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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 aw \leq 0.44 and the critical aw for water sorption-related crystallization (aw(cr)) of lactose were strongly affected by protein content based on DDI data. DEA results showed that the $\alpha\text{-relaxation}$ 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 aw up to 0.44 aw but the presence of WPI increased S. The linear relationship for aw(cr) and S for lactose/WPI mixtures was also established with R2 > 0.98. Therefore, DDI offers another structural investigation of water sorption-related crystallization as governed by aw(cr), and S may be used to describe real time effects of structural relaxations in noncrystalline multicomponent solids.

1	Water sorption-induced crystallization, structural relaxations and strength analysis of
2	relaxation times in amorphous lactose/whey protein systems
3	
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8 Abstract: Water sorption-induced crystallization, α -relaxations and relaxation times of 9 freeze-dried lactose/whey protein isolate (WPI) systems were studied using dynamic 10 dewpoint isotherms (DDI) method and dielectric analysis (DEA), respectively. The fractional water sorption behavior of lactose/WPI mixtures shown at $a_w \le 0.44$ and the 11 critical a_w for water sorption-related crystallization $(a_w^{(cr)})$ of lactose were strongly 12 13 affected by protein content based on DDI data. DEA results showed that the 14 α -relaxation temperatures of amorphous lactose at various relaxation times were 15 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 16 WPI increased S. The linear relationship for $a_w^{(cr)}$ and S for lactose/WPI mixtures was 17 also established with $R^2 > 0.98$. Therefore, DDI offers another structural investigation 18 of water sorption-related crystallization as governed by $a_w^{(cr)}$, and S may be used to 19 20 describe real time effects of structural relaxations in noncrystalline multicomponent 21 solids.

22

Keywords, Dynamic Dewpoint Isotherms; Crystallization; α-Relaxation; Relaxation
Times; Strength; Water Activity

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28 1. Introduction

30 Water is of key importance to food systems affecting processing, microbial safety, 31 sensory perception, and a storage stability and shelf life (Al-Muhtaseb, McMinn, & 32 Magee, 2002; Lodi & Vodovotz, 2008). Water sorption may be affected by 33 time-dependent phenomena, structural transformations, and phase transitions of food solids. Such transitions may affect rates of deteriorative changes and decrease the 34 35 storage stability of dehydrated foods, e.g., powdered milk (Silalai & Roos, 2011), 36 potato flakes (Turner et al., 2006), and dry pasta (Aguilera, Chiralt, & Fito, 2003; 37 Gowen, Abu-Ghannam, Frias, & Oliverira, 2008). Water sorption isotherms are 38 important to numerous applications, e.g., development of new products (Wang & 39 Brennan, 1991), determination of product stability and shelf life (Jouppila & Roos, 40 1994), and process design and control (Peng, Chen, Wu, & Jiang, 2007). The dynamic 41 dewpoint isotherm (DDI) method was developed to generate water sorption isotherms 42 using single samples in a dynamically changing water vapor pressure (Yuan, Carter, & 43 Schmidt, 2011). The DDI method developed along with dynamic vapor sorption 44 provides a continuous measurement of water content (c_w) and water activity (a_w) . DDI 45 differs from standard saturated salt solution methods (SSM), which measure c_w for equilibrated materials at known a_w (Schmidt & Lee, 2012). Also, DDI makes it possible 46 to generate complete dynamic isotherms with 50 to 200 data points quickly and 47 48 accurately without long equilibration times which are typical of SSM methods (Yuan et

al, 2011 ; Schmidt & 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.

53

Water sorption characteristics, as well as other interactions of food solids with water, 54 55 are defined by composition of nonfat components, i.e., carbohydrates and proteins 56 (Roos & Drusch, 2015). Characterization of glass formation of complex food solids 57 systems has been of particular interest in recent years (Ibach & Kind, 2007; Babu & 58 Nangia, 2011). Amorphous food materials exist in a supercooled and non-equilibrium 59 state blow their respective equilibrium melting temperature with no well-defined 60 structure. The nonequilibrium state may exhibit an indefinite number of glass structures 61 with varying levels of molecular packing and order. When temperature increases to 62 above glass transition temperature (T_g) , a rapid increase of molecular mobility occurs 63 and the glass-forming material transforms to a viscous liquid, which dramatically 64 affects various physicochemical properties of food solids (Slade, Levine, & Reid, 1991; 65 Bhandari & Howes, 1999). Structural relaxations in amorphous food materials around or above the glass transition occur as a result of molecular mobility changes due to 66 67 variations in external thermodynamic conditions e.g., pressure and temperature. Glass 68 transition may also result internally in materials because of changes in plasticizer or

69 solvent contents, e.g., water, which can induce dramatic changes in solids properties 70 and directly affect processing, storage, bioavailability, and delivery properties of food 71 materials (Yu, Li, & Sun, 2001; Roos & Drusch, 2015). Relaxation times (τ) 72 correspond to the kinetically impeded and time-dependent molecular rearrangements 73 that are responsible for solids structure and properties, e.g., flow characteristics, 74 viscous flow and collapse, mechanical or dielectric properties, and crystallization 75 (Sperling, 2005). Such properties may be used to control the quality and stability of 76 food materials during processing and storage (Champion, Le Meste, & Simatos, 2000).

