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Structural strength analysis of partially crystalline trehalose

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ABSTRACT

Strength concept, which is based on the Williams-Landel-Ferry (WLF) model, was developed using mixed structured powders containing amorphous and crystalline components. At the present study, semi-crystalline trehalose powders with various (100:0; 80:20; 60:40; 40:60; 20:80) amorphous to crystalline ratios were analyzed. Amorphous components were prepared from water solution by freeze-drying. Strength analysis, which included water sorption, differential scanning calorimetry, dynamic mechanical analysis and microscopy, was applied. The results indicated that water content significantly decreases glass transition (~100 °C) and α-relaxation temperatures (~90 °C) as well as structural strength parameter (~10 °C), while, the effect of crystalline component is less pronounced. This study can be used in processing and characterization of various partially crystalline food products including nutritional formulations and infant formulas.

1. Introduction

The improvement of processing and storage techniques requires a deep and fundamental knowledge of thermodynamics and kinetics. Food solids can exist in crystalline, amorphous or partially (e. g. semi) crystalline powders. Crystalline and amorphous materials show significantly different physicochemical properties (Bhandari, Bansal, Zhang, & Schuck, 2013, p. 660), due to differences in microstructure. Crystalline structures have long range molecular order, while amorphous structures are more disordered (short range molecular alignment) (Nurhadi & Roos, 2016). To preserve the taste, flavor and color of food the materials should be maintained in the amorphous form (Roos & Drusch, 2015, p. 368). Amorphous materials are thermodynamically unstable compared to crystalline structures, however they are fairly stable in the glassy state (e. g. glass) (Slade, Levine, & Reid, 1991). At temperatures close to the calorimetric glass transition temperature (T_g), physical properties of solids, such as molecular mobility, viscosity, etc. significantly change and materials are converted to supercooled liquids (e. g. rubber) showing time-dependent flow (Angell, Ngai, McKenna, McMillan, & Martin, 2000). Hence, obtaining the time-dependent characteristics of thermal, electric and mechanical changes is practically important. Structural strength concept, proposed by Roos and co-workers combine temperature differences ($T-T_g$) and a practically important time factor (critical change in structural relaxation time) (Roos et al., 2015).

Trehalose is a natural disaccharide of glucose with a high T_g (Green & Angell, 1989). Trehalose is widely used in food and biotechnology areas due to specific physicochemical properties such as prevention of biomolecules degradation (Crowe, Crowe, Rudolph, Womersley, & Appel, 1985; Uritani, Takai, & Yoshinaga, 1995); preservation of vaccines and medical proteins capabilities (Miller & de Pablo, 2000; Xie & Timasheff, 1997).

Amorphicity of materials can be detected gravimetrically from changing mass during water sorption (Buckton & Darcy, 1995; Lehto et al., 2006; Mackin et al., 2002; Nurhadi & Roos, 2016). Amorphous materials have larger porosity and more hydroscopic properties, hence amorphous structures show a higher sorption capacity than crystalline forms (Bhandari et al., 2013, p. 660; Nurhadi & Roos, 2016).

Differential scanning calorimetry (DSC) has been used as a method for detection and quantification of the amorphous components in carbohydrate systems. For this, sample is heated to above the T_g to get dehydration (T_h) (endotherm peak in DSC thermogram) and recrystallization (exotherm peak in DSC thermogram). The areas of exothermal and endothermal peaks are proportional to the amorphous content in a partially crystalline sample. Another approach to detect amorphous component in material by DSC is to determine the change of specific heat capacity (C_p) over the glass transition (Lehto et al., 2006; Saleki-Gerhardt, Ahlneck, & Zografi, 1994; Sebhatu, Angberg, & Ahlneck, 1994).

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Optical (light) microscopy usually shows that the partially crystalline structure tends to increase in transparency while approaching the transition temperature of dehydration without losing their external morphology (Sussich, Urbani, Princivalle, & Cesàro, 1998). A dynamic mechanical analysis (DMA) in multi-frequency mode is a useful tool to characterize mechanical properties including α, β, γ-relaxations, which happen due to variation in molecular mobility below and around T_g (Moates, Noel, Parker, & Ring, 2001). Knowing the frequency of measurements allows obtaining the value of structural relaxation time of α-relaxation process (Noel, Parker, & Ring, 2000), which may be related to particle structure, collapse and viscous flow. As the determination of viscous flow characteristics at temperatures close to the T_g is extremely difficult, strength concept provides an estimation of resistance to structural changes for amorphous materials above the calorimetry onset temperature during heating.

Strength analysis, which included water sorption, DSC and DMA, was successfully applied for various carbohydrate-protein, carbohydrate-carbohydrate and miscible models such as trehalose-whey protein isolate (WPI) (Fan & Roos, 2016a, b; Maidannyk & Roos, 2016), lactose-WPI (Fan & Roos, 2016a, b; Maidannyk & Roos, 2017), lactose-trehalose (Fan & Roos, 2016a) and trehalose-maltodextrin (Maidannyk, Nurhadi, & Roos, 2017). These studies showed that structural strength linearly depends on concentration of components and significantly decreases with increasing water content in a system. However, structural strength analysis of partially crystalline systems has not been addressed. The main aim of the present study was to develop the strength model using partially crystalline systems of trehalose. For this, effect of crystalline component on structural strength of amorphous trehalose was under investigation and effects of water content on structural strength of the partially crystalline systems were also studied.

