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## Water activity and glass transition in dairy ingredients

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**Abstract** – The glass transition temperatures ( $T_g$ ) of various dairy powders were determined by differential scanning calorimetry among the sorptions isotherm, and were also calculated using the extended Couchman–Karasz equation, taking into account the dry values of  $T_g$  and  $\Delta C_p$  (heat capacity changes during glass transition) and the contents in each amorphous component category. The results obtained showed a statistically significant correspondence between measured and calculated  $T_g$  inflection values: the model gives an approximate inflection value of  $T_g$  corresponding to the measured one  $\pm 14$  °C. This lack of fit can be explained both by the accuracy of measurement of  $T_g$  and by not considering minor constituents of dairy powders (minerals and oligosaccharides) in calculation. From the values of  $T_g$  and  $\Delta C_p$  measured and/or calculated in this study, it is possible to anticipate the behavior of a dairy powder under given temperature ( $T$ ) and water activity ( $a_w$ ) conditions during drying and storage with regard to stickiness and caking. We propose the calculation of a stickiness and caking sensitivity index according to the values of  $[T - T_g]$  and  $\Delta C_p$ , whose value is in agreement with the expected behavior of various dairy powders during drying and storage.

**water activity / glass transition / dairy powder / stickiness / caking**

**Résumé – Activité de l'eau et transition vitreuse de divers ingrédients laitiers.** Les températures de transition vitreuse ( $T_g$ ) de différents ingrédients laitiers ont été déterminées par calorimétrie différentielle sur l'ensemble de l'isotherme de sorption, et calculées par l'équation de Couchman-Karasz étendue à plus de trois constituants. Cette équation prend en compte les valeurs sèches de  $T_g$  et  $\Delta C_p$  (variation de chaleur spécifique mesurée lors de la transition vitreuse) et la fraction massique de chaque catégorie de constituant amorphe. Les résultats obtenus montrent une corrélation statistiquement significative entre les valeurs de  $T_g$  mesurées et calculées : le modèle utilisé permet ainsi d'obtenir une estimation de la valeur de  $T_g$  correspondant à la valeur mesurée  $\pm 14$  °C. L'écart d'ajustement peut s'expliquer par les erreurs de mesure et par la non-prise en compte des constituants mineurs dans le calcul (minéraux, oligosaccharides). À partir des valeurs de  $T_g$  et  $\Delta C_p$  mesurées et/ou calculées, il est possible d'anticiper le comportement d'une poudre laitière dans des conditions données de température ( $T$ ) et d'activité d'eau ( $a_w$ ) au cours du séchage et du stockage, vis à vis du collage et du mottage. Nous proposons le calcul d'un indice de sensibilité au collage et au mottage à partir des valeurs de  $[T - T_g]$  et  $\Delta C_p$ , dont la valeur est cohérente avec le comportement connu de différentes poudres laitières au cours du séchage et du stockage.

**activité de l'eau / transition vitreuse / poudre laitière / collage / mottage**

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## 1. INTRODUCTION

Spray drying, storage and quality of milk powder are significantly dependent on both the physical state of the lactose (one of the main components in skim milk powder) and on the proteins or other carbohydrates which themselves are dependent on the glass transition temperature ( $T_g$ ). The spray drying of skim milk concentrate is so quick that the lactose cannot crystallize [18]. Rapid removal of water in subsequent spray drying does not allow lactose crystallization, and when water is removed, lactose is transformed into a solid-like, amorphous glass directly from the dissolved state [9–11, 17, 18].

Many dehydrated foods contain amorphous components in the glass form. This is a non-equilibrium state with higher energy in relation to the corresponding equilibrium state. If the temperature of a material in this state rises above a certain critical value then it transforms into a rubber. This phenomenon is known as glass transition and the temperature at which it occurs is the glass transition range temperature. This transition results in an increase in mobility in the rubbery state and this in turn can lead to change in physical and chemical properties of the material. Carbohydrates, including sugars, starch and hemicelluloses can exist in the amorphous glassy state in dried foods. Low molecular weight sugars in the glassy state are usually extremely hygroscopic and have low glass transition temperatures [2]. This can lead to problems in spray drying and/or in storage. The addition of high molecular weight compounds to these low molecular weight sugars can lead to an improvement in spray drying and storage conditions. Proteins, including gelatin, elastin, gluten, glutenin, casein, whey proteins and lysozyme, are also found in the amorphous state in dried food. In the dry state, they have a relatively a high glass transition temperature [2, 12, 15].