77

78 The *a*-relaxation and relaxation times of glass forming food materials around calorimetric T_g could be studied and determined by dielectric analysis (DEA) (Moates, 79 80 Noel, Parker, & Ring, 2001; Clerjon, Daudin, & Damez, 2003). The α-relaxation 81 temperature (T_{α}) may also be taken from the dielectric loss (ε'') peak temperature at 82 various frequencies to obtain corresponding relaxation times (Silalai & Roos, 2011). 83 The Williams-Landel-Ferry (WLF) model is often used to model relaxation times of the 84 non-Arrhenius temperature dependence of relaxation processes occurring above T_g , 85 and the τ is shown against T-T_g (Slade, Levine, & Reid, 1991). The WLF-relationship 86 applies over the temperature range covering the rubbery or supercooled liquid state and 87 it was also used to describe time and temperature dependent behavior of food solids 88 systems. The "strength" concept and strength parameter (S) developed by Roos and 89 others (2015) combined the characterization of material state and relaxation times to 90 describe the critical temperature difference at which a sharp change in properties of the 91 material occurs. On the other hand, the S parameter based on WLF modeling was used 92 to describe amorphous food solids and their properties for typical processing and 93 storage conditions where a component or miscible components within food structure 94 may experience the glass transition (Fan & Roos, 2016a). Besides the strength of food 95 solids, the Deborah number was applied to provide a useful translation of measured 96 relaxation times to real timescales. Therefore, the strength concept gives a quantitative 97 measure to estimate compositional effects on relaxation times to describe properties of 98 food solids above measured T_g .

99

100 Lactose (β -D-galactopyranosyl (1–4)-D-glucopyranose) is one of the most common 101 and important ingredients in many formulated foods and pharmaceutical materials, and 102 it exhibits strong water-dependent properties, i.e., glass transition and crystallization 103 from its amorphous states during storage (Nickerson, 1979; Gänzle, Haase, & Jelen, 104 2008). Understanding glass transition-related structural relaxations and their coupling 105 with water sorption properties is essential for modeling the physical state of 106 dairy-based food systems at various conditions and the design of complex formulations. 107 The importance of glass transition to amorphous solids characteristics has been well 108 recognized but few studies have contributed to understanding effects of glass former or

109 polymer, i.e., protein, on the water sorption characteristics and structural relaxations in 110 food formulations. Therefore, the major objective of the present study was to 111 investigate the influence of food polymeric components (whey protein isolates, WPI) 112 on the water sorption properties of freeze-dried amorphous lactose/WPI mixtures using 113 the DDI measurement data at 25 °C. The strength analysis was carried out to determine 114 the S parameter for lactose/WPI systems by analyzing their relaxation times measured by DEA after storage at $a_w \le 0.44$ a_w and 25 °C. These data are useful for the 115 116 understanding of the effects of proteins on water sorption properties of amorphous 117 lactose and collective structural relaxation behavior when present with amorphous 118 lactose around the glass transition in well-mixed food and pharmaceutical materials.

119

- 120 **2.** Materials and Methods
- 121 **2.1. Sample preparation**

122

a-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

129	(semi-closed with septum) were frozen at -20 °C for 20 h and then subsequently
130	tempered at -80 °C for 3 h prior to freeze-drying using a laboratory freeze-dryer
131	(Lyovac GT2 Freeze-Dryer, Amsco Finn-Aqua GmbH, Steris [®] , Hürth, Germany).
132	After freeze-drying at pressure < 0.1 mbar, triplicate samples of each material were
133	stored in evacuated desiccators over P_2O_5 at 25 °C (Sigma-Aldrich, St. Louis, Mo.,
134	U.S.) prior to subsequent analysis.

