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# Water sorption-induced crystallization, structural relaxations and strength analysis of relaxation times in amorphous lactose/whey protein systems

Fanghui Fan [a], Tian Mou [b], Bambang Nurhadi [a], Yrjö H. Roos [a, *]

[a] School of Food and Nutritional Sciences, University College Cork, Cork, Ireland
[b] School of Mathematical Sciences, University College Cork, Cork, Ireland

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ABSTRACT

Water sorption-induced crystallization, α-relaxations and relaxation times of freeze-dried lactose/whey protein isolate (WPI) systems were studied using dynamic dewpoint isotherms (DDI) method and dielectric analysis (DEA), respectively. The fractional water sorption behavior of lactose/WPI mixtures shown at $a_w \leq 0.44$ and the critical $a_w$ for water sorption-related crystallization ($a_w^{(cr)}$) of lactose were strongly affected by protein content based on DDI data. DEA results showed that the α-relaxation temperatures of amorphous lactose at various relaxation times were affected by the presence of water and WPI. The α-relaxation-derived strength parameter ($S$) of amorphous lactose decreased with $a_w$ up to 0.44 $a_w$ but the presence of WPI increased $S$. The linear relationship for $a_w^{(cr)}$ and $S$ for lactose/WPI mixtures was also established with $R^2 > 0.98$. Therefore, DDI offers another structural investigation of water sorption-related crystallization as governed by $a_w^{(cr)}$, and $S$ may be used to describe real time effects of structural relaxations in noncrystalline multicomponent solids.



## 1. Introduction

Water is of key importance to food systems affecting processing, microbial safety, sensory perception, and a storage stability and shelf life (Al-Muhtaseb et al., 2002; Lodi and Vodovotz, 2008). Water sorption may be affected by time-dependent phenomena, structural transformations, and phase transitions of food solids. Such transitions may affect rates of deteriorative changes and decrease the storage stability of dehydrated foods, e.g., powdered milk (Silalai and Roos, 2011), potato flakes (Turner et al., 2006), and dry pasta (Aguilera et al., 2003; Gowen et al., 2008). Water sorption isotherms are important to numerous applications, e.g., development of new products (Wang and Brennan, 1995), determination of product stability and shelf life (Jouppila and Roos, 1994), and process design and control (Peng et al., 2007). The dynamic dewpoint isotherm (DDI) method was developed to generate water sorption isotherms using single samples in a dynamically changing water vapor pressure (Yuan et al., 2011). The DDI method developed along with dynamic vapor sorption provides a continuous measurement of water content ($c_w$) and water activity ($a_w$). DDI differs from standard saturated salt solution methods (SSM), which measure $c_w$ for equilibrated materials at known $a_w$ (Schmidt and Lee, 2012). Also, DDI makes it possible to generate complete dynamic isotherms with 50–200 data points quickly and accurately without long equilibration times which are typical of SSM methods (Yuan et al., 2011; Schmidt and Lee, 2012). Therefore, DDI method offers another real-time investigation of water sorption-related material properties, i.e., crystallization and deliquescence (Yao et al., 2011), in food processing as well as for the control of storage stability and shelf life of resultant products.

Water sorption characteristics, as well as other interactions of food solids with water, are defined by composition of nonfat components, i.e., carbohydrates and proteins (Roos and Drusch, 2015). Characterization of glass formation of complex food solids systems has been of particular interest in recent years (Ibach and Kind, 2007; Babu and Nangia, 2011). Amorphous food materials exist in a supercooled and non-equilibrium state blow their respective equilibrium melting temperature with no well-defined structure. The nonequilibrium state may exhibit an indefinite number of glass structures with varying levels of molecular packing and order. When temperature increases to above glass transition

* Corresponding author.
*E-mail addresses:* ffh11235813@gmail.com (F. Fan), yrjo.roos@ucc.ie (Y.H. Roos).

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temperature ($T_g$), a rapid increase of molecular mobility occurs and the glass-forming material transforms to a viscous liquid, which dramatically affects various physicochemical properties of food solids (Slade et al., 1991; Bhandari and Howes, 1999). Structural relaxations in amorphous food materials around or above the glass transition occur as a result of molecular mobility changes due to variations in external thermodynamic conditions e.g., pressure and temperature. Glass transition may also result internally in materials because of changes in plasticizer or solvent contents, e.g., water, which can induce dramatic changes in solids properties and directly affect processing, storage, bioavailability, and delivery properties of food materials (Yu et al., 2001; Roos and Drusch, 2015). Relaxation times ($\tau$) correspond to the kinetically impeded and time-dependent molecular rearrangements that are responsible for solids structure and properties, e.g., flow characteristics, viscous flow and collapse, mechanical or dielectric properties, and crystallization (Sperling, 2005). Such properties may be used to control the quality and stability of food materials during processing and storage (Champion et al., 2000).

