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Physical properties of maltodextrin DE 10: Water sorption, water plasticization and enthalpy relaxation

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ABSTRACT

Maltodextrins are hydrolysis products of starch. The present research aimed to study physical properties of maltodextrins (water sorption, water plasticization behavior and enthalpy relaxation) and highlighting their functions as food components. The GAB and GT equation were fitted successfully to water sorption and water plasticization data of maltodextrin DE 10. The critical water content and critical water activity values at 25 °C were 14 g water/100 g dry solid and 0.68 a_w, respectively. The Kohlrausch–Williams–Watt (KWW model) and extended Adam-Gibbs model fitted well the enthalpy relaxation kinetics data. The non-exponential parameter, β value of maltodextrin DE 10 was within in the range of 0.15–0.93 and its value was dependent on the water activity. At 25 °C, Maltodextrin with a_w <0.43 was stable glassy as indicated by very long enthalpy relaxation time. The KWW model gave a more accurate fit than the extended Adam-Gibbs model. Arrhenius model fitted well to enthalpy relaxation data and gave a free activation energy (E_a) of 459.5 kJ/mol.

1. Introduction

Maltodextrins are hydrolysis product of starch. The hydrolysis of starch to maltodextrin can be done by acid method or combined use of acids and enzymes (Linden and Lorient, 1999, Hobbs, 2009). The acid method is very fast to produce maltodextrin, but there are problems of discoloring, off-taste and high salt concentration of the maltodextrin product (Linden and Lorient, 1999). The problems of the acid method can be overcome by the enzyme method (Hobbs, 2009). The level of hydrolysis of starch to produce maltodextrin is indicated by dextrose equivalent (DE) Value. The higher the DE value, the higher the level of hydrolysis and as a result the lower is the molecular mass of the maltodextrin components. According to Linden and Lorient (1999), maltodextrins as a mixture of carbohydrates vary in composition and maltodextrins with corresponding DE value, may exhibit very different compositions.

Maltodexrins are classified as a GRAS ingredient (Hobbs, 2009). Maltodextrins are used as texturizing agents and fat replacers (Linden and Lorient, 1999). Maltodextrin is also used as a drying aid to increase the glass transition temperature of materials being dried especially materials with high sugar contents (with low glass transition temperature) to improve dehydration characteristic (Bhandari and Howes, 1999). Maltodextrins have glass transition temperatures, which depend on the DE value, often over the range of 140–180 °C (Roos and Karel, 1991). Maltodextrins are also used to increase processing and storage stability of solids in order to reduce caking, stickiness and improve flowability (Roos, 1995; Bhandari and Howes, 1999 and Descamps et al., 2013). According to Roos (1995) the addition of maltodextrin at level ≥50% (w/w per total dry solid) may be needed to achieve a significant effect on the glass transition.

Water sorption and water plasticization are important physical properties of food material. These properties are related to the stability of materials during processing and storage (Roos, 1995; Rahman, 2009). Water sorption relates water content and water activity across food solids while water plasticization relates water content and glass transition temperature of an amorphous phase. The correlation between water sorption and water plasticization is often used to determine the critical water content and critical water activity of materials at a chosen temperatures (Roos, 1995). The materials with water contents lower than their respective critical water content show enhanced stability especially in terms of physical stability (Roos, 1995).

In addition to glass transition temperatures (T_g), enthalpy relaxation is an important factor related to the glass transition of amorphous low water content materials (Liu et al., 2006). Below T_g,

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glassy state is a metastable non equilibrium state and, the amorphous structure still may relax towards a more stable state with a corresponding change in enthalpy and the relaxed enthalpy must be recovered during heating conditions allowing molecular arrangements (Hancock et al., 1995; Liu et al., 2006). Enthalpy relaxation is associated with structural changes such as structural relaxation and ageing (Liu et al., 2007). Enthalpy relaxation is related to molecular mobility in the glassy state and such mobility is connected to β and ɤ relaxations (Liu et al., 2007). However Hancock et al. (1995) stated that the translational mobility was still possible in the glassy state. Enthalpy relaxation may serve as a measure of macroscopic properties such as density, mechanical strength properties, volume and water permeability properties (Lourdin et al., 2002; Kim et al., 2003; and Liu et al., 2006). Thus it was suggested to store materials far below their T_g in order to maintain stability (Hancock et al., 1995 and Liu et al., 2007).

The relaxed enthalpy (enthalpy relaxation) increased during aging time and the increase of enthalpy relaxation followed non-linear and non-exponential function (Liu et al., 2006). Kawai et al. (2005) suggested two models, Kohlrausch–Williams–Watt (KWW) model and extended Adam-Gibbs model to explain the enthalpy relaxation kinetics. The KWW model is as the main model used to fit enthalpy relaxation data (Syamaladevi et al., 2010). The model is based on the stretched exponential function where the relaxation time obtained is the average relaxation time (Liu et al., 2006). The KWW model is presented in Equations (1) and (2).

$$\Delta H_{relax} = \Delta H_{\infty}\left\{1 - \exp\left[-\left(t/\tau^{KWW}\right)^{\beta}\right]\right\} \tag{1}$$

$$\Delta H_{\infty} = \Delta C_p\left(T_g - T_a\right) \tag{2}$$

Whereτ^{KWW} = constant is related to mean enthalpy relaxation timeβ = constant is related to the width of the relaxation time distribution spectrum ($0 \leq \beta \leq 1$)$\Delta H_{relax} = H_i - H_t$, the difference between enthalpy at the beginning of aging and after aging for t time at temperature, T_a.$\Delta H_{\infty} = H_i - H_{\infty}$, the difference between enthalpy at the beginning of aging time and after enthalpy reaching the equilibrium ($H\infty$) which enthalpy value on the extrapolated equilibrium liquid curve at T_a (Kawai et al., 2005).