- 135
- 136 **2.2. Water sorption experiment**
- 137

138 The water sorption of freeze-dried samples was studied using an AquaSorp isotherm 139 generator (AIG; Decagon Devices, Inc. Pulman WA, USA). The airflow continuously passes over the sample in AIG until certain interval time or when there 140 141 was a mass or a_w change of sample, then the flow stopped and the snapshot of the sorption process was taken by directly measuring mass and a_w based on a high precision 142 143 magnetic force balance and chilled-mirror dewpoint sensor (Decagon Devices, Inc. 144 Pulman WA, USA). Based on above principle the dynamic water sorption of DDI can 145 be comparable to real-time sorption process for a material with fast vapor diffusion or 146 by reducing the sample size. In the present study, approximately 600 mg of each sample 147 (dried powder), which could cover the bottom of stainless steel sample cup, was used in 148 measurements. Measurement parameters were 0.05 to 0.90 a_w at a temperature of 25 °C,

149	airflow of 300 ml/min (Schmidt & Lee, 2012). At certain interval time, the airflow
150	stopped automatically then the weight change and the a_w of the sample were recorded.
151	After initial c_w was determined, the mass was converted to the c_w of the sample at the
152	corresponding a_w and a plot of the dynamic sorption isotherm using the SorpTrac
153	software, version 1.03.3 (Decagon Devices, Pullman, WA, USA) was generated. Since
154	each DDI run is unique, the sorption section of the working isotherm was obtained in
155	duplicate, each on a different sample.

157 Fig 1.

158

The critical a_w value for water sorption-induced crystallization $(a_w^{(cr)})$ of lactose and 159 lactose/WPI mixtures were analyzed and determined by calculating the changes of c_w in 160 161 DDI of each sample using derivative analysis (Yuan et al., 2011). The procedures used 162 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 163 164 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^{\circ}), 165 166 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 167 function $(a_{wp}^{(cr)})$ based on smoothed DDI data was taken as acceleration point for 168

lactose crystallization. The smoothing and fitting procedures were repeated for the 1st 169 derivative after which the 2nd derivative was obtained from the 1st derivative. Water 170 sorption data showed that a substantial peak on the 2nd derivative developed with onset 171 around the calorimetric T_g corresponding a_w , $a_{wo}^{(cr)}$ (Fig. 1A). The water plasticization 172 173 to above the glass transition induced translational mobility of lactose. Such mobility 174 with further water plasticization could increase free volume to provide water sorption 175 sites and hydrogen bonding structuring of the lactose-water system to accommodate 176 water with less direct lactose-lactose interactions. The programmed codes for achieving 177 first and second derivative analysis in *R* programme were shown on Supplementary 178 Information.

179

180 **2.3. Dielectric analysis (DEA)**

181

DEA was used to measure dielectric properties from the dielectric constant or permittivity (ε'), dielectric loss (ε''), and their ratio tan $\delta = (\varepsilon''/\varepsilon')$ as a function of temperature. The ε' describes an alignment of dipoles and the ε'' describes an energy that is required to align dipoles (Talja & Roos, 2001). In the present study, the freeze-dried lactose and lactose/WPI at 7:3, 1:1 and 3:7 mass ratios were humidified for 120 h over saturated solutions of *CH*₃*COOK*, *MgCl*₂, and *K*₂*CO*₃ (Sigma Chemical Co., St. Louis, Mo., USA) to obtain respective water activities of 0.23, 0.33 and 0.44 a_w at 189 equilibrium in vacuum desiccators in incubators at storage temperature of 25 °C. 190 Dielectric properties of both dry and humidified samples were analyzed using dielectric 191 analyzer (DS6000, Triton Technology Ltd., UK), with titanium sample holders as the 192 electrodes. The LCR meter (inductance, capacitance, and resistance; LCR-819) and 193 DEA instrument were calibrated and zeroed with the open-short circuit of the 194 electrodes before starting experiments. Samples were ground and approximately 600 195 mg samples were placed between parallel plate titanium capacitors (diameter = 33 mm) 196 with the thickness less than 2 mm. Triplicate samples of each material were analyzed 197 using dynamic measurements and recorded using Triton Laboratory software (version 198 1.0.330). Samples were analyzed in triplicate using dynamic measurements and scanned from ~ 60 °C below to over the T_g region with cooling rate of 5 °C/min and 199 200 heating rate of 2 °C/min at frequencies of 0.5, 1.0, 5.0, 10.0 and 20.0 kHz. The 201 measuring head was connected to a liquid nitrogen tank (1L; Cryogun, Brymill 202 cryogenic systems, Labquip (Ireland) Ltd., Dublin, Ireland). As noted above, T_a 203 determined from the temperature of ε'' at the peak were used to determine the relaxation 204 times.

