Glasstransition temperature of regular and lactose hydrolyzed milk powders

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Abstract

The glass transition temperatures (Tg) of lactose hydrolyzed milk powder (HMP) was determined and compared to that of regular milk powders (MP). Some physical and chemical changes (loss of flowing ability, browning development) were also evaluated during storage of the different milk powders. Sugars of HMP (glucose, galactose, lactose) influenced, but did not define, the Tg values of the product, on the contrary lactose governed the observed Tg values of MP samples.

Changes in the flowing characteristics of milk powder and color development, stored at different water activity values, were much more evident in HMP than in regular milk powder. Results suggested that the Tg value is not the unique parameter governing the flowability and color development in stored milk powders.

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1. Introduction

Milk powders may contain amorphous solids, which can undergo a glassy-to-rubbery transition when stored at temperatures above the glass transition temperature (Tg). It has been shown that increasing the moisture content can lead to the formation of interparticle liquid bridges causing the particles to stick together (Peleg & Mannheim, 1977). Further absorption of water may result in collapse, caking and crystallization of the powder and formation of a hard mass. Physical changes (stickiness, collapse, crystallization and aroma retention) have been described as temperature–time–moisture-dependent phenomena (Chirife, Karel, & Flink, 1973; Tsouroufis, Flink, & Karel, 1976; To & Flink, 1978) that may cause problems in production and storage of dehydrated food products (Lazar, Brown, Smith, & Lindquist, 1956; White & Cakebread, 1966). The quality of milk powders during storage may also be decreased by fat oxidation (Shimada, Roos, & Karel, 1991) and nonenzymatic browning (Saltmarch, Vagnini-Ferrari, & Labuza, 1981).

Powders containing a considerable amount of sugars are particularly susceptible to caking or flowability loss as a result of moisture sorption or exposure to elevated temperature. The reduced flow of powder particles may lead to poor rehydration and dispersibility. Milk powders with hydrolyzed lactose contain large amounts of glucose and galactose, which render a product with lower Tg than regular milk powder (Jouppila & Roos, 1994).

The main objective of the present work was to determine the glass transition temperatures of milk powder with hydrolyzed lactose (HMP) as compared to regular milk powder (MP). Some physical and chemical changes (loss of flowability, browning development) were also evaluated during storage.

2. Materials and methods

2.1. Materials

The following materials were employed: (1) skim milk powder (per 100 g: 1.2 g fat, 35.3 g protein, 51.2 g lactose), (2) whole milk powder (Brand A per 100 g: 28.8 g fat, 25 g protein, 36.3 g lactose), (3) whole milk powder (Brand B per 100 g: 26 g fat, 25 g protein, 36 g lactose) and (4) whole milk powder with enzymatically hydrolyzed lactose (per 100 g: 26 g fat, 25 g protein, 8 g residual lactose, 15 g glucose, 15 g galactose). The
composition of these commercial products is informed in the label as minimum values. It is to be noted that the composition of the powders adds up to 100 g when moisture and ash contents are taken into account. Samples (2), (3) and (4) were defatted (Soxhlet extraction of the milk samples with ethyl ether for 48 h) prior to \( T_g \) determination. Milk powders were purchased from a local store. Amorphous sugar models having a composition which resembles that of hydrolyzed milk were also prepared and consisted of (on a dry basis): 22 g lactose/100 g (from Mallinckrodt Chem. Works, St. Louis, MO), 39 g glucose/100 g (from Mallinckrodt Chem. Works, St. Louis, MO), and 39 g galactose/100 g (Anedra, Buenos Aires). Distilled water (Mallinckrodt Chem. Works, St. Louis, MO), and 39 g amides and kept at 26°C over saturated salt solutions that provided constant relative humidities (RH) between 11% and 43% (Greenspan, 1977) or were exposed to dessicant.

2.2. Preparation of model systems

The amorphous systems were obtained by freeze-drying solutions containing 11 g/100 g of the different model systems. Aliquots of 1 mL of the solution were placed in 5 mL capacity vials, frozen 24 h at \(-26^\circ C\), immersed in liquid nitrogen and freeze-dried. The freeze-drying process lasted 48 h. A Heto–Holten A/S, cooling trap model CT110 freeze-dryer (Heto Lab Equipment, Denmark) was used which operated at \(-110^\circ C\) and at a chamber pressure of \( 4 \times 10^{-4} \text{ mbar} \).

The freeze-dried samples were transferred into desiccators and kept at 26°C over saturated salt solutions that provided constant relative humidities (RH) between 11% and 43% (Greenspan, 1977) or were exposed to dessicant.

2.3. Determination of total water content

The water content of the humidified samples was determined (in duplicate samples) by difference in weight before and after drying in a vacuum oven at 70°C during 48 h in the presence of dessicant.

2.4. Differential scanning calorimetry (DSC)

DSC was used to determine glass transition temperatures (\( T_g \)). Glass transitions were recorded as the onset temperature of the discontinuities in the curves of heat flow versus temperature. In the low RH range (0–43%) commercial milk products show a fat melting endotherm that hinders the glass transition. For this reason, milk powders were previously defatted (Jouppila & Roos, 1994). The instrument used was a DSC 30 Mettler TA 4000 Thermal Analysis System with a TC11 TA processor and Graph Ware TA72 thermal analysis software. The instrument was calibrated using indium. All measurements were made at \( 10^\circ C/\text{min} \), using hermetically sealed aluminum pans (Mettler, 40 \( \mu L \) capacity), and an empty pan was used as a reference. An average value of two replicate samples was reported.