The Adam-Gibbs model was previously used to explain relaxation kinetics above T_g and this model was based on the cooperative rearrangement region (CRR) model (Kawai et al., 2005). In simple form, the extended Adam-Gibbs model relates the change of unreleased enthalpy as a function of effective enthalpy relaxation time, and the enthalpy relaxation time itself depends on the aging time (Kawai et al., 2005).

$$\frac{d[\Delta H_{\infty} - \Delta H_{relax}]}{dt} = -\frac{1}{\tau^{eff}(t)}[\Delta H_{\infty} - \Delta H_{relax}] \tag{3}$$

$$\ln \tau^{eff}(t) = \ln \tau^{eff}_{\infty} + B[\Delta H_{\infty} - \Delta H_{relax}] \tag{4}$$

Where, $\tau^{eff}(t)$ is effective relaxation time and its value depend on aging time B and τ^{eff}_{∞} are constants.

Enthalpy relaxation time depends on the temperature where the aging process takes place or how far the aging temperature is below the glass transition temperature. Arrhenius equation was reported to fit to the enthalpy relaxation time as function of temperature (Hancock et al., 1995; Shamblin et al., 1999; Noel et al., 2000; Meste et al., 2002 and Kawai et al., 2005). The present research aimed to study the water sorption, water plasticization behavior and enthalpy relaxations of maltodextrin DE 10.

2. Materials and methods

2.1. Materials

Maltodextrin (M 100) with DE 9-12 (or in average DE 10) was purchased from Grain Processing Corporation, IA, USA and deionized water was obtained from KB scientific, Cork, Ireland. Salts for water sorption experiment: LiCl (PubChem CID: 433294), CH_3COOK (PubChem CID: 517044), $MgCl_2$ (PubChem CID: 5360315), K_2CO_3 (PubChem CID: 11430), $Mg(NO_3)_2$ (PubChem CID: 25212), $NaNO_2$(PubChem CID: 23668193), and NaCl (PubChem CID: 5234) were obtained from Sigma Chemical Co., (St. Louise, MO. U.S.A).

2.2. Water sorption method

Maltodextrin solution (total solid of 20%) was prepared in vials and dried by a freeze-dryer. First maltodextrin solution was prepared in glass vials (Schott, Mùllheim, Germany). The samples then were stored in freezer (HLLF-240, Heto, Jouan Nordic A/S, Allerød, Denmark) at temperature −20 °C for overnight and in freezer (Icebird/Mini Freeze 80, Heto, Jouan Nordic A/S, Allerød, Denmark) at −80 °C for about 3 h before freeze drying. After freezing all the samples were transferred to the freeze drier (Lyovac GT 2, Steris®, Hurth, Germany). Each vial contained 5 ml of solution and after drying each vial contained approximately 1 g of dried maltodextrin. The water content of maltodextrin after drying and closing of vials in the freeze-dryer under vacuum at the end of drying was assumed as zero. The vials were opened and stored in desiccators over various saturated salt solutions. The saturated salt solution used were LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, and NaCl with water activity values of 0.11, 0.23, 0.33, 0.43, 0.52 and 0.75 respectively (Roos and Karel, 1991). During storage in a vacuum desiccator, the vials were weighed regularly for 8 days. The leveled-off water content for maltodextrin at each water activity was calculated based on the weight gain (the curve levelled off). Analysis were carried out in triplicate. The Guggenheim–Anderson–deBoer (GAB) equation was used to relate water activity of maltodextrin and their water content.

$$X = \frac{X_m C K a_w}{(1 - K a_w)(1 + (C - 1) K a_w)} \tag{5}$$

Where,X = water content (g water/g dry solid)a_w = water activityX_m = monolayer water contentX_m, C and K are constants.

2.3. Water plasticization method

About 10 mg of sample of maltodextrin DE 10 was prepared in a standard 40 µl aluminum pan (Mettler Toledo, Schwerzebach, Switzerland) and equilibrated in desiccators over various relative humidities for 3 days. The pans then were hermetically sealed and analyzed by a differential scanning calorimeter (DSC). Three cycles of scanning were used (heating-cooling-heating) at same heating/cooling rate of 5 °C/min. The temperature profile scanning of maltodextrin at various water activities of 0.11; 0.23; 0.33; 0.43; 0.53; 0.65 and 0.76 were of 50–125 °C; 40–105 °C; 10–100 °C; 10–90 °C; 0–85 °C; 0–80 °C and −20 − 70 °C, respectively. The second heating scans were used to determine glass transition temperatures of the samples. The glass transition temperature was determined using the STAR^e software version 8.10 (Mettler Toledo Schwerzenbach, Switzerland). The relationship between glass transition temperature and water content for maltodextrin at various water activities were modelled using the Gordon–Taylor equation.