205

206 2.4. Strength analysis

208	The relaxation times and T_{α} corresponding to ε'' peak above T_g were modeled using the
209	WLF equation (Eq. 1). The relaxation times were defined by frequency set in DEA
210	measurements ($\tau = 1/2\pi f$). The WLF model constants C_1 and C_2 were derived from a
211	plot of $1/log(\tau/\tau_g)$ against $1/(T-T_g)$ using experimental τ with the assumption of $\tau_g = 100$
212	s at the calorimetric onset temperature of the T_g (Angell 2002). A decrease in the
213	number of logarithmic decades for flow, e.g., that being critical for stickiness, could be
214	used as the critical parameter, d_s , of Eq. (2) and the corresponding T - T_g was defined as
215	the strength of the solids, S. As the S values are given as temperature corresponding to a
216	critical τ for a key amorphous component within a material, it also provides a measure
217	of resistance to structural changes, i.e., the higher value of S refers to a stiffer system at
218	a corresponding T - T_g .

$$\log\left(-\frac{1}{g}\right) = \frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$
(1)

$$S = \frac{d_s C_2}{C_1 d_s} \tag{2}$$

222

Where, T, T_g , τ , τ_g , C_1 and C_2 and d_s shown in Eq (1) and (2) refer to the experimental temperature, onset glass transition temperature, experimental structural relaxation time and structural relaxation time at the glass transition ($\tau_g = 100$ s), material-specific WLF constants and the decrease in the number of logarithmic decades for τ ($d_s = 4$ was used

227	for various biological materials as reported by Roos et al. (2015) and Fan and Roos
228	(2016b), respectively.

230 **2.6. Statistical analysis**

231

The second derivative analysis of DDIs sorption data was carried out in *R* Programme and the strength analysis of dielectric α -relaxation associated relaxation times were calculated and fitted by using Microsoft Office Excel 2011 (Microsoft, Inc., USA). All measurements were repeated three times, as well as the average values with the standard deviation of triplicate measurements were calculated.

237

238 **3. Results and Discussion**

239 **3.1. Dynamic Water Sorption**

240

243	The DDI for pure lactose ($a_w \le 0.50$), WPI and lactose/WPI mixtures with the mass
244	ratios of 7:3 ($a_w \le 0.70$), 1:1 ($a_w \le 0.80$) and 3:7 followed the typical sigmoid shape of
245	water sorption isotherms (type II) in Fig. 1B, respectively. The fractional water
246	sorption of components, exhibited by amorphous sugar/protein mixtures, has been

Table 1 and Fig. 2

247	reported by previous studies (Roos & Potes, 2015). Similarly, the fractional water
248	sorption properties were proved in DDIs as the sorbed water in amorphous lactose/WPI
249	mixtures could be calculated as the sum of fractional quantities at $a_w \le 0.44$ (Fig. 1B).
250	However, if water sorption rates of components vary DDI data may reflect such
251	differences. Fig. 2 gives the DDI water sorption and literature SSM data for
252	freeze-dried lactose and lactose/WPI mixtures at 7:3, 1:1 and 3:7 mass ratios at 25 °C
253	(Fan & Roos, 2015). The water contents in DDIs of lactose were lower than those of
254	corresponding SSM isotherms (Fig. 2A). Such differences in the DDI sorption data
255	reflected the non-equilibrium state of amorphous solids and the relatively short
256	equilibration time in comparison to SSM giving a systematic error for the water content
257	as full dehydration may not take place at low a_w . The SSM-isotherms comparable c_w
258	data are shown on the DDIs of lactose/WPI mixtures at various protein contents (Fig.
259	2B-D). The DDI sorption data of pure amorphous WPI, however, showed
260	shape-comparable sorption isotherms to corresponding SSM isotherms (Fig. 2E). Such
261	similarity in water sorption by the two methods indicated that the amorphous WPI
262	showed a slow equilibration reducing time to water vapor diffusion and water
263	penetration during DDI sorption. The DDI sorption data for amorphous lactose leveled
264	off at high water activities ($\geq 0.50 a_w$) as a result of lactose crystallization (Fig. 2A). In
265	lactose/WPI systems lactose molecules form a continuous phase around WPI
266	molecules, but WPI components may hinder diffusion of the noncrystalline lactose. In
267	comparison to pure lactose, therefore, the presence of WPI in lactose/WPI mixtures

delayed crystallization and extended the sigmoid sorption behaviors to a higher a_w range (Fig. 2B-C). This phenomenon agreed with previous studies, which indicated that the crystallization of lactose could be delayed by the presence of polymeric components (Silalai & Roos, 2011). As noted above, the presence of other components, e.g., protein, with amorphous sugars, affected water sorption as well as the crystallization as a result of water plasticization.

