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Structural strength and crystallization of amorphous lactose in food model solids at various water activities

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ABSTRACT

Freeze-dried lactose and lactose/whey protein isolate (WPI) mixtures were used as amorphous food models at various a_w, and the effects of temperature and water and WPI contents on physical state were analyzed. Thermal behavior and mechanical properties were studied and Williams-Landel-Ferry (WLF) model was fitted to structural relaxation times (τ). The WLF-analysis gave a strength parameter (S) that was used to describe structural strength of the food solids. Our results showed that lactose and WPI in mixtures exhibited fractional water sorption. Thermal properties and structural strength of the solids were affected by water and WPI while T_g measured for the lactose/WPI systems followed that of the lactose component and showed phase separation of lactose and proteins. A relationship between S and water content was established, whereas the crystallization of amorphous lactose was more rapid in systems with a smaller S. Therefore, S provided a simple and convenient measure of τ controlling structure formation in food processing as well as to control lactose crystallization.

Industrial relevance: Sugars are common ingredients and often used as a mixture with other components, e.g., proteins, in the food and pharmaceutical industries. Thus, understanding the physical state and thermal behavior of sugar containing food materials has a great importance in the development of processing and shelf life control procedures for such ingredients and relevant products. This study provides physicochemical information about thermal and mechanical properties of freeze-dried lactose/whey protein systems used as food models at various water activities. Data on water sorption, time-dependent lactose crystallization, calorimetric glass transition and crystallization temperatures, and structural relaxation times can be used to understand and predict structural changes during processing and storage of relevant foods. Moreover, the structural strength concept, described in this study, allows of the control of crystallization behavior as a physical state and time-dependent phenomenon, and therefore, stability of food and pharmaceutical materials

1. Introduction

The physical state of food solids, e.g., sugars, polysaccharides and proteins, has received an increasing attention in food and pharmaceutical industries because of its importance to both processing and shelf life control (LeBail et al., 2003; Sperling, 2005). Industrial dehydration technologies, e.g., freeze-drying and spray-drying, remove water and provide many reconstituted products with sensorial properties resembling those of the original foods, e.g., powdered milk (Silalai & Roos, 2011), potato flakes (Turner, Whyte, Hudson, & Kaltovei, 2006) and dry pasta (Aguilera, Chiralt, & Fito, 2003; Gowen, Abu-Ghannam, Frias, & Oliveira, 2008). Dehydrated foods show stability achieved by converting at least some of the solids to an amorphous solid state, i.e., temperature and water content are controlled to reduce structural relaxations within the non-crystalline solid state (Lloyd, Chen, & Hargreaves, 1996; Slade & Levine, 1991). In various dehydrated food and biological materials, therefore, the physical state of solid food components may determine the success of structure formation (Biliaderis, 1991; Roos et al., 2015). Lactose (β-D-galactopyranosyl (1–4)-D-glucopyranose) is a common and typical non-crystalline food component (Gänzle, Haase, & Jelen, 2008). Lactose in dehydrated products may exist either as a very viscous glass or as a more liquid-like "rubbery" amorphous structure and in any ratio of the crystalline and amorphous states. The solid-like glass exhibits a high viscosity ($\approx 10^{12}$ Pa s) with solid appearance and strong hygroscopic properties (Gänzle et al., 2008). Moreover, amorphous lactose may undergo time-dependent changes, i.e., crystallization, with increasing rates at increasing temperatures and water contents (Slade & Levine, 1991; Sperling, 2005). Therefore, the physical state and physicochemical characteristics of amorphous lactose were important parameters in processing and storage of dehydrated lactose-based products such as powdered milk (Jouppila, Kansikas, & Roos, 1997).

Recent studies have shown that dried foods exhibit glass transitions when exposed to a humid atmosphere, which may greatly affect chemical and physical changes during food processing and storage. The

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change of amorphous materials from the glassy state to the rubbery state occurs above glass transition temperature (T_g), which is specific for each food component (Champion, Le Meste, & Simatos, 2000). When temperature increases to above T_g, a rapid increase of molecular mobility occurs, which is detected from decreasing viscosity and increasing flowability of glass-forming materials. The effects of the glass transition on component crystallization have shown that glass transition affects and often explains the occurrence of such behavior in foods (Chung, Woo, & Lim, 2004; Roos & Drusch, 2015; Slade & Levine, 1991). Structural relaxations, as often measured above or somewhat below the glass transition region, reflect the spontaneous approach of amorphous materials towards equilibrium at a rate, which depends on temperature and water activity (a_w) of the material. The corresponding structural relaxation time (τ) is the time that is necessary for the recovery from perturbations (Le Meste, Champion, Roudaut, Blond, & Simatos, 2002; Liu, Bhandari, & Zhou, 2006). Structural relaxations measured around the glass–liquid transition are of similar timescale to the experimental time scale. Therefore, structural relaxations and τ may be related to particle structure, flow characteristics, viscous flow and collapse, and mechanical properties, which control the quality and stability of food materials, particularly in the vicinity and above the onset of the calorimetric glass transition (Fan & Roos, 2016a). The Williams-Landel-Ferry (WLF) model is often fitted to structural relaxation times above T_g to show the non-Arrhenius temperature dependence of molecular mobility and the rate of diffusion-limited relaxation processes as related to T_g and expressed in terms of τ dependence on T–T_g (Angell, 2002; Sperling, 2005).

