Carbohydrate Polymers 89 (2012) 1050–1059

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Additivity of water sorption, alpha-relaxations and crystallization inhibition in lactose–maltodextrin systems

Naritchaya Potes, Joseph P. Kerry, Yrjö H. Roos *

School of Food and Nutritional Sciences, University College Cork, Cork, Ireland

ARTICLE INFO

Article history:
Received 2 December 2011
Received in revised form 12 March 2012
Accepted 16 March 2012
Available online 28 March 2012

Keywords:
Crystallization
Glass transition temperature
Lactose
Maltodextrin
Molecular size
Water sorption

ABSTRACT

Water sorption of lactose–maltodextrin (MD) systems, structural relaxations and lactose crystallization were studied. Accurate water sorption data for non-crystalline lactose previously not available over a wide range of water activity, a_w (<$0.76a_w$) were derived from lactose–MD systems data. Structural relaxations and crystallization of lactose in lactose–maltodextrin (MD) systems were strongly affected by water and MD. At high MD contents, inhibition of crystallization was significant. Inhibition with a high dextrose equivalent (DE) MD was more pronounced possibly because of molecular number and size effects. At 0.55–$0.76a_w$, inhibition increased with increasing MD content. At $a_w > 0.66$, the rate of lactose crystallization decreased at increasing MD contents. Different MDs with similar T_g in lactose–MD systems showed different crystallization inhibition effects. The results of the present study showed that the DE in selection of MD for applications has important effects on component crystallization characteristics.

1. Introduction

Crystallization is an important factor affecting physical stability of materials containing amorphous sugars during storage. It often results from an increase in molecular mobility (decrease of viscosity) above glass transition allowing formation of the highly ordered crystalline, equilibrium state, and leads to release of water sorbed by the amorphous material prior to crystallization (Roos, 1995). The rate of crystallization of amorphous sugars is governed by water content and temperature of storage above the glass transition temperature, $T - T_g$ (Roos & Karel, 1991a). Increasing water content leads to water plasticization and increased molecular mobility, which accelerate crystallization of amorphous sugars by decreasing the T_g (Roos & Karel, 1991a, 1992).

Previous studies showed that crystallization of amorphous sugars was delayed in mixtures with high molecular weight carbohydrate components, e.g., starch (Iglesias & Chirife, 1978; Roos & Karel, 1991a), MD (Iglesias, Chirife, & Buera, 1997; Kouassi & Roos, 2001; Labrousse, Roos, & Karel, 1992; Mazzobre, Buera, & Chirife, 1997) and corn syrup solids or MD with the DE above 20 (Gabarra & Hartel, 1998). Miscible high molecular weight components generally increase viscosity, and the average molecular weight, and decrease molecular mobility of amorphous systems (Roos & Karel, 1991b; Sillick & Gregson, 2009). They may also increase the T_g value. Below the T_g, molecular mobility of amorphous materials is restricted to vibrations and rotations due to decreased free volume and packing of molecules. However, the effect of addition of high molecular weight components to decrease the rate of crystallization is not entirely a result of the increased T_g of the amorphous system (Gabarra & Hartel, 1998; Roos & Karel, 1991a) depending on the type of sugars. Roos and Karel (1992) suggested that the rate of crystallization of lactose at varying water contents and temperatures was controlled by the T_g. Crystallization of amorphous sugars can be reduced or delayed by increasing viscosity, decreasing diffusion, and reduced molecular mobility above the T_g (Roos & Karel, 1991a, 1991c), including effects of the presence of various other molecular species and impurities. Iglesias and Chirife (1978) reported that changes in physical state and the apparent rate of crystallization of freeze-dried sucrose was reduced by the presence of others components (starch, carboxymethylcellulose, microcrystalline, cellulose, guar gum, garrofin gum, and sodium alginate). In the same way, as reported of Gabarra and Hartel (1998), the crystallization of freeze-dried sucrose was interfered by the addition of 10 and 20% (w/w) and prevented by the addition above 50% (w/w) of DE 20 and 42 corn syrup solids. Mazzobre, Soto, Aquilera, and Buera (2001) reported that the addition of a second sugar component, such as trehalose, to an amorphous lactose system delayed crystallization, without affecting the T_g value. This may be related to interactions between sugars and other components which reduced or delayed the rate of diffusion or mobility of sugar molecules to form crystals (nucleation) or crystal growth, lattice interference or steric hindrance effects, above T_g. It should, however, be noted that

---

* Corresponding author. Tel.: +353 21 4902386; fax: +353 21 4276398.
E-mail address: yrjo.roos@ucc.ie (Y.H. Roos).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2012.03.061

the T_g values of lactose and trehalose are similar and the sugars may be mixed in any ratio with no significant effects on the T_g of the blend.

Dielectric (DEA) and dynamic-mechanical analyses (DMA) may be used in studies of molecular mobility, including secondary relaxations (γ- and β-relaxations) below the calorimetric T_g and the α-relaxation (primary relaxation) of glass forming carbohydrate polymers (Kilmartin, Reid, & Samson, 2004; Pagnotta, Cerveny, Alegria, & Colmenero, 2009) and amorphous solids formulations (Ermolina, Polygalov, Bland, & Smith, 2007; Kalichevsky & Blanshard, 1993; Lievonen & Roos, 2003; Noel, Parker, & Ring, 2000; Silalai & Roos, 2011). Such measurements have been used to study dynamic (Massalska-Arodz, Williams, Thomas, Jones, & Dabrowski, 1999; Mijovic, 1998; Talja & Roos, 2001; Wurm, Soliman, & Schick, 2003) and isothermal crystallization (Alie et al., 2004; Bhugra et al., 2007; Massalska-Arodz et al., 1999; Mijovic, 1998; Wurm et al., 2003) of sugars and polymers. Crystallization behavior of amorphous materials may be observed from a sharp frequency-independent change of permittivity (dielectric constant, ε') and dielectric loss (ε'') from dielectric analysis data, and storage modulus (E'; mechanical energy storage) and loss modulus (E''; mechanical energy dissipation) from dynamic mechanical analysis measurements above the α-relaxation temperature. Rapid changes in dielectric and mechanical properties result from the transformation of the amorphous components into crystals, growth of crystalline regions, and migration of charges and orientation of dipoles (Gonnet, Guillet, Sirakov, Fulchiron, & Seytre, 2002; Mijovic, 1998; Talja & Roos, 2001). Gonnet et al. (2002) reported that the crystallization process of Kynar 710 poly (vinylidene fluoride) (semi-crystalline polymer) showed an increase in ε' when measured using DEA corresponding to a sharp increase of the E' measured by DMA. The onset temperature of crystallization found by DEA and DMA was approximately the same as the onset temperature of crystallization recorded in DSC measurements. Thus, the DEA and DMA were powerful and suitable techniques for monitoring of the crystallization of polymers.

The objectives of the present study were to determine effects of DE and glass transition of MD with lactose on water sorption, lactose crystallization behavior and to investigate dielectric and dynamic mechanical properties at crystallization of lactose in lactose–MD systems. This study is useful for understanding effects of MD on the crystallization of lactose in food and pharmaceutical materials as the DE of MD may have an important role in preventing sugar crystallization.

2. Materials and methods

2.1. Preparation of amorphous freeze-dried materials

MDs were of low DE of 4–7, 9–12, and high DE of 23–27 (Maltrin M040, M100, and M250, respectively; Grain Processing Corp., IA, U.S.A.). Freeze-dried amorphous solids of MD DE 4–7, 9–12, and 23–27, α-lactose (monohydrate, Sigma Chemical Co., St. Louise, MO, U.S.A.), and lactose–MD were prepared from solutions containing 20% (w/w) total solids. The ratios of lactose:MD DE 4–7 in solid was 40:60 and lactose:MD DE 9–12 and 23–27 in solids were 90:10, 80:20, 70:30, and 40:60. Aliquots of 5 mL (approximately 1 g of freeze-dried material) of MD, lactose, and lactose–MD solutions in preweighed 10 mL glass vials (semi-closed with septum) were frozen at −20 °C for 24 h, followed by −80 °C for 3 h, and then freeze-dried for 60 h at pressure (p) < 0.1 mbar (Lyovac GT 2, Steris®, Hürth, Germany) to obtain amorphous materials. All vials were hermetically closed with vacuum inside the freeze dryer at p < 0.1 mbar and kept over P_2O_5 in vacuum desiccators (Roos & Karel, 1990) at room temperature (20 ± 2 °C) to protect samples from water uptake.

