DIELECTRIC RELAXATIONS AND STICKINESS AROUND GLASS TRANSITION OF MALTODEXTRIN-MILK SOLIDS SYSTEMS

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Abstract:

Maltodextrins are often mixed with low molecular weight sugars to increase glass transition temperature (T_g) and improve dehydration properties of food solids. Around the glass transition, molecular motions are affected by solid-like characteristics of amorphous systems and their α-relaxation shows the onset of long-range molecular motions. Dielectric α-relaxations of dairy powder were investigated by dielectric analysis (DEA). Changes in dielectric properties such as α-relaxations occurred at temperature above glass transition. In the present study, the α-relaxation temperatures were measured from the onset temperatures of dielectric constant or permittivity (ε'). Stickiness behavior of milk powders was determined from the increased torque values in stirring by using a viscometer technique. At the same maltodextrin (DE9 and DE17) content, T_g values of maltodextrin-milk solids with the higher DE maltodextrin (DE17) were lower than those of systems with the lower DE maltodextrin (DE9). Increasing maltodextrin contents increased T_g and α-relaxation temperature (T_α); also the peak magnitudes of dielectric loss above T_g were lower. The maltodextrin-milk solids with low DE maltodextrins showed improved stability characteristics and the T_g and dielectric properties provide complementary information for the production of modified dairy-based powders. At temperatures above the glass transition, the α-relaxations were recorded and the corresponding sticky points (SPT) were determined. The α-relaxation occurred at higher T - T_g for SMP. The T – T_g decreased at SPT because of added MD. The results indicated that compositional effects on T_g and the α-relaxation of skim milk-maltodextrin solids systems were associated with molecular mobility and powder stickiness. Dielectric α-relaxations were significant to understanding flow characteristics and the stickiness behavior of food solids.

Introduction:

Glass transition temperatures (T_g) of mixtures of miscible food solids are dependent on the component compounds. Amorphous, low-molecular-weight sugars such as mono- and disaccharides are hygroscopic and show glass transitions at low temperatures [1,2]. Addition of high-molecular-weight substances into mixtures leads to a glass forming and increasing T_g. The evaluation of compositional effects on physical properties may often be based on the effects of food components on the T_g of their binary or tertiary mixtures [3]. Maltodextrins are widely used as food components to increase T_g of food solids, as maltodextrins are mixtures of homologous carbohydrate polymers [4,5], which have high T_g values [2]. Therefore, they are often mixed with foods containing low-molecular-weight sugars to obtain solids with increased T_g and improved dehydration properties [6]. However, maltodextrins are supplied with different dextrose equivalent (DE) values, which link to the number-average molecular weight and their T_g [6,7]. Glass transition reflects the molecular mobility in formulations with miscible components and can be measured from changes in material characteristics [2]. Dielectric analysis is one of the thermal analytical techniques often used for characterizing dielectric properties at temperatures above the glass transition. Dielectric properties of amorphous food systems are related to molecular mobility and reflect the temperature dependence of changes in textural characteristics, particularly at temperatures around and above the glass transition [8,9]. Above T_g, the increased molecular motions result in softening of amorphous components. Mechanical and dielectric relaxations of mixtures of two miscible glass-formers, such as mixtures of low-molecular-weight sugars have been studied by several researchers [10,11]. The α-relaxation showed the onset of long-range molecular motions [10] and was located from a change in complex modulus occurring at the α-relaxation temperature (T_α). Amorphous materials exhibit enhanced molecular mobility, time-dependent changes and rapidly decreasing viscosity above the glass transition, which make the glass transition responsible for liquid-like behavior, viscous flow and stickiness [2]. The glass transition properties of maltodextrins, lactose and lactose/protein mixtures have been well documented [6,12]. However, several studies have confirmed that stickiness is controlled by the glass transition [2,6,12]; no information reported the correlation of changes in dielectric properties of food powders and powder stickiness around the glass transition. The effect of solids composition (milk solids and maltodextrins) on their glass transitions, dielectric properties and stickiness has not been reported neither.