The aim of the present study was to evaluate the moisture sorption isotherm, glass transition temperature ( $T_g$ ) and state diagrams ( $T_g$  vs. moisture) for various dairy ingredients (caseinate, whey proteins, and crystallized and non-crystallized whey, skim milk and hydrolyzed skim milk powders).

From this information, we should be able to determine the glass transition temperature of any product with regard to the physical properties of its major ingredients by using the Couchman-Karasz equation [5], modified and extended in tertiary mixtures of casein, carbohydrates and water. From this thermodynamic information, one should be able to anticipate the behavior of a powder under given temperature and  $a_w$  conditions.

## 2. MATERIALS AND METHODS

### 2.1. Dairy powders

The native phosphocaseinate suspension (NPCS) was prepared by microfiltration and diafiltration (pore diameter: 0.1  $\mu\text{m}$ ) on MFS 19 equipment (Tetra-Laval, Århus, Denmark; 4.6  $\text{m}^2$ ) at 50 °C [6, 16], at  $200 \pm 5 \text{ g}\cdot\text{kg}^{-1}$  total solids. The whey protein isolate (WPI) was obtained by ultrafiltration and diafiltration on a DDS module (Gea, Soeborg, Denmark) with a plane membrane (10000  $\text{g}\cdot\text{mol}^{-1}$  molecular mass cut-off, 9  $\text{m}^2$ ; 50 °C) at  $200 \pm 2 \text{ g}\cdot\text{kg}^{-1}$  total solids. Concentrated milk and whey were produced in a two-stage falling film vacuum evaporation (GEA, Niro Atomizer, St Quentin en Yvelines, France) at Bionov (Rennes, France). The first evaporation stage was carried out at 60 °C and led to a concentrated milk and whey temperature of 40 °C. The evaporation capacity was 180  $\text{kg}\cdot\text{h}^{-1}$ . A part of the concentrated whey was crystallized at 25 °C for 5 h to obtain a crystallized whey concentrate. The spray drying of concentrates of NPCS, WPI, skim milk (SM), crystallized (CW) and non-crystallized whey (NCW) were performed at Bionov (Rennes, France) in a 3-stage pilot-plant spray dryer (GEA, Niro Atomizer, St Quentin en Yvelines, France) [22]. The atomizer was equipped with a pressure nozzle (0.73-mm diameter orifice) and a 4 slot core (0.51-mm nominal width), providing a 60° spray angle. Evaporation capacity was 70 to 120  $\text{kg}\cdot\text{h}^{-1}$  (depending on inlet and outlet air temperature and air flow). The hydrolyzed skim milk (HSM) and sodium caseinate (Na caseinate) powders were produced by “La Laiterie de Montaigu” (Montaigu, France)

**Table I.** Biochemical composition of dairy powders.

Powders	Casein	Whey proteins	Lactose	Glucose	Galactose
	(g·100 g <sup>-1</sup> TS)				
Non-Crystallized Whey	–	13.2 ± 0.2	78.9 ± 1.2	–	–
Crystallized Whey	–	13.5 ± 0.2	76.3 ± 1.2	–	–
Skim Milk	27.2 ± 0.1	5.4 ± 0.2	54.8 ± 0.9	–	–
Hydrolyzed Skim Milk	28.3 ± 0.2	5.7 ± 0.5	6.7 ± 1.2	23.1 ± 1.5	20.7 ± 1.5
Native Phosphocaseinate Suspension (NPCS)	84.5 ± 0.2	4.3 ± 0.5	1.8 ± 0.5	–	–
Whey Protein Isolate (WPI)	–	85.8 ± 0.1	3.8 ± 0.5	–	–
Na Caseinate	91.9 ± 0.2	–	2.2 ± 0.5	–	–

with a lactose hydrolysis ratio of 89% and by “Armor Proteines” (Saint Brice en Coglès, France), respectively.

## 2.2. Chemical and physical analysis

Free water content was calculated by weight loss after drying 5 g of the samples with sand in a forced air oven at 105 °C for 7 h (liquid) or 5 h (powder). Total water content was determined by weight loss after drying 5 g of the sample under vacuum with sand in a forced air oven at 105 °C for 5 h [20]. Crystallization ratios were determined by calculating the difference between total water and free water content [20]. Casein and whey protein contents were determined according to [1, 19]. The lactose, galactose and glucose contents were determined by enzymatic reactions (Boehringer Mannheim, Biopharm AG, Darmstadt, Germany). The biochemical composition of the dairy powders is reported in Table I.

Water activity ( $a_w$ ) was measured in a water activity-meter ( $a_w$ -meter; Novasina RTD 200/0 and RTD 33, Pfäffikon, Switzerland) at 20 °C.