274

275 Fig. 3

276

The $a_w^{(cr)}$ values of amorphous lactose and lactose/WPI mixtures at each ratio are 277 shown in Table 1, respectively. Fig. 2F showed a linear relationship with high 278 correlation coefficient ($R^2 > 0.98$) for $a_w^{(cr)}$ values against lactose content of amorphous 279 lactose/WPI systems at 25 °C, which indicated that the $a_w^{(cr)}$ was that of the lactose 280 component rather than for the entire system although protein affected structural 281 relaxation times (Roos & Potes, 2015). In the present study, the $a_{wo}^{(cr)}$ was considered 282 283 as a critical a_w point for glass-forming lactose plasticized by water to flow and 284 accommodate increasing free volume and water uptake during DDI sorption process. The $a_{wp}^{(cr)}$ was a turning point where the rate of water uptake became less than the rate 285 286 of lactose crystallization. Corresponding to previous X-ray study (Jouppila et al., 1997), therefore, we assumed that the $a_{wo}^{(cr)}$ and $a_{wp}^{(cr)}$ were the onset and half-crystallinity 287

point of lactose crystallization, respectively. In the present study, the $a_{wo}^{(cr)}$ of pure 288 289 amorphous lactose occurred at 0.381 a_w at 25 °C (Table 1). This result agreed with 290 previous calorimetric studies that the glass transition of freeze-dried lactose after 291 humidification at 0.44 a_w at room temperature was around 15 °C as well as the critical a_w of 0.37 of amorphous lactose (Fan & Roos, 2016a). Both onset and peak $a_w^{(cr)}$ values 292 293 of lactose/WPI mixtures increased concomitantly with increasing protein content 294 (Table 1). Fig. 3 gives a schematic diagram for the dynamic water sorption process of 295 amorphous lactose and lactose/WPI mixtures. From I to II (Fig. 3A), the water sorbed 296 by amorphous lactose could plasticize the structure of glass formers resulting in 297 breaking the hydrogen bonds between lactose molecules and the relaxation times of amorphous lactose decreased (Slade et al., 1991). As a_w increased to above $a_{wo}^{(cr)}$, the 298 299 mobilization of glass formers was strongly enhanced by water plasticization (Fig. 3A II-III). When the a_w exceeded $a_{wp}^{(cr)}$, the lactose crystallinity rapidly increased until 300 301 most of lactose crystallized during the DDI sorption process (Fig. 3A III-IV). However, the presence of WPI hindered water plasticization effects as the $a_{wo}^{(cr)}$ increased in 302 lactose/WPI mixtures (Fig. 3B II-III). Moreover, the $a_{wp}^{(cr)}$ of lactose/WPI mixtures 303 304 increased concomitantly with the WPI content and delayed the lactose crystallization in mixtures (Fig. 3B III-IV). Therefore, the $a_w^{(cr)}$ values of the DDI data indicate the glass 305 306 transition resulting in mobilization and crystallization of amorphous lactose in food and 307 pharmaceutical materials.

309 **3.2. Dielectric properties and** T_{α}

310

- 311 Table 2 and Fig. 4
- 312

313 Fig. 4 shows the dielectric loss (ε'' peaks at a frequency of 1.0 kHz) for lactose and 314 lactose/WPI mixtures with mass ratios of 7:3, 1:1 and 3:7 after storage below 0.44 a_w at 315 25 °C. Dielectric properties of the materials were affected by molecular interactions 316 and water plasticization. The magnitude of the ε'' peak correlated directly to a_w of 317 amorphous lactose at low water activities ($0.23 \le a_w \le 0.44$) as water content increased 318 and plasticization enhanced the mobility of lactose molecules. This agreed with Silalai 319 and Roos (2011) who reported that ε'' peaks found for skim milk powder increased in magnitude with increasing a_w (Fig. 4A). The ε'' describes an energy loss that is used by 320 321 polar groups in materials under the alternating electric field. The lower levels of WPI 322 containing lactose/WPI mixtures (≤ 30 %) showed higher magnitudes of ε'' peaks than 323 pure lactose after humidification at the same a_w and 25 °C (Fig. 4B-D). Therefore, the ε'' 324 data followed the amorphous lactose content of the mixtures as WPI and lactose exist in 325 separate phases. Table 2 gives the T_{α} value of each material in dielectric analysis at 1.0 kHz, which occurred above the corresponding calorimetric onset T_g measured by 326 327 differential scanning calorimeter (DSC) in agreement with Silalai and Roos (2011). The presence of water, in the present study, decreased the T_{α} values of amorphous 328 lactose and lactose/WPI mixtures as the peak temperature of ε'' concomitantly 329

