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UNIVERSITY COLLEGE, CORK

SCHOOL OF FOOD AND NUTRITIONAL SCIENCES



MALTODEXTRIN-INCORPORATED-VACUUM-DRIED HONEY POWDER: PROCESSING AND STABILITY

Thesis presented by

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DEDICATION

"To My Parents and My Family (Desi, Naufal and Misyal) with Love, Respect and Gratitude".

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"O mankind, remember the favor of Allah upon you. Is there any creator other than Allah who provide for you from heaven and earth? There is no deity except Him, so how are you deluded? [Quran 35:1]"

"Every soul will taste death. We test you with evil and with good as trial, to Us you will be returned [Quran 21:35]"

Bambang Nurhadi

October, 2016

ABSTRACT

Honey is rich in sugar content and dominated by fructose and glucose that make honey prone to crystallize during storage. The crystallization in honey will reduce honey quality. In an alternative solution, honey could be processed into powder form. Due to honey composition, the anhydrous glass transition temperature of honey is very low that makes honey difficult to dry alone and drying aid or filler is needed to dry honey. Maltodextrin is a common drying aid material used in drying of sugar-rich food. Maltodextrin is a starch hydrolysis product that shows properties based on the level of hydrolysis that is stated as dextrose equivalent (DE value). Vacuum drying is a simple drying method where the drying process occurs at lowered pressure that allows water evaporate at lower temperature and thus increasing drying rate. The present study aims to study the processing of honey powder by vacuum drying method and the impact of drying process and formulation on the stability of honey powder. To achieve the objectives, the series of experiments were done. Firstly the water sorption isotherm, water plasticization and enthalpy relaxation properties of maltodextrin DE 10 was investigated. Secondly studying the effect of temperature on the structural properties of honey powder was done by using DDI method as a tool of analysis. Thirdly water sorption isotherm and water plasticization properties were studied on honey powder obtained from different treatments of total solid concentration, DE value and maltodextrin concentration and lastly addition of anti-caking agent to honey powder was studied to determine their effect to stability and flow-ability.

The Guggenheim-Andersen and de-Boer (GAB) and Gordon-Taylor (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. Based on the KWW model, 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. Maltodextrin with water activity lower than 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.

Dynamic dew point isotherm (DDI) method was developed as analysis tool to determine amorphous content, which records the change of water activity and weight change (or water content) of a sample continuously. The DDI method was calibrated using pre-known amorphous contents of amorphous sucrose for sucrose and mixtures of sucrose and maltodextrin. Amorphous materials often exhibit higher sorption of water than crystalline materials. In the DDI approach, water sorption data were differentiated numerically and plotted against water activity. The water sorbed by the sample during recrystallization was measured by integrating the area of the new derived water sorption curve against water activity. The water sorbed was correlated with the amorphous content of the system. The honey powder also exhibited recrystallization of its amorphous sugar during water sorption. The result showed that the higher the drying temperature, the higher the amorphous content of vacuum-dried honey powder.

The present study investigated effects of total solids content of honey maltodextrin systems and the component ratio on water sorption isotherm and water plasticization behavior of the vacuum dried solids. The GAB model fitted well to the water sorption data with monolayer water contents over the range of 4.8 – 6.2 g water/100 g of solids. Water plasticization of the powder followed the Gordon-Taylor equation, with the T_g of dry solids of 30 – 43 ^oC depending on composition. The water content depressing the T_g to ambient temperature was less than the monolayer water

content. It appeared that the highest maltodextrin ratio decreased water sensitivity to the highest extent.

Anti-caking agent, calcium silicate and calcium stearate were added into honey powder. The addition of anti-caking agent influenced water sorption and flow-ability properties of honey powder. Calcium silicate addition seemed not to affect water sorption isotherm properties of honey powder, however calcium stearate showed inhibiting effect of recrystallization and collapse structure of amorphous components of honey powder. Addition of anti-caking agent to honey powder increased flow-ability of honey powder and calcium stearate seemed increase flow-ability better than calcium silicate.

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INTRODUCTION

Honey is a natural food from bees that has high sugar content. Its sugar content could be up to 65 % and dominated by fructose (35.7 – 41.7 %, w/w) and glucose (29.7 – 34.9 %, w/w) (Chmielewska, 2004). The ratio of fructose to glucose is in average 1.2 to 1 (Ram, 2011). High sugar content of honey makes it easy to crystallize during storage. The crystallization of honey is called granulation. In honey, glucose crystallizes into glucose monohydrate. Optimal granulation of honey occurs over the temperature range of 13 – 17 °C (Chmielewska, 2004; Venir, Spaziani and Maltini, 2010). The easiness of granulation of honey is determined by the ratio of glucose to water. If the ratio of glucose to water more than 2.1, honey is categorized as rapidly granulated honey and if the ratio is less than 1.7, honey is categorized as non-granulating honey (Lupano. 1997). Ratio between fructose to glucose is another criterion for assessing the granulation easiness of honey where honey with ratio fructose to glucose less than 1.14 is called as fast granulating honey while honey with the ratio more than 1.58 is classified as non-granulating honey (Venir, Spaziani and Maltini, 2010). The impact of granulation reduces quality of honey and increases water activity of honey that makes honey susceptible to microbial deterioration by osmophilic yeast (Zamora and Chrife, 2006; Gleiter, Horn and Isengard, 2006; Shi, Fang and Bhandari, 2013). Honey can be transformed into powder form to make it easier to handle, transport and store.

Honey solely is impossible to dry alone into powder. Almost 80-85% of honey solid is fructose and glucose (Lupano, 1997, Sahu, 2008, Venir, Spaziani and Maltini, 2010, Nurhadi et al., 2012). Fructose and glucose has low glass transition temperature (T_g), 5 °C and 31 °C respectively (Bhandari and Howes, 1999). The water content of honey could be more than 20 % and the water itself has very low T_g (-135 °C). Honey

has also a low pH of 3.8-5.0 (Ahmed et al., 2007). Thus by this composition, honey has also very low T_g of -59.8 - -48.7 °C over the water content range of 18.4 – 23.2 % (Nurhadi et al., 2012) while in the range of -51.14 to -33.64 °C was also reported (Ahmed, 2007). The glass transition temperature of anhydrous honey solids was reported 15 °C (Lazaridou et al., 2004) and these properties make honey difficult to dry solely. Honey with very low glass transition temperature could be dried by adding a material with a high glass transition temperature (Bhandari and Howes, 1999). The material for that purpose were maltodextrin and Arabic gum (Nurhadi et al., 2012), combination of whey protein isolate and maltodextrin (Shi, Fang and Bhandari, 2013). Maltodextrin is common filler or drying aid material for sugar-rich powder (Roos, 1995; Roos and Drusch, 2015). Maltodextrin is a starch derivative product and it can be differentiated by its molecular weight (level of hydrolysis), stated as dextrose equivalent (DE). The higher is the DE maltodextrin, the higher is the level of hydrolysis of starch and the lower is the molecular weight (Linden and Lorient, 1999).

Different drying methods could process honey liquid into honey powder. Honey powder is usually produced by spray drying (Shi, Fang and Bhandari, 2013). Honey powder may also be produced with highest quality by freeze-drying due to drying process involving sublimation at low temperature thus maintaining all the functional properties of honey. Vacuum drying as a simple drying method was reported to produce honey powder with optimum maltodextrin ratio 43 to 50 % (solid/solid) (Sahu, 2008; Nurhadi et al., 2012). In vacuum drying method, the drying rate is very high due to low pressure condition (vacuum pressure process) and water can evaporate at lower temperature. Different mechanisms of drying is occurring in spray drying and vacuum drying processes. The drying process in spray drying is very fast and water evaporates from small tiny droplet of samples that allows amorphous structure formation. The drying rate in vacuum drying is also high but still lower than in spray drying and the different properties of powders might be produced. The ratio of maltodextrin, DE value of maltodextrin and drying temperature could affect the

honey powder properties resulted. In addition to storage at temperature lower than its T_g, the stability of honey powder could be maintained by anti-caking agent addition.

Our studies in the present study has objectives to study the processing of honey powder by vacuum drying method and the impact of the drying process and formulation on the stability of the resultant honey powder.

The main hypotheses of the present study were:

i. Maltodextrin as a drying aid material affects the stability of honey powder.
ii. Drying temperature (drying rate) affects the structure (amorphous content) of honey powder.
iii. Anti-caking agents affect stability of honey powder.

The hypotheses were tested by series of experiment with the objectives:

i. Characterization properties of maltodextrin as drying aid materials: water sorption isotherm, water plasticization and enthalpy relaxation properties.
ii. Investigation the effect of ratio of maltodextrin, dextrose equivalent and initial total solid ratio on honey powder properties: water sorption and water plasticization properties.
iii. Investigation of the effect of drying temperature on the structure (amorphicity) of honey powder resulted.
iv. Investigation of dynamic dew point isotherm method as a simple method in measuring amorphous content of honey powder.
v. Investigation the effect of anti-caking agent on stability of honey powder which indicated by its corresponding water sorption isotherm and flow-ability properties.

CHAPTER I

LITERATURE REVIEW

1.1. Water Sorption Isotherm

Since ancient times, water content was an indicator of food stability (Chirife and Fontana, 2007). In 1950s, the concept of water activity as an indicator of stability was more acceptable than water content in terms of microbial, chemical and physical deterioration (Slade and Levine, 1991; Chirife and Fontana, 2007). Water activity in food states energy status of water in food that explains effectiveness to act as a solvent and participating in chemical or biochemical reaction (Rizvi, 2005; Chirife and Fontana, 2007). Water sorption isotherm (WSI) is a property that correlates water content and its equilibrium water activity at certain temperature. This property is essential to assess, control and evaluate foods in terms of processing, storage, handling and packageing (Chirife and Fontana, 2007; Okos et al., 2007).

Water activity describes the energy state of water in a system, if the systems have different water activities to surroundings there will be a transfer of water from or onto the system depending on the higher water activity and the transfer of water would stop if equilibrium is reached. Water activity concept has been used in formulation technology in predicting final mixture's water activity from mixtures two or more ingredients with different water activity, water contents and WSI properties (Welti-Chanes et al., 2007). In this assumption the initial water content from each ingredient would be the final water content of mixture and the amount of each ingredient would affect the final mixture water activities (Welti-Chanes et al., 2007). Water activity approach is also used in hurdle concept to preserve food where water activity is combined with other hurdles such as pH, temperature, anti-microbial agent to stop microbial growth in a food material (Welti-Chanes et al., 2007).

1.1.1. Water Activity

Water activity describes energy state of water in a material. If a material has water activity different from surroundings, there will be vapor exchange between each other until equilibrium is reached. The concept of water activity has thermodynamic explanation and derived based on ideal gas law and ideal Raoult's solution law (Rizvi, 2005, Bhandari and Adhikari, 2008).

Based on the fundamental thermodynamic equation, the chemical potential of water vapor (μ_w) can be stated as

$$\partial\mu_w = \overline{V_w}\partial P - \overline{S_w}\partial T \quad (1)$$

(Notes: P = pressure, S = entropy and subscript w for water)

At constant temperature, $\partial T = 0$, $\overline{V_w}$ and $\overline{S_w}$ refer to molar volume and molar entropy respectively,

$$\partial\mu_w = \overline{V_w}\partial P \quad (2)$$

For ideal gas, $\bar{V} = \frac{RT}{P}$

$\partial\mu_w = \frac{RT}{P}\partial P$ Then becoming

$$\partial\mu_w = RT\partial lnP \quad (3)$$

The chemical potential is stated with inclusion of standard reference, μ_w^0, at standard pressure (1 atm), P_0, thus the equation (3) can be expressed as :

$\int_{\mu_w^0}^{\mu_w} \partial\mu_w = \int_{P_0}^{P_w} RT\partial lnP$, then

$$\mu_w - \mu_w^0 = RT\{lnP_w - lnP_0\} = RTln\frac{P_w}{P_{0=1\ atm}} = RTlnP_w$$

$$\mu_w = \mu_w^0 + RTlnP_w \quad (4)$$

The equation 4 is valid for ideal gas, whereas, the water vapor does not follow the ideal gas. As consequence fugacity, f, was used instead of pressure, P.

$$\mu_w = \mu_w^0 + RTlnf_w \quad (5).$$

For water vapor pressure close to zero, it follows ideal gas law where $\lim_{P\to 0} \frac{f_i}{P_i}$=1, for the real condition the correlation between fugacity and pressure: $f_w = \gamma_f P_w$. Where

γ_f if fugacity coefficient and its value is varied depending on the temperature (Rizvi, 2005).

The second assumption used is the Raoult's Law for ideal solution. For the ideal solution, the amount of component water, w, in the solution can be stated as moles fraction of w which is proportional to the partial pressure of component w.

$$x_w = \frac{f_w}{f_w^{\square}} \; or \; f_w = x_w f_w^{\square} \qquad (6)$$

For the pure water solution, $x_w = 1$, $f_w = f_w^{\square}$ is the fugacity of pure water solution. Thus for pure water solution is in equilibrium with its surrounding, the chemical potential of water between liquid (solution, $\mu_w^{\square}$) and vapor phase are equal.

$$\mu_w^{\square} = \mu_{w(vapor)} = \mu_w^0 + RTlnf_w^{\square} \quad (7)$$

$$\mu_w^0 = \mu_w^{\square} - RTlnf_w^{\square} \quad (8)$$

Food or not pure water solution is in equilibrium with the surrounding, the chemical potential of water is expressed

$$\mu_{w(soln)} = \mu_w^0 + RTlnf_w \quad (9)$$

By combining equation (6) and (8)

$$\mu_{w(soln)} = \mu_w^0 + RTlnx_w + RTlnf_w^{\square} \qquad (10)$$

Roults law is followed for very dilute solution and not followed by food as non-ideal solution, thus instead of using x_w, water activity is used, a_w. Thus the equation (10) is becoming

$$\mu_{w(soln)} = \mu_w^0 + RTlna_w + RTlnf_w^{\square} \quad (11)$$

Thus where food in equilibrium, the chemical potential of water in vapor (eq. 5) and in food (eq. 11) is equal

$$\mu_w^0 + RTlnf_w = \mu_w^0 + RTlnf_w^{\bullet} + RTlna_w$$

$$lna_w = lnf_w - lnf_w^{\square} \text{ Or } a_w = \frac{f_w}{f_w^{\square}} \quad (12)$$

Where

$$a_w = \frac{f_w}{f_w^{\square}} = \frac{\gamma_f P_w}{\gamma_{f=1} P_w^{\square}} = \frac{\gamma_f P_w}{P_w^{\square}} \quad (13)$$

The value of fugacity constant is close to one at temperature range of 0 – 140 °C (Rizvi 2005). Thus the value of water activity of food is equal to ratio of vapor pressure to its corresponding pure water vapor pressure at a certain temperature.

1.1.2. WSI Determination

There are two methods for the determining WSI, differential and integration method (Rizvi, 2005). In integration method, series of samples are stored inside desiccators with various relative humidities and the sample weight is periodically measured until reaching equilibrium which is indicated by a constant weight (Rizvi, 2005). In differential method, a small amount of sample is stored in a chamber with controlled relative humidity and the humidity changes gradually until reaching the desired or set humidity (Rizvi, 2005). True equilibrium at each water activity takes a very long time and is impossible to reach and the equilibrium is said adequate when the measurement of the weight is changed by less than 2 mg/g sample (Bhandari and Adhikari, 2008) or 1 mg /g sample (Sablani, Kasapis and Rahman, 2007).

The WSI can be done in different direction, adsorption and desorption. For adsorption direction, the water activity of sample should be as low as possible as or at least lower than the starting water activity of WSI measurement (Bhandari and Adhikari, 2008). Sample could be prepared by drying with freeze-drying or vacuum drying or stored in desiccator with P_2O_5 or $CaSO_4$ for few days or weeks (Bhandari and Adhikari, 2008). For desorption direction, samples should have a_w higher than the highest a_w being used or used originally as they are (Bhandari and Adhikari, 2008). WSI obtained from two directions are not overlapped at each other and the phenomenon is called as hysteresis (Figura and Teixera, 2007).

The calibration of WSI was explained by Wolf et al (1984) and Kiranoudis et al. (1993). Avicel or microcrystalline cellulose was used as a standard material in WSI measurement (Wolf et al., 1984). WSI measurement is considered appropriate if the mean value of five measurements at 10 different a_w of avicel differ from the reference

value by not more than 0.498 g water/100 g dry solids (Wolf et al., 1984, Kiranoudis et al., 1993). The reference value of water activity of avicel at different a_w could be seen in **Table 1.1**

Table 1.1. The mean value of water content of avicell at different a_w (Wolf et al., 1984).