2.2. Water sorption study

Sorbed water of stored freeze-dried MD DE 9–12 and 23–27, lactose, and lactose–MD DE 9–12 and 23–27 at 90:10, 80:20, and 70:30 ratios were monitored for 5 days (non-crystallizing components) and 25 days (crystallizing components) over saturated solutions of LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, and NaCl (Sigma Chemical Co., St. Louise, MO, U.S.A.) at 0.11, 0.23, 0.33, 0.44, 0.55, 0.66, and 0.76a_w, respectively, in vacuum desiccators at room temperature. Freeze-dried lactose–MD DE 4–7, 9–12, and 23–27 at 40:60 ratios were monitored for 25 days over a series of saturated salt solutions with a_w from 0.55 to 0.76. Samples were weighed at intervals during storage. All vials, when removed and during transfers for weighing, were closed with septums. The crystallization of lactose was investigated from the loss of sorbed water. Water contents of the materials were measured as a function of time, and the average weight of triplicate samples was used in calculations. The average water contents at 5 days for freeze-dried MD and at 25 days for freeze-dried lactose and lactose–MD systems were used as water contents at steady state for water sorption isotherms. The Guggenheim–Anderson-de Boer equation (GAB) (Eq. (1)) was fitted to experimental data to model water sorption isotherm.

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

2.3. Differential scanning calorimetry (DSC)

Freeze-dried "anhydrous" materials (MD DE 9–12 and 23–27, lactose, and lactose–MD DE 9–12 and 23–27 at 90:10, 80:20, and 70:30 ratios) were transferred to preweighed DSC aluminum pans (40 μL, Mettler Toledo Schwerzenbach, Switzerland), hermetically sealed before weighing, and analyzed using punctured pans. At varying a_w, the freeze-dried materials were transferred to preweighed DSC aluminum pans and weighed. These unsealed pans with samples were rehumidified for 72 h over a series of saturated salt solutions with a_w from 0.11 to 0.44 in vacuum desiccators at room temperature. After equilibration the pans were hermetically sealed and reweighed. An empty punctured pan was used as a reference and the instrument was calibrated for temperature and heat flow as reported by Roos and Karel (1991a). The lids of DSC aluminum pans of anhydrous samples were punctured to allow evaporation of any residual water during the measurement. Freeze-dried materials with varying water contents were scanned in DSC using hermetically sealed pans. 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. The second heating scan was run to well above the T_g. The onset T_g values were recorded using STARe software, version 8.10 (Mettler Toledo Schwerzenbach, Switzerland). Triplicate samples were analyzed and average values of onset T_g were calculated. The Gordon and Taylor equation (Eq. (2)) was fitted to the average values of onset T_g.

$$T_g = \frac{w_1T_{g_1} + kw_2T_{g_2}}{w_1 + kw_2} \qquad (2)$$

2.4. Dielectric (DEA) and dynamic mechanical analyses (DMA)

Dielectric properties of freeze-dried anhydrous materials (lactose and lactose–MD DE 9–12 and 23–27 at 90:10, and 70:30 ratios) were analyzed using a dielectric spectrometer, DEA (DS6000, Triton Technology Ltd., UK), with titanium sample holders as the electrodes. Before starting an experiment, the LCR meter (LCR-819) and DEA instrument were calibrated at frequency 0.103 kHz with open-short circuit of the electrodes and zeroed in bridge RQ on a regular basis at 1 kHz with open-short circuit of the electrodes to ensure that the electrodes were clean (resistance value < 2 Ω).

Anhydrous materials were rehumidified for 5 days over a saturated salt solution with a_w 0.33 ($MgCl_2$) in vacuum desiccators at room temperature. Humidified samples were ground and approximately 100 mg samples were transferred onto the lower cup electrode (40 mm diameter) and then pressed with the upper electrode (33 mm diameter). Two electrodes were placed into a dielectric cell. The sample thickness was less than 2 mm. Triplicate samples of each material were analyzed using dynamic measurements and recorded using Triton Laboratory software, version 1.0.330. Samples were scanned from −50 to 200 °C with cooling rate of 5 °C/min and heating rate of 3 °C/min at frequencies of 0.012–10 kHz (Silalai & Roos, 2011). The measuring head was connected to a liquid nitrogen tank (1 l; Cryogun, Brymill cryogenic systems, Labquip (Ireland) Ltd., Dublin, Ireland). The α-relaxation temperature (T_α) was determined from the peak temperature above glass transition temperature of dielectric loss (ε'') and the crystallization temperature (T_{cr}) was determined from the onset temperature of increasing ε'' above the T_α region. Average values of triplicate samples for peak T_α and onset T_{cr} of ε'' were calculated. The ε'' describes an energy that is required to align ions and dipoles in an altering electric field.

Dynamic-mechanical properties of freeze-dried anhydrous materials (lactose and lactose–MD DE 9–12 and 23–27 at 90:10, and 70:30 ratios) were studied using a dynamic mechanical analyzer, DMA (Tritec 2000 DMA, Triton Technology Ltd., UK), by measuring the loss modulus (E'') as a function of temperature. The DMA instrument was balanced or set at zero to determine the zero displacement position and return the force to the zero position before starting an experiment. Anhydrous materials were rehumidified to 0.33a_w for 5 days as described for DEA experiments, and samples were ground to powder. Approximately 60 mg of the grinded samples were spread on a metal pocket-forming sheet (Triton Technology Ltd., UK). The sheet with sample was crimped along a pre-scored line to form a thin sandwich pocket. This pocket was attached directly between the clamps (the fixed clamp and the driveshaft clamp) inside the measuring head of DMA. The length, width, and thickness (<2 mm) of sample and pocket between the clamps were measured. Triplicate samples of each material were analyzed using dynamic measurements and recorded using DMA control software version 1.43.00. Samples were scanned from −50 to 180 °C with cooling rate of 5 °C/min and heating rate of 3 °C/min at frequencies of 0.5 to 20 Hz by using the single cantilever bending mode (Silalai & Roos, 2011). The measuring head was connected to a liquid nitrogen tank (1 l; Cryogun, Brymill Cryogenic Systems, Labquip (Ireland) Ltd., Dublin, Ireland). During dynamic heating, the samples were analyzed for T_α determined from the peak temperature of loss modulus (E'') above the glass transition, and the T_{cr} determined from the onset temperature of E''. Average values for triplicate measurements of peak T_α and onset T_{cr} of E'' were calculated.

The relaxation times of average values for peak T_α and onset T_{cr} measuring by DMA and DEA at various frequencies were calculated using the relationship; $\tau = 1/(2\pi f)$ (Noel et al., 2000). The peak T_α and onset T_{cr} were modeled using the Vogel–Tammann–Fulcher (VTF) equation (Eq. (3)) (Angell, 1997).