The objectives of the present study were to produce spray-dried milk solids/maltodextrin powders and to determine the effects of added maltodextrins on the glass transition, dielectric relaxation and stickiness properties of the materials.

Materials and Methods:

Skim milk powder (SMP) was supplied by Dairygold (Mitchelstown, Co. Cork, Ireland). Maltodextrins Glucidex® 9 and Glucidex®17, with respective dextrose equivalents of 8–10 (DE9) and 15–18 (DE17), were obtained from Roquette UK Ltd (Corby, UK). The powders of milk solids with maltodextrins were produced by spray drying at the Bio-Functional Food Engineering facility of Moorepark Food Research Centre (Fermoy, Co. Cork, Ireland). The SMP was mixed with different proportions (10, 35, 65 and 90%, w/w) of maltodextrins (DE9 and DE17) and suspended at 45% solids in water using a Silverson mixer (Zuiveltechnologies BV, Aarlanderveen, The Netherlands) at 55°C and stirred for approximately 1 h prior to spray drying. The reconstituted mixtures were spray dried using a two-fluid nozzle atomizer (Anhydro MicraSpray 750-3, Søborg, Denmark). The inlet and outlet temperatures were 180 and 90°C, respectively, while the internal and external fluid bed temperatures were 70 and 25°C, respectively. Dried powders of milk solids with maltodextrins (DE9 and DE17) were stored in sealed plastic bags at 15°C to protect the materials from water uptake and physicochemical changes prior to analysis.

Glass transition temperatures, T_g (onset), were derived from DSC (Mettler Toledo 821e with liquid N_2 cooling) thermograms, which were analyzed using STAR^e thermal analysis software, version 6.0 (Mettler Toledo Schwerzenbach, Switzerland). Samples of spray-dried powders (1 g) were transferred to glass vials and dried in a vacuum oven (50-55°C). Samples of dehydrated powders (5-15 mg) were prepared in DSC aluminum pans (40 µl; Mettler Toledo-27331, Schwerzenbach, Switzerland) and equilibrated in evacuated desiccators over P_2O_5 and saturated salt solutions for 120 h as described for water sorption. The DSC pans with samples were hermitically sealed. Triplicate samples of each powder were analyzed. An empty pan was used as a reference. The samples were scanned first to 40°C above the predetermined T_g (onset) at 5°C/min, then cooled at 10°C/min to 40°C below the T_g (onset), and the second heating scan at 5°C/min was run to well above the glass transition temperature range. Anhydrous samples were scanned using pans with punctured lids to allow evaporation of residual water during the measurements.

A dielectric thermal analyzer (Triton DS6000 DETA, Triton Technology Ltd, Loughborough, UK) was used to determine dielectric relaxations of dairy solids. Dielectric α-relaxation was observed from changes in dielectric constant or permittivity (ε'), dielectric loss (ε''), and tan δ (ε''/ε'). Tα was determined from the onset temperature of the permittivity (ε') change. Approximately 1 g samples of the powders were transferred to glass vials and dried in a vacuum oven (55°C) and humidified in evacuated desiccators over constant relative vapor pressures using saturated salt solutions. Steady-state water contents were obtained in 5 d. Approximately 60 mg of humidified powders were placed as samples between parallel plate capacitors with a diameter of 33 mm and thickness of <2 mm. The samples were scanned with heating rate of 3°C/min from 40°C below to above the α-relaxation range at various frequencies (0.5, 1, 5, 10 and 20 kHz).

A rotational viscometer (Brookfield viscometer model R/S Rheometer, Harlow Essex CM195TJ, England) was used to determine the sticky-point temperatures (SPT) of the dairy powders using a modified method of Özkan et al. (2002) [13]. Samples of powders (25 g) were transferred into Petri dishes and dried in a vacuum oven (55°C). The samples were stored in desiccators over saturated salt solutions until steady-state water contents were obtained. A pile of the humidified samples (approximately 50 g) was transferred to a water-jacketed cylinder. The samples were left in the water-jacketed cylinder connected to a temperature-controlled water bath for 20-30 min to reach measurement temperatures. Then, a L-shape stirrer was inserted. The torque values were measured for rotation of the stirrer in the powders as a function of time at 0.3 rpm every second for 40 s (Brookfield RHEO 2000 Version 2.7). The average torque value for each sample was calculated using the last 20 data points (20-40 s).