Water activity (a_w)	Water Content (g water/ 100 g dry solids)
0.11	2.02
0.23	3.19
0.33	4.06
0.44	5.04
0.53	5.82
0.58	6.48
0.71	8.21
0.75	8.83
0.84	10.95
0.90	12.96

Saturated salt solution is a commonly used means to vary water activity in WSI measurement (Bhandari and Adhikari, 2008). Some saturated salt preparations and their corresponding water acitivity as a function of temperature is presented in **Table 1.2**. Other solutions used are NaCl solution at various concentration, sulphuric acid-water solution, glycerol solution and mechanical humidifier (Bhandari and Adhikari, 2008). The suggested techniques to do WSI include the use of different a_w (at least 5 different a_w), triplicate samples, storage for 3 weeks (might be longer at high a_w), constant temperature ($\pm$ 1 °C fluctuation), ratio surface salt area to sample higher than 10/1 and ratio air volume to sample volume less than 20/1 (Rizvi, 2005, Bhandari

and Adhikari, 2008). Vacuum condition could shorten time needed to reach equilibrium (Bhandari and Adhikari, 2008).

Table 1.2. Saturated salt solutions, their preparation and effect of temperatures.

Salt	a_w at 25 °C[a]	gram in 100 ml of water[a]	Effect of Temperature (K)[b]
LiCl	0.11	> 175	ln a_w =(500.95/T)- 3.85
CH_3COOK	0.23	> 300	ln a_w =(861.39/T) - 4.33
$MgCl_2$	0.33	> 82	ln a_w = (303.35/T) - 2.13
K_2CO_3	0.44	> 168	ln a_w =(145.0/T) - 1.30
$Mg(NO_3)_2$	0.53	> 188	ln a_w = (356.6 /T) - 1.82
NaBr	0.58	> 110	
$SrCl_2$	0.71	> 81	
NaCl	0.75	> 54	ln a_w = (228.92 /T) - 1.04
KCl	0.84	> 53	ln a_w = (500.95 x 1/T) - 3.85
$BaCl_2$	0.90	> 57	

Sources**:** [a] Bhandari and Adhikari, 2008 and [b] Labuza, Kaanane and Chen, 1985.

1.1.3. Factors Affecting WSI

Some factors affect WSI including temperature, pressure and food composition. Pressure effect is less pronounced than temperature except at food process using a high pressure and temperature such as extrusion process (Labuza and Altunakar, 2007). Temperature is a main factor affecting water activity which follow the Clayperon-Equation. This approach is based on two assumptions: the determination of q_{st} is done at constant water content and the value of Q_{st} is just a function of water content and independent to temperature effect (Rizvi, 2005).

For equilibrium liquid-vapor boundary

$$\frac{\partial P}{\partial T} = \frac{\Delta S}{\Delta V} = \frac{\Delta Q}{T\Delta V} \quad \text{(Note Q = heat, T = temperature)} \quad (14)$$

Due to $V_g \gg V_l$, thus ΔV is affected mainly by the volume of gas (vapor) only,

$$\frac{\partial P}{\partial T} = \frac{\Delta Q}{TV_g}$$

Or the equation can be expressed in molar quantity (per mole).

$$\frac{\partial P}{\partial T} = \frac{\overline{\Delta Q}}{T\overline{V}} \quad (15)$$

For ideal gas, $\overline{V} = \frac{RT}{P}$, then the eq. 15 becoming

$$\frac{\partial P}{\partial T} = \frac{\overline{\Delta Q}}{T\overline{V_g}} = \frac{P\overline{\Delta Q}}{T^2 R} \quad (16)$$

Or $\frac{\partial P}{P} = \frac{\overline{\Delta Q}}{\overline{T^2}R}\partial T \rightarrow \partial lnP = -\frac{\overline{\Delta Q}}{R}\partial\frac{1}{T}$ (17)

For the pure water solution

$$\partial lnP_w^{\square} = -\frac{\overline{\Delta_{vap}H}}{R}\partial\frac{1}{T} \quad (18)$$

And for solution or food system

$$\partial lnP_w = -\frac{Q_{st}}{R}\partial\frac{1}{T} \quad (19)$$ (note Q_{st}= isosteric heat of sorption)

Thus combining eq. (18) and (19)

$$\partial lnP_w - \partial lnP_w^{\bullet} = dln\frac{P_w}{P_w^{\bullet}} = -\frac{Q_{st} - \overline{\Delta_{vap}H}}{R}\partial\frac{1}{T}$$

$$\partial lna_w == -\frac{Q_{st} - \overline{\Delta_{vap}H}}{R}\partial\frac{1}{T} = -\frac{q_{st}}{R}\partial\frac{1}{T}$$

$$q_{st} = Q_{st} - \overline{\Delta_{vap}H}$$

$$q_{st} = nett\ isosteric\ heat\ sorption$$

As temperature increases, usually their corresponding equilibrium water content at different a_w would decrease (Muhtaseb, Mc Minn and Magee, 2002). The value of q_{st} is determined by plotting $ln\ a_w$ vs $\frac{1}{T}$ at same water content and the value of q_{st} increased when the water content decreased (Kiranoudis et al., 1993). The net isosteric heat of sorption is positive and means that to evaporate water in food needs more heat than the latent evaporative heat of pure water at corresponding temperature. At very high a_w, the nett isosteric heat of sorption value close to zero means that water tends to act as pure water which needs evaporative heat given by latent evaporative heat of pure water (Rizvi, 2005).

The WSI of food could be determined by additive rule of water sorption for each component based on their dry weight composition (Welti-Chanes et al., 2007). Fat does not contribute to water sorption except glycerol that contain polar phosphate group (Arslan and Togrul, 2005). For carbohydrate, their structure could be in amorphous, crystalline or partially amorphous (Bhandari, 2013). Amorphous structure would adsorb more water at low a_w than crystalline structure (Bhandari, 2013). The higher water sorption in amorphous structure than in crystalline structure due to more number of hydrogen bonding site available for water molecules (Haque and Roos, 2005). Crystalline material water sorption will increase significantly when reaching deliquescent point due transformation from crystalline solid to saturated solution (Lipasek, Taylor and Mauer, 2011, Lipasek et al., 2012). Amorphous sugar could crystallize during WSI which characterized by the loss of water and result in a break in WSI curve (Bhandari and Adhikari, 2008). Potes, Kerry and Roos (2012) used fractional water sorption method in determining WSI of lactose by mixing lactose with maltodextrin at different ratios.

1.1.4. WSI Models

Water in food could be found as a "free water" at high a_w that attach to food solid by capillary adsorption (the heat of sorption is equal to evaporative latent heat of water at corresponding temperature) and "bound water" through molecular adsorption mechanism (Figura and Teixeira, 2007). At low water activity, water adhere through molecular attraction such as H-bond and Van de Waals attraction and the increasing number of ionic or polar type molecules resulting in more water "bounded" through this mechanism (Figura and Teixeira, 2007). In addition, Ghorab et al. (2014) stated the various interaction of water with solid through surface adsorption, capillary condensation, and adsorption into bulk/solid matric, crystal formation and deliquescence.

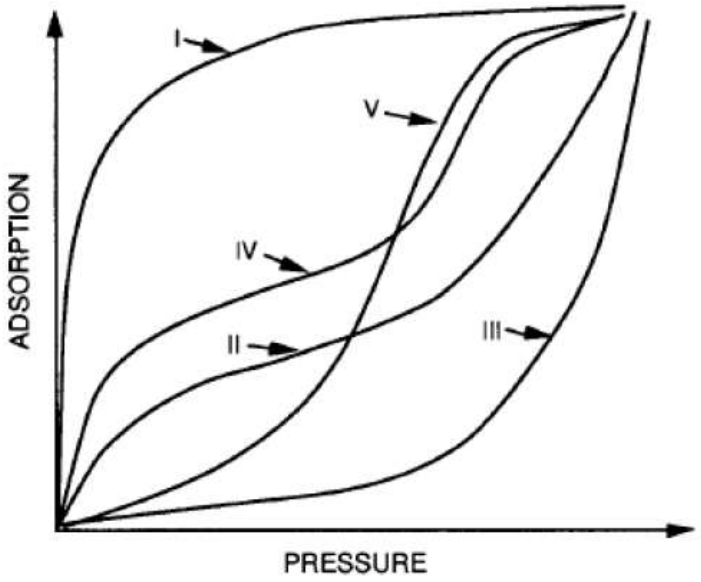


Fig. 1.1. Five WSI types of Brunauer Classification (Source: Roos, 1995).

There are five WSI sorption models based on Brunauer classification (Roos, 1995). The five WSI models could be seen in **Fig. 1.1.** Type I WSI corresponds to porous solid material with finite volume of voids showing saturation water sorption at high a_w (Langmuir isotherm), while type II WSI is owned by soluble product such as sugar and called as sigmoid Isotherm (Mathlouthi and Roge, 2003, Bhandari and Adhikari, 2008). Type III is for material above its corresponding glass transition temperature, type IV is for material with swell able hydrophilic properties and type V is a combination of type II and III for material such as charcoal (Mathlouthi and Roge, 2003, Bhandari and Adhikari, 2008). An amorphous sugar that crystallize during WSI experiment show broken curve at certain water activity due to water loss as a result of crystallization (Makower and Dye, 1956; Bhandari and Adhikari; 2008 and Potes, Kerry and Roos, 2012).

There are many WSI models involving two or three parameters and most of them are empirical and just a few have a theoretical background and explanation (Rizvi, 2005; Bhandari and Adhikari, 2008). Two WSI models, BET (Brunauer, Emmet

and Teller) and GAB (Guggenheim, Andersen and de Boer), are most commonly used and the models are semi-empirical with parameters having meaning (Chirife and Fontana, 2007). The two models are

$$X = \frac{a_w X_m}{(1-a_w)(1+(c-1)a_w)} \quad \text{(BET equation)}$$

$$X = \frac{CKa_w X_m}{(1-ka_w)(1+K(C-1)a_w)} \quad \text{(GAB equation)}$$

Where X = water content (g water/g dry solids)

C, K = Constants related to energy constant

X_m = monolayer water content

BET and GAB parameter could be determined by transformation of the equation and least square method (Kiranoudis et al., 1993).

In BET assumption, water in food is divided as monolayer water and "free water" with its corresponding heat of sorption given by evaporative latent heat of pure water at corresponding temperatures (Figura and Teixeira, 2007). Water below monolayer water content is attached to polar and ionic group site and considered as an optimal water content for stability during storage especially in term of microbial stability (Roos et al., 1998; Rizvi, 2005, Rahman, 2006, Sablani, Kasapis and Rahman, 2007). BET model is valid for a_w range of 0.05 to 0.35-0.5 (Rizvi, 2005). Based on the C value, food with C value 50 – 200 follow type I WSI of Brunauer Classification and C value between of 2 - 50 and less than 2 follow type II and type III, respectively (Rizvi, 2005). The monolayer water content (X_m) obtained from BET model is considered as stable water content and thus used as desired final water content in drying of foods (Welti-Chanes et al., 2007). Below X_m, the energy to remove water from system needs high amount energy (Q_{st}) and a drying process should be stopped when X_m reached otherwise the drying process is not efficient anymore (Welti-Chanes et al., 2007).

GAB model is an extension of BET model and the model could cover wider a_w range up to a_w 0.9 (Rizvi, 2005). The model is chosen as formal WSI model by European Project COST 90 on physical properties of Food (Rizvi, 2005). In this assumption, water

above X_m attaches as multi-layer whose heat of sorption is higher than the evaporative latent heat of pure water and at higher water activity, water would act as a pure water (Rizvi, 2005). The constant C and K correspond to energy difference between water molecule in upper layer and in the monolayer and difference energy correspond pure liquid state to upper layer, respectively (Timmermann, Chirife, Iglesias, 2001).

In addition of BET monolayer water content (X_m), another WSI related properties, hygroscopicity, is also used as indicator of food stability. Hygroscopicity is defined as the final equilibrium water content of sample after exposing over 75 % RH (saturated NaCl) (Jaya and Das, 2004, Shi, Fang and Bhandari, 2013, Vidovic et al., 2014) or the linear slope of curve that correlate water activity and water content at certain a_w range (Figura and Teixeira, 2007). Hygroscopicity is affected and related to the porosity or amorphous structure in samples (Vidovic et al., 2014). Samples with more amorphous structure tend to be more hygroscopic than the lower amorphous structure (Bhandari, 2013). Hygroscopicity of samples depends on its corresponding anhydrous solid glass transition temperature, with the lower the T_g, the more hygroscopic samples are (Bhandari and Howes, 1999). Increasing maltodextrin as filler in sugar-rich powder decreases the hygroscopicity of samples due to the increasing of the T_g (Vidovic et al., 2014).

In addition to R square value, the relative percentage square (%RMS) are also used to evaluate the goodness of fit of the models (Rizvi, 2005).

$$\%RMS = 100\left\{\frac{\sum_1^N \left(X_i - X_i^* / X_i\right)^2}{N}\right\}^{\frac{1}{2}}$$

Where: X_i = experimental water content (g water/ g dry solids)

X_i^* = BET or GAB calculated water content (g water/ g dry solid)

N = number of data

If the %RMS value is less than 10, then the BET or GAB model is considered good as WSI model of samples (Rizvi, 2005).

1.1.5. Static and Dynamic Dew Point Isotherm

Conventional WSI used gravimetric/static method which involved storage of a series of samples at different desiccators with various water activities (integration method) (Rizvi, 2005). Dynamic water sorption follows a differential method (Rizvi, 2005). There are two dynamic WSI, dynamic vapor sorption (DVS) and dynamic dew point isotherm (DDI) methods (Ghorab et al., 2014). In DVS, principally the method has more similarities to static method in terms of equilibrium requirement between samples and their surrounding at each water activity. The WSI data from DVS method are comparable to static method (Ghorab et al., 2014)

In contrast to DVS, DDI method does not need equilibrium conditions (Li, 2010; Allan and Mauer, 2015). In DDI method, a small amount of sample is put in a pan at air flow with high/low relative humidity (depends on adsorption or desorption direction) passed over the sample, then the sample will adsorb/desorb water during the process and at certain interval time, water activity above sample and sample weight are recorded then the process continues until reaching the set condition (Decagon, 2014). More number of data is collected in DDI method than in the conventional method, however the GAB and BET parameter could not be calculated from the data due to different principle to conventional static method (Schmidt and Lee, 2012). The higher number of data set in DDI method could increase resolution of DDI curve and this is important for the study of water sorption related properties (Carter and Schmidt, 2012). The DDI data are used to evaluate the water sorption related properties such as determining deliquescent point (Lipasek, Taylor and Mauer, 2011; Lipasek et al., 2012 and Ghorab et al., 2014,) and critical water activity (Li, 2010, Carter and Schmidt, 2012). Critical water activity (Ca_w) and critical water content are

water activity and water content whose corresponding glass transition temperature equals to ambient temperature (25 °C) (Roos, 1995, Roos and Drusch, 2015).

In DDI curve, critical water activity is characterized by the significant increase of water sorption by a food system due to state transition from glassy to rubbery state (Yu et al., 2008; Yuan, Carter and Schmidt, 2011; Carter, Schmidt, 2012). The critical water activity was determined by firstly smoothing the DDI data and water activity where a peak from second derivation of DDI data refers to the critical water activity (Yu et al., 2008; Yuan, Carter and Schmidt, 2011; Carter, Schmidt, 2012). The comparison of critical water activity obtained from DDI method and thermal method was compared and showed a good agreement (Carter and Schmidt, 2012). Deliquescent is first order water induced temperature dependent phase transition from crystalline solid to saturated liquid (Lipasek et al., 2012). DDI method showed the good result and comparable deliquescent point of some crystalline materials compared to other methods (Lipasek et al., 2011, Lipasek et al., 2012, Schmidt and Lee, 2012). Romani et al (2015) used DDI data to explain biscuit water sorption curve changed from J-shape to more sigmoid curve due to structural changes of biscuit during storage.

1.2. Glass Transition Temperature

Since 1980, polymer science approach has been used in food science (Slade and Levine, 1991). Some food components are polymers like carbohydrates (starch) and proteins. The polymer science approach, focuses on the importance of glass transition temperature as a key parameter that determines the properties of food during processing and storage (Slade and Levine, 1991). The role of water in glass transition approach is based on dynamic aspect of water mobility while in water activity approach, it focuses on the thermodynamic aspect of energy equilibrium (Muhtaseb, Mc Minn and Magee, 2002). Glass transition temperature and water activity have been used together to assess and control food properties during

processing, handling and storing (Roos, 2002). Food itself is a complex system that is composed of a mixture components that might be thermodynamically stable (such as crystal) or non-thermodynamically non-equilibrium amorphous state (Roos, 1995). Water is distributed in food non-uniformly and affected by some factors like composition, amorphous or crystalline structure and presence of microscopic capillaries (Slade and Levine, 1991).

