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Short review

Keeping quality of dairy ingredients

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Abstract – The most widely used process for dehydration of dairy products is spray drying. This is an effective method for preserving biological products as it does not involve severe heat treatment and allows storage of powders at ambient temperature. Various authors have reported the physico-chemical properties of free and bound water and the effects of water on physical state, transition temperatures, sticking temperature, reaction kinetics and stability of milk products. The emphasis is on the physical state of non-fatty solids and the effects of water and its physical state on chemical reaction rates, growth of micro-organisms and stability. Spray-drying, storage and quality of dairy powders are significantly dependent on both the physical state of lactose (one of the main components of dairy powders) and other carbohydrates, which themselves are dependent on the glass transition temperature (T_g) and water activity (a_w). The maximum moisture content of a dairy powder (4% for skim milk powder) is defined in the product specification in relation to a_w, and this must be close to 0.2 at 25 °C for optimal preservation. In these conditions of water content and a_w, the T_g will be close to 50 °C. This paper is a short review of the different physical properties required to maintain the quality of dairy ingredient powders.

dairy powder / water activity / glass transition / stickiness

摘要 – 保持乳品成分质量。喷雾干燥是最广泛使用的乳制品脱水方法。如果不采用剧烈的加热处理,乳粉是在室温下保持乳制品中生物成分的有效方法。关于乳粉中自由水和结合水的物理化学特性以及水分对物理状态的影响、转变温度、粘性温度、反应动力学和乳制品稳定性等问题已经有过很多的文献报道。本文着重强调非脂固形物的物态及水分和水分的物态对化学反应速率、微生物的生长速率和稳定性的影响。喷雾干燥、贮藏和乳粉的质量主要取决于乳糖的物态（乳粉中一种主要化合物）和其他碳水化合物, 而这些化合物的状态则完全依赖于玻璃相转变温度(T_g)和水分活度(a_w)。乳粉产品中最大水分含量（脱脂粉在4%）的限定与水分活度直接相关, 乳粉在25 °C下贮存的最佳水分活度应该在0.2, 在此水分含量和水分活度下,玻璃相转变温度接近50 °C。本文综述了保持乳品成分质量所需要满足的物理特性。

乳粉 / 水分活度 / 玻璃相转变 / 黏度

Résumé – Conservation de la qualité des ingrédients laitiers. Le procédé le plus largement utilisé pour la déshydratation des produits laitiers est le séchage par atomisation. C'est une méthode efficace pour préserver les produits biologiques puisqu'elle ne nécessite pas de traitement thermique sévère et permet le stockage des poudres à température ambiante. Plusieurs auteurs ont reporté les

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propriétés -ysico-chimiques de l'eau libre et liée, et les effets de l'eau sur l'état physique, les températures de transition vitreuse, la température de collage, la cinétique de réaction et la stabilité des poudres de produits laitiers. L'accent est mis ici sur l'état physique des solides non gras, les effets de l'eau et de son état physique sur les taux de réaction chimique, la croissance des microorganismes et la stabilité. Le séchage par atomisation, le stockage et la qualité des poudres laitières sont significativement dépendants de l'état physique du lactose (un des principaux constituants des poudres laitières) et de celui des autres hydrates de carbone, qui sont eux-mêmes dépendants de la température de transition vitreuse (T_g) et de l'activité de l'eau (a_w). La teneur en humidité maximale d'une poudre laitière (4 % pour une poudre de lait écrémé) est définie dans la spécification du produit en relation avec l'a_w, qui doit être proche de 0,2 à 25 °C pour une conservation optimale. Dans ces conditions de teneur en eau et d'a_w, la T_g sera proche de 50 °C. Ce papier est une courte revue des différentes propriétés physiques requises pour maintenir la qualité des ingrédients laitiers en poudre.

poudre de lait / activité de l'eau / transition vitreuse / collage

1. INTRODUCTION

Spray-drying, storage and quality of milk powder are significantly dependent on both the glass transition temperature (T_g) and water activity (a_w).

Concerning the T_g, the spray-drying of skim milk concentrate is so quick that the lactose cannot crystallize [19]. Rapid removal of water in subsequent spray-drying does not allow lactose crystallization, and when water is removed, lactose is transformed to a solid-like amorphous glass directly from the dissolved state [11, 13, 14, 18, 19].

Many dehydrated foods contain amorphous components in the glass form. This is a non-equilibrium state with higher energy compared 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 (in the spray dryer → stickiness; during the storage → cakiness). This phenomenon is known as glass transition and the temperature range at which it occurs is the glass transition temperature range. It results in an increase in mobility in the rubbery state, and this in return can lead to changes in the physical and chemical properties of the material. Around and beyond this temperature, powders may become sticky, caked, or collapsed, resulting in both degradation of overall quality and difficulties during processing, storage and handling operations. To avoid such consequences, care must be taken when operations are carried out at or around T_g, provided that the T_g is known [2, 3]. Each component (content, physical state) has a contribution to the overall T_g value. Low molecular weight sugars are usually extremely hygroscopic in the glassy state and have low glass transition temperatures [4]. This can lead to problems in spray drying and/or in storage. On the other hand, the addition of high molecular weight compounds can lead to improvements 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 [4, 15, 16].