“Working” moisture adsorption isotherms were determined using the method proposed by [15]. Approximately 2-g samples of dairy powders were weighed in stainless steel dishes and placed in a desiccator which contained a saturated salt solution at an  $a_w$  between 0.11 and 0.66. The saturated salt solutions used were LiCl, CH<sub>3</sub>COOK, MgCl<sub>2</sub>, NaI, K<sub>2</sub>CO<sub>3</sub>, NaBr,

Mg(NO<sub>3</sub>) and NaNO<sub>2</sub> with relative humidity (RH) of 11, 22, 33, 39, 43, 54, 57 and 66% (± 1% RH), respectively, giving  $a_w$  of 0.01 × percentage of RH at equilibrium [15]. The desiccators were then placed in temperature-controlled chambers (± 2 °C) at 20 °C, and samples were allowed to equilibrate for 15 d. Preliminary experiments showed that the dairy powders reached relative humidity equilibrium at 20 °C, whether by adsorption or desorption, within 10 d. However, to ensure a constant  $a_w$ , dairy powder samples were equilibrated for fifteen days prior to use.

Glass transition temperatures ( $T_g$ ) and heat capacity changes ( $\Delta C_p$ ) were determined using differential scanning calorimetry (DSC) (Q-1000, TA Instruments, Saint Quentin en Yvelines, France) calibrated with indium (melting point 156.6 °C). The samples were scanned twice to eliminate the hysteresis effect of thermal relaxation that is typical for glass transition. The initial scanning rate was 5 °C·min<sup>-1</sup> from –70 °C to +70 °C for the skim milk, hydrolyzed skim milk, and crystallized and non-crystallized whey powders, and from 0 °C to +130 °C for the NPCS and WPI powders. Samples were cooled at 10 °C·min<sup>-1</sup> at –70 °C, and the  $T_g$  range was determined from the DSC curve of the second scan at 5 °C·min<sup>-1</sup> from –70 °C to +250 °C (Fig. 1), giving three values:  $T_g$  onset,  $T_g$  inflection and  $T_g$  endset. The  $\Delta C_p$  value was given by the change in heat capacity between onset and endset  $T_g$  values.

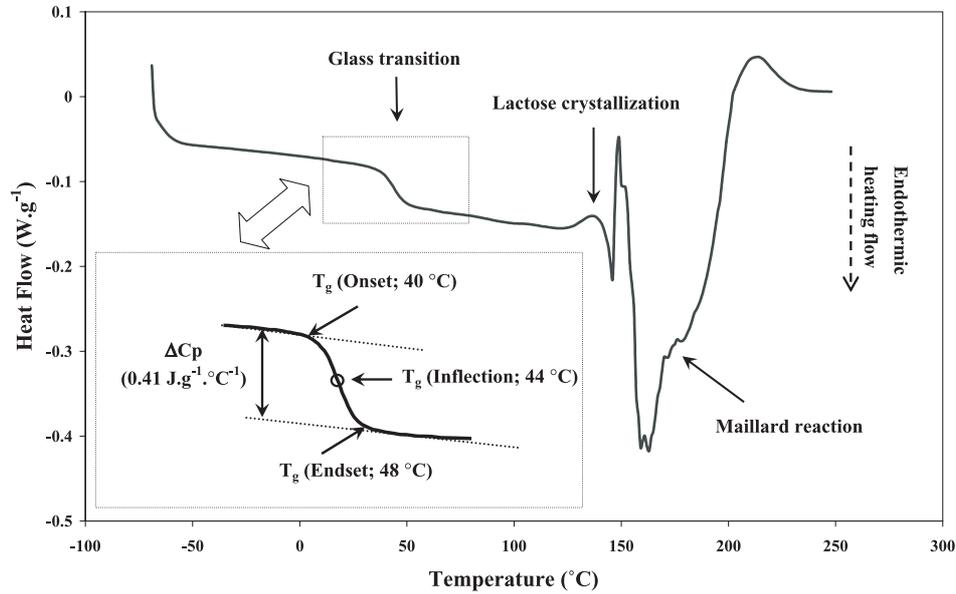


Figure 1. DSC curve of the second scan obtained with non-crystallized whey powder at 0.22  $a_w$ .

### 2.3. Statistical analysis

For each powder from the same batch, three replications of moisture adsorption isotherms, glass transition temperatures and heat capacity change determination were performed. The Student's  $t$  test was used as a guide for pair comparisons of the trial means. Differences among trials that are subsequently described as being significant were determined at  $P < 0.05$ .

