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Structural strength analysis of amorphous trehalose-maltodextrin systems

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ABSTRACT

Fundamental knowledge of physical state of materials gives practically important information for food, biological and pharmaceutical industry. Based on Williams-Landel-Ferry (WLF) equation, the strength concept was introduced. This concept provides a simple parameter, S, to express resistance of solids to flow above the glass transition temperature. To develop this approach, miscible trehalose-maltodextrin (0:100; 20:80; 40:60; 60:40; 80:20 and 100:0) systems with different ratios of components were used in the present study. Such systems represent various food products including infant formula and many nutritional formulations. Amorphous solids were prepared from 20% solids in water solutions by freeze-drying. Fractional water sorption analysis of trehalose-maltodextrin miscible systems allows control of water content at high water activities. Glass transition temperatures were measured by DSC. DMA and DEA in a multi-frequency mode allowed determination of corresponding α-relaxation temperatures at various structural relaxation times. Volume rheology gives structural relaxation time – temperature dependence for high water content systems. The strength showed linear dependence on maltodextrin concentration and its value decreased significantly with increasing water content in miscible systems.

1. Introduction

Knowledge of thermodynamic and kinetic characteristics is fundamental for understanding of processing and storage of materials. The glass transition temperature (T_g) is an important physical parameter which is often measured by differential scanning calorimeter (DSC). At temperatures below T_g low molecular weight sugars (mono- and disaccharides) exist in an amorphous solid form. However, during heating to above the T_g, physical properties such as molecular mobility, viscosity, etc. are significantly changing and amorphous solids (e.g. glass) are converted to supercooled liquids (e.g. rubber), showing time-dependent flow (rapid change in structural relaxation time) (Angell, Ngai, McKenna, McMillan, & Martin, 2000; Roos, 2008). Unfortunately, T_g of a material alone does not provide sufficient information about kinetics of the transition process. Therefore, measurements of the time-dependent characteristics of electric, thermal and mechanical changes give very important practical data. Structural strength determination, proposed by Roos and co-workers is a simple approach, which combines temperature change and practically important time factors (Fan & Roos, 2016a, 2016b; Maidannyk & Roos, 2016, 2017; Roos et al., 2015). The strength (S) shows a temperature difference ($T - T_g$), at which a structural relaxation times decrease to a critical level (Fan & Roos, 2016a, 2016b; Maidannyk & Roos, 2016, 2017; Roos et al., 2015).

T_g of complex multicomponent systems depends on components miscibility (Roos, 2008). In the present study systems of trehalose-maltodextrin with various component contents were used as a miscible carbohydrate model. Trehalose is a natural disaccharide of glucose monomers with a high T_g (Green & Angell, 1989) and represents a suitable material for uses in food and biotechnological areas due to its physicochemical properties (stabilization of protein structure and membrane structure in a dry state, inhibition of biological damage) (Crowe, Crowe, Rudolph, Womersley, & Appel, 1985; Xie & Timasheff, 1997). Maltodextrins are products of starch hydrolysis and their molecular size/weight can be characterized by Dextrose Equivalent (DE). Even with the same DE, maltodextrin is a mixture of different carbohydrates, therefore usually maltodextrins have a very complex composition (Linden & Lorient, 1999; Nurhadi, Roos, & Maidannyk, 2016). Systems with maltodextrin of low DE usually form mixtures with sugars which have higher T_g than pure sugars (Silalai & Roos, 2011).

The presence of water dramatically decreased T_g of anhydrous carbohydrates as a result of water sorption. Water sorption isotherm of each system allows knowing water content during storage at various relative humidities (Blahovec & Yanniotis, 2009; Potes, Kerry, & Roos,

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2012). Measurement of T_g, at a very high water content in the system, is practically complicated, thereby T_g may be obtained from the Gordon-Taylor relationship (Arvanitoyannis, Blanshard, Izzard, Lillford, & Ablett, 1993).

Dynamic mechanical (DMA) and dielectric (DEA) analyses in a multi-frequency mode are suitable methods to measure α-, β- and γ-relaxations which occur due to molecular mobility around and below T_g. These methods were applied for analyses of different amorphous carbohydrates at low water contents (Moates, Noel, Parker, & Ring, 2001; Kilmartin, Reid, & Samson, 2004; Ermolina, Polygalov, Bland, & Smith, 2007; Silalai & Roos, 2011; Potes et al., 2012). The structural relaxation time of the α-relaxation process can be obtained from the frequency of primary α-relaxation (Noel, Parker, & Ring, 2000). For systems with high water contents, data of structural relaxation times may be obtained from volume rheology (Angell, 2002).