Results and Discussion:

Effect of compositional solid on glass transition temperature

T_g of milk solids/maltodextrin systems, taken from the onset temperature of the glass transition measured by DSC, varied with maltodextrin (DE9 and DE17) content. Several previous studies found that T_g of skim milk solids was similar to T_g of amorphous lactose [4,12,14,15]. Therefore, the effect of milk solids and maltodextrin contents on the T_g of binary milk solids/maltodextrin systems was determined in the present study. According to Roos (1995) [2], the Gordon–Taylor (GT) model is often applied in predicting water plasticization of several food components. In the present study, application of the G-T equation to predict the composition dependence of T_g of milk solids/maltodextrin (DE9 and

DE17) systems required determination of the empirical constant (k). We found that the G-T model fitted the experimental data for mixtures of milk solids and maltodextrins. The T_g values of milk solids/maltodextrin systems increased with increasing maltodextrin contents (Figure 1.). This suggested the high miscibility of amorphous carbohydrate phase. Moreover, depression of T_g with high DE of maltodextrin in the systems resulted from an introduction of additional free volume by low-molecular-weight compounds [2]. This was in agreement with previous studies [16].

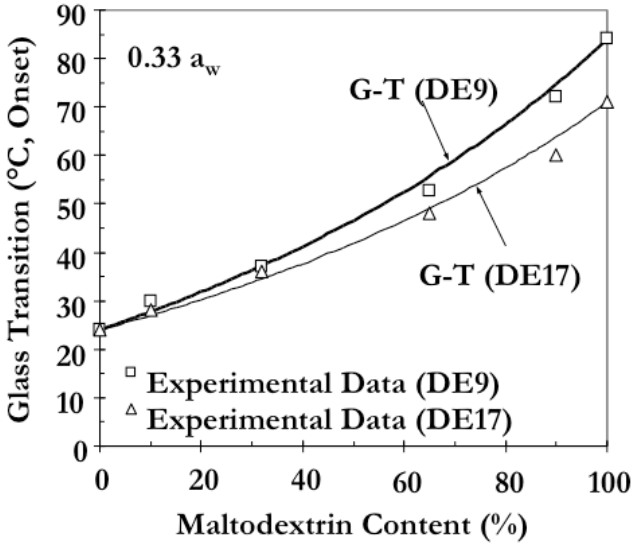

Figure 1. Effect of maltodextrin contents on glass transition temperature (T_g) of milk solids systems at 0.33 a_w.

Dielectric properties

Dielectric properties of maltodextrin-milk solid systems around glass transition are shown in Figure 2. At temperatures below the glass transition, dielectric constant or permittivity was quite low as a result of low molecular mobility in a glassy state. The permittivity increased dramatically at temperatures above the glass transition as the polar groups of molecules exhibited increasing mobility and peaks above the glass transition in the permittivity were observed [10,17]. The magnitudes of dielectric changes indicated dielectric α-relaxations, which were relative to molecular mobility [18,19,20]. In addition, the magnitudes of dielectric permittivity showed a smaller decrease for the milk solids with higher maltodextrin contents due to the reduction of molecular mobility added with high molecular weight substances [18,20]