$$\tau = \tau_0 \exp\left[\frac{DT_0}{T - T}\right] \tag{3}$$

3. Results and discussion

3.1. Water sorption of components and carbohydrate mixtures

The GAB sorption isotherms, experimental data for the amorphous MD DE 9–12 and 23–27 (0.11–0.76a_w), lactose (0.11–0.44a_w), lactose–MD DE 9–12 and 23–27 at 70:30 ratio (0.11–0.55a_w), and predicted water contents for non-crystalline, amorphous lactose (0.55–0.76a_w) and lactose–MD DE 9–12 and 23–27 at 70:30 ratio (0.66–0.76a_w) are shown in Fig. 1 and Table 1. Previous studies showed that the GAB relationship could be fitted to experimental data of amorphous lactose below 0.55a_w (Bronlund & Paterson, 2004; Jouppila & Roos, 1994; Roos & Karel, 1990; Shrestha, Howes, Adhikari, & Bhandari, 2007; Silalai & Roos, 2010; Zhou & Roos, 2011) at 20–25 °C due to the limitation of crystallization of lactose at intermediate and high water activities. The maximum extent of lactose crystallization occurred at 0.70a_w at 24 °C, shown by a parabolic relationship with storage water activity (Jouppila, Kansikas, & Roos, 1997). At higher water activities, the extent of lactose crystallization decreased due to increased solubilization of lactose in sorbed water (Jouppila et al., 1997). However, the extrapolated sorption data above 0.44a_w extensively exceed true sorbed water contents and are not valid. *In the present study we found that the experimental data at 0.11–0.44a_w and calculated water contents at 0.55–0.76a_w, derived from lactose–MD DE 9–12 or 23–27 at 40:60 ratio (steady state sorbed water contents of non-crystalline components) water sorption data, for non-crystalline lactose could be used in the GAB equation* (Fig. 1)*. Also water sorption data of non-crystalline lactose–MD systems could be derived from the sum of water contents of amorphous components over a wide range of a_w, including high a_w (0.55–0.76a_w), i.e., the sorbed water contents of lactose–MD mixtures were additive and agreed with the sum of the water contents of individual amorphous components at each a_w*. Therefore, this result could be used to obtain the GAB sorption isotherms for non-crystalline lactose–MD DE 9–12 and 23–27 mixes at all ratios. Water contents of non-crystalline lactose–MD at 70:30 ratio systems were available from experimental data for systems in the absence of crystallization of lactose (0.11–0.55a_w) and calculated water content at higher a_w (0.66–0.76a_w) were total water contents of non-crystalline lactose, given by non-crystallizing lactose–MD DE 23–27 at 40:60 ratio (0.66–0.76a_w), and amorphous MD (Fig. 1 and Table 1). *These results for the first time make available sorbed water contents for non-crystalline lactose up to 0.76a_w and the GAB isotherm can be used for lactose systems to predict their water sorption.*

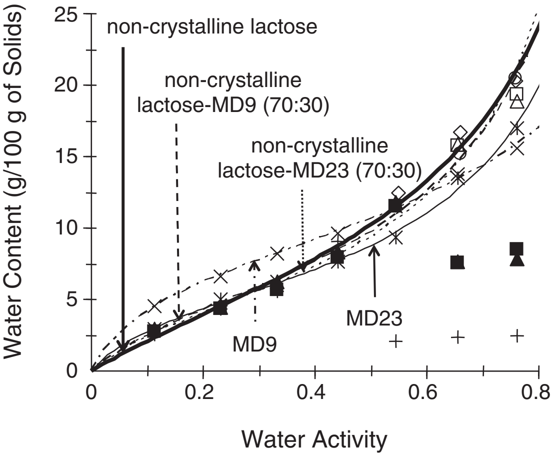

Fig. 1. The experimental data (solid symbols) and calculated water contents (clear symbols) for amorphous lactose, lactose–MD DE 9–12 (MD 9) at 70:30 ratio (▲, △), and lactose–MD DE 23–27 (MD 23) at 70:30 ratio (■, □) systems were compared to experimental data of MD 9 (×) and 23 (⋇). The thick solid (amorphous lactose), dashed (lactose–MD 9 (70:30)), dotted (lactose–MD 23 (70:30)), dashed-dotted (MD 9), and solid lines (MD 23) correspond to the GAB sorption isotherms. The GAB sorption isotherm of non-crystalline lactose was obtained using experimental data at 0.11–0.44a_w (+) and water contents derived from lactose–MD 9 (○) and lactose–MD 23 (◇) at 40:60 ratio at 0.55–0.76a_w. The GAB sorption isotherms for non-crystalline lactose–MD systems at 70:30 ratio used experimental data at 0.11–0.55a_w and fractional water contents calculated for non-crystalline lactose and measured for MD 9 and 23 to predict sorbed water contents for lactose–MD mixtures at 0.66 and 0.76a_w.

Table 1
Water contents and water activity (a_w) for non-crystalline lactose (NCL), amorphous MD DE 9–12 (MD 9) and 23–27 (MD 23), and NCL–MD 9 and 23 at 70:30 ratio. The water content of NCL at 0.55 to 0.76 a_w was derived from experimental NCL–MD 23 at 40:60 ratio. Water contents of NCL–MD systems were obtained from experimental data at 0.11 to 0.55 a_w and fractional water contents calculated for NCL and measured for MD 9 and 23 to predict sorbed water contents for lactose-MD mixtures at 0.66 and 0.76 a_w.

a_w	Water content (g/100 g of dried solids)									
	NCL by experiment and weight fraction	70% lactose by weight fraction	Amorphous MD by experiment		30% MD by weight fraction		NCL-MD by weight fraction		Lactose–MD by experiment	
			MD 9	MD 23	MD 9	MD 23	MD 9	MD 23	MD 9	MD 23
0.11	2.57	1.80	4.57	2.95	1.37	0.89	3.17	2.69	2.95	2.77
0.23	4.39	3.07	6.64	4.96	1.99	1.49	5.06	4.56	4.43	4.38
0.33	5.53	3.87	8.20	6.24	2.46	1.87	6.33	5.74	6.22	5.70
0.44	9.03	6.32	9.58	7.60	2.87	2.28	9.19	8.60	8.26	7.90
0.55	12.50	8.75	11.55	9.32	3.47	2.80	12.21	11.54	11.76	11.50
0.66	16.71	11.70	13.73	13.46	4.12	4.04	15.82	15.74	7.63	7.51
0.76	20.28	14.20	15.59	17.02	4.68	5.11	18.87	19.30	7.83	8.48

The additivity principle of sorbed water contents of components is likely to apply similarly to other carbohydrate mixtures.

3.2. Glass transition

The T_g values and a_w for anhydrous and humidified freeze-dried MD DE 9–12 and 23–27, lactose, and lactose–MD systems are shown in Fig. 2. The amorphous lactose showed similar T_g values to lactose–MD DE 9–12 and 23–27 at all ratios from 0 to 0.44a_w, and MD DE 9–12 and 23–27 did not significantly affect the T_g of the systems. The T_g values of anhydrous and humidified lactose at 0.11, 0.23, 0.33, and 0.44a_w were 105, 52, 42, 32, and 13 °C, respectively, in agreement with Haque and Roos (2006). The MD DE 9–12 had significantly higher T_g than MD DE 23–27, which was close to the T_g of lactose at 0.11–0.44a_w. Lactose–MD DE 9–12 and 23–27 systems at all ratios showed similar T_g and water contents to those of lactose at corresponding a_w up to 0.44a_w. These results showed that the addition of MD DE 9–12 and 23–27 at ratios 90:10, 80:20, and 70:30 had minor effects on the T_g values and water contents of the systems. This was in accordance with Roos and Karel (1991b), who reported that sucrose–MD mixtures with less than 50% (w/w) MD showed no significant increase of the T_g. Gabarra and Hartel (1998) also reported that the mixtures of amorphous sucrose: corn syrup solids with DE 20 and 42 at 80:20 and 90:10 ratios showed similar T_g. The T_g values of the mixture systems were mainly dependent on number average rather than weight average molecular weight of components. The relationship between number average molecular weight and T_g was linear (Avaltroni, Bouquerand, & Normand, 2004; Gabarra & Hartel, 1998; Roos & Karel, 1991b, 1991d).

Sugar–MD mixtures in previous studies were used to increase the T_g to control and inhibit crystallization of amorphous sugars (Iglesias et al., 1997; Kouassi & Roos, 2001; Mazzobre et al., 1997; Mazzobre, Hough, & Buera, 2003). For crystallization inhibition, however, the presence of small molecular weight components described by the DE value of maltodextrins may be more important than the T_g of a sugar–MD alone as also found by Gabarra and Hartel (1998). The freeze-dried lactose–MD DE 9–12 systems at 90:10, 80:20, and 70:30 ratios showed similar T_g to the amorphous lactose–MD DE 23–27, but the inhibition of crystallization of lactose above the T_g, as assessed from the water sorption data (Fig. 3), was different. It is well known that the crystallization kinetics of amorphous sugars is governed by $T - T_g$. Adding a second component is a general principle to control crystallization by disturbing the mobility of sugar molecules, and a carbohydrate mixture may show an increased T_g of the system depending on the molecular weight and concentration of the second component. Mazzobre, Soto, Aquilera, and Buera (2001) found that lactose crystallization was inhibited in freeze-dried lactose-trehalose systems with respective ratios of 80:20 and 70:30 of solids, but the T_g values did not differ from that of lactose. However, our systems emphasized that the crystallization inhibition of lactose was affected by the glass transition of the systems as well as the number average molecular weight of the MD while the lactose-trehalose system of Mazzobre et al. (2001) had a composition independent T_g.