Crystallization of an amorphous food component results in a dramatic change in structure of dried food materials; particularly mechanical properties and time-dependent flow characteristics are affected (Roos & Drusch, 2015; Sperling, 2005). The rate of amorphous lactose crystallization depends on several factors, such as the rate of nucleation, the time required to remove water, molecular anomerization and storage temperature above T_g, T–T_g (Ibach & Kind, 2007). Crystallization of amorphous lactose is of practical importance and it may enhance physical and chemical deterioration in food ingredients and is typical of dairy powders at high storage humidities or temperatures causing a rapid loss of shelf life (Gänzle et al., 2008; Ibach & Kind, 2007). Mechanical properties of amorphous sugars could be affected by their degree of crystallinity and the presence of other components affecting glass transition e.g., water (Slade & Levine, 1991), carbohydrates (Cruz, Oliveira, & MacInnes, 2001) and proteins (Regand & Goff, 2006). The frequency-dependent α-relaxation of amorphous sugars is governed by water content, relative humidity and temperature (Faivre et al., 1999). As the measurements of solid flow characteristics over the glass transition region are extremely difficult, Roos et al. (2015) defined a measure for solids flow characteristics given by "structural strength, S" and introduced a William-Landel-Ferry (WLF) model-based analysis of structural relaxation times within solids affecting flow characteristics in food materials. The strength concept gave a measure of resistance to structural changes for glass-forming solids and could be used to describe the solids properties, such as crystallization, in mixes of sugars and polymeric food components (Fan & Roos, 2016b).

Whey protein isolates (WPI) may act as stabilizers, which are widely used in sugar–protein systems during spray drying and freeze-drying in the food and pharmaceutical industries (Wang, Langrish, & Leszczynski, 2010; Zhou & Labuza, 2007). Our previous studies showed that WPI could affect crystallization of amorphous sugars in powders at high relative humidity (RH) storage (Fan & Roos, 2016b). However, the effects of the structural strength of the amorphous compounds on properties of dried milk and other food materials in processing and shelf life need to be established. Therefore, the objectives of the present study were to investigate the influence of water and WPI on the calorimetric glass transition and lactose crystallization, structural relaxation times and structural strength of freeze-dried amorphous food models (lactose/WPI systems) after storage at various a_w. We expected that the relationship between structural strength and crystallization of the glass former and their interaction with other solids could contribute to powder characteristics, which could be widely used in practical applications.

2. Materials & methods

2.1. Preparation of food models

The food models in our study were prepared using α-lactose monohydrate (Sigma-Aldrich, St. Louis, Mo., U.S.A.) and whey protein isolate (WPI; Isolac®, Carbery Food Ingredients, Co., Ballineen, Ireland; impurities including carbohydrates and lipids < 3%). De-ionized water (KB Scientific, Cork, Ireland) was used for all experimental work. Lactose was dissolved in de-ionized water to obtain 20% (mass) solution. WPI solution with 20% (mass) solids was prepared using continuous stirring for 4 h at room temperature (~23 °C). Lactose and WPI solutions at room temperature were used to obtain mass ratios of 7:3, 1:1, and 3:7 of lactose/WPI by mass, respectively. Samples (5 mL in total) were prepared in pre-weighted 20 mL glass vials (10 mL, diameter 24.3 mm × height 46 mm; Schott Müllheim, Germany). All samples in the vials (semi-closed with septum) were frozen in a still air freezer at −20 °C for 20 h and then subsequently tempered at −80 °C for 3 h prior to freeze-drying using a laboratory freeze-dryer (Lyovac GT2 Freeze Dryer, Amsco Finn-Aqua GmbH, Steris®, Hürth, Germany). After freeze-drying at pressure <0.1 mbar, triplicate samples of each material were stored in evacuated vacuum desiccators over P_2O_5 (Sigma-Aldrich, St. Louis, Mo., U.S.A.) prior to subsequent analysis.

2.2. Water sorption and time-dependent crystallization

Water sorption by freeze-dried lactose, lactose/WPI mixtures and WPI at each ratio was monitored for 120 h (non-crystallizing samples) and 240 h (crystallizing samples) over saturated solutions of *LiCl*, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$ and *NaCl* (Sigma Chemical Co., St. Louis, Mo., U.S.A.) at respective water activities of 0.11, 0.23, 0.33, 0.44, 0.54, 0.65 and 0.76 a_w at 25 °C, in vacuum desiccators. The a_w measured (Dew Point Water Activity Meter 4TE, Aqualab, WA, USA) for each sample at 25 °C is given in Table 1. Evacuated desiccators in incubators (Series 6000, Termaks, Bergea, Norway) were stored at 25 °C. Vials with samples were weighted to monitor water sorption at 0, 3, 6, 9, 12 and 24 h followed by 24 h intervals up to 240 h, respectively. Lactose crystallization was monitored from release of sorbed water during storage over saturated solutions of $NaNO_2$ and *NaCl* at 25 °C. Water contents of the materials were measured as a function of time, and the average weights of triplicate samples were used in calculations. The Guggenheim-Anderson-de Boer (GAB) equation (Eq. (1)) was used to fit the experimental data of water sorption at 25 °C, where m is water content, m_0 is the monolayer value, C and K are respectively calculated from m_0 (Timmermann, Chirife, & Iglesias, 2001).

$$\frac{m}{m_0} = \frac{CKa_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \quad (1)$$

2.3. Thermal analysis

The onset glass transition temperature (T_g), onset and peak crystallization temperature (T_{cr1} and T_{cr2}) for each material was determined using differential scanning calorimeter (DSC) (Mettler Toledo Schwerzenbach, Switzerland). Samples of all materials were transferred to preweighed standard DSC aluminum pans (~40 μL, Mettler Toledo Schwerzenbach, Switzerland), and hermetically sealed before weighing. An empty punctured pan was used as a reference. Samples were scanned from ~60 °C below to over the T_g region at 5 °C/min and then cooled at 10 °C/min to initial temperature. A second heating scan was