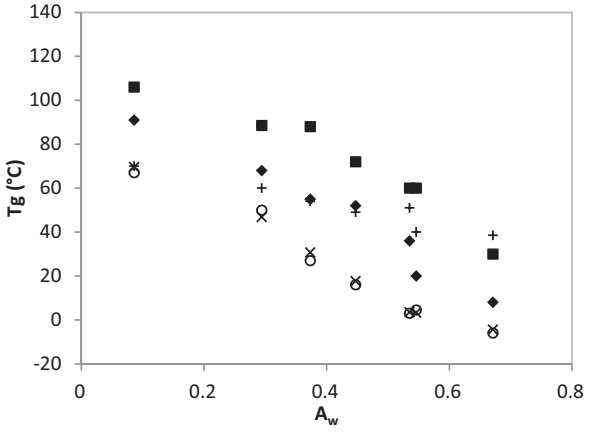

Fig. 6. Evolution of glass transition temperatures versus A_w for sucrose (+) samples. (o) T_{g1}, (♦) T_{g2}, (■) T_{g3}, + peak temperature of enthalpy relaxation, × literature values for sucrose[0].

The other transitions were observed at higher temperature but at lower values than the flour-rich phase of the sucrose (−) sample. Thus, we could suggest that one (T_{g2}) would be associated with a "flour-sucrose" mixed phase, whereas the other one (T_{g3}) could be resulting from a "sucrose-plasticized flour" rich phase, with a higher flour content. The enthalpy relaxation peak could then be associated with the highest glass transition temperature in each type of system.

As shown Figs. 4 and 6, the various transition temperatures deduced from the deconvolution expectedly decreased with an increase in hydration. It is noteworthy that the 2 types of samples differed not only by the number of thermal transitions but also by the "calculated" component that can be associated with the transition detected on the "original" raw DSC thermogram. Indeed, in the sucrose (+) sample, the glass transition detected on the original thermogram corresponded to the component with the lowest glass transition temperature whereas it was the one with the highest T_g in the sucrose (−) sample. This was possibly due to the differences in ΔC_p between sugar and flour.

The fact that T_{g1} coincided well with the glass transition of pure sucrose suggested the presence of a sucrose separated phase in these samples.

Having determined the glass transition temperatures of the various phases, the theoretical weight fractions of sugar and "flour" present in each phase for all A_w's were calculated using the

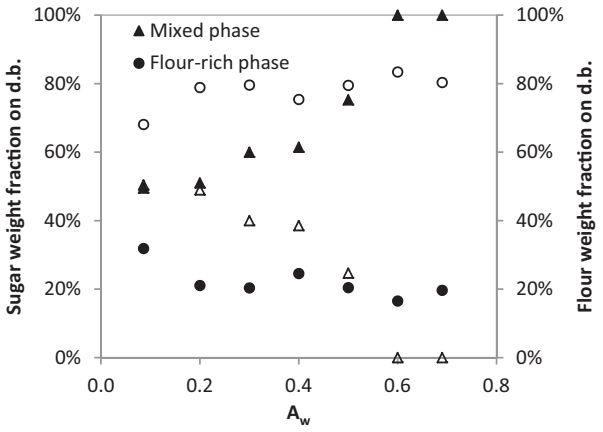

Fig. 7. Sugar weight fraction (y_s, full symbols) and flour weight fraction (y_f, empty symbols) of the mixed phase (triangle) and flour-rich phase (circle) as function of A_w.

Couchman–Karasz relation for a ternary polymer/sugar/water system:

$$T_g = \frac{y_w \Delta C_{p,w} T_{g,w} + y_s \Delta C_{p,s} T_{g,s} + y_f \Delta C_{p,f} T_{g,f}}{y_w \Delta C_{p,w} + y_s \Delta C_{p,s} + y_f \Delta C_{p,f}}$$

together with:

$$\sum_i y_i = 1$$

The mass fractions of water (y_w) were obtained from the moisture sorption data. Values for the ΔC_p (1.94, 0.76 and 0.43 kJ/kg K) and T_g (136, 343 and 440 K) of respectively water (Oliver & Meinders, 2011), sucrose (Kalichevsky et al., 1992) and flour ((Kaletunç & Beslauer, 1996; van der Sman & Meinders, 2011) were used. The ΔC_p value for "flour" was set at 0.426 kJ/kg K as calculated by van der Sman for polysaccharides and structural (proline-rich) proteins (van der Sman, 2013; Oliver & Meinders, 2011). This approximation was performed due to the fact that 2 glass transitions were detected in the sugar (−) samples with their respective ΔC_p, thereby making it difficult to attribute a specific ΔC_p value for the weight fraction calculations. The results are summarized in Fig. 7.

It was calculated that the mixed phase contained about 50% of sucrose and flour at low water content. It was then observed that this phase became richer in sucrose and more and more depleted from flour with increasing A_w values, pointing toward a segregation of both components. The flour-rich phase consisted at low A_w of about 30% of sucrose and 70% of flour. With increasing A_w values, this phase became richer in flour, pointing toward a preferential migration of the sugar toward the mixed phase.

4. Conclusions

The present work pinpointed the need to analyse and interpret the individual phase behaviors of composite materials rather than directly analyse the "overall" thermal signature obtained in DSC. The latter usually reflects the dominating transition (largest ΔC_p) of a multiphasic material, thereby hiding the presence of smaller relaxations. This approach brings new insights to the generally acknowledged data on amorphous dry food systems and invites one to question most data published in the last decades on these complex matrices considered homogeneous due to their dominating glass transition. Among the perspectives, considering the phase behavior of complex systems and thus the properties of their individual phases (individual T_gs and composition changes) could lead to a better understanding of the physical stability of the products.

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