Comparison between measured and predicted  $T_g$  values was performed using linear regression. Fitting between values provided by the extended Couchman-Karasz equation and the experimental data was estimated by the multiple correlation coefficient ( $R^2$ ) and a Fisher  $F$  test. Significance was determined at  $P < 0.001$ .

## 3. RESULTS AND DISCUSSION

The  $T_g$  and  $\Delta C_p$  measured at various relative humidities are reported in Tables II, III, IV, V, VI and VII for the non-crystallized whey (NCW), crystallized whey (CW), skim

milk (SM), hydrolyzed skim milk (HSM), and NPCS and WPI powders, respectively.

In all cases and according to the literature, the increase in the relative humidity during the sorption isotherm involves that of the product water content, leading to a reduction in the glass transition temperature  $T_g$  [8, 13]. Indeed, and according to the Couchman-Karasz equation [5] extended in tertiary mixtures of casein, carbohydrates and water (Eq. (1)), the glass transition temperature from a product is the gravity center of the glass transition temperatures from its components:

$$T_g = \frac{W_1 \Delta C_{p1} T_{g1} + W_2 \Delta C_{p2} T_{g2} + W_3 \Delta C_{p3} T_{g3}}{W_1 \Delta C_{p1} + W_2 \Delta C_{p2} + W_3 \Delta C_{p3}} \quad (1)$$

where  $T_{gi}$  is the glass transition temperature of a component  $i$  (K),  $\Delta C_{pi}$  is the change in heat capacity of this component at  $T_{gi}$  ( $J \cdot kg^{-1} \cdot ^\circ C^{-1}$ ) and  $W_i$  its weight fraction. The components taken into account are supposed to be miscible, which excludes the insoluble fractions such as crystallized lactose or calcium phosphate precipitate, for example.

**Table II.** Non-crystallized whey powder: free water content, glass transition temperature ( $T_g$ ), change in heat capacity ( $\Delta C_p$ ) and crystallization ratio at various relative humidities.

Relative Humidity (%)	Free water content (g·100 g <sup>-1</sup> TS)	Glass transition temperature (onset -°C)	Glass transition temperature (inflection -°C)	Glass transition temperature (endset -°C)	Change in heat capacity (J·g <sup>-1</sup> ·°C <sup>-1</sup> )	Crystallization ratio (%)
11	4.2 ± 0.1	49 ± 2	51 ± 1	52 ± 1	0.38 ± 0.02	12.2
22	4.8 ± 0.2	40 ± 1	44 ± 1	47 ± 1	0.42 ± 0.05	13.9
33	7.4 ± 0.1	24 ± 1	29 ± 1	32 ± 2	0.50 ± 0.02	11.6
39	8.9 ± 0.1	17 ± 2	21 ± 2	25 ± 2	0.51 ± 0.02	11.9
43	10.1 ± 0.1	12 ± 1	15 ± 1	18 ± 1	0.53 ± 0.02	13.9
53	5.7 ± 0.1	-28 ± 2	-15 ± 2	-10 ± 2	0.09 ± 0.02	72.8
57	5.9 ± 0.1	-37 ± 2	-22 ± 2	-14 ± 3	0.12 ± 0.02	76.2
66	7.4 ± 0.2	-54 ± 2	-35 ± 3	-24 ± 2	0.15 ± 0.03	81.5

**Table III.** Crystallized whey powder: free water content, glass transition temperature ( $T_g$ ), change in heat capacity ( $\Delta C_p$ ) and crystallization ratio at various relative humidities.

Relative Humidity (%)	Free water content (g·100 g <sup>-1</sup> TS)	Glass transition temperature (onset -°C)	Glass transition temperature (inflection -°C)	Glass transition temperature (endset -°C)	Change in heat capacity (J·g <sup>-1</sup> ·°C <sup>-1</sup> )	Crystallization ratio (%)
11	2.2 ± 0.1	39 ± 1	44 ± 1	48 ± 1	0.18 ± 0.01	61.9
22	2.6 ± 0.2	25 ± 2	30 ± 1	36 ± 2	0.24 ± 0.02	68.0
33	3.9 ± 0.2	14 ± 1	15 ± 2	17 ± 1	0.06 ± 0.02	70.7
39	4.3 ± 0.1	1 ± 1	2 ± 1	3 ± 2	0.04 ± 0.01	72.8
43	4.8 ± 0.2	-3 ± 1	-2 ± 1	-1 ± 1	0.03 ± 0.01	72.4
53	4.6 ± 0.1	-22 ± 3	-16 ± 3	-6 ± 3	0.10 ± 0.02	82.8
57	4.9 ± 0.2	-35 ± 3	-21 ± 3	-13 ± 2	0.11 ± 0.02	82.8
66	6.5 ± 0.1	-42 ± 4	-27 ± 3	-21 ± 2	0.15 ± 0.02	91.1