Glass transition is a reversible state transition of amorphous materials between a glassy solid and super cooled liquid (rubbery state) (Roos, 2002, Roos, 2010). Amorphous states are comprised of glassy state, glass transition temperature range, rubbery plate region, rubbery flow region and liquid flow regions (Roos, 1995). Glassy materials are characterized by a very high viscosity (> 10^{12} Pa.s), corresponding structural relaxation times of more than 100 s, transparent appearance and brittle structure (Roos, 1995; Roos and Drusch, 2015). Glassy solid and rubbery states are not in equilibrium even though in the glassy state, the molecular mobility is restricted to short range vibrational and rotational motion (Liu, Bhandari and Zhou, 2006). Molecular mobility in rubbery state is more free where long range translational and rotational motions of molecules occur (Liu, Bhandari and Zhou, 2006).

Some properties are affected by the transition from glassy to rubbery state including the increasing of specific volume, coefficient of thermal expansion, specific heat, enthalpy, entropy, viscosity and decreasing of mechanical modulus (Roos and Drusch, 2015). Glass formation in food can be obtained by rapid cooling from melting process such as in hard sugar candy processing and rapid removal of water in drying, baking, evaporation, and freezing process (Roos, 1995, Roos and Drusch, 2015).

1.2.1. Water Plasticization

Differential scanning calorimetry (DSC) is the most common method to determine glass transition temperatures (T_g) of food and other systems (Roos, 1995; Roos and Drusch, 2015). The T_g is indicated by a step change in the heat capacity

(Roos, 1995). Other techniques are also used for the measurement of T_g such as thermal mechanical analysis measuring dimensional change, dynamic mechanical analysis measure mechanical modulus, while dielectric analysis and dynamic dew point isotherm measuring dielectric loss and moisture sorption properties, respectively (Carter and Schmidt, 2012). Determination of T_g is influenced by internal factors such as sample composition and thermal history and external factors such as heating and cooling rate (Slade and Levine, 1991). The effect of carbohydrates on T_g of dried powder is more significant than fat and protein, while the increasing heating rate would increase T_g (Roos, 1995; Roos and Drusch, 2015).

Some consideration should be taken out in T_g determination. The preparation of sample is needed to determine T_g of anhydrous sample. The sample could be prepared by drying in vacuum oven at 60 °C for 24 hours or store the sample in P_2O_5 for a week (Liu, Bhandari and Zhou, 2006). To erase thermal history of sample or to remove a peak interfering T_g determination, the sample should be heated until reaching temperature higher than its corresponding T_g by 40 °C or higher its melting point (Liu, Bhandari and Zhou, 2006). The T_g of sample should be stated with two parameters, onset or mid-point temperature and glass transition temperature ranges (Liu, Bhandari and Zhou, 2006). Heating and cooling rate used during measurement should also be stated (Liu, Bhandari and Zhou, 2006).

In addition to temperature, water acts as plasticizer to food that decreases its T_g (Slade and Levine, 1991; Roos, 1995; Roos and Drusch, 2015). The relationship between water content and T_g is modelled by Gordon-Taylor equation

$$T_g = \frac{X_s T_{g,s} + K X_w T_{g,w}}{X_s + K X_w}$$

Where: $T_{g,s}$, K = constants

X_w = fraction weight of water

X_s = fraction weight of food solid

$T_{g,s}$ = glass transition temperature of anhydrous food solid

$T_{g,w}$ = glass transition temperature of water (-135 °C) (Roos, 1995).

The assumption of Gordon-Taylor equation is ideal volume mixing where two components are miscible and their volumes are additives (Liu, Bhandari and Zhou, 2006). The value of K should be valid for the temperature range used and should not be extrapolated to wider range in state diagram (Cabrera and Schmidt, 2015).

Water plasticization properties are used in building state diagrams of food. State diagram is a map of different phases and states of a substance as a function of water content (Roos, 1995; Rahman, 2006; Guizani et al., 2010; Roos and Drusch, 2015). The relationship between water plasticization properties and water sorption is used to determine critical water activity and critical water content (Ca_w and CX) (Roos, 1995, Roos and Drusch, 2015). Low hygroscopic food products usually have high critical water acitivity while low Ca_w for may apply to hygroscopic food powder (Roos, 1995, Roos et al., 1998, Roos and Drusch, 2015). Physical or mechanical properties of low water content products changed drastically when their corresponding critical water activity and water content were reached (Welti-Chanes et al., 2007). Those changes are caused by increasing of water mobility that is associated with glassy to rubbery transition that promote physical and chemical changes (Welti-Chanes et al., 2007). For sugar-rich powder, these changes involve collapse phenomena such as stickiness, crystallization, agglomeration and caking (Roos, 1995). Thus sugar-rich powders must be stored below its corresponding glass transition temperature and critical water activity and low water vapor permeability packageing material should be used to keep the product stable (Welti-Chanes et al., 2007).

Amorphous food below T_g is considered as metastable and the difference ($T-T_g$) is used as an indicator for stability (Roos, 1995; Roos and Drusch, 2015). Glass transition temperature is a good indicator correlated to phenomena occurring in food handling and storage due to effect of water sorption and temperature such as collapse in freeze-drying, stickiness in spray drying, crystallization, agglomeration and caking of amorphous food component during storage, crispness of extruded product and

diffusivity of volatile component in food system (Roos et al., 1998; Bhandari and Howes, 1999; Roos, 2010). However the glass transition approach is not successful in some cases. Le Meste et al. (2002) reported that pigment oxidation in glassy matrix and enzymatic reaction still occurred at high rate and temperature itself rather than the difference ($T-T_g$) controlled non-enzymatic browning reaction.

1.2.2. Enthalpy Relaxation

In addition to glass transition, enthalpy relaxation is another important property of amorphous solids (Liu, Bhandari and Zhou, 2006). Glassy state is a metastable non equilibrium state where molecular relaxations still are possible in order to reach more stable state whose lower energy state and as a result decreasing its corresponding enthalpy (energy lost) (Liu, Bhandari and Zhou, 2006). As shown in **Fig.1.2.** When amorphous glassy solid is stored under its T_g, the enthalpy will decrease and needs to be recovered during heating scan in DSC measurement (Liu, Bhandari and Zhou, 2006, Syamaladevi et al., 2012). This phenomenon is called enthalpy relaxation or structural ageing (Liu, Bhandari and Zhou, 2006). The recovered energy in enthalpy relaxation is related to molecular mobility of the system in amorphous glassy region (Syamaladevi, Sablani and Swanson, 2010).

Enthalpy relaxation is a reversible phenomenon (Syamaladevi et al., 2012). Thermal history of a sample and time scale of observation would determine endothermic or exothermic nature of the enthalpy relaxation process (Roos, 1995). Enthalpy relaxation is related to $\beta \; or \; \gamma$ relaxation which involves short range motion of specific chemical groups such as the side group branches in polymer chains (Liu, Bhandari and Zhou, 2006; Roos, 2010). The γ relaxation occurs at lower temperature and is much weaker than β relaxation (Liu, Bhandari and Zhou, 2006). Enthalpy relaxation would result in more compact molecular organization and strengthening of its interaction (Kim et al., 2003). Enthalpy relaxation can explain some physical properties such as increased rigidity and brittleness and decreased dimension and

transport properties (Kim et al., 2003). Some macroscopic properties of glassy materials change during physical ageing like volume, enthalpy, refractive index, electrical conductivity and viscosity (Syamaladevi et al., 2012). Kim et al. (2003) reported the decreasing of water vapor permeability of glassy starch as stored under its corresponding T_g

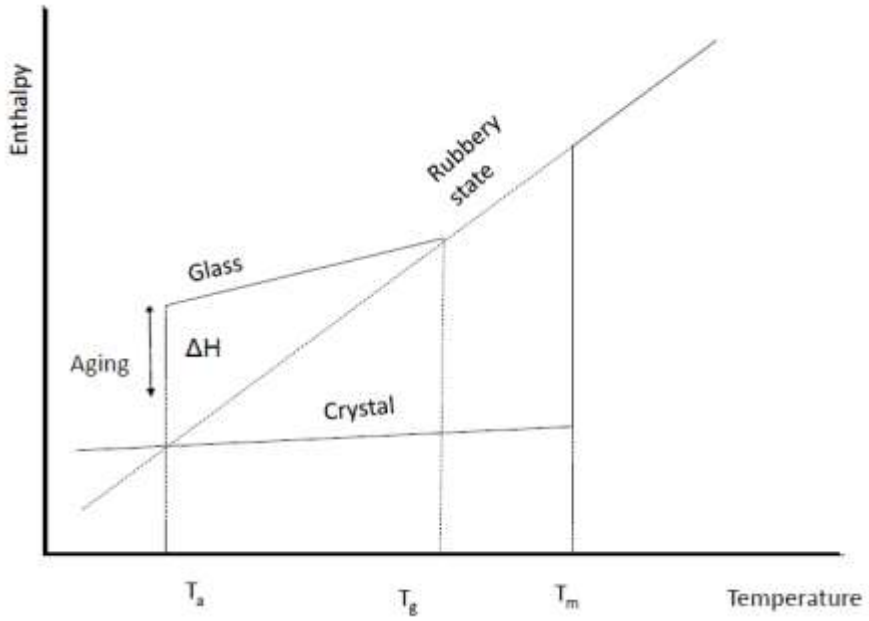


Fig. 1.2. Schematic diagram of enthalpy relaxation.

Enthalpy relaxation could be studied by storing a sample below its glass transition temperature (physical ageing) or by changing cooling and reheating scan rate in T_g determination by DSC (Roos, 1995). Physical ageing of sample could be done in two ways, firstly by storing sample below its corresponding T_g and then varying storing temperatures (temperature annealing) and secondly by storing at same storing/ageing temperature but below its corresponding water activity and stored at different water activities (water annealing) (Descamps, Palzar and Zuercher, 2009). Temperature is more efficient than water in enhancing relaxation of maltodextrin below T_g (Descamps, Palzar and Zuercher, 2009). In physical ageing experiment, any

previous thermal treatment history should be erased by heating an amorphous sample to temperature higher than its T_g by 30 °C and thermal decomposition of a sample should be avoided (Liu, Bhandari and Zhou, 2006).

Enthalpy relaxation kinetics was done by storing the amorphous glass food below its T_g at various temperatures and ageing times (Kawai et al., 2005; Haque, Kawai and Suzuki, 2006; Liu, Bhandari and Zhou, 2016). Kawai et al. (2005) used two equations in correlating enthalpy relaxation and ageing time, KWW (Kohlrausch-Williams-Watt) and Adam-Gibbs model.

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

Where, $\Delta H_{\infty} = \Delta C_p(T_g - T_a)$

$$\frac{d[\Delta H_{\infty} - \Delta H_{relax}]}{dt} = \frac{1}{t^{eff}(t)}[\Delta H_{\infty} - \Delta H_{relax}]$$ (Adam-Gibbs model)

And $lnt^{eff}(t) = lnt^{eff}_{\infty} + B\left[[\Delta H_{\infty} - \Delta H_{relax}]\right]$

Where

τ^{KWW} = constant is related to mean enthalpy relaxation time

β = constant is related to the width of the relaxation time distribution spectrum ($0 \leq \beta < 1$)

$\Delta H_{relax} = H_i - H_t$, the difference between enthalpy at the beginning of ageing and after ageing for t time at temperature, T_a.

$\Delta H_{\infty} = H_i - H_{\infty}$, the difference between enthalpy at the beginning of ageing time and after enthalpy reaching the equilibrium (H_{∞}) which enthalpy value on the extrapolated equilibrium liquid curve at T_a (Kawai, et al., 2005).

$\tau^{eff}(t)$ = effective relaxation time and its value depend on ageing time

B, τ^{eff}_{∞} = constants

KWW model was the most common model used in studying enthalpy relaxation in a polymer and small saccharides (Kim et al., 2003; Syamaladevi, Sablani and Swanson, 2010). The β value refer to distribution of molecular motion under glassy region and the smaller the β value, the more the distribution of molecular motion deviates from a single exponential behavior. The individual component in amorphous structure have their own relaxation time and the constant, τ^{KWW} obtained from KWW model refers to the mean relaxation time of whole amorphous system (Kawai et al., 2005; Syamaladevi, Sablani and Swanson, 2010). Enthalpy relaxation in large molecular weight food such as starch and protein-based food are much smaller compared to the small molecular weight components such as sugar (Syamaladevi, Sablani and Swanson, 2010). Enthalpy relaxation is measured as endothermic peak following T_g curve and its value increases when ageing time increases (Kim et al., 2003). The enthalpy relaxation decreases when amorphous glassy solid is stored far below its T_g which means its molecular mobility was much more reduced (Syamaladevi, Sablani and Swanson, 2010). Thus it is suggested to store a glassy amorphous solid at a temperature below its T_g by 50 °C to maintain their structural and macroscopic stability (Hancock, Shamblin and Zografi, 1995). The Adam-Gibbs model approach is based on the decreasing of configurational entropy of a system under glassy region with ageing time (Kawai et al., 2005). The value of $\tau^{eff}_{0 \text{ and }} \tau^{eff}_{\infty}$ refer to relaxation time of minimum and maximum of amorphous glass solid system (Kawai et al., 2005).

Enthalpy relaxation studied by varying heating rates of scanning was done by using the Tool-Narayanaswamy-Moynihan equation (TNM), however the application of the equation is more difficult than the method in physical ageing (Kawai et al., 2005). Liu, Bhandari and Zhou (2006) explained that at constant ageing time, the higher the heating rate, the higher the T_g, while at constant heating rate, increasing ageing time would increase T_g.

Enthalpy relaxation time depend on temperature and its dependency was well explained by Arrhenius equation (Shamblin et al., 1999; Kawai et al., 2005). Kawai et al (2005) reported the higher activation energy of glucose enthalpy relaxation than the activation energy of β relaxation of glucose and they suggested that the high value of activation energy related to molecular mobility in the glassy state (translational diffusion) rather than local mobility such as in β relaxation. Trehalose was reported having highest enthalpy relaxation time related activation energy among other sugars (glucose, maltose and sucrose) which explained trehalose is the most stable glass among other sugar under glassy region (Kawai et al., 2005).

1.3. Sugar-Rich Food Powder

Food powder is classified into sticky and non-sticky powder (Jaysundera et al., 2011). Sticky powder is the powder produced from sugar-rich food such as honey, fruit juice, and vegetable extract (Jayasundera et al., 2011). The composition of main sugar of some fruit juices is presented in Table 1.3. Fructose is the highest amount of sugar found in almost all fruit juices except juices of prunes, nectarine, peach and cherry (Gorsel et al., 1992, Karadeniz and Eksi, 2002). Sucrose is the main sugar composition of juices of prune, nectarine and prune while cherry juice is composed of highest amount of glucose (Gorsel et al., 1992). The acid content in fruit juice is in the range 4-6 g/l (Gorsel et al., 1992) and the most common acids found are citric acid, ascorbic acid, malic acid, quinic acid and tartaric acid (Gorsel et al., 1992). Malic acid is the common acid found in fruit juices in highest amount (Gorsel et al., 1992).

Table 1.3. Main sugar composition in selected fruit juices.

Juice	Composition (g/l)		
	Glucose	Fructose	Sucrose
Apple [a]	9.3-32.2	66.1-96.0	8.5-55.1
Apple [b]	17.1-25.7	43.7-62.5	6.9-9.5
Prunes [b]	23.5-63.5	3.0-55.0	54.0-68.0
Cherry [b]	66.9-83.1	60.9-75.7	0.6-1.0
Grape [b]	85.6-106.2	94.9-115.7	2.1-3.7
Nectarine [b]	8.1-8.9	5.7-6.1	76.5-91.1
Peach [b]	6.1-7.3	4.8-5.0	51.6-62.0
Pear [b]	13.2-20.4	65.6-96.8	4.3-6.7
Plum [b]	31.0-54.6	35.6-61.6	1.5-8.7
Kiwi fruit [b]	40.9-97.9	48.1-116.7	10.9-25.3
Strawberry [b]	16.4-19.6	19.9-23.7	1.1-2.3

Notes: [a] Karadeniz and Eksi, 2002; [b] Gorsel et al., 1992

High sugar and acid foods have very low glass transition temperature that could cause stickiness problem during drying (Bhandari and Howes, 1999). Adhikari and Bhandari (2009) added that sugar rich food such as fruit juices and honey have very high fructose and acid content that make it difficult to dry solely (Adhikari and Bhandari, 2009). The T_g of some monosaccharides and disaccharides and acids are presented in Table 1.4. Filler or drying aids with high molecular weight to increase T_g and special drying methods are needed to produce sugar-rich food powder (Roos, 1995; Woo and Bhandari, 2013; Roos and Drusch, 2015).

Table 1.4. Glass transition temperature of some sugars and acids.