In terms of water activity (a_w), water content is not sufficient to evaluate food stability during storage. The study of water activity has been developed to take into account any interactions of water with the other food components. a_w can be understood as a description of water availability; the greater the water availability, the higher the a_w value, involving certain biological (growth of moulds, yeast or bacteria), biochemical (lipid oxidation, enzymatic or non-enzymatic reaction) or physical changes (stickiness, caking, collapse, lactose crystallization) [19].

The aim of this short review was to correlate certain thermodynamic information (moisture sorption isotherm, a_w, T_g and state diagrams) to be able to understand the behaviour of a powder under given temperatures and a_w conditions with regard to the quality of dairy ingredients and the rehydration behavior. From this thermodynamic information, it should be possible to anticipate the behavior of a powder under given temperature and a_w conditions.

2. GLASS TRANSITION

Glass transition of dairy solids has been observed using differential scanning calorimetry (DSC). DSC measures any change in heat capacity that occurs over the glass transition temperature range [19]. DSC is also the most common method for the determination of glass transition temperatures, taken from the onset or midpoint temperature of a change in heat capacity [12]. Many sugars, including lactose, are transformed rapidly from the solid glassy state to a syrup-like, sticky liquid.

The glass transition of anhydrous lactose, as observed using DSC, has an onset temperature of 101 °C [15], which is one of the highest temperatures measured for "anhydrous" disaccharides [12]. Glass transition temperatures for anhydrous milk components and solids are given in Table I. The glass transitions observed in milk solids are very close to those of pure lactose [6, 7]. However, if lactose is hydrolyzed, the T_g observed decreases dramatically, because of the much lower T_g of the galactose and glucose components [6]. This also results in significant changes in the spray drying behavior and storage stability of lactose-hydrolyzed milk solids [12]. Amorphous carbohydrates, including lactose and its hydrolysis products, are significantly plasticized by water, demonstrated by a rapidly decreasing T_g with increasing water content. The effect of water on the T_g of milk solids may be predicted using the Gordon-Taylor equation [6, 12], or the Couchman-Karasz equation [8] according to Schuck et al. [20]. Information regarding water plasticization can also be demonstrated by water sorption properties, which allow evaluation of the extent of water plasticization of dairy powders in various storage conditions.

Several studies have shown that the stickiness of dehydrated powders results from particle surface plasticization and concurrent decrease in viscosity, allowing the formation of liquid bridges between powder particles [10]. It may be assumed that similar mechanisms control particle properties in the spray drying process. However, the process involves removal of the solvent and plasticizer, which has to occur at a rate competing with particle velocity and the formation of a dry surface to allow free flow of individual particles throughout the dehydration process. The glass transition temperature of skim milk solids, showing the stickiness and caking zone at about 10 °C above T_g or higher measured by DSC is shown in Figure 1.

3. STICKINESS

Some studies tried to relate stickiness behavior and glass transition [2,3]. Various techniques and types of instrumentation have been developed to characterize the stickiness behavior of the powder particles. The instrumental measurement concepts are generally based on the properties of food materials, such as resistance to shear motion, viscosity, optical properties and glass transition temperature. The first two concepts provide a direct interpretation of the stickiness behavior, whereas the results obtained from the latter measurement concept can be indirectly correlated to stickiness. Stickiness characterization techniques may, therefore, be divided into direct and indirect techniques. The direct techniques can also be further classified as conventional,

Table I. Powder behaviors during drying and storage as a function of [T - T_g] and ΔCp values [20].

Powder	Free moisture content ($g \cdot kg^{-1}$)	Water activity (25 °C)	Calculated T_g temperature (Inflection - °C)	Calculated ΔCp (25°C) ($J \cdot g^{-1} \cdot °C^{-1}$)	Powder temperature T (°C)	$T-T_g$ (°C)	SCSI	Observed effects on powder
STICKING PROPERTIES								
Crystallized sweet whey	15.6 ± 1	0.13 ± 0.01	43	0.19	55 ± 3	+12	3	No
	22.5 ± 1	0.22 ± 0.02	25	0.24	51 ± 3	+26	6	Yes
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
	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
	45.2	0.26 ± 0.01	49	0.28	20 ± 2	–29	2	No
Non crystallised 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