3.3. Crystallization kinetics

No crystallization of amorphous lactose in lactose and lactose–MD systems occurred at low a_w (a_w 0.11–0.44) during 25 days of storage. At intermediate and high a_w (a_w 0.55–0.76), lactose crystallization was affected by MD at all ratios with the rate of crystallization decreasing with increasing MD content at the same a_w. Freeze-dried lactose lost sorbed water most rapidly at a_w 0.55, 0.66, and 0.76 at 5, 2, and 2 days of storage, respectively. At 0.55a_w, crystallization of lactose–MD DE 23–27 at 90:10 and 80:20 ratios was complete with loss of sorbed water at 11 and 19 days, respectively, but lactose–MD DE 9–12 at 90:10 and 80:20 ratios showed high variation of the time of loss of sorbed water. The MD DE 23–27 was the strongest crystallization inhibitor in lactose–MD systems at 40:60 ratio within 25 days of storage at 0.55a_w. The lactose–MD DE 4–7 and 9–12 at 40:60 ratio systems showed a minor loss of sorbed water (partial crystallization) after storage at 0.55a_w for 1 and 3 days, respectively. This result proved that lower molecular weight carbohydrates present in the high DE MD could exhibit molecular motions and diffusion rates exceeding those of the higher molecular weight (low DE) MD carbohydrates, as described by Gabarra and Hartel (1998). The smaller carbohydrates could also retard lactose mobility, reduce and disturb lactose nucleation and crystal growth. The MD DE 23–27 prevented crystallization of lactose in lactose–MD at 40:60 ratio up to 0.55a_w. The effective concentration of MD in crystallization prevention in this study was lower than found in previous studies. Iglesias et al. (1997), and Gabarra and Hartel (1998) reported that above or equal to 50% MD DE 10 and corn syrup solid DE 20 could prevent crystallization of trehalose (up to 0.52a_w for 15 days of storage), and sucrose (dry mixtures), respectively. According to the present study, MD at ratios up to 70:30 lactose–MD could delay crystallization of lactose up to 0.55a_w during storage at room temperature without being substantially affected by storage close to the T_g of the systems.

Water sorption of amorphous freeze-dried lactose and lactose–MD systems at 0.66 and 0.76a_w for 25 days is shown in Fig. 3. The amorphous freeze-dried lactose showed water contents of 2.0–2.4 g/100 g of dried solids at 0.55–0.76a_w, which showed that amorphous lactose did not crystallize as α-lactose monohydrate (Fig. 3A and B). Haque and Roos (2005) reported that amorphous freeze-dried lactose crystallized as mixtures of α-lactose monohydrate, anhydrous β-lactose, and anhydrous forms of crystals with α- and β-lactose in a molar of 4:1 ratio at $a_w > 0.55$, but also that recrystallization to α-monohydrate took place. Final water contents

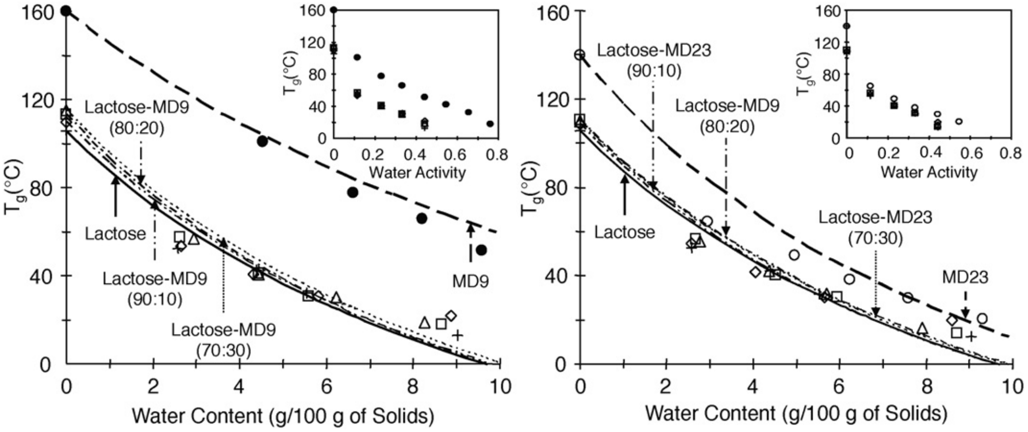

Fig. 2. Glass transition temperature (T_g), water content, and water activity (a_w) for the freeze-dried MD DE 9–12 (MD 9) and 23–27 (MD 23), lactose, and lactose–MD systems at 90:10, 80:20, and 70:30 ratios. Experimental data are shown for MD 9 (●), MD 23 (◯), lactose (+), lactose–MD (90:10) (◊), lactose–MD (80:20) (□), and lactose–MD (70:30) (△). The solid (lactose), dashed (MD), long dashed double dotted (lactose–MD (90:10)), long dashed dotted (lactose–MD (80:20)), and dotted lines (lactose–MD (70:30)) correspond to the T_g predicted by the Gordon-Taylor equation. Data for T_g of anhydrous MD 9 are from Roos and Karel (1991b).

of lactose–MD DE 9–12 and 23–27 systems increased with increasing MD content at 0.66 and 0.76a_w (Fig. 3A), and corresponded to water retained in the amorphous MD proportion (Roos & Karel, 1992). This result was in accordance with Nowakowski and Hartel (2002), who reported that mixtures of sucrose-corn syrup solid with DE 43 showed higher water contents with increasing contents of corn syrup solid. At 0.66a_w, the lactose–MD DE 9–12 and 23–27 at 40:60 ratios seemed to have no crystallization of lactose during 25 days of storage, but lactose–MD DE 9–12 and 23–27 showed partial crystallization of lactose after storage for 9 and 15 days, respectively. Lactose–MD DE 4–7 at 40:60 ratio showed partial crystallization after 5 days of storage. This result showed that MD DE 23–27 inhibited crystallization of lactose more strongly than MD DE 9–12 and 4–12 in lactose–MD systems at 40:60 ratio at 0.66a_w, which indicated that the crystallization of lactose was affected by the number average molecular weight of the MD in lactose–MD systems. At 0.76a_w, crystallization of lactose in lactose–MD DE 4–7, 9–12, and 23–27 at 40:60 ratio occurred after 7 days of storage in all systems (Fig. 3B). The systems of lactose–MD DE 23–27 lost sorbed water after reaching a maximum water uptake less rapidly than lactose–MD DE 9–12 at 80:20, 70:30, and 40:60 ratios and lactose–MD DE 4–7 at 40:60 ratio with a_w 0.76 (Fig. 3B). It should be noted that the use of MD DE 9–12 in lactose–MD systems at 90:10–70:30 ratios increased the rate of water uptake from 0.10 (lactose) up to 0.27 day^{-1} at 0.66a_w and from 0.20 (lactose) up to 0.32 day^{-1} at 0.76a_w, but lactose–MD DE 23–27 at 90:10–70:30 ratios did not show differences in water uptake from lactose.

Kinetics of loss of sorbed water used as an indicator for the rate of lactose crystallization from amorphous lactose and lactose–MD DE 9–12 and 23–27 systems at all ratios are shown in Fig. 4. The rate of loss of water sorbed by lactose–MD systems decreased with increasing MD content at 0.66 and 0.76a_w. The lactose–MD DE 9–12 and 23–27 systems at all ratios showed rate constants for loss of sorbed water (k_1) from −1.47 (lactose) up to 0 and 0 day^{-1} (no loss of water sorbed), respectively, at 0.66a_w and −0.79 to −0.04 and −0.02 day^{-1}, respectively, at 0.76a_w. Therefore lactose–MD DE 23–27 showed a smaller rate of loss of water sorbed than lactose–MD DE 9–12 and lactose systems at 0.76a_w. The relations between the k_1 and content of lactose in lactose–MD DE 9–12 and 23–27 systems at 0.66 and 0.76a_w are shown in Fig. 5. At 0.66 and 0.76a_w, the rate of loss of sorbed water of lactose–MD systems decreased (close to zero) with increasing MD content. Systems containing MD DE 23–27 showed a stronger effect on the rate of loss of sorbed water than MD DE 9–12. Also lactose–MD systems at 90:10 ratio showed that MD DE 23–27 (k_1 = −0.19 day^{-1}) gave a lower rate of loss of sorbed water than MD DE 9–12 (k_1 = −0.40 day^{-1}) at 0.66a_w. The rate of loss of sorbed water of lactose–MD DE 9–12 system did not show significant differences from lactose–MD DE 23–27 (k_1 = −0.20 day^{-1}) system at 0.76a_w (Fig. 5). Therefore, the effect of DE of the MD on lactose crystallization was dependent on a_w. This further confirmed that the MD with the higher DE more effectively delayed lactose crystallization from lactose–MD systems.