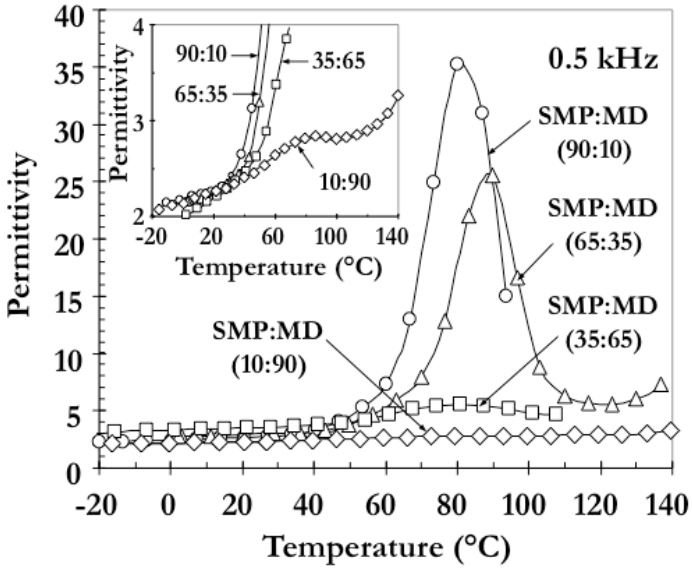

Figure 2. Dielectric relaxations of milk solids systems with varying maltodextrin contents at 0.33 a_w.

Stickiness Behavior of Skim Milk-Maltodextrin Solids Systems

In the present study, we emphasized the effect of maltodextrins (DE9 and DE17) on dielectric relaxations and relaxation times relative to stickiness development of milk solids-maltodextrin systems. Stickiness behavior of milk solids with maltodextrin (DE9 and DE17) contents was observed from an increase in torque values with increasing temperature. Plots of torque values against the T - T_g for milk solids-maltodextrin systems are shown in Figure 3. A steep increase in torque values of each skim milk-maltodextrin solids system occurred above the glass transition in agreement with many studies [12,16,21]. An increase in torque occurred as the solid particles adhered and caused a retarded flow of the powder [13,22,23]. Our previous study showed a relationship between temperature dependence of α-relaxations and flow characteristics of milk solids systems above T_g where dramatic changes in α-relaxation and stickiness occurred as a result of enhanced molecular mobility and consequent liquid bridging between particles [15,24].

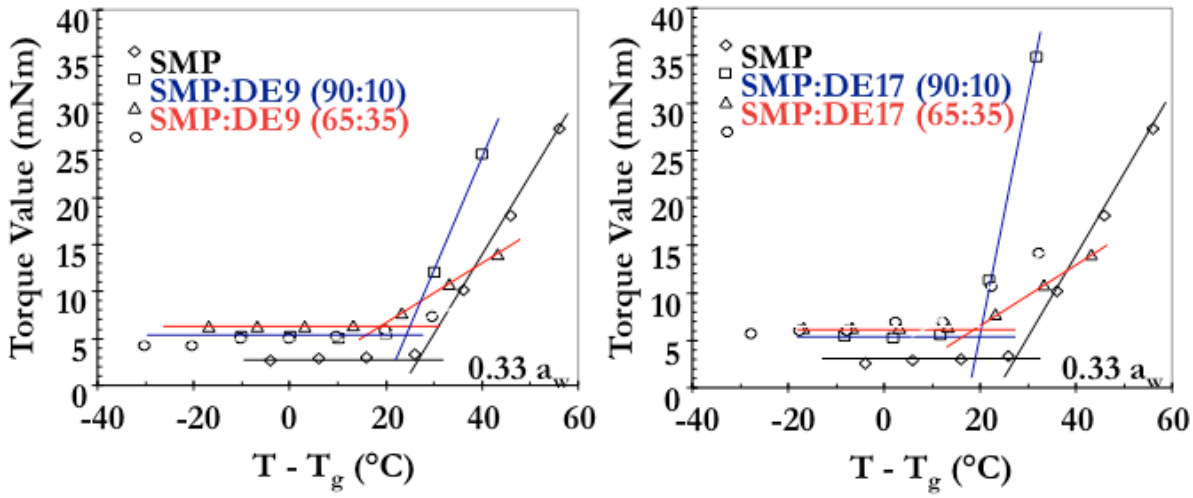

Figure 3. Torque values at 0.33 a_w for skim milk solids (SMP) and skim milk-maltodextrin (DE9 and DE17) solids systems as a function of temperature difference to the glass transition temperature (T – T_g).

Dielectric α-Relaxation Times and Stickiness

In the present study, the temperature dependence of relaxation times of skim milk-maltodextrin solids systems above the glass transition as described by the Vogel-Tammann-Fulcher (VTF) relationship with $T_0 = T_g$ and $T = T_\alpha$ is shown in Figure 4.

