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Structural relaxations of amorphous lactose and lactose-whey protein mixtures

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A R T I C L E I N F O

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Structural relaxations and relaxation times, τ, of lactose in freeze-dried amorphous lactose and lactose-WPI mixture systems were studied with glass transition data. The results indicated that T_g, enthalpy relaxation and α-relaxation temperature, T_α, of amorphous lactose was affected by the presence of lactose crystals and WPI at 0.33 a_w (25 °C) due to water migration. The τ and $T_\alpha - T_g$ relationship of the materials was successfully modeled by the WLF equation with the material-special constants ($-C_1$ and C_2). A strength parameter, S, indicating decrease of τ from 10^2 to 10^{-2} s, could be used to measure the structural stability of lactose systems above their glass transition. The strength of amorphous lactose decreased with a_w increasing up to 0.44 and enhanced by α lactose crystals and WPI in storage at 0.33 a_w. Hence, the strength parameter provided a simple and convenient means to measure compositional effects on structure formation in food processing.

1. Introduction

Structural relaxations, as often measured above and somewhat below the glass transition region, reflect the spontaneous approach of an amorphous material towards equilibrium at a rate which often depends on temperature and water activity, a_w, of the material (Shamblin and Zografi, 1998; Liu et al., 2006). Structural relaxation times correspond to the kinetically impeded molecular rearrangements and relate to the time-dependent changes of thermodynamic, mechanical or dielectric properties, following a perturbation such as a change in temperature or pressure (Chung et al., 2004a; Surana et al., 2004; Haque et al., 2006). A change in enthalpy around the glass transition reflects the non-equilibrium nature of the glassy state and is often referred to as enthalpy relaxation, which is dependent on the kinetics of molecular freezing around glass transition (Liu et al., 2006). Enthalpy relaxation occurs concomitantly with increasing local translational molecular motions of molecules or parts of polymer molecules when a glassy material is heated to above its glass transition (Roos, 1987; Shamblin and Zografi, 1998; Wungtanagorn and Schmidt, 2001a, b; Liu et al., 2006; Haque et al., 2006). Since the enthalpy relaxation is recognized as an important factor relating to the physical properties of polymers, differential scanning calorimetry, DSC, is routinely used to study enthalpy relaxations associated with the glass transition (Yoshida, 1995; Le Meste et al., 2002; Surana et al., 2004; Roos and Drusch, 2015).

The molecular arrangement in a non-equilibrium glass often tends to lose its “quenched in” excess enthalpy or free volume with time (Hancock et al., 1995). Variations in molecular mobility, including molecular displacement or deformation, molecular migration, molecular diffusion reflecting Brownian movements and rotation of functional groups or polymeric segments around covalent bonds, could be related to processability and stability of food products upon storage (Roudaut et al., 2004). In the glass, long-range cooperative motions are restricted and motions (vibrations of atoms, reorientation of small groups of atoms) are mainly local not involving the surrounding atoms or molecules. A temperature increase to above the T_g results in a rapid increase of molecular mobility, which is shown by the decreasing viscosity and increasing flowability of the material (Hancock et al., 1995). The relaxation time, τ, is the time that is necessary for the recovery from perturbations (Le Meste et al., 2002). Structural relaxations around the glass–liquid transition could show relaxation times of similar timescale of the experimental time scale (Champion et al., 2000). Thus, structural relaxations and τ may be related to particle structure, flow characteristics, viscous flow and collapse, and

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mechanical properties, which control the quality and stability of food materials, particularly in the vicinity and above the onset of the calorimetric glass transition.

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 (Roos and Karel, 1992). It is a dramatic change in material structure that results in complete changes of physicochemical properties. Mechanical properties of amorphous sugars could be affected by their degree of crystallinity (Chung et al., 2002; Chung et al., 2004b) and the presence of other components affecting their glass transition, e.g. water (Downton et al., 1982; Slade and Levine, 1991), carbohydrates (Cruz et al., 2001; Miao and Roos, 2005) and proteins (Silalai and Roos, 2011a; Fan and Roos, 2015). A characteristic feature of mechanical properties of amorphous sugars, such as the T_g-dependence, could affect food quality and shelf life during storage (Slade and Levine, 1991; Silalai and Roos, 2011a, b). The glass transition appears as the primary α-relaxation, which could cover a wide range of time and temperature scales (Urbani et al., 1997; Faivre et al., 1999; Talja and Roos, 2001; Yu, 2001). The frequency-dependent α-relaxation of amorphous sugars is governed by water content, relative humidity and temperature (Roos and Karel, 1991). Dynamic-mechanical analysis (DMA) may be used in studies of structural relaxations below the calorimetric T_g, the α-relaxation (primary relaxation) of glass forming carbohydrates, and to derive the α-relaxation temperature, T_α, (Silalai and Roos, 2011b; Potes et al., 2012). The T_α may be taken from loss modulus peak temperatures at various frequencies to obtain the corresponding τ. In general, Williams–Landel–Ferry (WLF) model, as an interrelated relationship, is often used to define mobility in terms of the non-Arrhenius temperature dependence of the rate of any diffusion-limited relaxation process occurring at the temperature T, compared to the rate of the relaxation at the reference temperature, e.g., T_g, expressed in terms of τ dependence on $T-T_g$ (Williams et al., 1955; Slade and Levine, 1995; Angell, 1997; Roos and Drusch, 2015).