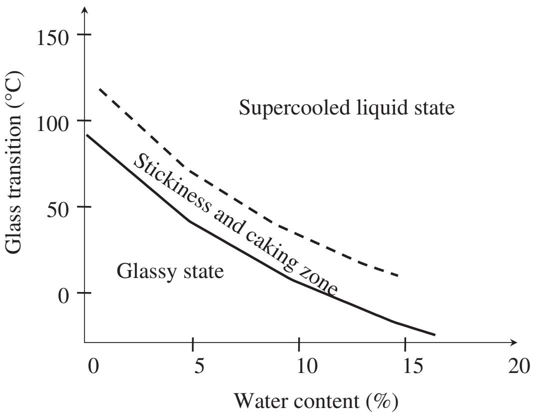

Figure 1. Relationship between glass transition temperature and water content of skim milk powder [18, 19].

pneumatic and in situ techniques according to the testing mechanism used. Conventional techniques involve mechanical movement, shearing or compression of the powder sample (propeller-driven methods, shear cell method, ampoule method or optical probe method), whereas pneumatic techniques involve the use of an air stream with predetermined temperature and humidity to blow or suspend the powder particles (fluidization test, cyclone stickiness test, blow test method) [2, 3, 6]. The in situ technique involves measurement of surface stickiness of single liquid droplets during hot air drying. Certain indirect methods such as T_g determination and the thermal compression test have been described by Boonyai et al. [2, 3].

Several techniques have been developed to characterize the stickiness behavior of food powders. All the tests are empirical in nature. Those techniques are still in development due to inaccuracy and the difficulty of application to real processing and handling situations. Glass transition is an instrumental approach, which has been proposed to correlate with stickiness. Due to the significant negative economic consequences in the industrial processing and handling of sticky products, investigations to find an accurate, simpler and cheaper technique to characterize the stickiness behavior of these types of product are still required.

4. WATER ACTIVITY AND SORPTION ISOTHERM

The water activity (a_w) of dried milk products is largely correlated to moisture content and temperature. The composition and state of individual components as influenced by various processing techniques also play an important role. The composition of the solids reflects more or less the protein content. At low moisture content characterized by $a_w < 0.2$, the casein is the main water absorber. Within the intermediate range of > 0.2 to < 0.6, sorption is dominated by the transformation of the physical state of lactose. Above this level, salts have a marked influence [17].

The water activity of milk powders consisting of non-fat milk solids and milk fat is mainly controlled by the moisture content expressed in non-fat solids since the fat has no influence. Thus, differences in a_w are due mostly to the state of proteins and the physical state of the lactose. The main

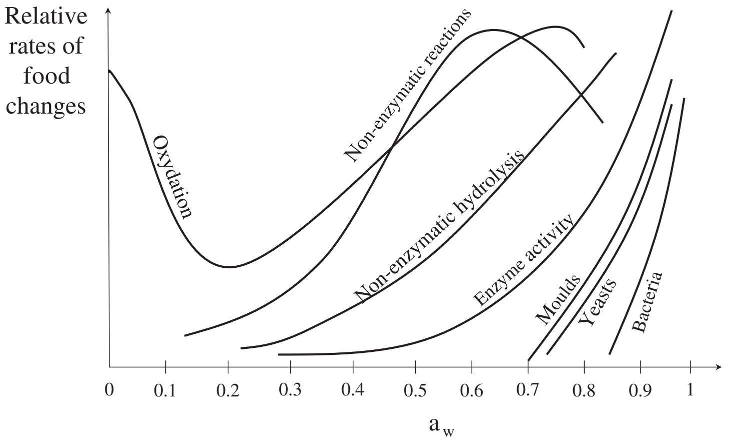

Figure 2. Relative rates of food changes [19].

value of this relationships lies in the control of the shelf life of foods [19] (Fig. 2). The methods to determine a_w consist of putting the product in equilibrium with the surrounding atmosphere then measuring the thermohygrometric characteristics of the air in equilibrium with the product. The a_w should be close to 0.2 at 25 °C for optimal preservation [9].

According to Pisecky, and as a_w plays an important role during the dehydration process, understanding of sorption isotherms can provide valuable guidelines for the engineering design, control of the drying process (isothermal desorption curves) and storage stability (isothermal adsorption curves). In practical terms, all milk powder isotherms found in the literature were obtained using final products as starting materials. The starting material is exposed to air of defined relative humidity and brought to equilibrium, after which the moisture content is determined. Thus, the published isotherms are designated as adsorption or desorption. Establishing equilibrium can very often take weeks. Many mathematical equations, both theoretical and empirical, have been reported in the literature to express the water sorption isotherms of dairy powders. For example, there are the BET model (Brunauer-Emmett-Teller) [5], the GAB model (Guggenheim-Anderson-de Boer) [21] and other published models [1, 11, 17]. With practical or theoretical sorption isotherms, the ideal moisture content can be determined for the optimal stabilization (at 0.2 a_w and at 25 °C) of some dairy powders. For example, the corresponding moisture content must be close to 4%, 2–3% and 6%, corresponding to skim milk, whey and caseinate powders, respectively.