330	decreased with increasing a_w (Table 2). The T_a values of amorphous lactose could be
331	significantly increased by WPI in lactose/WPI mixtures (Table 2). Lactose can be
332	assumed to exist separated from protein. The frequency-dependent T_{α} indicated an
333	apparent relaxation time of lactose in WPI mixtures. Water plasticization enhanced the
334	molecular mobility of lactose molecules which consequently decreased the peak
335	temperature of ε'' . However, the WPI contained in mixtures hindered the molecular
336	mobility of lactose and increased the apparent relaxation times and T_{α} . In our previous
337	studies, similarly, the presence of other components, i.e., water and protein, affected
338	the structural relaxations, relaxation times and T_{α} of glass-forming sugars in
339	freeze-dried sugars/protein systems based on dynamic-mechanical analysis (DMA)
340	(Fan & Roos, 2016a,b).

3.3. Relaxation times and *S* **parameter**

344 Fig. 5

Both DEA and DMA measurements allowed determination of structural relaxation
times from the α-relaxation data at various frequencies. The structural relaxation times
can be related to stickiness characteristics of food powders as well as other mechanical

349	properties of food solids, such as the collapse of structure or viscosity and diffusion
350	(Clerjon et al., 2003). Fig. 5 shows structural relaxation times from our experiments
351	and literature (Fan & Roos, 2016a). The WLF-relationship of Williams et al. (1955)
352	was developed on the basis that most inorganic and organic glass formers showed
353	similar decreases in τ and viscosity over the temperature range of T_g to T_g +100K. The
354	use of WLF-relationships often assumes that the structural relaxation time obtained
355	using dielectric measurements reach 100 s at the calorimetric onset T_g (Angell, 2002;
356	Roos et al., 2015). In the present study, the WLF-relationship with "universal"
357	constants ($C_1 = -17.44$ and $C_2 = 51.6$) did not fit the experimental data but
358	material-specific constants gave a good fitting performance for lactose and lactose/WPI
359	mixtures at a_w below 0.44 and 25 °C (Fig. 5). Table 2 gives material-specific WLF
360	constants for amorphous lactose and lactose/WPI mixtures obtained from structural
361	relaxation times of the DEA and published DMA measurements. The material-specific
362	C_1 for amorphous lactose increased concomitantly with a_w increasing, whereas both C_1
363	and C_2 decreased by the presence of WPI content at a_w below 0.44 (Table 2). It is
364	important to note that fitting of the WLF model to experimental relaxation times may
365	result in positive or negative values or negative values for the constants C_1 and C_2
366	(Roos & Drusch, 2015). In the present study, the C_1 and C_2 with negative values
367	determined the downward concavity for WLF relationship, which showed the profiles
368	for the decreases of relaxation times of amorphous lactose at temperatures above
369	calorimetric T_g . Therefore, the material-specific WLF constants could be used to

describe material properties and structural relaxation processes of amorphous lactose at
various water activities. The presence of other components, e.g., water and protein,
affected the structural overall relaxation processes as well as apparent relaxation times
of lactose/WPI mixtures.

374

The decrease of relaxation times to 10^{-2} corresponded to a decrease in viscosity from 375 10^{12} Pa s to 10^5 Pa s reaching critical viscosities for collapse and stickiness of 376 377 amorphous food solids (Bellows & King, 1973; Downton, Flores-Luna, & King, 1982). 378 Roos et al. (2015) recommended a WLF model-based strength analysis for amorphous 379 sugars/protein systems. The S parameter for glass-forming components calculated by using material-specific WLF constants defined an allowable increase in temperature 380 above the onset of the calorimetric T_g until $\tau = 0.01$ s. As the lactose and protein 381 382 diffusion was uncoupled the S parameter followed relaxation times of amorphous 383 lactose. Table 2 gives the S values of amorphous lactose and lactose/WPI mixture at low a_w based on the strength analysis using experimental structural relaxation times 384 385 derived from DEA and published DMA data. In the present study, the S values of 386 freeze-dried lactose with different water activities agreed with our earlier data (Fan & 387 Roos, 2016a). The presence of water decreased the structural strength of amorphous lactose at a_w below 0.44, whereas the S values of lactose/WPI mixtures were 388 389 significantly higher than was found for pure lactose (Table 2). As the S parameter

390 provides a measure of structural transformation, a low S value referred to a more rapid 391 structural change. Such rapid changes occurred in the presence of water as the 392 structural relaxations of amorphous lactose were enhanced by water plasticization. 393 However, the relatively higher S exhibited by lactose/WPI mixtures indicated that the 394 mixes were strengthened against structural deformation as protein offered a structural 395 supporting effect. Therefore, the S parameters based on dielectric/mechanical 396 relaxations can be used to describe compositional effects of amorphous food solids 397 systems. Such data can be used to control shrinkage in dehydration and possibly rates 398 of physicochemical changes in food storage.