Components	T_g (°C)	References
Fructose	5	Roos, 1995
Glucose	31	
Galactose	30	
Sucrose	62	
Maltose	87	
Lactose	101	
Lactic acid	-60	Intipunya and Bhandari, 2010
Malic acid	-16	
Citric acid	12	
Tartaric acid	18	

Sugar-rich food powder usually showed type II WSI of Brunauer classification (Moraga, Martinez and Chiralt, 2006; Sablani and Kasapis, 2007; Syamaldevi, Sablani and Swanson, 2010; Mosquera, Moraga, Navaretta, 2012). Sugar-rich food powder have critical water activity and critical water content lower than the water activity at its corresponding equilibrium BET monolayer water content (Rahman, 2006; Moraga, Martinez and Chiralt, 2006; Sablani, Kasapis, Rahman, 2007; Syamaladevi, Sablani and Swanson, 2010; Mosquera, Moraga, Navaretta, 2012). Due to high sugar content, sugar rich food powder is hygroscopic in nature and this make difficult in handling and storing.

1.3.1. Filler or Drying Aid Materials

Several factors needs to consider in the use of filler or drying aid materials. Those factors are compatibility with core material and external environment, safety, cost effectiveness, good encapsulation ability and compliance to the specification of the final product (Anandharamakrishnan and Ishwarya, 2015). The use of filler or drying aid would improve drying rate, prevent stickiness, reduce hygroscopicity,

maintain flowability, encapsulate flavor or aroma and maintain quality of powder during storage (Wang and Zhou, 2012). Carbohydrate such as maltodextrin and gum Arabic and proteins (whey protein isolate/ WPI, casein and gelatin) are used as a filler or drying aid for sugar-rich food powder production (Anandharamakrishnan and Ishwarya, 2015).

Maltodextrin is a common drying aid for sugar-rich food powder due to its efficiency in reducing stickiness (Roos, 1995; Anandharamakrishnan and Ishwarya, 2015; Roos and Drusch, 2015). Maltodextrin is a starch hydrolysis product by acid or enzyme method (Linden and Lorient, 1999). The hydrolysis level is characterized by its corresponding dextrose equivalent (DE), where the higher the DE value, the lower the molecular weight of maltodextrin (Linden and Lorient, 1999). Thus the higher the DE value of maltodextrin, the lower the glass transition temperature and the correlation of DE value and its corresponding T_g is described by equation.

T_g = -1.4(DE) + 449.5 (Kelvin) (Roos, 1995, Roos, 2002).

Maltodextrin is a mixture of carbohydrates and even at the same DE value could have different composition (Linden and Lorient, 1999). Maltodextrin is a safe food ingredient and classified as GRASS (Generally Recognized as Safe) (Hobbs, 2009). Maltodextrin with different DE also showed different water sorption properties. At lower relative humidity (RH < 40%), maltodextrins with lower DE had higher water sorption than the higher DE and at higher RH, reverse phenomenon occured (Ghorab et al., 2014).

The mechanism of maltodextrin to reduce stickiness in sugar-rich powder production is by increasing its T_g and as a result increasing anhydrous solid T_g and finally reducing stickiness (Fang and Bhandari, 2012; Shi, Fang and Bhandari, 2013). Maltodextrin at ratio more than 50 % would affect T_g significantly (Roos, 1995, Roos and Drusch, 2015). Maltodextrin ratio impact to powder recovery and high ratio would increase the recovery (Shi, Fang and Bhandari, 2013). Potes, Kerry and Roos (2012) reported the high ratio of maltodextrin and the high DE value contributed to

reduced crystallization of lactose during storage. The ratio of maltodextrin use depends on the material being dried and also the drying method. At same maltodextrin ratio, vacuum drying produced higher yield (powder recovery) than that produced by spray drying method (Nurhadi et al., 2012).

Gum Arabic is a glycan exudate of certain ligneous plants (Linden and Lorient, 1999). Gum Arabic is a highly branched and complex polymers with units of D-galactose, L-arabinose and minor portion of 4-o-methyl-D-Glucuronate and L-rhamnose (Anandharakrishnan and Ishwarya, 2015). Gum Arabic also contains small portion of protein (1-2 %) which makes it having emulsification properties (Anandharakrishnan and Ishwarya, 2015). The high price of gum Arabic and its variability due to various natural source limit its use (Anandharakrishnan and Ishwarya, 2015). Mechanism of gum Arabic is considered similar to maltodextrin (Nurhadi et al., 2012, Mosquera, Moraga and Navarreta, 2012). Gum Arabic at the same ratio as maltodextrin gave higher T_g of anhydrous strawberry solids and as a result higher critical water activity (Mosquera, Moraga and Navarreta, 2012).

WPI is produced from a byproduct of cheese production which contains of 4 key protein fractions of α-lactalbumin, β-lactoglobulin, immunoglobulins and serum albumin as a minor protein fraction (Anandharakrishnan and Ishwarya, 2015). WPI is a protein with globular structure and denatured by heat and isoelectric point at pH 5 decreasing its solubility (Anandharakrishnan and Ishwarya, 2015). Protein as a filler or drying aid has emulsification properties and its mechanism involving the migration of protein molecules to droplet air-interface (in spray drying process) to form protein-rich film and as a result reducing stickiness (Adhikari et al., 2009, Fang and Bhandari, 2012). The use of protein as filler material depends on sample being dried. Adhikari et al (2009) reported the use of higher ratio of sodium caseinate at 30 % (solid/solid) in spray drying of fructose with lower T_g than sucrose that needed lower quantity sodium caseinate at 0.5 %.

1.3.2. Drying Method

Based on pressure and temperature used, drying method could be classified as oven drying, vacuum drying and freeze drying (Fig. 1.3). In oven drying, drying condition is done at ambient pressure while in vacuum drying, the drying process is occurred at pressure lower than ambient pressure (Fig. 1.3.). In the both drying method, water is removed by evaporation (liquid to vapor) while in freeze drying, water is removed from material by sublimation (ice to vapor). Sugar-rich food powder could be in purely amorphous, purely crystalline or partially amorphous structures (Bhandari, 2013). Drying method would affect the structure of resultant product. Three types of drying methods in producing sugar-rich powder are spray drying, freeze-drying and vacuum drying.

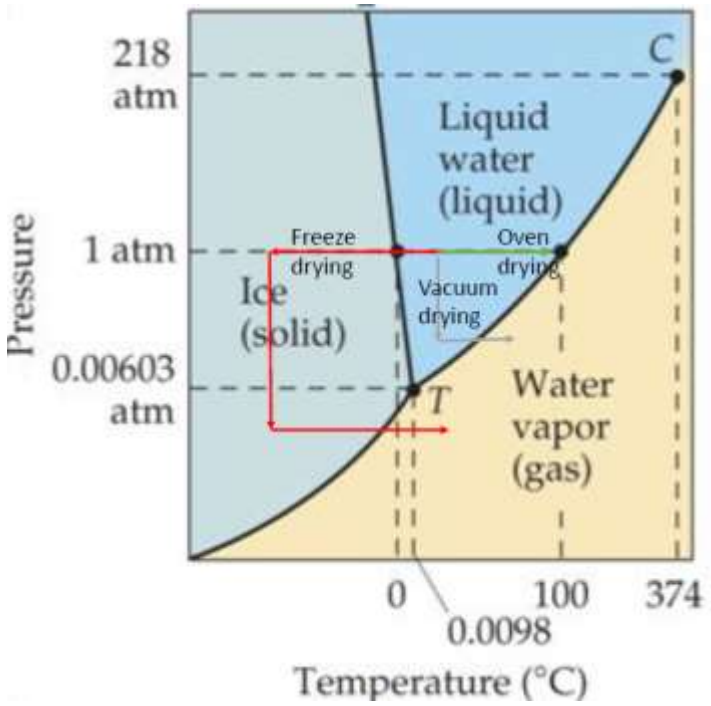


Fig. 1.3. The triple point diagram of water and different drying method (Source: http://s3.amazonaws.com/answer-board-image/ce08287e-469e-4431-a502-4886997b60e2.png).

Spray drying is the major operation unit in producing powder recently (Bhandari, Patel and Chen, 2008, Roos and Drusch, 2015). In spray drying of sugar-rich food, the process of water evaporation from a tiny droplet of samples is very fast thus

not allowing nucleation and crystallization of solutes (Bhandari, Patel and Chen, 2008). By adjusting drying process condition, partially amorphous product with various amorphous content could be obtained (Chio, Langrish and Braham, 2008; Wang and Langrish, 2009; Jayasundera et al., 2011).

The principle of successful spray drying process is rapid removal of water so particle surface can approach its corresponding T_g before colliding with other particles or drier walls (Roos, 2002) or at least the particle surface droplet temperature not more than 20 °C of its T_g to avoid stickiness problem (Bhandari and Howes, 1999, Roos, 2002). Successful spray drying is indicated with product recovery more than 50 % from total feed solid (Bhandari and Howes, 1999). Total solid concentration of feeding solution in spray drying process is varied in the range of 20 – 50 % (Bhandari, Patel and Chen, 2008). The solid feed concentration depend on the viscosity, type of atomizer and final product requirement where low solid content would produce smaller size particle with poor reconstitution properties (Bhandari, Patel and Chen, 2008).

There are four main units in spray drying systems; drying gas supply and heating system, atomizer system, drying chamber and powder separator (Bhandari, Patel and Chen, 2008). Spray drying could be considered as a convective adiabatic drying which means the difference between inlet and outlet temperature determines the amount of water removed from samples upon drying (Bhandari, Patel and Chen, 2008). The common outlet temperature in spray drying is usually over the range of 60 – 80 °C (Bhandari, Patel and Chen, 2008). This means for successful spray drying process, the glass transition temperature of droplet surface being dried should be higher than 40 - 60 °C in order to avoid stickiness when approaching drier walls.

Freeze-drying is the most energy intensive operation in producing sugar rich food powder but the product resulted is considered having superior quality (Bhandari, Patel and Chen, 2008). The principle of freeze-drying is sublimation (transformation from ice solid phase into vapor phase) that occurs below triple point (0.01 °C, 612 Pa)

(Ratti, 2008). The sugar-rich food resulted from freeze-drying is considered as purely amorphous structure (Roos, 1995). The reason is during sublimation process, frozen water is removed from the samples and the solute solid in glassy state with limited molecular mobility to induce crystallization (Roos, 1995, Roos and Drusch, 2015).

The water removal process in freeze-drying involves two processes, sublimation and desorption (Ratti, 2008, Ratti, 2013). In sublimation, the phase transformation from solid ice to vapor phase may occur at constant temperature and the temperature should be lower than that maximally freeze concentrated solids glass transition temperature (T_g') to prevent collapse (Roos, 1995; Ratti, 2008). After all ice is removed by sublimation, remaining water is removed by desorption and upon desorption the product temperature increases to ambient temperature or set heating temperature (Ratti, 2008, Ratti, 2013). The product temperature should be less than its T_g to prevent collapse (Ratti, 2008, Ratti, 2013). Collapse affects drying due to reduced drying rate with effect on quality of dried product such as resultant poor aroma retention, poor rehydration and uneven dryness (Bhandari and Howes, 1999, Roos, 1995, Roos and Drusch 2016). Addition of high molecular weight drying aid or filler would prevent collapse due to increasing both of T_g' and T_g (Roos and Drusch, 2015).

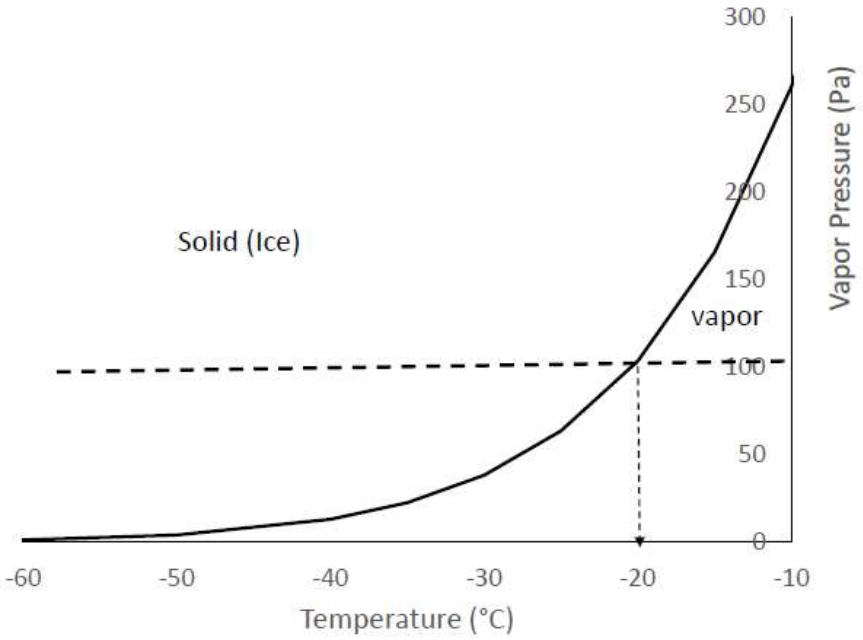


Fig. 1.4. The vapor pressure and temperature during equilibrium condition between ice (water solid phase) and vapor (gas phase) of water.

The common sublimation process is done at a pressure of 1 mbar (100 Pa or 0.1 kPa) lower which corresponds to sublimation at -20 °C or lower (**Fig. 1.4**.)(Ratti, 2008, Ratti, 2013). For a product with very low T_g, sublimation needs a lower temperature achieved at lower pressures (Ratti, 2008, Ratti, 2013). The product obtained from freeze-drying usually has high porosity which may show higher water sorption than the dried materials produced by other drying methods (Ratii, 2008, Ratti, 2013). Haque and Roos (2005) reported similar crystallization behavior of lactose obtained using freeze-drying and spray drying.

Vacuum drying refers to drying process below ambient pressure condition. Vacuum drying is suitable to dry heat and oxygen sensitive products. At normal conditions water will boil at 100 °C. Boiling of water will occur if the vapor pressure is equal to ambient pressure (Toledo, 2007). At lower pressure water will boil at lower temperature (**Fig. 1.5**.). As shown in **Fig. 1.5**, at 100 °C, the water vapor pressure is

equal to 100 kPa which is also the normal ambient pressure and as a result water will boil.

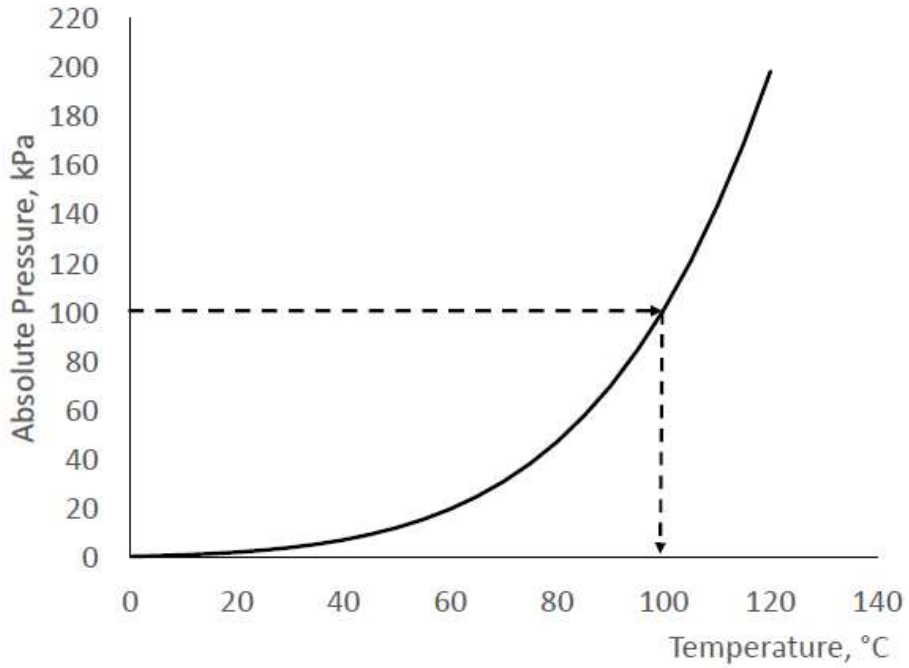


Fig. 1.5. The water vapor pressure at different temperatures (Data from Toledo, 2007).

The common pressure used in vacuum drying is 1 – 10 kPa which corresponds to 10 – 50 °C for water boiling (Toledo, 2007; Land, 2012), However the drying temperature may be higher than the temperature range and as a result excessive boiling occurs (Land, 2012). Excess boiling would promote frothy or puffed structural appearance which results in increasing heat and mass transfer rate due to high surface area to volume ratio (Land, 2012). As a result at same temperature, drying rate in vacuum drying is higher than normal drying at ambient pressure condition. Vacuum drying is often combined to other methods to increase drying rate such as reported by Cui et al. (2008) who combined vacuum drying and microwave heating system in producing honey powder. Grinding operation is needed to produce powder from freeze-drying and vacuum drying techniques. During grinding, heat might be released and might plasticize amorphous samples or cause melting of crystalline structure to

produce amorphous structure. Vidovic et al. (2014) reported that grinding leads to the formation of amorphous region on the surface of crystalline sucrose.