Structural strength analysis was successfully applied for various carbohydrate-protein and carbohydrate-carbohydrate models such as trehalose-whey protein isolate (WPI), (Fan & Roos, 2016a, 2016b; Maidannyk & Roos, 2016), lactose-WPI (Fan & Roos, 2016a, 2016b; Maidannyk & Roos, 2016, 2017) and lactose-trehalose (Fan & Roos, 2016a). These previous studies have confirmed that structural strength depends on composition and significantly decreases upon increasing of water content of the material. However, structural strength analysis including water sorption, glass transition, rheological, mechanical and dielectric properties data for miscible carbohydrates systems has not been addressed. The main purpose of the present study was to develop the strength concept using miscible trehalose-maltodextrin systems. For this, the effect of maltodextrin on structural strength of amorphous trehalose was under investigation. In addition, effects of water content on structural strength of miscible systems were also in focus.

2. Materials and methods

2.1. Materials

D-(+)-Trehalose crystalline dihydrate (Hayashibara Co., Ltd., Okayama, Japan) and Maltodextrin (M 100) with DE 9–12 or in average DE 10 (Grain Processing Corporation, IA, USA) were used without purification. De-ionized water was obtained from KB scientific, Cork, Ireland.

2.2. Determination of the initial water content

Samples of powders with various ratios of trehalose and maltodextrin (0:100; 20:80; 40:60; 60:40; 80:20 and 100:0 trehalose-maltodextrin systems) with final mass 0.5–1.0 g were dried at 70 °C with absolute pressure $P_{abs} < 10$ mbar for 24 h in a WTB Binder vacuum oven (Mason Technology®, Tuttingen, Germany) to measure the initial water content of the materials. The difference in mass of samples before and after drying was defined as initial water content.

2.3. Preparation of amorphous freeze-dried materials

Trehalose and maltodextrin solutions (total solid of 20%) in water were prepared separately. After that, solutions were mixed in required proportions. The ratio of solid components trehalose:maltodextrin was 0:100; 20:80; 40:60; 60:40; 80:20 and 100:0. 5 ml aliquots of these solutions were frozen in pre-weighted and semi-closed with septum 10 ml glass vials at −20 °C for 24 h, then at −80 °C for 3 h, followed by freeze-drying for 60 h at pressure $p < 0.1$ mbar (Lyovac GT2, Steris®, Hürth, Germany) to obtain amorphous materials. All vials were hermetically sealed under the vacuum conditions inside the freeze dryer at $p < 0.1$ mbar and stored over P_2O_5 in vacuum desiccators (Roos & Karel, 1990) at room temperature (25 ± 1 °C) to protect samples from water uptake.

2.4. Water sorption analysis

Freeze-dried and closed under vacuum conditions samples with various ratios of trehalose and maltodextrin (described above) were stored in desiccators over P_2O_5. Each system was stored at an evacuated desiccator (25 ± 1 °C) for 10 days over the saturated solutions of LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, NaCl and KCl (Sigma Chemical Co., St. Louise, MO. U.S.A.), which at equilibrium provided 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., NE) 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, 120 and 144 h (up to 192 h for 0:100 trehalose:maltodextrin system) upon storage. Possible crystallization of trehalose was assessed from the release 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 study water activity dependence in amorphous trehalose-maltodextrin systems on water content (Eq. 1):

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

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

The fractional water sorption method, shown by Potes et al. (2012) allows calculation of fractional water content of material, stored at high water activities (Eq. 2):

$$W_t = n_1 W_1 + n_2 W_2 \quad (2)$$

where, W_t is the total equilibrium water content in the system; n_1 and n_2 are multipliers of each component in the system (for example $n_1 = 0.2$, $n_2 = 0.8$ for 20:80 trehalose-maltodextrin system); W_1 and W_2 are water contents in each non-crystallized component (Potes, 2014).

2.5. Differential scanning calorimetry (DSC)

Differential scanning calorimeter (DSC) (Mettler Toledo Schwerzenbach, Switzerland) was used to measure the glass transition temperature of amorphous trehalose-maltodextrin 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 from ~30 °C below to over T_g region with 5 °C/min heating rate and cooled at 10 °C/min to initial temperature. Then, second heating scan was run to well above (>50 °C) the T_g at 5 °C/min heating rate. The onset of T_g was determined by the STAR^e software version 8.10 (Mettler Toledo Schwerzenbach, Switzerland). The Gordon-Taylor equation (Eq. 3) was used to estimate T_g for high water content systems (60, 70, 80 and 80% of water).

$$T_g = \frac{w_1 T_{g1} + kw_2 T_{g2}}{w_1 + kw_2} \quad (3)$$

where, w_1 and w_2 are the mass fractions of amorphous sugar and of water, T_{g1} and T_{g2} are glass transition temperatures, respectively, and k is a constant.

2.6. Dynamical mechanical analyses (DMA)

Dynamic mechanical analyzer (DMA) (Tritec 2000 DMA, Triton Technology Ltd., UK) was used to measure mechanical properties (E″ – loss modulus, E′ – storage modulus and $\tan\delta = E''/E'$) of anhydrous