During 25 days of storage, we noted that freeze-dried lactose–MD systems except DE 4–7 at 40:60 ratio at 0.66 and 0.76a_w had collapsed structures. The collapse phenomenon of dehydrated materials occurs above T_g and before complete crystallization of amorphous compounds (Roos & Karel, 1991c). This occurred as a result of a lower T_g and viscous flow. The collapsed structure formed at the end of water uptake was likely to reduce water loss, it caused thickening of the microstructure, and the materials could retain higher water contents. Lactose–MD DE 4–7 at 40:60 ratio had highest water sorption of MD components and no collapse or changes in volume during storage at 0.76a_w, and it showed a higher water content than lactose–MD DE 9–12 (Fig. 3B). The highest residual water content of the lactose–MD DE 23–27 system could be related to the slow desorption from the collapsed structure during lactose crystallization. The lactose–MD DE 9–12 at 40:60 ratio appeared more opaque (higher crystallinity) than amorphous lactose–MD DE 23–27 with a_w 0.66 and 0.76 at 7 and 2 days, respectively. Our results showed that lactose crystallization in lactose–MD systems was more affected by MD components hindering lactose movement than their glass transition. This finding emphasized the importance of concentration, molecular size effects, molecular interactions, lattice interference or steric hindrance effects of the mixed components that disturbed nucleation or crystal growth (Iglesias & Chirife, 1978; Mazzobre et al., 2001; Roos & Karel, 1991a, 1991c).

3.4. Dielectric and dynamic-mechanical properties

The T_α of amorphous lactose and lactose–MD DE 9–12 and 23–27 at 90:10 and 70:30 ratios at 0.33a_w above the onset T_g measured by DSC was taken from peak temperature of ε'' and E'' of dielectric and dynamic mechanical analyses, and the T_{cr} was the onset temperature of a subsequent increase in ε'' and E'' giving a higher temperature peak above T_α (Figs. 6 and 7). The peak

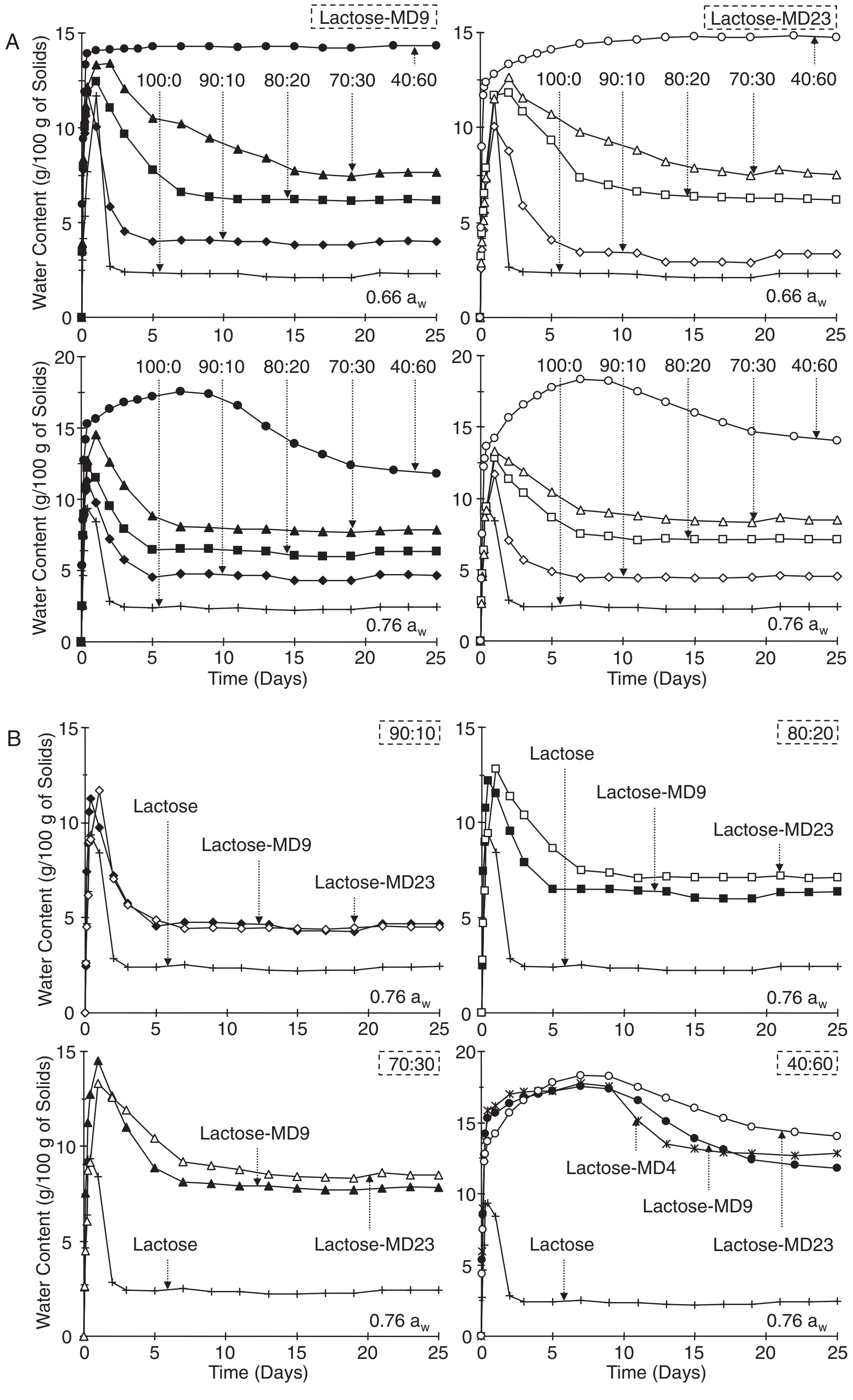

Fig. 3. Water sorption for (A) freeze-dried lactose and lactose–MD DE 9–12 (MD 9), 23–27 (MD 23) systems at all ratios (90:10, 80:20, 70:30, and 40:60) at a_w 0.66 and 0.76 and (B) freeze-dried lactose–MD DE 4–7 (MD 4) at 40:60 ratio, 9–12, and 23–27 at all ratios at a_w 0.76 for 25 days.