1.3.3. Sugar-Rich Food Powder Stability

Plasticization is a major factor that leads to instability of sugar-rich food powder. Plasticization could be caused by temperature or water (Roos and Drusch, 2015). Plasticization promotes transformation of amorphous structure in the powder from glassy to rubbery state. The plasticization of glassy amorphous solids in sugar-rich powders results in time-dependent physical changes such as collapse phenomena (Roos and Drusch, 2015). Those phenomena include stickiness and caking of the powder, crystallization of amorphous material in the powder and structural collapse (Roos, 1995, Roos and Drusch, 2015). The physical changes of the powder lead to initially free-flowing powder to become more difficult to handle and flow.

Water acts as a plasticizer in food and decreases T_g (Roos, 1995, Roos and Drusch, 2015). Water plasticization is material dependent. The same amount of water might result in different level of plasticization in different materials (Sablani, Kasapis and Rahman, 2007). There was more plasticizing effects in amorphous structures of sugar-rich powder than low-sugar powders although the presence of small amount of water had little influence on water activity (Sablani, Kasapis and Rahman, 2007). As a result sugar-rich powder had critical water activity (Ca_w) lower than a_w which corresponds to mono layer water content (Sablani, Kasapis and Rahman, 2007; Mosquera, Moraga, Navaretta, 2012). Ca_w was determined by combining Gordon-Taylor equation for water plasticization behaviour and GAB equation for water sorption isotherm behaviour (Roos et al., 1998, Sablani, Kasapis and Rahman, 2007). Increasing ratio of filler material such as maltodextrin and using higher molecular weight material (material with low DE) in sugar-rich powder would increase the value of Ca_w (Roos, 1995, Roos and Drusch, 2015).

Some actions could be done to maintain stability of sugar-rich food powder. Those actions include storing the product at temperatures lower than T_g, using packageing materials with low vapor permeability and using anti-caking agents (Welti-Chanes et al., 2007). Anti-caking agent is a food additive usually added to food powder (up to 2 %) to increase stability and retain free-flowing properties of host material (Barbosa-Canovas et al., 2005). The mechanism of anti-caking involves competing with host powder for water, being physical barrier between particles, increasing glass transition temperature and acting as water protective barrier (Barbosa-Canovas et al., 2005; Msagati, 2013).

1.4. Honey Powder

Honey powder has some advantages over honey liquid in term of easiness in handling, transport and longer stability (Shi, Fang and Bhandari, 2013). Uses of honey powder are many. It can be as a replacer of honey liquid. Honey powder is mixed into dry mixes, seasoning or dry coating (Cui et al., 2008). Tong et al. (2010) reported the use of honey powder in bread processing as a dough improver.

1.4.1. Honey

Honey is a naturally sweet substance produced by bees from plants, secretion of living part of plants and excretion of plant-sucking insect (Chmielewska, 2004). These substances are combined with specific substances and stored until ripen and mature (Chmielewska, 2004, Sahun, 2008). The processing of honey liquid involves separation from honey comb by centrifugal force and gravity, filtering and straining (Cui et al., 2008). Honey is used as a food or ingredients of many manufactured foods such as bakery, confectionery, beverages, spreads, dairy, dressings and sauces, meats, and snacks (Bellik and Iguerouada, 2014). Honey is used as an ingredient for its sweetness, color, flavor and functional properties related to health (Kolayli et al., 2014).

Table 1.5. Composition and Some Properties of Honey.

Composition/Properties	
Water (g/g honey)	0.18[a]; 0.18-0.20[b]; 0.19[c]; 0.18[d]
Glucose (g/g honey)	0.34[a]; 0.32-0.33[b]; 0.33[c]; 0.33[d]
Fructose (g/g honey)	0.38[a]; 0.37-0.38[b]; 0.37[c]; 0.39[d]
Water activity (a_w)	0.59[c]; 0.59[d]
Glass transition temperature (T_g)	-42 °C[c]; -40 °C[d]

Notes: [a] Lupano, 1997, [b]Sahu, 2008, [c] Venir, Spaziani and Maltini, 2010 and [d] Nurhadi et al., 2012.

The composition of honey varies and depends on many factors such as botanical origin and bees type (Kolayli et al., 2014). The chemical composition of honey will affect the physicochemical properties of honey such as viscosity, water activity and color. As can be seen in Table 1.5, more than 85 % of honey solids are mono saccharide sugars, fructose and glucose. The main disaccharide sugars are mainly maltose (up to 3.8 %) and sucrose (up to 1.4 %) (Chmielewska, 2004). Protein content in honey is up to 1 % consisting mainly globular proteins such as enzymes (Invertase and α-amylase and β-amylase) (Chmielewska, 2004). Color of honey is affected by natural pigments or by heating process. The natural pigments found are carotenoids, flavones and anthocyanins (Kolayli et al., 2014). Darker honey is considered to have more antioxidant properties than lighter colored honey (Kolayli et al., 2014). The major minerals found in honey are K, Na, Ca, Mg and Mn and very small amounts of Fe, Zn, Cu and Se (Bellik and Iguerouda, 2014). The pH value of honey is around 3.8-5.0 (Ahmed et al., 2007) and the main acids in honey are citric acid and gluconic acid (Chmielewska, 2004). Aroma of honey is affected by origin of plant source such as methyl anthronilate in citrus honey (Kolayli et al., 2014).

Honey is classified as Newtonian fluid, where the viscosity is independent of shear rate and having the viscosity around 7.7-15.4 Pa s at 21 °C (Sopade et al, 2002).

The increasing temperature will decrease honey viscosity and up to 40 °C, Temperature dependency of viscosity was well described by the WLF (William-Landel-Ferry) model (Sopade et al., 2002).

The high sugar content in honey makes it easy to crystallize and the phenomenon is called granulation. The granulation of honey is due to the formation of glucose monohydrate (Zamora and Chirife, 2006). The tendency of honey to granulate is determined by the high glucose content. The honey with ratio glucose to water more than 2.1 is classified as rapidly granulated honey (Lupano, 1997). Honey with ratio of fructose to glucose less than 1.4 is also classified as rapidly granulated honey (Venir, Spaziani and Maltini, 2010). Granulation of honey is also affected by temperature where temperature around 13-17 °C is considered as optimum temperature for granulation of honey (Chmielewska, 2004 and Venir, Spaziani and Maltini, 2010). The granulation of honey reduces the quality of honey. The impacts of honey granulation are characterized by its difficulty in handling and pouring, subtle haze appearance and increased water activity which makes honey prone to microbial deterioration especially by osmophilic yeasts (Zamora and Chirife, 2006, Gleiter, Horn and Isengard, 2006). Granulation of honey is prevented by storing honey at temperatures higher than 25-40 °C or below -35 °C (Venir, Spaziani and Maltini, 2010). The heating treatment to honey at temperature higher than 40 °C should be avoided because it might damage functional components in honey (Venir, Spaziani and Maltini, 2010). The processing of honey into honey powder is an alternative solution to avoid granulation problem of honey.

1.4.2. Drying of Honey

Honey is sugar rich food that is difficult to dry. As reported in Table 1.5., more than 85 % of honey solids are fructose and glucose. Fructose occurs in a higher amount than glucose with an average ratio of 1.2 to 1 (Ram, 2011). The T_g values of fructose and glucose are very low, 5 and 31 °C, respectively. The pH of honey is also

very low around 5. Water is the third main component of honey after fructose and glucose with a T_g of water is very low, -135 °C (Roos, 1995, Roos and Drusch, 2015). Thus the T_g of honey is very low as given in Table 1.5 and some publications reported T_g for honey at -51.14 to -33.64 °C (Ahmed et al., 2007), -51 to -42 °C (Kantor, Pitsi and Thoen, 1999) and -47.3 to -42.3 °C (Shi, Fang and Bhandari, 2013).

The low T_g of honey will cause stickiness problem during the spray drying process thus drying aids should be used (Shi, Fang and Bhandari, 2013). Shi, Fang and Bhandari (2013) reported the use of maltodextrin, WPI and their combinations in producing honey powder. The level of success of honey powder drying with spray drying method is characterized by the powder yield that should reach more than 50 % (Shi, Fang and Bhandari, 2013). Maltodextrin alone at ratio up to 60 % (solid/solid) and WPI ratio up to 40 % is needed to dry honey powder successfully (Shi, Fang and Bhandari, 2013). The use of maltodextrin could be reduced to 40 % when combined with WPI and the less was the WPI added the less was the powder yield obtained (Shi, Fang and Bhandari, 2013). Nurhadi et al (2012) reported the yield of honey powder of 50 % (per total solid feed solution) when maltodextrin was used at a ratio of 50 % (solid/solid). Maltodextrin allowed to overcome stickiness problem during spray drying of honey by increasing glass transition temperature (Roos, 1995, Roos and Drusch, 2015). WPI acted by not only increasing glass transition temperature but also by migrating into the droplet surface of honey thereby reducing stickiness problem (Shi, Fang and Bhandari, 2013). In order to dry successfully by spray drying, the droplet should dry into glassy state due to rapid evaporation (Roos, 2002) or the difference of temperature between droplet surface and T_g ($T-T_g$) should be less than 20 °C as a critical limit of stickiness (Bhandari and Howes, 1999, Roos, 2010). The higher was the ratio of maltodextrin, the higher was the honey powder yield by spray drying method (Shi, Fang and Bhandari, 2013).

In addition to spray drying method, vacuum drying was also reported to produce honey powder (Sahu, 2008, Cui et al., 2008; Nurhadi et al., 2012,). Cui et al.

(2012) combined microwave and vacuum drying technique to increase drying rate and decrease drying temperature in producing honey powder. The drying condition of vacuum drying reported for honey powder were 1.33-6.7 kPa and 70 °C (Sahu, 2008), and 16 kPa and 60 °C (Nurhadi et al., 2012). At the same maltodextrin ratio, vacuum drying produced higher honey powder yield than spray drying process (Nurhadi et al., 2012). In vacuum drying, low pressure would make evaporation of water to occur at a lower temperature. Drying temperature used in vacuum drying usually is higher than boiling temperature of water at corresponding pressure which promotes internal evaporation/excess boiling and as a result frothy structure may be formed. The frothy structure would increase heat and mass transfer rate due to high ratio of surface area to volume (Land, 2012).

The hygroscopicity, water content and water activity of honey powder produced by spray drying were not different, when maltodextrin and WPI were used as drying aids (Shi, Fang and Bhandari, 2013). Hygroscopicity of honey powder decreased in line with increasing maltodextrin ratio (Sahu, 2008, Shi, Fang and Bhandari, 2013). The hygroscopicity of honey powder obtained by vacuum drying process was lower than for honey powder from spray drying process (Nurhadi et al., 2012) and it might be due to the difference in amorphous structure. Partially amorphous material with higher amount of crystalline material would have less tendency to water sorption (Bhandari, 2013). Hydroxy methyl furfural (HMF) is used as an indicator of heating process and a high HMF in honey means excessive heating process (Chmielewska, 2004). HMF is a substance that is produced from loss of three water molecules either from D-glucose or D-fructose due to heating process (Chmielewska, 2004, Kolayli et al., 2014). Nurhadi et al. (2012) reported that higher amount of HMF was found in honey powder from vacuum drying than in honey powder produced using the spray drying process.

1.5. Conclusions

Honey is classified as a high sugar food with up to 85 % of total solids being glucose and fructose. The transformation of high sugar food into a dried form needs drying aids or filler materials and special drying methods. Maltodextrin is a common drying aids with high T_g. Maltodextrin is available at different molecular weight (different T_g) which indicated by DE value. Vacuum drying method is a simple drying method among other drying methods (freeze-drying and spray drying) to produce high-sugar dried foods. The honey formulation with maltodextrin in term of DE value, maltodextrin ratio, total solids and drying temperature may affect the resultant vacuum-dried honey powder stability. Water sorption isotherm and water plasticization properties is used to assess the stability of honey powder.

CHAPTER II

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

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Physical Properties of Maltodextrin DE 10: Water Sorption, Water Plasticization and Enthalpy Relaxation

ABSTRACT

Maltodextrins are hydrolysis products of starch. The present research aimed to study physical properties of maltodextrins and their characteristics (water sorption, water plasticization behavior and enthalpy relaxation) 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 KWW model and extended Adam-Gibbs model fitted well the enthalpy relaxation kinetics data. Based on the KWW model, 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. Maltodextrin with water activity lower than 0.43 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.

Key Words: Maltodextrin DE 10, Water Sorption, Water Plasticization, Enthalpy Relaxation

2.1. 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 and 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.

Maltodextrins 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 $\geq$ 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, enthalpy relaxation is an important factor related to the glass transition of amorphous low water content materials (Liu, Bhandari and Zhou, 2006). Below T_g, 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, Shamblin and Zografi, 1995; Liu, Bhandari and Zhou, 2006). Enthalpy relaxation is associated with structural changes such as structural relaxation and ageing (Liu, Bhandari and Zhou, 2007). Enthalpy relaxation is related to molecular mobility in the glassy state and such mobility is connected to β and ɤ relaxations (Liu, Bhandari and Zhou, 2007). However Hancock, Shamblin and Zografi (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, Bhandari and Zhou, 2006). Thus it was suggested to store materials far below their glass transition temperature in order to maintain stability (Hancock, Shamblin and Zografi, 1995 and Liu, Bhandari and Zhou, 2007).

The relaxed enthalpy (enthalpy relaxation) increased during ageing time and the increase of enthalpy relaxation followed non-linear and non-exponential function (Liu, Bhandari and Zhou, 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, Sablani and Swanson, 2010). The model is based on the stretched exponential function where the relaxation time obtained is the average relaxation time (Liu, Bhandari and Zhou, 2006). The KWW model is presented in equations 1 and 2.

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

$$\Delta H_{\infty} = \Delta C_p (T_g - T_a) \quad (2)$$

Where

τ^{KWW} = constant is related to mean enthalpy relaxation time

β = 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 ageing and after ageing for t time at temperature, T_a.

$\Delta H_{\infty} = H_i - H_{\infty}$, the difference between enthalpy at the beginning of ageing 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 glass transition temperature 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 ageing time (Kawai et al., 2005).

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

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

Where, $\tau^{eff}(t)$ is effective relaxation time and its value depend on ageing time

B and τ^{eff}_{∞} are constants

Enthalpy relaxation time depends on the temperature where the ageing process takes place or how far the ageing temperature is below the glass transition temperature. Arrhenius equation was reported to fit to the enthalpy relaxation time as function of temperature (Hancock, Shamblin and Zografi, 1995; Shamblin et al., 1999; Noel, Parker and Ring, 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. The maltodextrin DE 10 (M100) was chosen as an object due to its properties in term of molecular weight (still having high T_g) and good solubility in water.

2.2. Materials and Methods

2.2.1. 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).

2.2.2. 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 dryingwas 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, 0.65 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.

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

Where,

X = water content (g water/ g dry solid)

a_w = water activity

X_m = monolayer water content

X_m, C and K are constants

2.2.3. 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.

$$T_g = \frac{(1-X)T_{g(ds)} + k_{G-T}XT_{g(w)}}{(1-X) + k_{GT}X} \qquad (6)$$

Where,

T_{g1} = glass transition temperature of dry solid maltodextrin

T_{g2} = glass transition temperature of water

X = fraction of water

K_{G-T} = constant

The goodness of fit for both water sorption and water plasticization were analyzed using the value of relative percentage square (%RMS) which the %RMS value less than 10 indicate the very good fit of model (Rizvi, 2005).

$$\%RMS = 100\left\{\frac{\sum_{i=1}^{N}\left\{\frac{X_i - X_i^{\square}}{X_i}\right\}}{N}\right\} \qquad (7)$$

Where;

N = number of data

X_i = experimental data

$X_i^{\square}$ = calculated data from the model chosen

2.2.4. Enthalpy Relaxation

Enthalpy relaxation experiments were done as described in Fig. 1. About 10 mg of maltodextrin was prepared in 40 µl aluminum pan and stored at various water

activities for 3 days. The pans were sealed hermetically. Each samples then was heated to 30 °C higher than the glass transition temperature (process 1 in **Fig. 2.1**) to erase the thermal history of samples (Hancock, Shamblin and Zografi, 1995) , then the sample was cooled to 40 °C below respective glass transition temperatures to convert samples into glassy state (process 2). The samples then were reheated directly to 30 °C higher than the respective glass transition temperatures (process 3) for unaged samples. The samples were cooled to room temperature (25 °C) and stored/aged for 10, 20 and 30 days (process 4) at 25 °C. Thus the difference between glass transition temperature and ageing temperature (T_g-T) for maltodextrin at 0.11, 0.23, 0.33, 0.43, 0.53, 0.65 and 0.76 were 70, 50, 39, 26, 16, 9 and -8 °C respectively. After storage, the samples were heated from 40 °C below the glass transition to 30 °C higher than glass transition (process 5). All heating and cooling rates were at 5 °C/min. After analysis by DSC, the samples were reweighed to ascertain that no leakage (water loss) occurred.