$\Delta C_p$  is representative of the extent of the biochemical modifications that occur during glass transition (i.e. around the  $T_g$  range) or changes in state (crystallization and fusion). In the case of glass transition, which corresponds to the change from a high viscosity amorphous liquid to a low viscosity amorphous liquid, its value is directly in relation to the amplitude of the changes within the product. The results obtained in this study show that  $\Delta C_p$  is extremely variable according to the product with constant water activity. As an example, for a 0.22  $a_w$ , its value is between 0.13 (WPI) and 0.42 (NCW). Generally, the value of  $\Delta C_p$  is determined by the concentration and the nature (amorphous, crystallized) of the lactose present.

The values obtained for the crystallized and non-crystallized whey are given in

Tables II and III. We observed a reduction in  $T_g$  in relation to the increase in relative humidity and free water content, which is in agreement with the literature [17]. At the same time,  $\Delta C_p$  value increased until crystallization of lactose occurred beyond 43% of HR in both cases (in accordance with the literature), and then decreased. In the first part of the sorption isotherm (below 43% of HR), the values of  $T_g$  and  $\Delta C_p$  of the NCW were significantly higher than those of the CW, corresponding to the quantity of amorphous lactose present in these powders. Glass transition can occur only on amorphous components, and is not related to the crystallized state.

Simultaneous reduction in water content, related to the release of water molecules by lactose [18], and considerable reduction in

**Table IV.** Skim milk powder: free water content, glass transition temperature ( $T_g$ ), change in heat capacity ( $\Delta C_p$ ) and crystallization ratio at various relative humidities.

Relative Humidity (%)	Free water content (g·100 g <sup>-1</sup> TS)	Glass transition temperature (onset -°C)	Glass transition temperature (inflection -°C)	Glass transition temperature (endset -°C)	Change in heat capacity (J·g <sup>-1</sup> ·°C <sup>-1</sup> )	Crystallization ratio (%)
11	4.4 ± 0.1	45 ± 2	49 ± 1	51 ± 1	0.23 ± 0.02	0.3
22	5.4 ± 0.2	39 ± 1	42 ± 1	46 ± 1	0.25 ± 0.03	-2.1
33	7.3 ± 0.1	22 ± 1	25 ± 1	30 ± 1	0.32 ± 0.02	5.5
39	8.6 ± 0.1	15 ± 1	20 ± 1	23 ± 1	0.33 ± 0.01	6.0
43	9.3 ± 0.1	5 ± 1	12 ± 2	17 ± 2	0.26 ± 0.01	7.4
53	8.4 ± 0.1	-9 ± 3	-1 ± 3	1 ± 3	0.29 ± 0.01	30.2
57	8.8 ± 0.2	-16 ± 3	-9 ± 2	-2 ± 3	0.33 ± 0.00	50.6
66	9.2 ± 0.2	-31 ± 4	-24 ± 4	-6 ± 3	0.36 ± 0.01	57.6

**Table V.** Hydrolyzed skim milk powder: free water content, glass transition temperature ( $T_g$ ), change in heat capacity ( $\Delta C_p$ ) and crystallization ratio at various relative humidities.

Relative Humidity (%)	Free water content (g·100 g <sup>-1</sup> TS)	Glass transition temperature (onset -°C)	Glass transition temperature (inflection -°C)	Glass transition temperature (endset -°C)	Change in heat capacity (J·g <sup>-1</sup> ·°C <sup>-1</sup> )
11	5.8 ± 0.1	10 ± 2	13 ± 1	18 ± 1	0.28 ± 0.01
22	7.7 ± 0.1	-5 ± 1	2 ± 1	9 ± 2	0.32 ± 0.02
33	9.9 ± 0.1	-15 ± 1	-10 ± 1	-5 ± 3	0.41 ± 0.03
39	11.9 ± 0.1	-21 ± 1	-15 ± 1	-10 ± 1	0.42 ± 0.03
43	12.4 ± 0.1	-27 ± 2	-18 ± 2	-14 ± 2	0.45 ± 0.05
53	15.8 ± 0.2	-34 ± 3	-28 ± 1	-22 ± 2	0.48 ± 0.01
57	16.4 ± 0.1	-38 ± 3	-30 ± 2	-23 ± 3	0.51 ± 0.02
66	17.4 ± 0.2	-40 ± 3	-32 ± 3	-25 ± 3	0.52 ± 0.00

$\Delta C_p$  occurred during the isothermic crystallization of lactose in the powders (from 43% of HR).