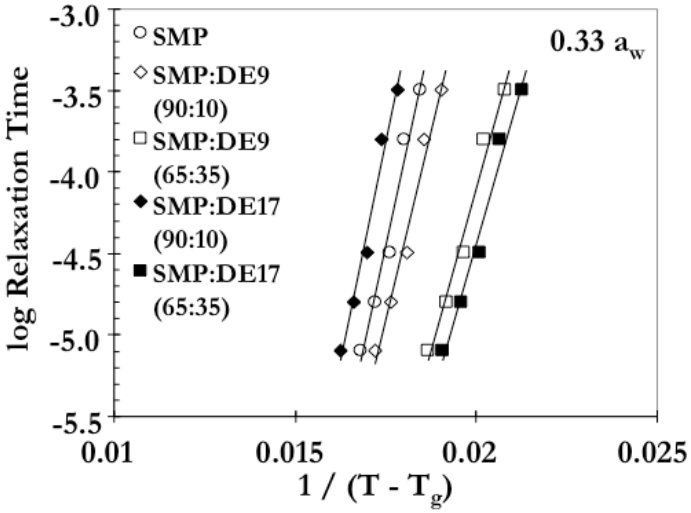

Figure 4. Plots of log relaxation time against temperature difference 1/(T – T_g). The α-relaxation temperatures (T_α) were taken from the temperatures at the dielectric peaks at various frequencies (0.5, 1, 5, 10 and 20 kHz) at 0.33 a_w.

It indicated that the α-relaxation times corresponding to sticky point temperature (SPT) occurred at higher T - T_g for skim milk-maltodextrin solids systems. They occurred over a more narrow temperature range at various frequencies (smaller T - T_g). The systems showed the large slopes of the VTF plots of skim milk-maltodextrin solids, which were similar to those of SMP. In addition, the T - T_g decreased with increasing maltodextrins content (Figure 5). The results indicated that compositional effects on the α-relaxation of skim milk-maltodextrin solids systems were associated with molecular mobility and powder stickiness.

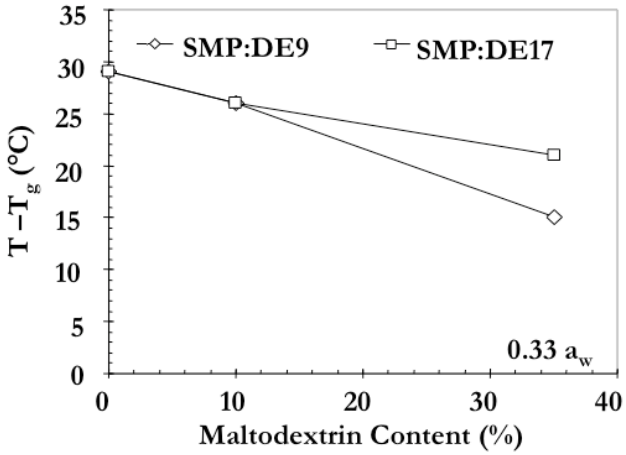

Figure 5. Plot of the T - T_g corresponding to SPT as a function of maltodextrin (DE9 and 17) contents.

Conclusion:

Temperature dependence of α-relaxations observed from changes in dielectric properties of skim milk-maltodextrin solids systems was affected by glass transition, solids composition and water content. The primary α-relaxations of skim milk-maltodextrin solids systems were mainly governed by miscible carbohydrate phase and shifted to higher temperatures with increasing maltodextrin content. Increasing maltodextrin content resulted in smaller changes in dielectric properties and longer relaxation times of skim milk-maltodextrin solids systems around and above glass transition. Effects of composition on relaxation times of skim milk-maltodextrin solids systems can be related to flow characteristics and stickiness around and above glass transition. Low DE maltodextrins were efficient in reducing mobility of carbohydrate molecules and stickiness as predicted from the increased T_g and T_α as well as smaller changes in dielectric α-relaxations. High molecular weight maltodextrins increased temperature and relaxation times needed for inter-particle liquid bridging. Dielectric α-relaxations were significant to understanding flow characteristics and the stickiness behavior of food solids.

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