399

400 **3.4.** Sorption-induced crystallization, relaxation times and *S* parameter

401

402 Fig. 6

403

The relationships between a_w and T- T_g of amorphous lactose and lactose/WPI mixtures against their corresponding relaxation times are shown in Fig. 6A. The water-induced structural relaxations of food solids systems, observed in isothermal water sorption, are likely to correlate with crystallization above glass transition. The relaxation times of lactose dramatically decreased with increasing T- T_g as the T_g was depressed by water

409	(Fig. 6A). The crystallization of lactose was initialized above $a_{wo}^{(cr)}$ and rapidly
410	occurred along decreasing structural relaxation times during water sorption process.
411	The water sorption-induced lactose crystallization could stop at 0.7 a_w based on the
412	DDI sorption data, where the τ decreased approximately 4 logarithmic decades (Fig.
413	6A). As we expected, the $a_{wo}^{(cr)}$ for water-induced crystallization was delayed to occur
414	at higher a_w in the presence of WPI (Fig. 6A). The decrease of structural relaxation
415	times, $a_{wp}^{(cr)}$ and crystallization of amorphous lactose can be controlled by WPI during
416	exposures to high humidities (Fig. 6A). Fig. 6B shows a plot of onset and peak $a_w^{(cr)}$
417	against S for anhydrous lactose and lactose/WPI mixtures. There was a linear
418	relationship between $a_w^{(cr)}$ and S with high correlation ($R^2 > 0.97$). The pure lactose had
419	a lower $a_w^{(cr)}$ and S value than WPI containing systems (Fig. 6B). This result indicated
420	that the structural strength could be related to water-induced crystallization of
421	amorphous sugars during isothermal water sorption. Therefore, we believe that the DDI
422	provided parameters describe the structural changes and crystallization behavior of
423	amorphous sugars during water plasticization. The S parameter could be used to
424	estimate time-dependent water sorption-induced solid properties of amorphous food
425	mixtures during storage at various water activities, i.e., structural transformations and
426	deformation. Moreover, proteins as commonly used components could be used in food
427	and pharmaceutical systems to control water sorption properties as well as structural
428	relaxation rates and crystallization.

430 4. Conclusion

431

432 We have shown that the freeze-dried lactose and lactose/WPI mixtures have fractional 433 water sorption properties. Water sorption-induced relaxations and crystallization were 434 delayed in the presence of WPI in amorphous lactose/WPI mixtures. The T_{α} values of amorphous lactose in lactose/WPI mixtures at $a_w \le 0.44$ were affected by the mixture 435 composition, i.e., water, and WPI. The WLF analysis based S parameter with relaxation 436 437 times data from DEA and DMA was dependent on mixture composition. It was used to 438 interpret water sorption-induced crystallization of amorphous lactose in mixtures with 439 WPI. The combination of dielectric and mechanical properties offers a new approach in 440 understanding glass transition-related structural relaxations occurring in food 441 processing and storage. Such information also advances innovations in food 442 formulation through mapping of structural relaxation times of food components and 443 their mixes.

444

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Figure 1. The $a_w^{(cr)}$ for freeze-dried lactose respectively taking the peak a_w of first derivative $(a_{wp}^{(cr)})$ and onset a_w of the second derivative $(a_{wo}^{(cr)})$ on DDI sorption data at 25 °C (A). B shows the DDI curves for lactose and lactose/WPI mixtures with 7:3, 1:1 and 3:7 mass ratios by running at 25 °C, respectively.



Figure 2. The comparison diagram between DDI and literature SSM data of freeze-dried lactose and lactose/WPI mixtures (7:3, 1:1 and 3:7, w/w) at flow rates of 300 ml/min at 25 °C (A-E). The $a_w^{(cr)}$ shows a highly linear relationship with lactose content ($R^2 > 0.98$) in lactose/WPI mixtures (F). The literature SSM sorption data were derived from Fan and Roos (2015).



Figure 3. Schematic diagrams for water-induced α -relaxation and crystallization on amorphous lactose (A) and lactose/WPI mixtures (B) in dynamic water sorption processes, respectively. The symbols do not represent the real size and quantity of components.



Figure 4. The DEA spectra and peak temperature of ε'' as T_{α} of amorphous lactose (A) and lactose/WPI mixtures with 7:3, 1:1 and 3:7 mass ratios after storage at 0.23 a_w (B), 0.33 a_w (C), and 0.44 a_w (D) under 25 °C.