In the last part of the sorption isotherm (above 43% of HR), these two powders behaved almost equally, the NCW being within the same range as the CW in terms of  $T_g$ , crystallization ratio and low value of  $\Delta C_p$ .

The  $T_g$  and  $\Delta C_p$  values obtained with skim milk (SM; Tab. IV) and their evolution among the sorption isotherms were comparable with those obtained with NCW. However, the extent of the modifications observed was limited compared with those of NCW, reflecting a smaller proportion of amorphous lactose in skim milk at the beginning of the isotherm ( $a_w = 0.11$ ). Indeed, the amorphous lactose

content can be obtained from the total lactose content (Tab. I) and the crystallization ratios measured for each of these powders (Tabs. II and IV). At 0.11  $a_w$ , it was, respectively, equal to 54.6% and 69.3% for SM and NCW, leading to a lower  $\Delta C_p$  value for SM.

In the case of hydrolyzed skim milk (HSM; Tab. V), the values of free water content and  $T_g$  were higher and lower, respectively than those of skim milk at the same water activity. In accordance with the literature [7, 18], these results are explained by the fact that hydrolysis of lactose in glucose and galactose leads to an increase in powder hygroscopicity and, in accordance to the  $T_g$  values of these monosaccharides (Tab. VIII), to a reduction in the overall  $T_g$  value of the powder.  $\Delta C_p$  was significantly

**Table VI.** NPCS powder: free water content, glass transition temperature ( $T_g$ ) and change in heat capacity ( $\Delta C_p$ ) at various relative humidities.

Relative Humidity (%)	Free water content (g·100 g <sup>-1</sup> TS)	Glass transition temperature (onset -°C)	Glass transition temperature (inflection -°C)	Glass transition temperature (endset -°C)	Change in heat capacity (J·g <sup>-1</sup> ·°C <sup>-1</sup> )
11	8.0 ± 0.1	112 ± 3	122 ± 0	130 ± 2	0.34 ± 0.03
22	9.9 ± 0.1	99 ± 2	103 ± 0	112 ± 0	0.37 ± 0.05
33	11.2 ± 0.2	86 ± 3	99 ± 2	105 ± 1	0.48 ± 0.04
39	11.6 ± 0.1	81 ± 3	90 ± 2	92 ± 1	0.53 ± 0.04

**Table VII.** WPI powder: free water content, glass transition temperature ( $T_g$ ) and change in heat capacity ( $\Delta C_p$ ) at various relative humidities.

Relative Humidity (%)	Free water content (g·100 g <sup>-1</sup> TS)	Glass transition temperature (onset -°C)	Glass transition temperature (inflection -°C)	Glass transition temperature (endset -°C)	Change in heat capacity (J·g <sup>-1</sup> ·°C <sup>-1</sup> )
11	8.5 ± 0.1	102 ± 1	106 ± 1	112 ± 3	0.10 ± 0.00
22	9.5 ± 0.1	90 ± 3	95 ± 0	106 ± 1	0.13 ± 0.01
33	11.2 ± 0.1	77 ± 3	80 ± 2	85 ± 3	0.13 ± 0.03
39	12.5 ± 0.2	49 ± 3	59 ± 3	66 ± 2	0.15 ± 0.02