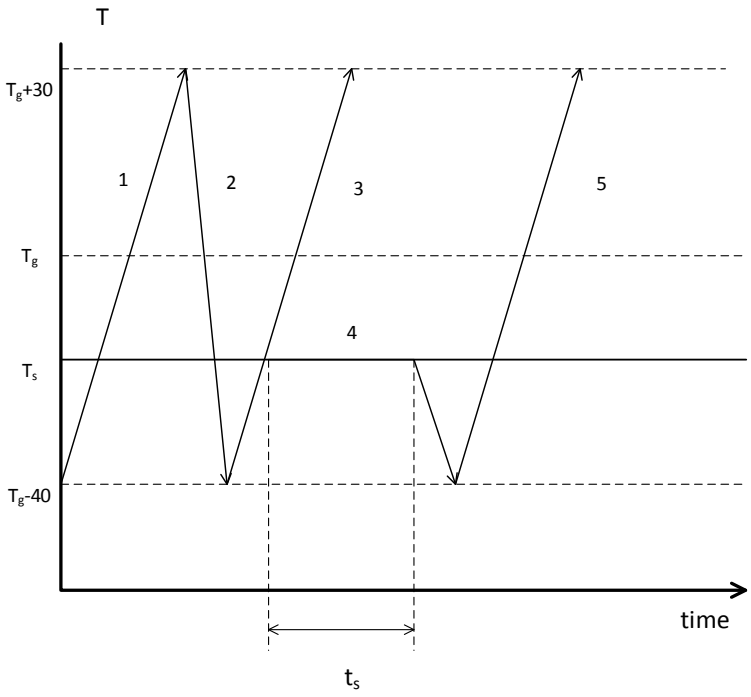


Fig. 2.1. Temperature Profile of Enthalpy Relaxation of Measurements using DSC.

Two approaches were used to explain the kinetics of enthalpy relaxation of maltodextrin DE 10. The KWW model and extended Adam Gibbs Model were used (Kawai et al., 2005). Enthalpy relaxation was determined by measuring endothermic peak area around glass transition temperature using the STARe software version 8.10 (Mettler Toledo Schwerzenbach, Switzerland) (Hancock, Shamblin and Zografi, 1995; Kawai et al., 2005 and Liu, Bhandari and Zhou, 2007). The Arrhenius equation was used to study the dependence of relaxation time on temperature (Hancock, Shamblin and Zografi, 1995).

2.3. Result and Discussion

2.3.1. Water Sorption and Water Plasticization

From water sorption isotherm experiments, the weight gain of maltodextrin started to level off after 3 days of storage except for maltodextrin stored over high 0.85 a_w which took about 6 days. The equilibrium water contents of maltodextrins and water activities are given in Table 2.1. The GAB equation fitted well to water sorption data of maltodextrin with high value of R square.

Table 2.1. The water sorption and water plasticization of maltodextrin DE 10 and the Parameter of GAB and GT equation.

a_w	X (g water/ 100 dry solid)	T_g (°C)	GAB Equation Parameters	GT Equation Parameters
0.11	4.0 ± 0.06	95 ± 0.9	*) X_m=6.6; C=5.3; K=0.74; R^2=0.33	*) K_{GT}=7.2; $T_{g(ds)}$=152 °C; $T_{g(w)}$=-135 °C; R^2=0.98
0.23	6.6 ± 0.01	75 ± 2.0		
0.33	7.8 ± 0.02	64 ± 1.7		
0.43	9.3 ± 0.08	51 ± 1.2	**) X_m=6.7; C=14.6; K=0.81; R^2=0.94	**) K_{GT}=5.5; $T_{g(ds)}$=147 °C; $T_{g(w)}$=-135 °C; R^2=0.98
0.53	11.1 ± 0.03	41 ± 01		
0.65	12.7 ± 0.04	34 ± 0.3		
0.75	15.4 ± 0.09	17 ± 0.7		

Note: *) Analysis was done based on data from Roos and Karel, 1991
**) Present Study
X_m is monolayer water content stated as g water per 100 g dry solid

Water acted as plasticizer and the water content of maltodextrin DE 10 was inversely proportional to the glass transition temperature (Table 2.1). The Gordon-Taylor equation (GT equation) also fitted well to water plasticization of maltodextrin DE 10. Our findings for GT parameters were also very close to previous results of Roos and Karel (1991).

Endothermic peak of maltodextrin at various water activities (a_w of 0.11, 0.23, 0.33, 0.43, 0.53 and 0.65) occurred around 50 °C in first heating scan of maltodextrin and the peaks disappeared in second heating scan by DSC (Fig. 2.2). The endothermic peak was not seen clearly at water activities of 0.11 and 0.23, while for maltodextrin at a_w of 0.76 the exothermic peak occurred and disappeared after storage. Similar findings were also reported for starch and starch derived products such as native rice starch, breakfast cereals and wheat gluten by Borde et al., (2002), Kim et al., (2003) and Anzai et al., (2011). Maltodextrin as a starch derived product still showed the same phenomenon as shown by starch system. Borde et al (2001) explained the phenomenon was related to carbohydrate-water interaction and enthalpy relaxation of the amorphous carbohydrate. The endothermic and exothermic transition related to separate phenomena and the exothermic transition occurred directly after the endothermic transition for maltodextrin at 0.33 to 0.65 a_w (first heating scan). Endothermic transition is likely related to dehydration of water from maltodextrin and it was not present in an immediate reheating of the sample. The endothermic transition recovered during ageing especially for maltodextrin at low water activities (0.11 and 0.23, data not shown) while for maltodextrin at 0.33 to 0.65 a_w, it was not clear due to the overlapping with enthalpy relaxation (Fig. 2.2). The exothermic transition for maltodextrin at 0.33 to 0.65 a_w was due to glass transition and it disappeared at the second heating scan and was not recovered during ageing/storing (Fig. 2.2).

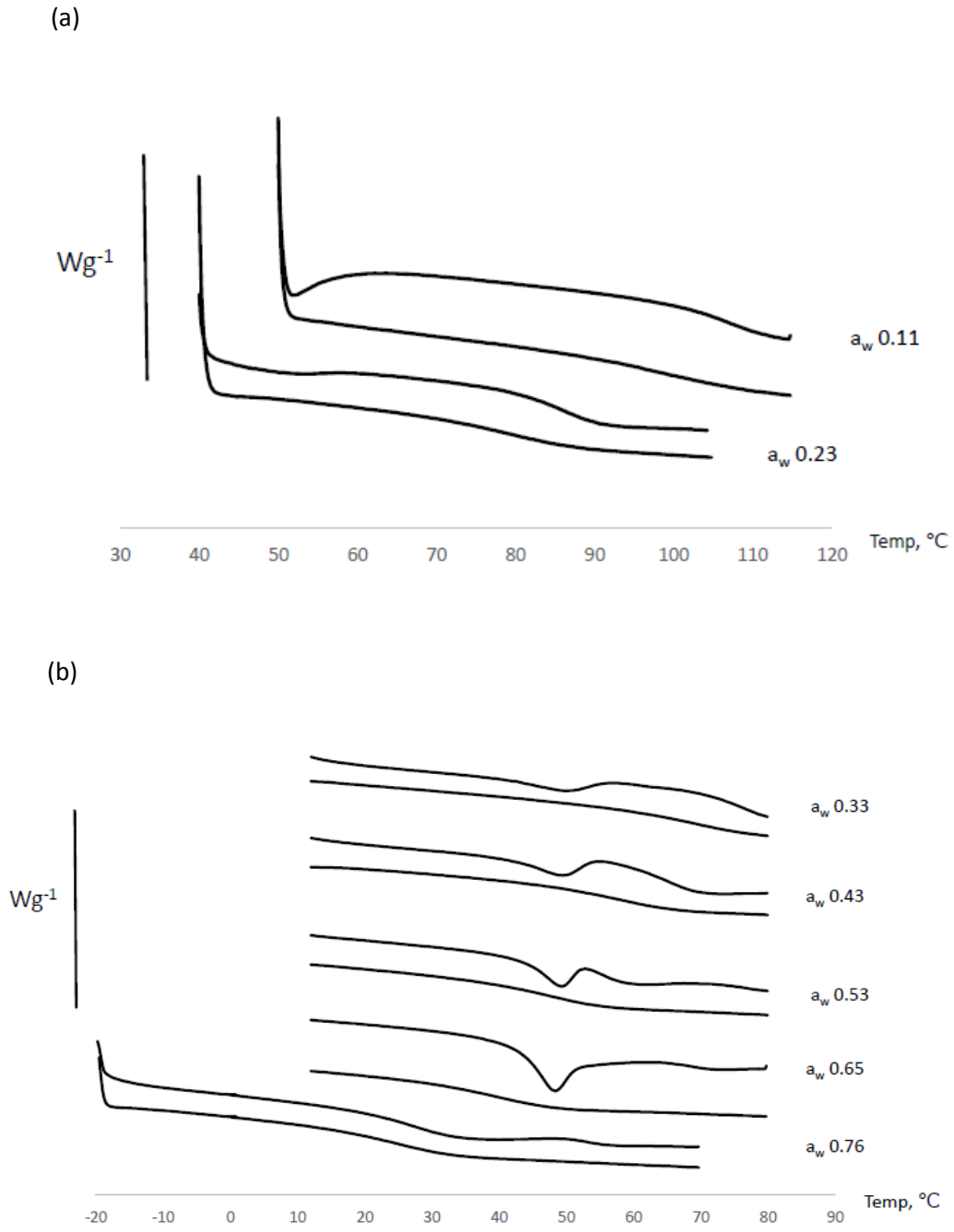


Fig. 2.2. DSC thermogram for Maltodextrin DE 10 at various water activities. At each water activity, the curve from top to below show first and second DSC heating scan. (a). Maltodextrin at 0.11 and 0.23 a_w, (b). Maltodextrin at 0.33, 0.43, 0.53, 0.65 and 0.76 a_w.

Monolayer water content indicated the amount of water that was strongly attached to polar and ionic groups and corresponded to stability of low-moisture material (Rizvi, 2005). Rizvi (2005) stated that BET's monolayer content is not significantly different from that given by GAB model. According to Sablani, Kasapis and Rahman, (2007) materials at their monolayer water content should be stable against microbial deterioration. Apart from monolayer water content, the critical water content and water activity obtained from correlating water sorption and water plasticization is used as an indication of stability especially physical stability (Roos, 1995).

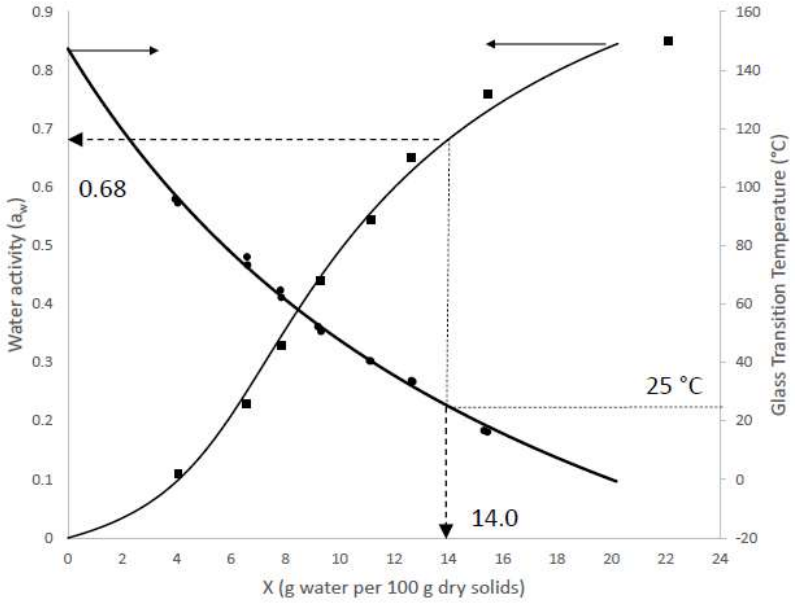


Fig. 2.3. Water activity of Maltodextrin DE 10 and water content data and calculated water content using GAB equation and water content of Maltodextrin DE 10 and glass transition temperature data and calculated glass transition temperature using GT equation. The curve show critical water content and critical water activity at 25 °C.

The critical water content and water activity of maltodextrin determination are shown in Fig. 2.3. The critical water activity and water content of maltodextrin DE

10 were of 0.68 and 14.0 g water/100 g dry solid, respectively. Due to the high value of critical water activity and water content of maltodextrin DE 10, it is usually added to increase the critical water activity and water content for high sugar materials such as reported by Mosquera, Moraga and Navarreta (2012) that the increasing critical water activity of strawberry powder after maltodextrin addition was increased from 0.094 to 0.23.

2.3.2. Enthalpy Relaxation

Enthalpy relaxation is often measured as the area of overshoot (endothermic peak) around the glass transition temperature (Hancock, Shamblin and Zografi, 1995) although it may also be found as an exotherm depending on the state of molecular arrangement within the glass. As shown in Fig. 2.4, the endothermic peak relaxation occurred around the glass transition at 50 – 60 °C. Similar result was also reported by Kim et al. (2003). According to Liu, Bhandari and Zhou (2006) the overshoot (enthalpy relaxation) was caused due to the return to a higher enthalpy state as rapid molecular movements appeared at the glass transition and molecular rearrangements corresponding to the dynamic heating could take place. Unclear endothermic relaxations of Maltodextrin at a_w of 0.11 and 0.23 were less apparent and longer relaxation times at the higher temperature and lower water content were expected. However for maltodextrin at a_w 0.76, the ageing temperature was higher than its glass transition temperature (onset) and consequently no endothermic relaxation appeared.

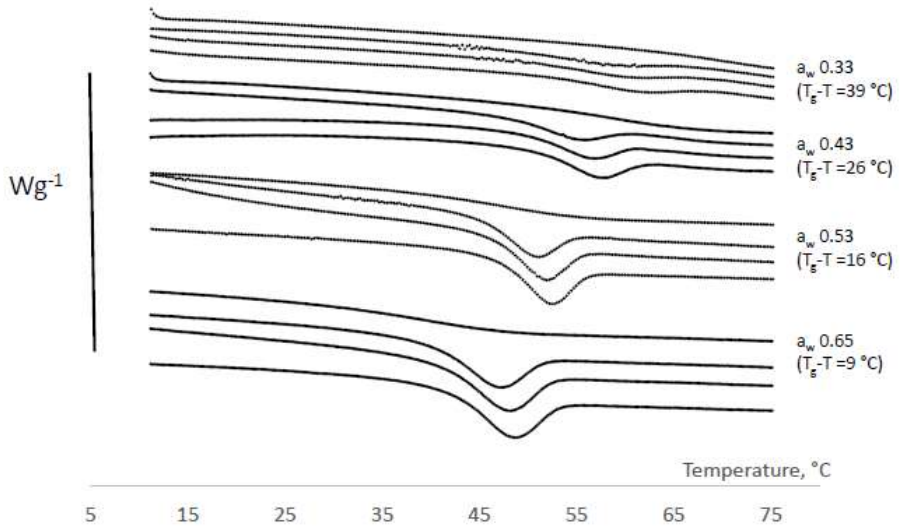


Fig. 2.4. Enthalpy relaxation of Maltodextrin DE 10 at various water activity. At each water activity, the curve from top to below show maltodextrin after aged for 0 (unaged samples), 10, 20 and 30 days at 25 °C.

As shown in Fig. 2.4, the endothermic peak temperature decreased as the water activity of maltodextrin DE 10 increased. It can be understood as the endothermic peak occurred around glass transition temperature and the higher the water activity of Maltodextrin, the lower was the glass transition temperature. Corresponding results for maltodextrin DE 21 were reported by Descamps, Palzer and Zuercher (2009). Fig. 2.4 illustrates that the endothermic peak tended to increase as the ageing time increased. These finding agreed with Kim et al. (2003) and Haque et al. (2012) who reported the increasing of enthalpy relaxation as ageing time increased.

2.2.1. Enthalpy Relaxation: KWW model

The KWW model fitted well to enthalpy relaxation data of maltodextrin DE 10 (Fig. 2.5). The curve was not linear and not exponential (Hancock, Shamblin and Zografi, 1995, Le Meste et al., 2002, Liu, Bhandari and Zhou, 2006 and Descamps, Palzer and Zuercher, 2009). The parameter value of KWW's model of maltodextrin DE

10 was presented in Table 2.2. As can be seen in Fig. 5, maltodextrin at high water activity (a_w 0.65), with β value close to 1, had the curve close to exponential curve. The β value varied depending on water activity of maltodextrin DE 10 (Table 2.2). At ageing temperatures close to glass transition temperature (maltodextrin at high water activity), the β value increased. At high water activity (a_w 0.65), the enthalpy relaxation increased dramatically with β value close to 1 (0.93) while at low water activity (a_w 0.33), the enthalpy relaxation distributed widely with low β value of 0.15.