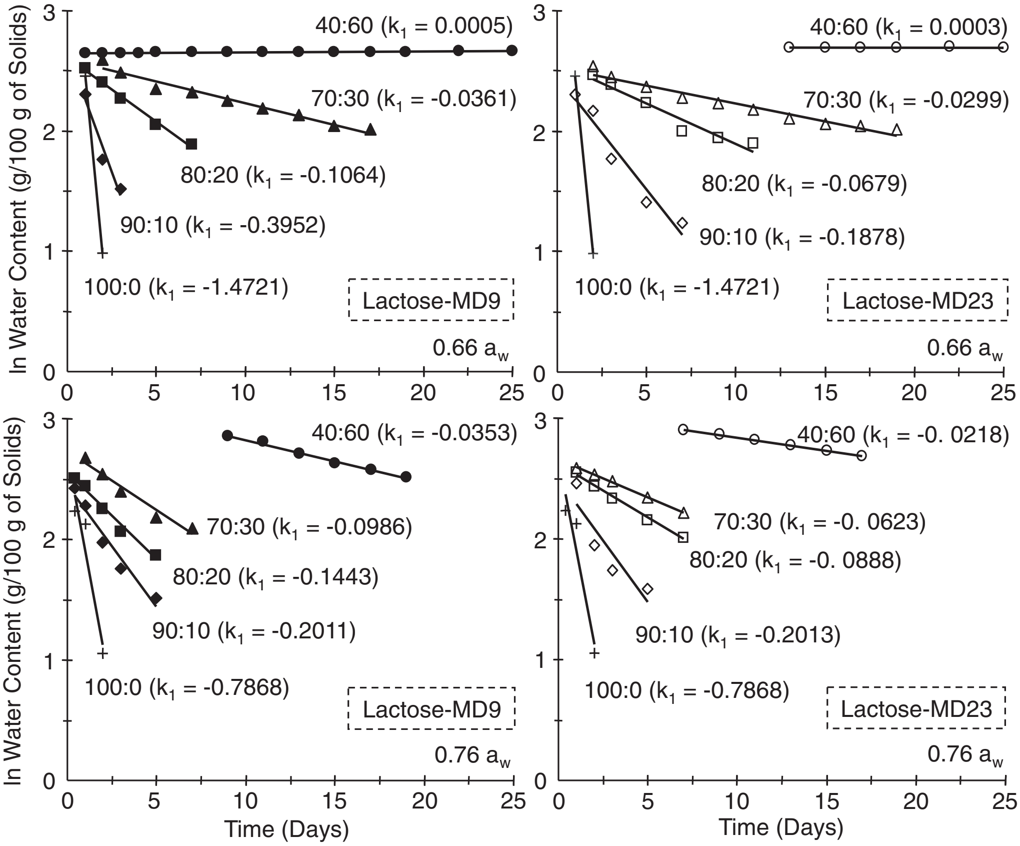

Fig. 4. Kinetics of loss of water sorbed by lactose (+) and lactose–MD DE 9–12 (MD 9), 23–27 (MD 23) systems at ratios 90:10 (◆, ◇), 80:20 (■, □), 70:30 (▲, △), and 40:60 (●, ○) at 0.66 and 0.76a_w.

temperatures of ε'' at 0.5 kHz for freeze-dried lactose and lactose–MD DE 9–12 and 23–27 at 90:10 and 70:30 ratios (Fig. 6) were not significantly different in accordance with the glass transition data and the peak temperature of E'' (Fig. 6). The T_α of amorphous lactose and lactose–MD systems at 0.33a_W occurred at ~30 °C and ~20 °C above the onset T_g measured by DSC in dielectric analysis at 0.5 kHz and dynamic mechanical analysis at 0.5 Hz, respectively, in agreement with Silalai and Roos (2011). It should be noted that the T_α from dielectric and dynamic mechanical analyses are highly dependent on the frequencies of the measurements (Talja & Roos, 2001). The lactose–MD at 70:30 ratio showed higher magnitudes of dielectric loss and loss modulus peaks in the region of T_α than lactose–MD at 90:10 ratio. Increasing MD content affected the water content of the amorphous systems. This was dependent on the DE of MD and water sorption, which increased the number of dipoles responding to the electric field. Lactose–MD DE 9–12 at 90:10 and 70:30 ratios showed a higher magnitude of the dielectric loss and loss modulus peaks at T_α than lactose–MD DE 23–27 at the same ratios. The height of magnitude of dielectric loss and loss modulus correlated directly to water content of lactose–MD systems at 0.33a_W. This result agreed with Silalai and Roos (2011), who found that dielectric loss and loss modulus peaks of skim milk powders increased in magnitude with increasing water content.

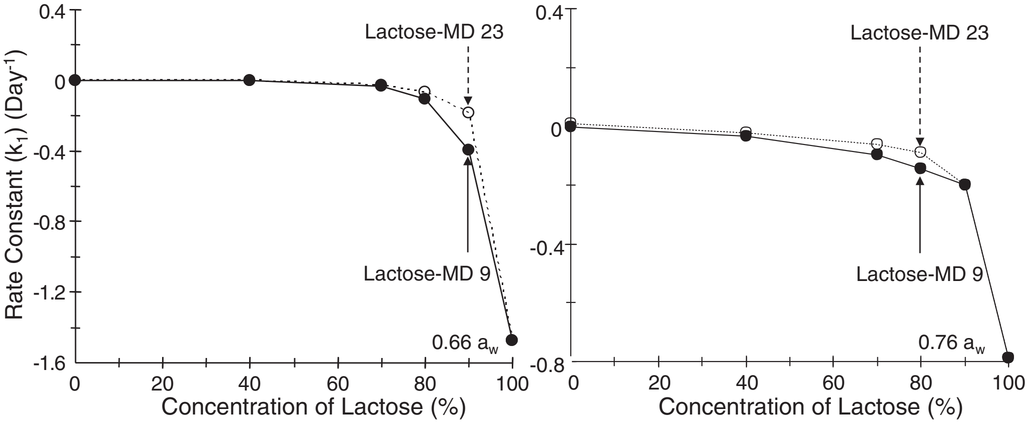

Fig. 5. Rate constants (k_1) from kinetics of loss of water sorbed from freeze-dried lactose, MD DE 9–12 (MD 9) and 23–27 (MD 23), and lactose–MD 9 (●) and 23 (○) systems at 90:10, 80:20, 70:30, and 40:60 ratios at 0.66 and 0.76a_w (from Fig. 4).

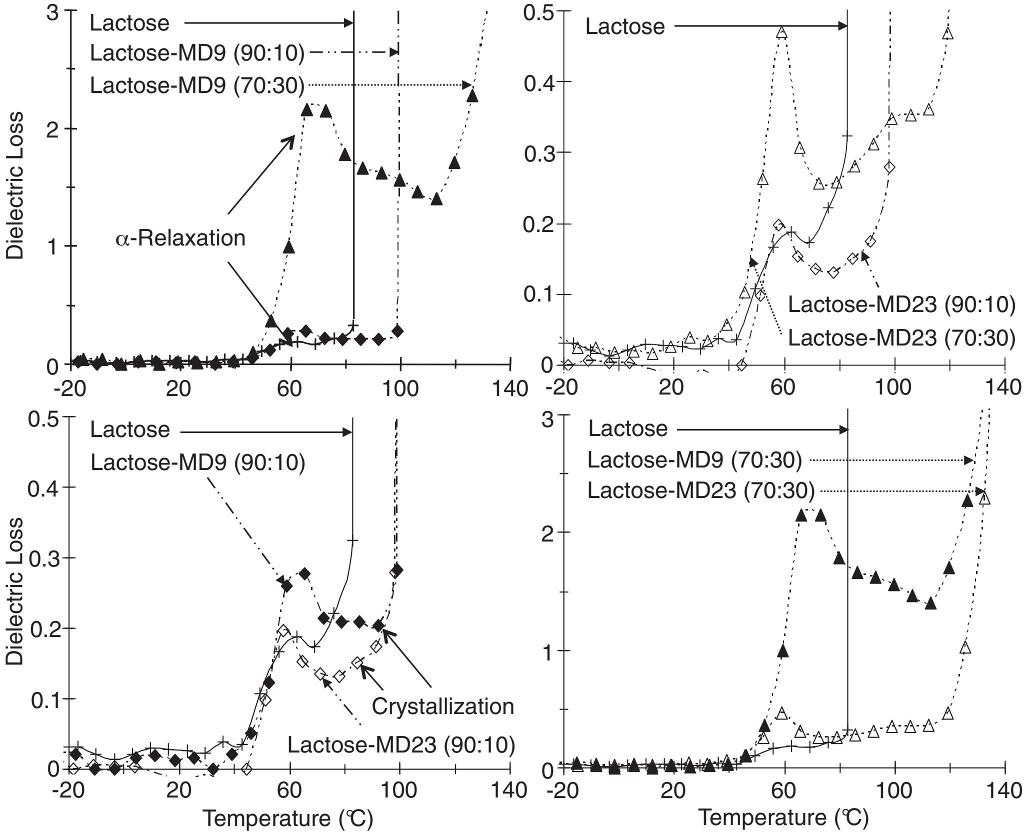

Fig. 6. Dielectric loss and onset temperature of crystallization for freeze-dried lactose, lactose–MD DE 9–12 (MD 9) and 23–27 (MD 23) at 90:10 and 70:30 ratios at 0.5 kHz. Experimental data are shown for lactose (+), lactose–MD 9 (90:10) (◆) and (70:30) (▲), and lactose–MD 23 (90:10) (◇) and (70:30) (△).