**Table VIII.** Calorimetric characteristics of various dairy ingredients.

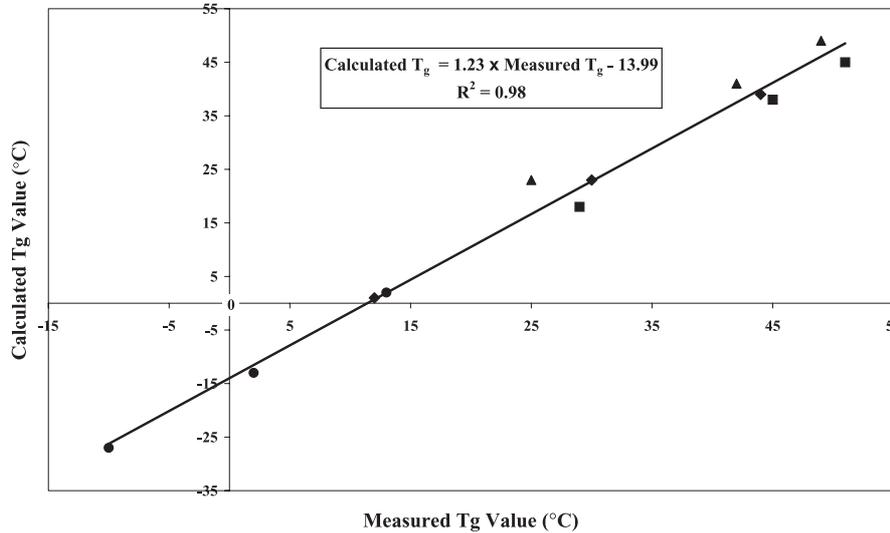
Dairy ingredients	Dry glass transition temperature (inflection -°C)	Change in heat capacity (J·g <sup>-1</sup> ·°C <sup>-1</sup> )	References
Water	-139	1.94	[12]
Casein	132	0.26	Table VI; [12; 14; 15]
Whey proteins	127	0.09	Table VII; [14]
Lactose	98	0.38	[23]
Glucose	31	0.24	Table V; [3, 4, 18]
Galactose	30	0.24	Table V; [3, 4, 18]

higher for HSM than for SM, which could be due to the higher thermoplasticity of glucose and galactose as compared with lactose. This hypothesis needs, however, to be confirmed. For the whole sorption isotherm, the continuous evolution of  $\Delta C_p$  observed could have been due to the absence of crystallization of glucose and galactose (not measured).

The quasi-total elimination of lactose and minerals (WPI and NPCS powders) resulted in a significant increase in  $T_g$  at a given  $a_w$  (Tabs. VI and VII). Within the  $a_w$  range investigated, and in agreement with

the literature [12, 14, 15], whey proteins and caseins were more hygroscopic than the other powders, except for hydrolyzed skim milk. One interesting finding of this study relates to the values of  $\Delta C_p$  obtained for caseins and whey proteins (0.37 and 0.13 J·g<sup>-1</sup>·°C<sup>-1</sup> at 0.22  $a_w$ , respectively). These differences can be explained both by their composition in amino acids and by their degree of organization [14].

Table VIII gives  $T_g$  and  $\Delta C_p$  values for the different constituent types at 0.0  $a_w$ , given in the literature or linearly extrapolated from the results obtained in this study



**Figure 2.** Calculated  $T_g$  values as a function of measured  $T_g$  inflection values for various dairy powders and  $a_w$  in the range 0.11 to 0.33. The different marker styles correspond to dairy powders. ■: NCW; ◆: CW; ▲: SM; ●: HSM.

at  $a_w$  lower than 0.39 (included), i.e. before lactose crystallization (Tabs. II to VII). According to the data of Tables I and VIII, and using the Couchman–Karasz equation extended to more than three constituents (water, amorphous lactose, glucose and galactose, casein and whey proteins), it is possible to predict the  $T_g$  value of each powder. Figure 2 represents the calculated (predicted)  $T_g$  values as a function of measured  $T_g$  inflection values for SM, HSM, CW and NCW,  $a_w$  being in the range 0.11 to 0.33. The model obtained by linear regression is statistically significant at the  $P < 0.001$  level, with a  $R^2$  coefficient of 0.98. This shows that the extended Couchman–Karasz equation makes it possible to obtain a satisfying approximate inflection value of  $T_g$ , corresponding to the measured one  $\pm 14$  °C (intercept value of the model). Moreover, the higher the value of  $T_g$ , the better the estimation by the extended Couchman–Karasz equation, in accordance with the fact that the dry glass transition and  $\Delta C_p$  values used in this equation (Tab. VIII) were extrapolated from the results obtained at  $a_w$  lower than 0.39. The lack of fit and

**Table IX.** Calculation of stickiness and caking sensitivity index.

$T - T_g$ (°C)	$\Delta C_p$ ( $J \cdot g^{-1} \cdot ^\circ C^{-1}$ )	Number of points
$[T - T_g] \leq 5$	$\Delta C_p < 0.1$	0
$5 < [T - T_g] \leq 10$	$0.1 \leq \Delta C_p < 0.2$	1
$10 < [T - T_g] \leq 15$	$0.2 \leq \Delta C_p < 0.3$	2
$15 < [T - T_g] \leq 20$	$0.3 \leq \Delta C_p < 0.4$	3
$20 < [T - T_g] \leq 30$	$0.4 \leq \Delta C_p < 0.5$	4
$30 < [T - T_g]$	$0.5 \leq \Delta C_p$	5

underestimation of  $T_g$  by the model can be explained both by the accuracy of measurement of  $T_g$  and  $\Delta C_p$  and by not considering minerals and oligosaccharides (especially in the case of HSM) in calculation. However, this approach makes it easily possible to reach an approximate value for  $T_g$  from the biochemical composition and the crystallization ratio of lactose. It is therefore a particularly interesting operational tool, already validated on an industrial scale.