As can be seen in Fig. 2.5, the higher the water activity of maltodextrin (or the closer the ageing temperature to glass transition temperature), the higher was the relaxed enthalpy (ΔH_{relax}) of maltodextrin. This result was agreement with Syamaladevi et al. (2010) who stated that the enthalpy relaxation increased with the ageing temperature towards glass transition temperature.

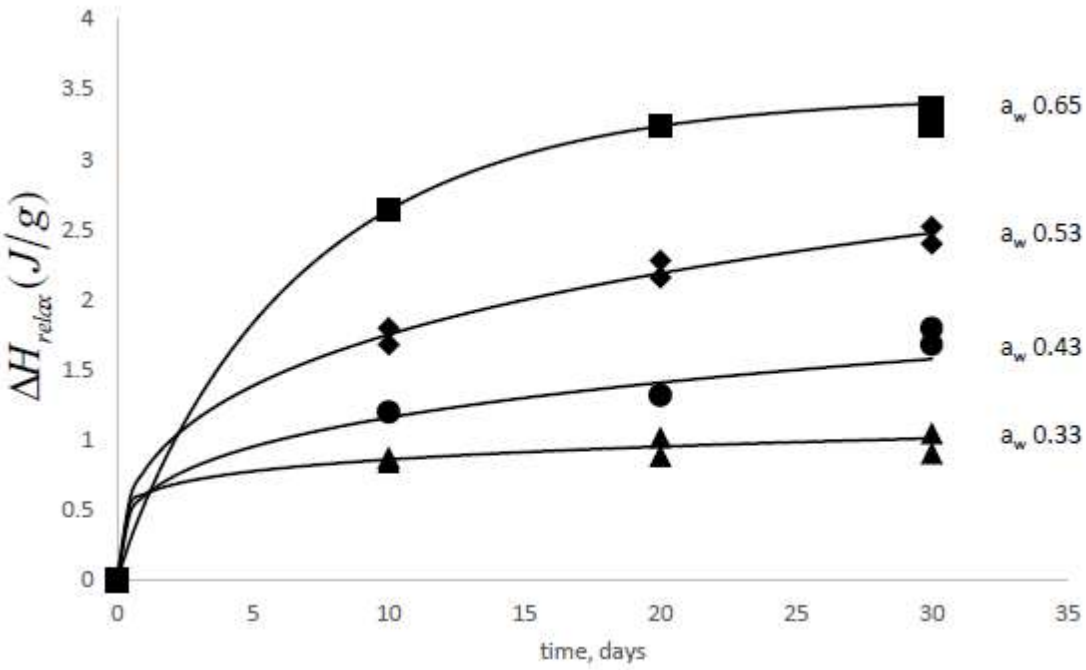


Fig.2.5. Enthalpy relaxation (ΔH_{relax}) data and calculated enthalpy relaxation using KWW model against ageing time of Maltodextrin at various water activities.

Table 2.2. The KWW's model parameter of Maltodextrin DE 10 at various water activities.

a_w	β	τ (days)	ΔH_∞ (J/g)	R^2
0.33	0.15	1.8×10^9	15.8	0.99
0.43	0.30	11833.2	10.3	0.98
0.53	0.40	127.8	5.8	0.99
0.65	0.93	6.8	3.5	0.99

The enthalpy relaxation of small saccharides is higher than that of more complex saccharides (polysaccharides) (Kawai et al., 2005 and Syamaladevi et al., 2010). The enthalpy relaxation of maltodextrin stored at 10 °C below its glass transition temperature (a_w 0.65) had enthalpy relaxation (around 3.5 J/g) smaller than trehalose (disaccharides) (5.2 J/g) stored at the same conditions (Data from Kawai et al., 2005).

Relaxation time of maltodextrin DE 10 increased as the ageing temperature far below the T_g (T_g-T increased or a_w decreased) (Table 2.2). It can be concluded from data of Table 2.2, the relaxation time of maltodextrin at water activity lower than 0.43 (or T_g-T > 30 °C) was extremely long. It means that molecular mobility in the glassy state of maltodextrin DE 10 stored more than 30 °C below its glass transition temperature was very limited and could be negligible. Hancock, Shamblin and Zografi (1995) suggested that materials stored at 50 °C below their glass transition temperature could maintain their structural and macroscopic stability.

2.2.2. Enthalpy Relaxation: Extended Adam-Gibbs Model

Despite using relaxation time as an independent parameter to ageing time in KWW model, the extended Adam Gibbs model used effective enthalpy relaxation time (τ^{eff}) as function of ageing time (Kawai et al., 2005).

$$\frac{d(\Delta H_{\infty} - \Delta H_{relax})}{dt} = -\frac{1}{\tau^{eff}(t)}\left(\Delta H_{\infty} - \Delta H_{relax}\right)$$

$$\frac{d(\Delta H_{\infty} - \Delta H_{relax})}{\left(\Delta H_{\infty} - \Delta H_{relax}\right)} = k(t)dt \quad where \;\; k(t) = -\frac{1}{\tau^{eff}(t)}$$

$$\ln(\Delta H_{\infty} - \Delta H_{relax}) = \int k(t)dt$$

$$\ln(\Delta H_{\infty} - \Delta H_{relax}) \quad vs \quad t$$

Thus we plotted ln (ΔH_{∞}-ΔH_{relax}) against ageing time and we found that the relationship followed well an exponential function. As an example, for maltodextrin at a_w 0.33 we found

$$\ln(\Delta H_{\infty} - \Delta H_{relax}) = \int k(t)dt = 2.6961 + 0.0637e^{-0.2107t}$$

$$\frac{d\int k(t)dt}{dt} = \frac{d(2.6961 + 0.0637e^{-0.2107t})}{dt}$$

$$k(t) = 0.0637(-0.2107)e^{-0.2107t} = -0.0134e^{-0.2107t}$$

$$because \quad k(t) = -\frac{1}{\tau^{eff}(t)}$$

$$\tau^{eff}(t) = \frac{-1}{-0.0134e^{-0.2107t}} = 74.627e^{0.2107t}$$

$$\tau^{eff}(t) = 74.63e^{0.21t}$$

For maltodextrin at water activity of 0.43, 0.53 and 0.65 were presented in equation below respectively

$$\tau^{eff}(t) = 59.52e^{0.093t}$$

$$\tau^{eff}(t) = 18.55e^{0.092t}$$

$$\tau^{eff}(t) = 4.93e^{0.047t}$$

Then according to Kawai et al. (2005), the correlation of ln τ^{eff} and (ΔH_{∞}-ΔH_{relax}) followed linear equation as below:

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

The plot of ln τ^{eff} and (ΔH_{∞}-ΔH_{relax}) for maltodextrin DE 10 at different water activities are shown in Fig. 2.6. From equation above, we get the parameters $\tau^{eff}{}_{o}$ and $\tau^{eff}{}_{\infty}$ for maltodextrin at each water activity (or different T_g-T). The value of $\tau^{eff}{}_{o}$ and $\tau^{eff}{}_{\infty}$ were related to time at which enthalpy has not relaxed yet and enthalpy has relaxed to reach its lowest state (Kawai et al., 2005). If we compare the two models, it seemed that KWW model fitted better than extended Adam Gibbs model based on the value of their R squares. However these two models should be complementary to each other. The KWW model gave a mean/average enthalpy relaxation time while the extended Adam Gibbs model gave relaxation time when enthalpy relaxation started and reached an infinite state (Kawai et al., 2005).

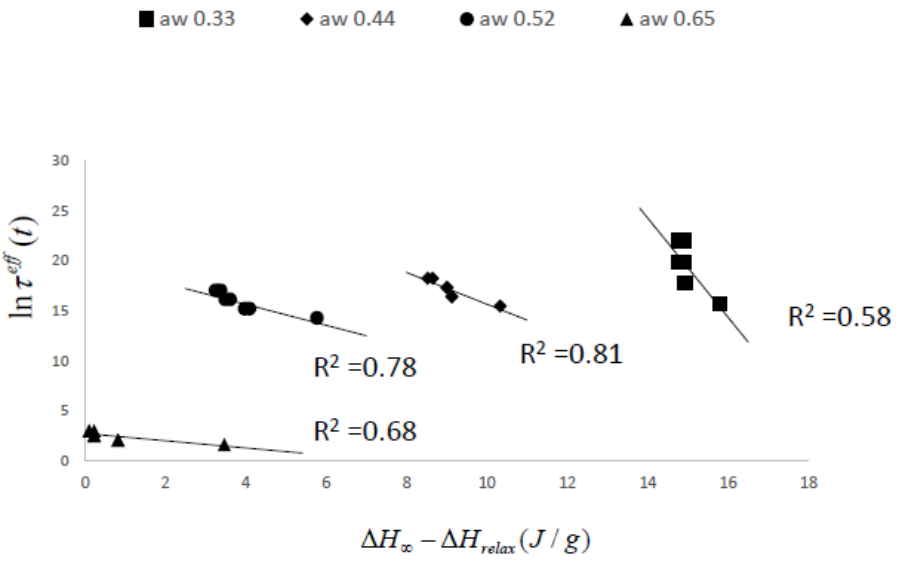


Fig. 2.6. Effective enthalpy relaxation time (τ^{eff}) and (ΔH_{∞}-ΔH_{relax}) of Maltodextrin at various water activities.

2.3.3. Temperature Dependence of Enthalpy Relaxation Time

Relaxation time below glass transition temperature is dependent on temperature and the Arrhenius approach was used to correlate the relaxation time as a function of temperature (Hancock, Shamblin and Zografi, 1995, Meste et al., 2002 and Kawai et al., 2005). In the present study, the ageing temperature of maltodextrin was kept constant at 25 °C. However maltodextrin had been stored and equilibrated over various water activities and having different glass transition temperatures. Thus the relationship of log relaxation time was plotted with the difference between the glass transition temperature and ageing temperature (T_g-T). The relationship of log relaxation time and (T_g-T) was derived as follow

$$\tau_T = \tau_o \exp\left(E_a \big/ RT\right)$$

$$\tau_{T_g} = \tau_o \exp\left(E_a \big/ RT_g\right)$$

$$\frac{\tau_T}{\tau_{T_g}} = \frac{\cancel{\tau_o} \exp\left(E_a \big/ RT\right)}{\cancel{\tau_o} \exp\left(E_a \big/ RT_g\right)} = \exp\left(\frac{E_a}{RT} - \frac{E_a}{RT_g}\right)$$

$$\frac{\tau_T}{\tau_{T_g}} = \exp\left(\frac{E_a}{RT} - \frac{E_a}{RT_g}\right) = \exp\left\{\left(\frac{E_a}{R}\right)\left(\frac{T_g - T}{T_g T}\right)\right\}$$

$$\ln\frac{\tau_T}{\tau_{T_g}} = \left(\frac{E_a}{R}\right)\left(\frac{T_g - T}{T_g T}\right)$$

$$\ln\tau_T = \ln\tau_{T_g} + \left(\frac{E_a}{R}\right)\left(\frac{T_g - T}{T_g T}\right)$$

Fig. 2.7 shows the relaxation time (both mean enthalpy relaxation time from KWW equation and effective enthalpy relaxation time from extended Adam Gibbs equation) increased as the difference between T_g and ageing temperature also increased. Arrhenius equation fitted better for data obtained from KWW model than extended Adam Gibbs model. The free activation energy (Ea) of relaxation time from KWW model was in the middle between two free activation energies of relaxation

time from extended Adam Gibbs model. As suggested by Kawai et al. (2005) the relaxation time of KWW model was an average value of enthalpy relaxation time, while in extended Adam Gibbs model, the relaxation time related to time at which enthalpy started (τ^{eff}_{o}) to relax and reach equilibrium (τ^{eff}_{∞}). Thus the Ea value of relaxation time from KWW model should be between Ea^{eff}_{o} and Ea^{eff}_{∞}.

Table 2.3. Comparison of Enthalpy relaxation characteristic of Maltodextrin to saccharides.

Compounds	T_g (K)	β	KWW model	Extended Adam-Gibbs Model	
			Ea^{KWW} (KJ/mol)	Ea_0^{eff} (KJ/mol)	Ea_∞^{eff} (kJ/mol)
Glucose*	309	0.46 – 0.53	179.5	152.8	310.9
Sucrose*	341	0.53 – 0.62	212.2	172.9	320.0
Maltose*	363	0.47 – 0.55	245.4	164.6	441.4
Trehalose*	386	0.51 – 0.75	360.8	238.8	589.1
Maltodextrin (M100)**	**422**	**0.15 – 0.93**	**459.5**	**338.6**	**2464.1**

Note : * from Kawai et al, 2005
** recent study

The activation energy of maltodextrin DE 10 and some simple sugars are shown in Table 2.3. Maltodextrin DE 10 had the highest activation energy compared to others and as suggested by Kawai et al (2005) it meant that maltodextrin DE 10 is the most stable glass below its glass transition temperature. This finding could be understood since maltodextrin having more complex structure and higher molecular mass and also higher glass transition temperature than sugars in Table 2.3.

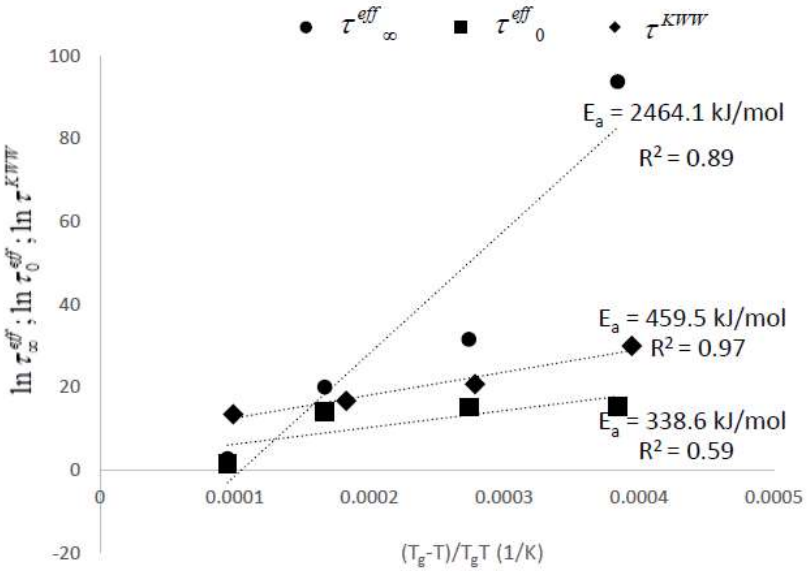


Fig.2.7. Temperature Dependence of Enthalpy Relaxation Time of Maltodextrin with different water activities (various glass transition temperature) from Both KWW and extend Adam Gibbs model.

2.4. Conclusion

The GAB and GT equation fitted successfully to water sorption and water plasticization behavior of maltodextrin DE 10. The critical water content and critical water activity of maltodextrin DE 10 at 25 °C were 14 g water/100 g dry solid and 0.68, respectively. The KWW model and extended Adam-Gibbs model was used to explain the enthalpy relaxation kinetics of maltodextrin DE 10. Based on the KWW model, the non-exponential parameter, β value, of maltodextrin DE 10 were in the range of 0.15-0.93 and its value depend on the water activity of maltodextrin. Maltodextrin with water activity lower than 0.43 and stored/aged at 25 °C had the “stable” glass indicated by very long enthalpy relaxation time. The KWW model seemed to fit better than the extended Adam-Gibbs model. Enthalpy relaxation time of maltodextrin DE 10 depend on the temperature with the free activation energy of 459.5 kJ/mol.

CHAPTER III

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Dynamic water sorption for the study of amorphous content of vacuum-dried honey powder

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Dynamic Water Sorption for the Study of Amorphous Content of Vacuum-Dried Honey Powder

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ABSTRACT

Amorphous components in food powders are important as they often provide a solid structure. They also affect powder properties such as physical and storage stability. Quantification of amorphous components of food powders may be challenging. We developed a dynamic water sorption by dynamic dew point isotherm (DDI) method, which records the change of water activity and weight change (or water content) of a sample continuously. The research was aimed to study the amorphous content of vacuum-dried honey powder produced from different drying temperatures. The DDI method was calibrated using known amorphous contents of amorphous sucrose and mixtures of amorphous sucrose and maltodextrin. Amorphous materials often exhibit higher sorption of water than crystalline materials. In the new approach, water sorption data were differentiated numerically and plotted against water activity. The water sorbed by the sample during recrystallization was measured by integrating the area of the new derived water sorption curve against water activity. The water sorbed was correlated with the amorphous content of the system. The honey powder also exhibited recrystallization of its amorphous sugar during water sorption. The result showed that the higher the drying temperature, the higher the amorphous content of vacuum-dried honey powder.