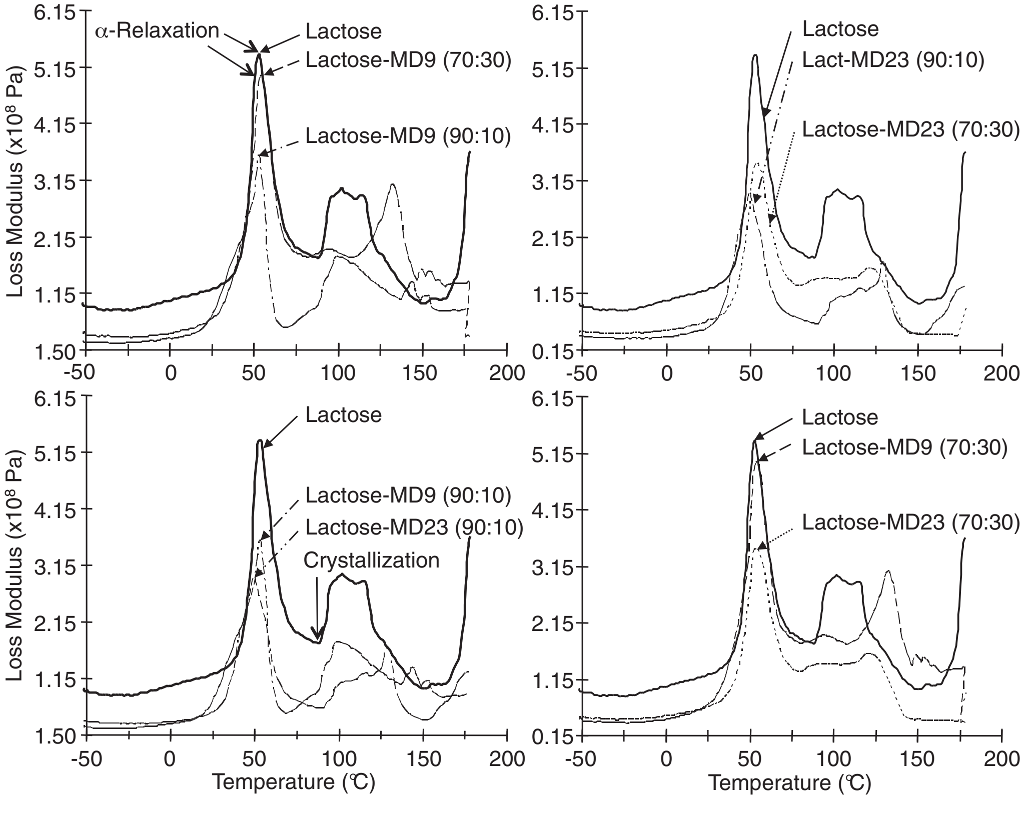

Fig. 7. Loss modulus and onset temperature of crystallization for freeze-dried lactose, lactose–MD DE 9–12 (MD 9) and 23–27 (MD 23) at 90:10 and 70:30 ratios at 0.5 Hz. Experimental data are shown for lactose (—), lactose–MD 9 (90:10) (–·–·) and (70:30) (– – –), and lactose–MD 23 (90:10) (–··–) and (70:30) (······).

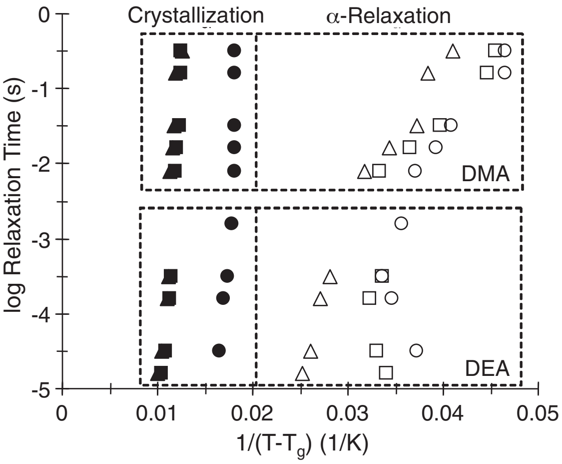

Fig. 8. The plots of relaxation times at peak temperature of α-relaxation (clear symbols) and onset temperature of crystallization (solid symbols) derived from dielectric loss and loss moduli measured by DEA and DMA for freeze-dried lactose (○, ●) and lactose–MD DE 9–12 (△, ▲) and 23–27 (□, ■) at 70:30 ratio. The VTF (Vogel–Fulcher–Tammann) model was fitted to all experimental data at 0.33a_w.

The intensity of the loss modulus peak of amorphous lactose showed water content independence (Fig. 7), which was different from dielectric loss peak of lactose (Fig. 6). The amorphous lactose–MD DE 9–12 at 90:10 and 70:30 ratios agreed with onset T_{cr} of ε'' with lactose–MD DE 23–27 at same ratio (Fig. 6). The onset T_{cr} of E'' of amorphous lactose and lactose–MD systems at 90:10 and 70:30 ratios did not differ at same ratio, but systems containing MD with high DE showed bigger changes in crystallization behavior of lactose than MD with low DE (Fig. 7). These results showed that increasing MD content in lactose–MD systems showed changes in crystallization behavior and the onset T_{cr} of ε'' and E'' was at higher temperatures and also the magnitudes of changes in dielectric loss and loss modulus were increased. The sharp increase or sudden variation of dielectric loss and loss modulus above the T_α in accordance with the results of Talja and Roos (2001) for xylitol and Gonnet, Guillet, Sirakov, Fulchiron, and Seytre (2002) for Kynar 710 poly (vinylidene fluoride) was frequency independent indicating crystallization of lactose (Figs. 7 and 8). The rate of lactose crystallization in lactose–MD might depend on content and DE of MD in the systems. Lactose–MD DE 9–12 and 23–27 systems with high contents of MD showed a frequency dependent change and a slower growth or progression rate of lactose crystallization.

The VTF model using $T_0 = T_g$ was fitted to experimental data of peak T_α and onset T_{cr} of dielectric loss and loss modulus for freeze-dried lactose and lactose–MD systems at 70:30 ratios at 0.33a_w as shown in Fig. 8. The retarded mobility of lactose–MD systems was shown by increasing τ_α at corresponding $T - T_g$, also increasing for the lower DE MD 9–12. The τ_α at high frequencies and corresponding high temperatures (DEA data for lactose and lactose–MD DE 23–27) showed decreasing $T - T_g$ probably because of some crystallization releasing water and consequent increase in mobility. Increasing MD content in lactose–MD systems showed increasing onset T_{cr} for ε'' and E'' (Figs. 6–8), but the crystallization temperature was almost frequency independent (Fig. 8). These results showed that small sugar molecules in MD with high DE gave a higher 'fragility', but disturbed crystallization of lactose more than MD with lower DE, which was in accordance with results of water sorption studies. It also appeared that instant lactose crystallization required about a constant mobility as shown by the frequency independent $T - T_g$. These results showed that the crystallization of lactose was inhibited with increasing MD content and the MD with high DE showed a stronger inhibition of crystallization of lactose than lower DE MD. Therefore an addition of a second component may delay crystallization of lactose, as it disturbs nucleation and crystal growth by hindering diffusion of lactose molecules.

4. Conclusions

We have shown that amorphous carbohydrate mixtures have additive water sorption properties, and the crystallization of lactose was delayed by the addition and increasing contents of MD. The DE of MD has an important role in preventing lactose crystallization. A smaller molecular size (high DE) of MD components increased the delay or was a stronger inhibitor of crystallization of lactose and also MD showed an individual property/role in water sorption of lactose–MD systems. Despite of a similar T_g of amorphous lactose–MD systems, they showed differences in τ_α and different inhibition effects on lactose crystallization. The capability of MD in preventing crystallization of lactose was water activity dependent, and systems containing smaller molecular size or lower molecular weight components showed stronger hindering effect and affected the rate of loss of water sorbed. These results proved that in amorphous systems the number average molecular weight, molecular size effects, and steric hindrance effects of components have significant effects on sugar crystallization.

Acknowledgements

This study was financially supported by the Food Institutional Research Measure (FIRM) of the Department of Agriculture, Food and the Marine project "Water activity control and texture stabilisation of high protein snack bars" (08/R&D/TMFRC/651) coordinated by Dr. Phil Kelly, Teagasc.

References

Alie, J., Menegotto, J., Cardon, P., Duplaa, H., Caron, A., Lacabanne, C., et al. (2004). Dielectric study of the molecular mobility and the isothermal crystallization kinetics of an amorphous pharmaceutical drug substance. *Journal of Pharmaceutical Sciences*, *93*(1), 218–233.