The $\alpha$-relaxation and relaxation times of glass forming food materials around calorimetric $T_g$ could be studied and determined by dielectric analysis (DEA) (Moates et al., 2001; Clerjon et al., 2003). The $\alpha$-relaxation temperature ($T_\alpha$) may also be taken from the dielectric loss ($\varepsilon''$) peak temperature at various frequencies to obtain corresponding relaxation times (Silalai and Roos, 2011). The Williams-Landel-Ferry (WLF) model is often used to model relaxation times of the non-Arrhenius temperature dependence of relaxation processes occurring above $T_g$, and the $\tau$ is shown against $T$-$T_g$ (Slade et al., 1991). The WLF-relationship applies over the temperature range covering the rubbery or supercooled liquid state and it was also used to describe time and temperature dependent behavior of food solids systems. The "strength" concept and strength parameter ($S$) developed by Roos et al. (2015) combined the characterization of material state and relaxation times to describe the critical temperature difference at which a sharp change in properties of the material occurs. On the other hand, the $S$ parameter based on WLF modeling was used to describe amorphous food solids and their properties for typical processing and storage conditions where a component or miscible components within food structure may experience the glass transition (Fan and Roos, 2016a). Besides the strength of food solids, the Deborah number was applied to provide a useful translation of measured relaxation times to real timescales. Therefore, the strength concept gives a quantitative measure to estimate compositional effects on relaxation times to describe properties of food solids above measured $T_g$.

Lactose (β-D-galactopyranosyl (1–4)-D-glucopyranose) is one of the most common and important ingredients in many formulated foods and pharmaceutical materials, and it exhibits strong water-dependent properties, i.e., glass transition and crystallization from its amorphous states during storage (Nickerson, 1979; Gänzle et al., 2008). Understanding glass transition-related structural relaxations and their coupling with water sorption properties is essential for modeling the physical state of dairy-based food systems at various conditions and the design of complex formulations. The importance of glass transition to amorphous solids characteristics has been well recognized but few studies have contributed to understanding effects of glass former or polymer, i.e., protein, on the water sorption characteristics and structural relaxations in food formulations. Therefore, the major objective of the present study was to investigate the influence of food polymeric components (whey protein isolates, WPI) on the water sorption properties of freeze-dried amorphous lactose/WPI mixtures using the DDI measurement data at 25 °C. The strength analysis was carried out to determine the $S$ parameter for lactose/WPI systems by analyzing their relaxation times measured by DEA after storage at $a_w \leq 0.44$ $a_w$ and 25 °C. These data are useful for the understanding of the effects of proteins on water sorption properties of amorphous lactose and collective structural relaxation behavior when present with amorphous lactose around the glass transition in well-mixed food and pharmaceutical materials.

## 2. Materials and methods

### 2.1. Sample preparation

α-Lactose monohydrate (>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. 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. Mixed solutions (5 mL in total) were prepared in pre-weighted glass vials (10 mL; Schott Müllheim, Germany). All solutions 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 $P_2O_5$ at 25 °C (Sigma-Aldrich, St. Louis, Mo., U.S.) prior to subsequent analysis.

### 2.2. Water sorption experiment

The water sorption of freeze-dried samples was studied using an AquaSorp isotherm generator (AIG; Decagon Devices, Inc. Pulman WA, USA). The airflow continuously passes over the sample in AIG until certain interval time or when there was a mass or $a_w$ change of sample, then the flowstopped and the snapshot of the sorption process was taken by directly measuring mass and $a_w$ based on a high precision magnetic force balance and chilled-mirror dewpoint sensor (Decagon Devices, Inc. Pulman WA, USA). Based on above principle the dynamic water sorption of DDI can be comparable to real-time sorption process for a material with fast vapor diffusion or by reducing the sample size. In the present study, approximately 600 mg of each sample (dried powder), which could cover the bottom of stainless steel sample cup, was used in measurements. Measurement parameters were 0.05–0.90 $a_w$ at a temperature of 25 °C, airflow of 300 ml/min (Schmidt and Lee, 2012). At certain interval time, the airflow stopped automatically then the weight change and the $a_w$ of the sample were recorded. After initial $c_w$ was determined, the mass was converted to the $c_w$ of the sample at the corresponding $a_w$ and a plot of the dynamic sorption isotherm using the SorpTrac software, version 1.03.3 (Decagon Devices, Pullman, WA, USA) was generated. Since each DDI run is unique, the sorption section of the working isotherm was obtained in duplicate, each on a different sample.

The critical $a_w$ value for water sorption-induced crystallization ($a_w^{(cr)}$) of lactose and lactose/WPI mixtures were analyzed and determined by calculating the changes of $c_w$ in DDI of each sample using derivative analysis (Yuan et al., 2011). The procedures used to obtain the first and the second derivative was as follows. Attempts to leave out noise and find the peak location, the $a_w$ and $c_w$ data derived from DDI were smoothed using LOESS (local polynomial regression fitting) smoothing (second-degree polynomial) with a span of 11 points using the $R$ programme, version 3.2.3 (The R Foundation©, Murray Hill, NJ, USA). The smoothed data set was fit using a smoothing cubic spline after which the first derivative of the fit was taken. The peak $a_w$ of the 1st derivative function ($a_{wp}^{(cr)}$) based on smoothed DDI data was taken as acceleration point for