Figure 5. Strength parameters (*S*) of freeze-dried amorphous lactose at various water activities (0-0.44 a_w) (A), lactose/WPI mixtures at mass ratio of at 7:3, 1:1 and 3:7 at frequency of 1.0 kHz after storage at 0.23 a_w (B), 0.33 a_w (C) and 0.44 a_w (D) at $d_s = 4$ decreasing τ as measured using DEA and literature DMA (Fan & Roos, 2016c) down to 0.01 s. Such decrease in τ is known to result in particle stickiness and aggregation at a contact time of 10 s (Roos et al., 2015).



Figure 6. The relationship between a_w and T- T_g of amorphous lactose and lactose/WPI mixture at 7:3 (w/w) with their corresponding relaxation times (A). B shows the relationship between strength parameter (S) and $a_w^{(cr)}$ for amorphous lactose and its WPI containing mixtures at 25 °C.

Figure Captions

Figure 1. The $a_w^{(cr)}$ for freeze-dried lactose respectively taking the peak a_w of first derivative $(a_{wp}^{(cr)})$ and onset a_w of the second derivative $(a_{wo}^{(cr)})$ on DDI sorption data at 25 °C (A). B shows the DDI curves for lactose and lactose/WPI mixtures with 7:3, 1:1 and 3:7 mass ratios by running at 25 °C, respectively.

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Table 1. The onset and peak $a_w^{(cr)}$ for water-induced crystallization ($a_{wo}^{(cr)}$ and $a_{wp}^{(cr)}$) in freeze-dried lactose, lactose/WPI mixtures at 7:3, 1:1 and 3:7 mass ratios during DDI sorption process at 25 °C.

Table 2. The literature onset T_g , T_a at 1.0 kHz, material-specific C_1 and C_2 , and S for freeze-dried lactose, lactose/ WPI mixtures at solid ratios of 7:3, 1:1 and 3:7 after storage at low a_w (≤ 0.44) at 25 °C.

solption process at 25°°C.						
Sample	Ratios	$a_{wo}^{(cr)}$	$a_{wp}^{(cr)}$			
Lactose	-	0.381 ± 0.010^{a}	0.467 ± 0.003			
Lactose/WPI	7:3	0.547 ± 0.018	0.643 ± 0.001			
Lactose/WPI	1:1	0.623 ± 0.028	0.708 ± 0.006			
Lactose/WPI	3:7	0.773 ± 0.013	0.857±0.001			

Table 1. The onset and peak $a_w^{(cr)}$ for water-induced crystallization $(a_{wo}^{(cr)} \text{ and } a_{wp}^{(cr)})$ in freeze-dried lactose, lactose/WPI mixtures at 7:3, 1:1 and 3:7 mass ratios during DDI sorption process at 25 °C.

^{*a:*} Values are mean \pm SD (n=3)

Sample	a_w	T_{g}	T_{α}	C_{I}	C_2	S
Lactose	0.00	105 ± 3^{a}	138±2	3.19±0.31	-54.63±0.63	30.4±0.7
	0.23	40±2	72 ± 1^{b}	3.47±0.23	-51.93±0.42	27.8±1.0
	0.33	30±3	64±3	4.93±0.19	-55.48±0.56	24.9 ± 0.8
	0.44	14±1	40±1	7.66±0.45	-61.36±0.66	21.0±1.6
Lactose/WPI 7:3	0.23	40±1	76±1	2.38±0.33	-50.31±0.64	31.5±0.9
	0.33	30±1	70±1	5.15±0.21	-85.88 ± 0.50	37.5±1.0
	0.44	13±1	41±3	4.13±0.35	-53.15±0.52	26.2±1.3
Lactose/WPI 1:1	0.23	41±1	84±1	0.98 ± 0.43	-49.55±0.41	39.8±0.5
	0.33	30±2	83±1	2.87 ± 0.44	-77.72±0.76	45.3±0.5
	0.44	14±2	48±5	1.83±0.25	-49.18±0.63	33.7±0.4
Lactose/WPI 3:7	0.23	41±2	87±0	1.07 ± 0.38	-54.47±0.66	43.0±0.7
	0.33	30±3	86±4	2.30±0.29	-77.28±0.73	49.1±0.5
	0.44	13±2	N/A	-	-	-

Table 2. The literature onset T_g , T_a at 1.0 kHz, material-specific C_1 and C_2 , and S for freeze-dried lactose, lactose/ WPI mixtures at solid ratios of 7:3, 1:1 and 3:7 after storage at low $a_w (\leq 0.44)$ at 25 °C.

^{*a*:} The onset T_g of lactose and lactose/WPI mixtures are derived from Fan and Roos (2016c); ^{*b*:} Values are mean \pm SD (n=3);

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