2.5. Determination of water activity

The water activity of the samples was determined with an Aquafal dew-point hygrometer. Decagon Devices, Inc, Pullman, Washington, USA (Schebor & Chirife, 2000).

2.6. Determination of flowability characteristics

Milk powder samples were poured in 4 cm diameter plastic dishes and placed in desiccators at different relative humidities at 37°C. At different times, samples were removed and flow behavior classified in an arbitrary scale from 1 to 5, being 5 a free flowing powder (control) and 1 a hard, not flowing mass.

2.7. Determination of nonenzymatic browning

Nonenzymatic browning was reordered as the color developed by milk samples stored during 1 month at 37°C at different relative humidities (eight replicates were measured). A spectrophotometer Minolta 508-d (Minolta Co. Ltd, Japan) with integrating sphere was used to measure \( L^*, a^* \) and \( b^* \) values of the CIELAB chromatic space of powders during storage. A standard calibration with white and black references was performed with illuminant \( D_{65} \) and an observation angle of \( 2^\circ \). To perform the measurements, samples were placed in a circular cell of 3 cm diameter. Color differences between control (commercial conditions) and stored samples was expressed as \( \Delta E_{ab} = \sqrt{\Delta L^*} + \Delta a^* + \Delta b^* \) (Lozano, 1979).

3. Results and discussion

\( T_g \) values of regular milk powder (MP), skim milk powder (SMP), and milk powder with HMP equilibrated at different relative humidities were determined by differential scanning calorimetry. It is to be noted that \( T_g \) values corresponding to regular milk powders could not be determined by DSC due to melting peaks of fat, and for that reason these products were previously defatted, as described before. Fig. 1a illustrates the thermograms showing the glass transition temperature of MP, SMP and HMP at 11% RH; values were 61°C, 62°C, and 36°C, (onset values, respectively). Fig. 1b shows \( T_g \) values versus water content (g/kg, dry basis) for different MP samples, HMP and sugar model systems. \( T_g \) values of HMP were dramatically lower than those observed for MP. This behavior was also observed by Jouppila and Roos (1994) in freeze-dried milk powders, and they attributed this fact to the
presence of glucose and galactose in the hydrolyzed milk samples. It is known that monosaccharides (glucose and galactose) have much lower glass transition temperatures than the disaccharide lactose (Roos, 1993). It is to be noted that $T_g$ values corresponding to regular milk powders were similar to those obtained for lactose alone; similar results were obtained by Jouppila and Roos (1994), Burin, Buera, Hough, and Chirife (2002); Shimada et al. (1991), Karmas, Buera, and Karel (1992) and Labrousse, Roos, and Karel (1992) reported that the $T_g$ values of food model systems based on lactose were similar to that of lactose which was their main component. It was suggested that either lactose governed the $T_g$ of the system (Jouppila & Roos, 1994) or lactose and other components may exist in different phases, as immiscible compounds, and DSC method could only detect the carbohydrate-rich phase. Jouppila and Roos (1994) reported that the $T_g$ values of freeze-dried skim milk powders with hydrolyzed lactose were higher than those of anhydrous galactose and glucose, and suggested that incomplete hydrolysis of lactose would render a system with a high $T_g$ component that should increase the $T_g$ of a carbohydrate mixture. However, our model system (lactose:glucose:galactose) had the same sugar composition that hydrolyzed milk; and we observed that HMP had higher $T_g$ values than those of the sugar model. This may indicate that the presence of proteins and other milk components may affect differently the glass transition behavior of lactose and the monosaccharides (glucose + galactose).

**Table 1** shows the flow behavior of commercial spray-dried MP and HMP exposed to different relative humidities during 4 weeks at 37°C. As mentioned before, the samples were rated from 5 (free-flowing) to 1 (hard-not flowing mass). Important flowability changes for HMP samples started at $a_w$: 0.22 (e.g. 3 in the scale adopted), and increased for higher $a_w$ values, the samples being almost a hard mass at $a_w$: 0.43. For MP samples, noticeable changes were only observed at $a_w$: 0.43.

Non enzymatic browning development was also recorded in spray-dried MP and HMP samples after 4 weeks storage at 37°C (Fig. 2). HMP samples showed higher color development than MP samples, and it increased drastically at $T - T_g > 0$. It is to be noted that the molar concentration of reducing sugars is doubled in lactose hydrolysis. Also, the higher color development in HMP samples could be due to the greater reactivity of glucose and galactose as compared to lactose (Buera, Chirife, & Resnik, 1990). Schebor, Buera, Karel, and Chirife (1999) observed noticeable browning development

**Table 1**

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1—Hard mass, not flowing; 5—free flowing.
higher molecular mobility (i.e. lower $T_g$ values in HMP samples), the presence of highly reactive monosaccharides also enhanced the development of this reaction.

We may conclude that in complex food systems, such as milk powder, the $T_g$ values of their main carbohydrates do not account completely for the observed behavior regarding the flowing characteristics and the development of chemical reactions as nonenzymatic browning. The presence of other components in these food systems (proteins, fat) may also play an important role in the physical and the chemical stability.

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**References**