2. Materials and methods

2.1. Materials

D-(+)-Trehalose crystalline dihydrate (Hayashibara Co., Ltd., Okayama, Japan) and de-ionized water (KB scientific, Cork, Ireland) were used without purification.

2.1.1. Amorphous structure

Amorphous structure was obtained by freeze-drying (Lyovac GT2, Steris®, Hürth, Germany). For this, trehalose solution (total solid of 20%) in water was prepared. After that, 5×10^{-3} L aliquots of solution were frozen in pre-weighted and semi-closed with septum in 1×10^{-2} L glass vials (Schott, Mulheim, Germany) at −20 °C for 24 h, then at −80 °C for 3 h, followed by freeze-drying for 60 h at pressure $p < 10$ Pa. All vials were hermetically sealed under the vacuum conditions inside the freeze dryer at $p < 10$ Pa and stored over P_2O_5 in vacuum desiccators (Roos & Karel, 1990) at room temperature (25 ± 1 °C) to protect samples from water uptake.

2.1.2. Crystalline structure

Crystalline trehalose powder was prepared by grinding commercial trehalose powder and stored in a desiccator over P_2O_5 at 25 ± 1 °C for 3 days. A small amount of amorphous structure can be detected after grinding procedure (Willart, Dujardin, Dudognon, Danede & Descamps, 2010; Nurhadi & Roos, 2016).

2.1.3. Partially crystalline structures

Partially crystalline trehalose systems were prepared by blending accurately weighted amount of 100% crystalline and 100% amorphous structures at 100:0; 80:20; 60:40; 40:60; 20:80 and 0:100 amorphous:crystalline ratios. Mixing was done by spatula and shaking the closed vials (Nurhadi & Roos, 2016).

2.2. Determination of the initial water content

Samples of trehalose powder with final weight 0.5–1.0 g were dried at 70 °C with absolute pressure $P_{abs} < 10^3$ Pa for 24 h in a WTB Binder vacuum oven (Mason Technology®, Tuttingen, Germany) to measure the initial water content of the material. The difference in mass of samples before and after drying was defined as initial water content.

2.3. Water sorption analysis

Partially crystalline systems with various ratios of amorphous and crystalline structures (described above) were stored at evacuated desiccators (25 ± 1 °C) for 10 days over the saturated solutions of P_2O_5, LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, NaCl and KCl (Sigma Chemical Co., St. Louis, MO. U.S.A.), which at equilibrium provided 0, 0.11, 0.23, 0.33, 0.44, 0.545, 0.66, 0.76 and 0.85 a_w, respectively. AQUALAB 4 (TE) (Decagon Devices Inc., Pullman, WA., U.S.A.) water activity meter was used to measure water activity for each material after storage. Samples were weighted at intervals of 0, 2, 4, 6, 8, 10, 24, 48, 72, 96 and 120 h upon storage. Possible crystallization of amorphous trehalose was assessed from the loss of sorbed water. The water content in each mixture was plotted as a function of time, and the Guggenheim-Anderson-deBoer (GAB) relationship was fitted to data to know water activity-water content dependence of amorphous trehalose systems (Eq. (1)):

$$\frac{m}{m_0} = \frac{Cka_w}{(1 - ka_w)(1 - ka_w + Cka_w)} \quad (1)$$

where, m is water content, m_0 is the monolayer value and C and k were respectively calculated from m_0.

Equation (2) was used to determine the combined effects of amorphous and crystalline components (Bronlund & Paterson, 2004):

$$W_{mixture} = n_1 W_{crystalline} + n_2 W_{amorphous} \quad (2)$$

where, $W_{mixture}$ is the total equilibrium water content in the mixture; n_1 and n_2 are mass fractions of crystalline and amorphous components in the system ($n_1+n_2 = 1$); $W_{crystalline}$ and $W_{amorphous}$ are water contents in crystalline and amorphous component.

2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimeter (DSC) (Mettler Toledo Schwerzenbach, Switzerland) was used to measure the glass transition temperature, dehydration and spontaneous recrystallization of partially crystalline trehalose mixtures with 0, 0.11, 0.23, 0.33 and 0.44 a_w. Samples of all mixtures were transferred to pre-weighted standard DSC aluminium pans (40 μL, Mettler Toledo, Schwerzenbach, Switzerland) and hermetically sealed. An empty punctured pan was used as a reference. For anhydrous systems only, the lids of DSC aluminium pans were punctured to allow evaporation of residual water upon the measurement. All samples were scanned with 5 °C/min heating rate. The onset of T_g, heat capacity of endotherm and exotherm were determined by the STAR^e software version 8.10 (Mettler Toledo, Schwerzenbach, Switzerland).

2.5. Dynamical mechanical analyses (DMA)

Dynamic mechanical analyzer (DMA) (Tritec 2000 DMA, Triton