Previous studies have shown that water and food components in mixed systems vary in their physical and chemical stability (Champion et al., 2000; Fan and Roos, 2015). The importance of glass transition to amorphous solids characteristics has been well recognized but few studies have contributed to the understanding of effects of crystals or glass former on the particle structure and properties in food materials. The objectives of the present study were to investigate the influence of water, two different crystalline phases (α-lactose monohydrate and anhydrous β-lactose crystals) and polymeric food component (whey protein isolates, WPI), on the calorimetric glass transition, enthalpy relaxations, α-relaxation, and τ of freeze-dried amorphous lactose in systems at low water activities ($\leq$0.44 a_w). We expect that the flow characteristics or "strength" of the glass former and their interaction with other solids could contribute to powder characteristics. This study is useful for the understanding of the effects of water and food components on the collective relaxation behavior when present with amorphous lactose around the glass transition in food and pharmaceutical materials.

2. Materials and methods

2.1. Sample preparation

α-lactose monohydrate, anhydrous β-lactose (>99% lactose) (Sigma–Aldrich, St. Louis, Mo., U.S.) and whey protein isolate (WPI; Isolac®, Carbery Food Ingredients, Co., Ballineen, Ireland; minor components including carbohydrates or lipids < 3%) were used. Lactose was dissolved in boiling (~100 °C) deionized water (KB Scientific Ltd. Cork, Ireland) to obtain 20% (mass) solution and then cooled to room temperature (20 ± 3 °C). WPI with 20% (mass) solids in deionized water at room temperature was prepared using continuous stirring for 4 h (Fan and Roos, 2015). Aqueous lactose and WPI with 20% (mass) solids at room temperature were used to obtain ratios of 7:3, 1:1 and 3:7 of lactose-WPI by mass. 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 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 desiccators over P_2O_5 (Sigma–Aldrich, St. Louis, Mo., U.S.) prior to subsequent analysis.

Freeze-dried lactose was monitored for 120 h over saturated solutions of LiCl, CH_3COOK, $MgCl_2$, and K_2CO_3 (Sigma Chemical Co., St. Louis, Mo., U.S.A.) at respective water activities, a_w, of 0.11, 0.23, 0.33, and 0.44 a_w depending on storage temperature of 25 °C (Greenspan, 1977; Labuza et al., 1985), in vacuum desiccators. The α-lactose monohydrate, anhydrous β-lactose, WPI and lactose-WPI at 7:3, 1:1 and 3:7 mass ratios were adjusted to 0.33 a_w (Dew Point Water Activity Meter 4TE, Aqualab, WA, USA) by humidification over saturated solution of $MgCl_2$ (Sigma Chemical Co., St. Louis, Mo., U.S.A.) in vacuum desiccators in incubators at 25 °C. All vials were closed with septum when removed out of desiccators for weighing and septum was removed when vials were loaded on the balance. All mixtures were made into powder using a mortar and pestle after humidification. After storage at 0.33 a_w and 25 °C, lactose, α-lactose monohydrates, anhydrous β-lactose and WPI were mixed in order to prepare the crystals containing systems. The solid ratios of α and β type of lactose crystal-lactose systems were 1:4, 2:3, 3:2 and 4:1 (by mass), respectively.

2.2. Thermal analysis

The onset of glass transition temperature, T_g, heat capacity changes, ΔC_p, and recovery of enthalpy, ΔH, for each material were determined around glass transition using 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 and the instrument was calibrated for temperature and heat flow as reported by Potes et al. (2012). Samples were scanned from ~30 °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 run to well above the T_g at 5 °C/min. The onset glass transition temperatures derived from two subsequent heating scans, T_{g1} and T_{g2}, were recorded using STARe software, version 8.10 (Mettler Toledo Schwerzenbach, Switzerland). The ΔH values were calculated from the endothermic peak around the glass transition (Surana et al., 2005; Haque et al., 2006). Fig. 1 gives a schematic diagram for the onset T_g, ΔC_p and the size of the relaxation peak, which was used to derive ΔH values, based on two heating scan using DSC.

2.3. Dynamic-mechanical analysis

Dynamic-mechanical properties of humidified pure lactose and composite materials were studied using DMA (Tritec 2000 DMA, Triton Technology Ltd., UK). The storage modulus, E', and loss modulus, E'', as a function of temperature at different frequencies were determined (0.5, 1, 3, 5, and 10 Hz). The DMA instrument was