**Table X.** Powder behavior during drying and storage as a function of  $[T - T_g]$  and  $\Delta C_p$  values.

Powder	Free Moisture content (g·kg <sup>-1</sup> )	Water activity (25 °C)	Calculated T <sub>g</sub> temperature (inflection -°C)	Calculated $\Delta C_p$ (J·g <sup>-1</sup> ·°C <sup>-1</sup> )	Powder temperature T (°C)	T - T <sub>g</sub> (°C)	SCSI	Observed effects on powder
STICKINESS PROPERTIES								
Crystallized sweet whey	15.6 ± 1	0.13 ± 0.01	43	0.19	55 ± 3	+ 12	3	No [21]
	22.5 ± 1	0.22 ± 0.02	25	0.24	51 ± 3	+ 26	6	Yes [21]
Sodium caseinate	69.0 ± 1	0.24 ± 0.02	34	0.25	45 ± 2	+ 11	4	No
	83.0 ± 2	0.34 ± 0.01	22	0.48	40 ± 3	+ 18	7	Yes
Skim milk	40.7 ± 2	0.20 ± 0.02	53	0.26	60 ± 2	+ 7	3	No [21]
	60.0 ± 1	0.34 ± 0.01	35	0.31	42 ± 3	+ 7	4	No
	75.0 ± 1	0.41 ± 0.02	24	0.34	38 ± 2	+ 12	5	Yes
CAKING PROPERTIES								
Skim milk	39.6	0.20 ± 0.01	55	0.26	20 ± 2	- 35	2	No [21]
	45.2	0.26 ± 0.01	49	0.28	20 ± 2	- 29	2	No [21]
Non-crystallized sweet whey	23.9	0.10 ± 0.02	65	0.37	20 ± 2	- 4	3	No
	81.6	0.39 ± 0.01	11	0.52	20 ± 2	+ 9	6	Yes

From these results, it is possible to consider the behavior of the different powders during drying (stickiness) and storage (caking) according to the range of variations in the parameters  $[T - T_g]$  (T corresponding to the temperature of the powder) and  $\Delta C_p$ . An increase in  $[T - T_g]$  leads to an increase in the speed of physico-chemical changes (thermoplasticity, crystallization and Maillard reaction) in the product [8, 18]. A stickiness and caking sensitivity index (SCSI, ranging between 0 and 10) can be determined for all powder,  $a_w$  and temperature conditions. This index (Eq. (2)) simultaneously integrates the values of  $[T - T_g]$  (ranging between 0 and 5) and  $\Delta C_p$  (ranging between 0 and 5) (Tab. IX):

$$\text{SCSI} = \text{Number of points}_{[T - T_g]} + \text{Number of points}_{[\Delta C_p]} \quad (2)$$

Considering the SCSI value calculated from this equation makes it possible to anticipate powder behavior during drying and storage, from the most favorable case

(SCSI ≤ 4: no stickiness and/or no caking) to the most unfavorable (SCSI ≥ 6: high to very high stickiness or caking hazard). Table X gives examples of SCSI and the stickiness and caking tendency observed during drying and storage of skim milk, native phosphocaseinate suspension, non-crystallized whey and crystallized whey powders. The SCSI values are clearly in agreement with the observed effects on the powder.

#### 4. CONCLUSIONS

In this study, the glass transition temperatures of various dairy powders were determined by differential scanning calorimetry, and were also calculated using the extended Couchman-Karasz equation, taking into account the values of  $T_g$ ,  $\Delta C_p$  and the contents in each component category. In the case of lactose, it is necessary to consider the crystallization ratio, since the calculation of  $T_g$  takes into account only the amorphous state of the components. The results obtained showed a good correspondence between measured and calculated  $T_g$  inflection

values, which provides easy access to this essential parameter for the control of drying and storage of dairy powders.

We particularly emphasize the importance of the  $\Delta C_p$  value in the understanding of the mechanisms and control of stickiness during drying and caking during storage. We propose the calculation of a stickiness and caking sensitivity index according to the values of  $[T - T_g]$  and  $\Delta C_p$ , making it possible to anticipate the behavior of a powder under given temperature and  $a_w$  conditions.

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