With T_g, water activity is one of the main factors governing many of the phenomena occurring during thermal dehydration, mainly:

- easiness of water evaporation from a liquid droplet;
- particle temperature history during the whole removal process;
- moisture content equilibrium which can be achieved under given conditions at infinite residence time;
- stickiness of the product (in relation to the T_g) and outlet conditions used for drying without occurring of sticking [17].

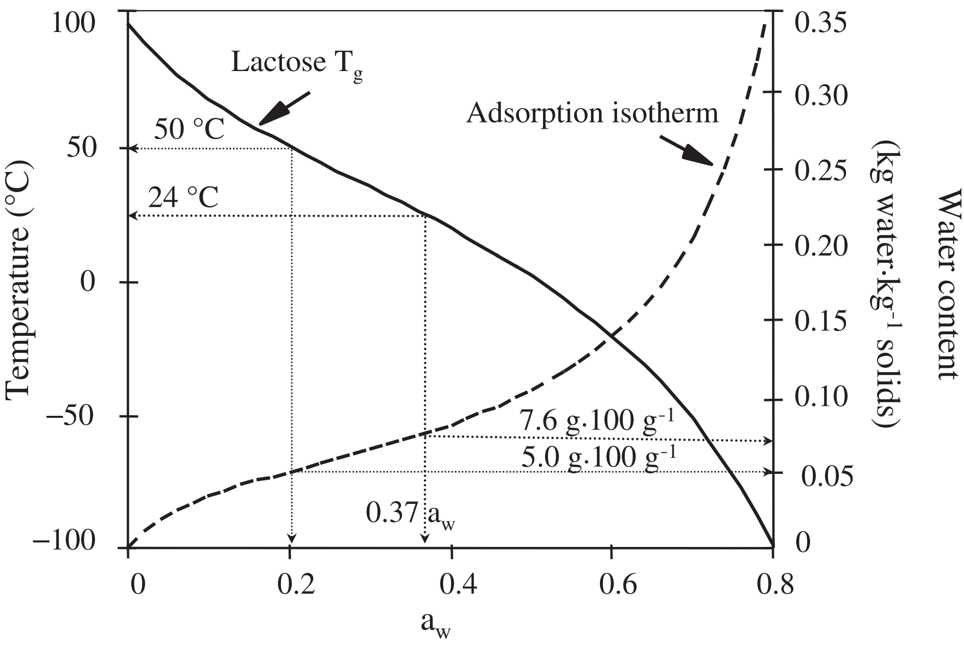

Figure 3. Glass transition temperature (T_g) and water adsorption isotherm for skim milk solids and T_g curve of lactose [18, 19].

5. WATER ACTIVITY IN RELATION TO GLASS TRANSITION

Combination of the T_g and a_w curves in relation to the moisture content provides to obtain a very interesting profile (Fig. 3) [19]. From this curve, it is easy to determine the moisture content and the T_g at different a_w values in relation to a skim milk powder. For example, the moisture content and the T_g at 0.2 a_w, will be close to 5% and 50 °C, respectively. If you want an a_w close to 0.4, the moisture content and the T_g will be close to 8.5% and 20 °C, respectively. Thus, for this powder some enzymatic and non-enzymatic reactions can begin at 0.4 a_w, which may increase deterioration and loss of quality. Moreover, it is not easy to stabilize this powder at a temperature lower than 20 °C.

6. EXAMPLES

It is possible from published results [19, 20] to consider the behaviors of different powders during drying (sticking) and storage (caking) according to the range of variations in the parameters $[T - T_g]$ (T corresponding to the temperature of the powder) and ΔCp (heat capacity changes during glass transition). An increase in $[T - T_g]$ leads to an increase in the speed of physico-chemical changes in the product (thermoplasticity, crystallization, Maillard reaction) [19]. A sticking and caking sensitivity index (SCSI, ranging between 0 and 10) can be determined for each powder, a_w and temperature condition. This index simultaneously integrates the values of $[T - T_g]$ (ranging between 0 and 5) and ΔCp (ranging between 0 and 5) [20].

With the SCSI value calculated, it is possible to anticipate the powder behavior during drying and storage, from the most favorable situation (SCSI ⩽ 4: no sticking and/or no caking) to the most unfavorable (SCSI ⩾ 6: high to very high risk of sticking or caking). Table I gives examples of SCSI and the sticking and caking tendencies observed during drying and storage of skim milk, sodium caseinate, non-crystallized whey and crystallized whey powders. The SCSI values are clearly in agreement with the effects observed regarding sticking and caking [2, 3, 20].

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