Angell, C. A. (1997). Why C_1 = 16–17 in the WLF equation is physical- and the fragility of polymers. *Polymer*, *38*(26), 6261–6266.

Avaltroni, F., Bouquerand, P. E., & Normand, V. (2004). Maltodextrin molecular weight distribution influence on the glass transition temperature and viscosity in aqueous solutions. *Carbohydrate Polymers*, *58*(3), 323–334.

Bhugra, C., Rambhatla, S., Bakri, A., Duddu, S. P., Miller, D. P., Pikal, M. J., et al. (2007). Prediction of the onset of crystallization of amorphous sucrose below the calorimetric glass transition temperature from correlations with mobility. *Journal of Pharmaceutical Sciences*, *96*(5), 1258–1269.

Bronlund, J., & Paterson, T. (2004). Moisture sorption isotherms for crystalline, amorphous and predominantly crystalline lactose powders. *International Dairy Journal*, *14*, 247–254.

Ermolina, I., Polygalov, E., Bland, C., & Smith, G. (2007). Dielectric spectroscopy of low-loss sugar lophiles. II. Relaxation mechanisms in freeze-dried lactose and lactose monohydrate. *Journal of Non-Crystalline Solids*, *353*, 4485–4491.

Gabarra, P., & Hartel, R. W. (1998). Corn syrup solids and their saccharide fractions affect crystallization of amorphous sucrose. *Journal of Food Science*, *63*(3), 523–528.

Gonnet, J-M., Guillet, J., Sirakov, I., Fulchiron, R., & Seytre, G. (2002). In situ monitoring of the non-isothermal crystallization of polymers by dielectric spectroscopy. *Polymer Engineering and Science*, *42*(6), 1159–1170.

Haque, M. K., & Roos, Y. H. (2005). Crystallization and X-ray diffraction of spray-dried and freeze-dried amorphous lactose. *Carbohydrate Research*, *340*, 293–301.

Haque, M. K., & Roos, Y. H. (2006). Differences in the physical state and thermal behavior of spray-dried and freeze-dried lactose and lactose/protein mixtures. *Innovative Food Science and Emerging Technologies*, *7*, 62–73.

Iglesias, H. A., & Chirife, J. (1978). Delayed crystallization of amorphous sucrose in humidified freeze dried model systems. *International Journal of Food Sciences and Nutrition*, *13*(2), 137–144.

Iglesias, H. A., Chirife, J., & Buera, M. P. (1997). Adsorption isotherm of amorphous trehalose. *Journal of the Science of Food and Agriculture*, *75*, 183–186.

Jouppila, K., Kansikas, J., & Roos, Y. H. (1997). Glass transition, water plasticization, and lactose crystallization in skim milk powder. *Journal of Dairy Science*, *80*(12), 3152–3160.

Jouppila, K., & Roos, Y. H. (1994). Water sorption and time dependent phenomena of milk powders. *Journal of Dairy Science*, *77*(7), 1798–1808.

Kalichevsky, M. T., & Blanshard, J. M. V. (1993). The effect of fructose and water on the glass transition of amylopectin. *Carbohydrate Polymers*, *20*, 107–113.

Kilmartin, P. A., Reid, D. S., & Samson, I. (2004). Dielectric properties of frozen maltodextrin solutions with added NaCl across the glass transition. *Journal of the Science of Food and Agriculture*, *84*, 1277–1284.

Kouassi, K., & Roos, Y. H. (2001). Glass transition and water effects on sucrose inversion in non-crystalline carbohydrate food systems. *Food Research International*, *34*(10), 895–901.

Labrousse, S., Roos, Y., & Karel, M. (1992). Collapse and crystallization in amorphous matrices with encapsulated compounds. *Sciences Des Aliments*, *12*, 757–759.

Lievonen, S. M., & Roos, Y. H. (2003). Comparison of dielectric properties and non-enzymatic browning kinetics around glass transition. *Innovative Food Science and Emerging. Technologies*, *4*, 297–305.

Massalska-Arodz, M., Williams, G., Thomas, D. K., Jones, W. J., & Dabrowski, R. (1999). Molecular dynamics and crystallization behavior of chiral isooctyloxycyanobiphenyl as studied by dielectric relaxation spectroscopy. *Journal of Physical Chemistry B*, *103*(20), 4197–4205.

Mazzobre, M. F., Buera, M. P., & Chirife, J. (1997). Protective role of trehalose on thermal stability of lactase in relation to its glass and crystal forming properties and effect of delaying crystallization. *Lebensmittel-Wissenschaft and Technologie*, *30*, 324–329.

Mazzobre, M. F., Soto, G., Aquilera, J. M., & Buera, M. P. (2001). Crystallization kinetics of lactose in systems co-lyofilized with trehalose. Analysis by differential scanning calorimetry. *Food Research International*, *34*, 903–911.

Mazzobre, M. F., Hough, G., & Buera, M. P. (2003). Phase transitions and functionality of enzymes and yeasts in dehydrated matrices. *Food Science and Technology International*, *9*(3), 163–172.

Mijovic, J. (1998). Monitoring Crystallization by dielectric spectroscopy. *Dielectrics Newsletter*, 1–3.

Noel, T. R., Parker, R., & Ring, S. G. (2000). Effect of molecular structure and water content on the dielectric relaxation behavior of amorphous low molecular weight carbohydrates above and below their glass transition. *Carbohydrate Research*, *329*, 839–845.

Nowakowski, C. M., & Hartel, R. W. (2002). Moisture sorption of amorphous sugar products. *Journal of Food Science*, *67*(4), 1419–1425.

Pagnotta, S. E., Cerveny, S., Alegria, A., & Colmenero, J. (2009). Dielectric relaxtions in ribose and deoxyribose supercooled water solutions. *Journal of Chemical Physics*, *131*(8), 0851021–851027.

Roos, Y., & Karel, M. (1990). Differential scanning calorimetry study of phase transitions affecting the quality of dehydrated materials. *Biotechnology Progress*, *6*(2), 159–163.

Roos, Y., & Karel, M. (1991a). Plasticizing effect of water on thermal behavior and crystallization of amorphous food models. *Journal of Food Science*, *56*(1), 38–43.

Roos, Y., & Karel, M. (1991b). Phase transitions of mixtures of amorphous polysaccharides and sugars. *Biotechnology Progress*, *7*(1), 49–53.

Roos, Y., & Karel, M. (1991c). Applying state diagrams to food processing and development. *Food Technology*, *45*(12), 66, 68–71, 107.

Roos, Y., & Karel, M. (1991d). Water and molecular weight effects on glass transition in amorphous carbohydrates and carbohydrate solutions. *Journal of Food Science*, *56*, 1676–1681.

Roos, Y., & Karel, M. (1992). Crystallization of amorphous lactose. *Journal of Food Science*, *57*(3), 775–777.

Roos, Y. H. (1995). *Phase transitions in foods*. San Diego: Academic Press Inc.

Shrestha, A. K., Howes, T., Adhikari, B. P., & Bhandari, B. R. (2007). Water sorption and glass transition properties of spray-dried lactose hydrolysed skim milk powder. *Lebensmittel-Wissenschaft and Technologie*, *40*, 1593–1600.

Silalai, N., & Roos, Y. H. (2010). Roles of water and solids composition in the control of glass transition and stickiness of milk powders. *Journal of Food Science*, *75*(5), 285–296.

Silalai, N., & Roos, Y. H. (2011). Coupling of dielectric and mechanical relaxations with glass transition and stickiness of milk solids. *Journal of Food Engineering*, *104*, 445–454.

Sillick, M., & Gregson, C. M. (2009). Viscous fragility of concentrated maltopolymer/sucrose mixtures. *Carbohydrate Polymers*, *78*, 879–887.

Talja, R. A., & Roos, Y. H. (2001). Phase and state transition effects on dielectric, mechanical, and thermal properties of polyols. *Thermochimica Acta*, *380*, 109–121.

Wurm, A., Soliman, R., & Schick, C. (2003). Early stages of polymer crystallization – a dielectric study. *Polymer*, *44*, 7467–7476.

Zhou, Y., & Roos, Y. H. (2011). Characterization of carbohydrate–protein matrices for nutrient delivery. *Journal of Food Science*, *76*(4), 368–376.