Key words: *Amorphous, Dynamic water sorption, sucrose, maltodextrin, Honey Powder*

3.1. Introduction

Powder components can be in pure amorphous, pure crystalline or partially amorphous structures (mixed amorphous and crystalline states) (Bhandari, 2013). The differences in structure between amorphous and crystalline order, Crystalline structures have long range molecular alignment, while amorphous structures have short range molecular alignment of limited order (Bhandari, 2013). Food processing, such as drying, may produce pure amorphous or partially amorphous structures (Roos, 1995). Roos (1995) stated that freeze-drying often results in pure amorphous materials as a result of freeze concentration of solutes and resultant removal of ice by sublimation. Chiou, Langrish and Braham (2008) reported that spray drying produced lactose powders with various amorphous structures (partially amorphous) at different inlet drying temperatures.

Amorphous and crystalline materials have different physicochemical properties. Amorphous structures are thermodynamically 67etastab as compared to crystalline structures and as a result, amorphous structures are 67etastable with reduced physical and chemical stability (Lehto et al., 2006). Powders with crystalline components have low porosities, easy to flow properties which make them easier to handle although hard to dissolve (Chiou, Langrish, and Braham, 2008, Bhandari, 2013). Meanwhile, powders with amorphous structure are more hygroscopic, more cohesive, and difficult to flow and disperse (Chiou, Langrish, and Braham, 2008, Bhandari, 2013). Amorphous structures have larger porosity and volume and as consequence amorphous structures have a higher sorption capacity than crystalline forms (Bhandari, 2013). In partially amorphous powders, the amorphous fraction is mostly found on the surface of the powder (Mackin et al., 2002, Adhikari et al., 2009).

Several methods can be used to detect amorphous powder components. Lehto et al. (2006) used x-ray powder diffraction, differential scanning calorimetry (DSC), step scan DSC, isothermal microcalorimetry, solution calorimetry, Raman spectrometry and gravimetric water sorption to quantify amorphous lactose in a dried

lactose system. Chiou, Langrish, and Braham (2008) used the water induced crystallization technique to detect amorphous contents by recrystallization of amorphous fractions in partially amorphous materials. Recrystallization measurement as a basis to detect amorphous contents of materials was also used in gravimetric water sorption, solution calorimetry, Raman spectrometry (Lehto et al., 2006) and dynamic vapor sorption (Mackin et al., 2002). Vollenbroek et al. (2010) and Burnet, Malde, and Williams (2015) used dynamic vapor sorption (DVS) to detect amorphous contents of components in dried materials. Vollenbroek et al. (2010) determined the amorphous contents of partially amorphous lactose based on the corresponding BET (Brunauer-Emmet-Teller) monolayer water content. Lehto et al. (2006) suggested to use combined techniques in detecting amorphous content in dried materials.

Dynamic dew point isotherm (DDI) is a recent technique developed along with dynamic vapor sorption (DVS) to measure water sorption properties of materials. The word 'dynamic' means that the measurement of water sorption variable (water content and water activity) is done continuously compared to conventional, static water sorption techniques which measure water content equilibrated materials at known water activity. The amount of data (water activity and water content) is very limited in conventional water sorption, compared to the dynamic method. DVS has more similarities to conventional water sorption, whereas the DDI method does not reach an equilibrium state (Li, 2010, Allan and Mauer, 2015). Thus, dynamic water sorption data from DDI can not be compared with water sorption from conventional water sorption method. In DDI, airflow (humid air or dry air depend on sorption direction) continuously pass over the sample for a certain interval time result in a_w change by 0.015 (Allan and Mauer, 2016), then the flow is stopped and a snapshot of water activity and weight change (water content) is recorded. The machine then starts to flow air over the sample again until the desired condition is met (Decagon, 2014). Principally, dynamic water sorption of DDI is comparable to water sorption for most

materials, especially those with fast vapor diffusion or small sample size (Decagon, 2014).

Despite limitations of dynamic water sorption from DDI, the technique has still been used effectively in determining time-dependent properties related to water sorption experiments (Romani et al., 2016). DDI was used to determine glass-rubbery transitions of polydextrose (critical water content and critical water activity) and the result was comparable to the DSC method (Carter and Schmidt, 2012, Yuan, Carter, and Schmidt, 2012). The critical water activity was determined as the water activity where peak occurred at second derivative of water sorption curve (Carter and Schmidt, 2012, Yuan, Carter, and Schmidt, 2012). DDI was also used to determine the deliquescence phenomena of crystalline substances (Ghorab et al., 2014).

The DDI method in the current research was used to detect the amorphous content of partially amorphous powders. The principle of determination was based on the recrystallization of the amorphous fraction of the sample being analyzed. This means that the sample must contain amorphous substances that could recrystallize during the water sorption measurement. Amorphous structure in the sample absorb more water than a crystalline fraction. Thus, the amount of water adsorbed is proportionally related to the amorphous content of the sample. Mackin et al. (2002) measured the amorphous content based on acetone uptake by amorphous benzyl derivate using DVS method. The current research is aimed at validating the use of DDI to determine the amorphous content of powder blend of pre-known amorphous content (sucrose and sucrose-maltodextrin system), to study the effect of drying type on properties of powder produced, and to study the amorphous content of vacuum dried honey powder produced from different drying temperatures.

3.2. Material and Methods

3.2.1. Materials

3.2.1.1. Amorphous Sucrose and Sucrose-Maltodextrin

Amorphous sucrose (Sigma-Aldrich, USA), amorphous sucrose-maltodextrin and maltodextrin DE 10 (M100) powder were obtained by freeze-drying (Lyovac GT 2, Steris®, Hurth, Germany) and vacuum oven drying (WTB Binder, Germany).

For freeze-drying, sucrose, sucrose-maltodextrin (7/3, solid/solid) and maltodextrin (Grain Processing Corporation, IA, USA) solution with 20 % of total solid were prepared in glass vials 10 ml (Schott, Mulheim, Germany). The vials were semi-closed with a septum. The samples in vials were frozen in a freezer (HLLF-240, Heto, Jouan Nordic A/S, Allerød, Denmark) at -20 °C overnight followed by tempering at -80 °C (Icebird/Mini Freeze 80, Heto, Jouan Nordic A/S, Allerød, Denmark) for 3 hours and freeze-drying. Each vial contained 5 ml of solution giving 1 gram of solids. The vials were closed under vacuum condition for the static water sorption experiment (amorphous sucrose-maltodextrin), while others were ground and stored in P_2O_5 (Sigma-Aldrich, USA) for further DDI analysis.

For vacuum oven drying, sucrose, sucrose maltodextrin and maltodextrin solutions with 40 % of total solid were prepared in Petri dishes sealed with a perforated cover. The drying process was done for 3 hours and after that, the samples were ground and stored over P_2O_5 for further DDI analysis.

3.2.1.2. Crystalline Powder

Crystalline sucrose powder was prepared by grinding crystalline sucrose and was stored in P_2O_5 for DDI analysis. The grinding process breaks the crystal and might give a small amount of amorphous structure in samples (Willart et al., 2010).

3.2.1.3. Blend of amorphous and crystalline sucrose

Amorphous-Crystalline Sucrose systems were prepared in five ratios of components. Samples were prepared by blending amorphous sucrose obtained from the vacuum oven and blended with crystalline sucrose at certain ratios in vials. Blending was done by spatula and shaking the closed vials. The mixed samples contained 100 %, 66.7 %, 50 %, 33.3 % and to 0 % of amorphous sucrose.

Amorphous-Crystalline Sucrose and Maltodextrin were prepared in the same way as above by blending all the components. The ratio of sucrose and maltodextrin for all treatments were fixed at 7 to 3 (solid ratio). Five samples were prepared by blending amorphous sucrose to crystalline sucrose at certain ratios of 100 %, 75 %, 50 %, 25 % and 0 %.

3.2.1.4. Vacuum Oven dried Honey

Honey-maltodextrin solutions (total solid 43 %, ratio honey: maltodextrin = 6:4) were prepared on petri dish sealed using perforated covers for drying in vacuum oven at temperature, 70, 60, 50 and 40 °C for 1.5, 3, 5, and 6 hours. The dried samples were ground and stored in P_2O_5 for further analysis.

3.2.2. Methods

3.2.2.1. Static water sorption of amorphous sucrose-maltodextrin powders

Static water sorption was done for amorphous sucrose- maltodextrin while data for water sorption of amorphous sucrose was obtained and calculated from Makower and Dye (1956). Seven saturated salts were used to vary the relative humidity of desiccator. The salts used were LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, Mg $(NO_3)_2$, $NaNO_2$, and NaCl were obtained from Sigma Chemical Co.,(St. Louise, MO. U.S.A), for relative humidities of 11 %, 23 %, 33 %, 43 %, 52 %, 65 % and 75 %, respectively (Roos, 1995). The freeze-dried samples in glass vials were closed under vacuum conditions. The vials were then opened and stored in desiccators over various saturated salt solutions with

RH values ranges from 11 % to 75 %. During storage in a vacuum desiccator, the vials were weighed regularly until 8 days for samples stored in desiccators with relative humidity up to 52 %, while for other samples (stored in 65 % and 75 % RH) were stored until 14 days. Then the water content of samples was measured by drying in a vacuum oven at 100 °C for 6 hours. The analysis was carried out in triplicate. The Guggenheim-Anderson-deBoer (GAB) equation was used to relate water activity of amorphous sucrose- maltodextrin and their water content.

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

Where,

X = water content (g water/g dry solid)

a_w = water activity

X_m = monolayer water content

X_m, C, and K are constants

3.2.2.2. Effective diffusivity

Effective diffusivity was calculated for vacuum dried honey powder at different temperatures. The water content of honey and maltodextrin had been previously determined as 18 % and 6 % (g water per 100 g sample). The water content of honey and maltodextrin were determined by vacuum oven at 70 °C and 100 °C, respectively (Park and Bell, 2004). Based on the known water content of honey and maltodextrin, the initial water content of the mixture of honey-maltodextrin before drying was known. During drying of the honey-maltodextrin solution in a vacuum oven, the weight change of samples were recorded every 15 minutes. Effective diffusivity was taken as the slope of the natural logarithm of a dimensionless water ratio against drying time (Okos et al., 2007). The water content was presented as g water per g dry solid. The water ratio was calculated as follows:

$\frac{X-X_\infty}{X_0-X_\infty}$ (2).

Where

X = water content at certain time

X_o = initial water content

X_∞ = final water content at the end of drying

3.2.2.3. Differential Scanning Calorimetry (DSC)

DSC analysis was done to measure the glass transition temperature of amorphous sucrose-maltodextrin samples which had been equilibrated to various a_w while water plasticization data of amorphous sucrose were obtained and calculated from Roos (1992). Samples of about 10 mg were prepared in pre-weighed aluminum pans and equilibrated for three days in desiccators over various saturated salt solutions over the range of 11 % to 44 % RH. The pans were then sealed hermetically and analyzed by differential scanning calorimeter (DSC). Scanning (heating-cooling-heating) was done at 5 ℃/min. The temperature limits in heating and cooling scanning of amorphous sucrose-maltodextrin at different water activities were as follows:

$a_w\, 0.44:\ -10\ to\ 70℃$

$a_w\, 0.33:\ 0\ to\ 85℃$

$a_w\, 0.23:\ 10\ to\ 90℃$

$a_w\, 0.11:\ 10\ to\ 100℃$

The glass transition temperature, T_g was determined from the second heating scan with STAR^e software (version 8.10, Mettler Toledo Schwerzenbach, Switzerland). The T_g and water content for sucrose-maltodextrin at various water activities were modeled using the Gordon-Taylor equation.

$T_g = \frac{(1-X)T_{g(ds)}+K_{G-T}XT_{g(w)}}{(1-X)+K_{G-T}X}$ (3).

Where,

$T_{g(ds)}$ = glass transition temperature of dry solid sucrose-maltodextrin

$T_{g(w)}$ = glass transition temperature of water

X = fraction of water

K_{G-T} = constant

DSC measurements were also done for vacuum-dried honey powder. Scanning was done in heating and cooling at 5 ℃/min. The temperature range was -30 ℃ to 100℃ and the endothermic melting heat of glucose monohydrate in samples was measured with STAR^e software (version 8.10, Mettler Toledo Schwerzenbach, Switzerland).

3.2.2.4. Dynamic Dewpoint Isotherm (DDI)

About 500 mg of sample (dried powder) was prepared in DDI (Aquasorp Decagon Devices, Inc. Pulman WA, USA) measurements. The water sorption with adsorption direction was started from 0.1 to 0.85 a_w, with temperature set constant at 25 ℃ and air flow 300 ml/min. The water content of initial samples was predicted by option provided by the DDI software (SorpTract Software, Decagon, Device Inc., Pulman WA, USA) with principle by decreasing sample water activity below 0.1 a_w then the weight decreasing as a basis to predict the water content. For the adsorption direction, small amount of wet air (the ambient air pass through dehumidifier and then pass through water container) pass over the sample, then the sample will adsorb moisture. During water sorption experiment, the machine automatically record the change of weight and water activity of sample at certain interval time by precision balance and chilled-dew point sensor water activity meter respectively. The water activity and the water content obtained were then used to plot the dynamic water sorption isotherm. The water content of samples obtained was not accurate, however, the water content changes that occurred during the water sorption experiment were useful in determining the first derivative to show amorphous content.

3.2.2.5. Adsorbed Water

Determination of water adsorbed by samples in the DDI method was based on two principles. Firstly, the amorphous part of a sample should be potentially re-crystallizable during water sorption and secondly, the crystalline fraction of samples will adsorb significantly less water as compared to the amorphous fraction. When the amorphous structure recrystallized, the adsorption curve leveled off until reaching the deliquescence water activity (Decagon, 2014), and an increase in sorption occurred only at higher humidity conditions as a result of deliquescence. Smoothing of the adsorption curve was used to reduce the noise from the data and the simplest smoothing technique of moving average was used (NIST/SEMATECH, 2012). A different smoothing technique was used in determining the critical water content of polydextrose by using DDI method (Yuan, Carter, and Schmidt, 2011, Carter and Schmidt, 2012). In the smoothing technique, the three closed data (X_1, X_2, X_3) were averaged and stated as a new value X_1' and then the next data (X_2, X_3 X_4) were averaged and stated as next new value X_2' and the calculation were continued for all data. The technique of moving average were used to smooth both a_w and water content data of sample obtained from DDI.

The adsorbed water was calculated by measuring the area under the first derivative curve of water sorption. The first derivation of the curve was calculated with the formula :

$$\left(\frac{dX}{da_w}\right)_1 = \frac{X_2 - X_1}{a_{w2} - a_{w1}}. \qquad (4)$$

The area of the peak was calculated using Trapezoidal Integration Rule (Toledo, 2007) (equation 5) starting from water activity where significant increasing of water sorption due to transition from a glassy to a rubbery state and ending at water activity where the water sorption curve leveled off.

$$area = \frac{1}{2}(a_{w2} - a_{w1})(X_2 + X_1) \qquad (5)$$

The total area was calculated from the cumulative summation of all trapezoids between the water activity range.

All treatments were repeated at least twice.

3.3. RESULT AND DISCUSSION

3.3.1. Amorphous and Crystalline Sucrose-Maltodextrin.

The water sorption of materials with different structure, crystalline and amorphous, have different water sorption curves (Mathlouthi, 2001, Mathlouthi and Roge, 2003). The interaction between the solid material and water may be related to surface adsorption, capillary condensation, adsorption by the solid bulk matrix, crystallization, and deliquescence (Ghorab et al., 2014). As shown in Fig. 3.1, crystalline sucrose adsorbed a small amount of water until deliquescence occurred as compared to amorphous sucrose and amorphous sucrose-maltodextrin which adsorbed more water at low water activities. Lipasek et al. (2012) stated that crystalline materials adsorbed a small amount of water below their deliquescence point and when the deliquescence point was surpassed, the water sorption curve dramatically changed. Deliquescence is a solvent induced phase transition of crystalline structure from a solid to a solution (Allan and Mauer, 2016). Fig. 3.1 shows that the deliquescence point (RH_o) of crystalline sucrose was around 0.8 a_w and this value complied with the RH_o value of crystalline sucrose reported as 0.83 a_w (Mathlouthi, 2001, Mathlouthi and Roge, 2013). Below the deliquescence point, the adsorption of water was surface adsorption (Ghorab et al., 2014) which involves less than 3 hydrogen bonding molecular layers of water (Lipasek et al., 2012). Above the RH_o , water sorption by crystalline sucrose increased significantly which according to Lipasek et al (2012) indicated dissolution of crystalline substance.

Fig. 3.1 shows that amorphous sucrose and amorphous sucrose-maltodextrin adsorbed small amount of water at very low water activities but their water

adsorption increased above 0.2 a_w where the critical water activity was surpassed. The critical water activity at 25 ℃ of amorphous sucrose and amorphous sucrose-maltodextrin was very similar as presented in Fig. 2 as 0.29 and 0.26, respectively. Carter and Schmidt (2012) stated that adsorption of water in the amorphous glassy state is limited to surface sorption and limited hydrogen bonding. The critical water activity is the water activity where the amorphous structure transforms from a glassy to a rubbery state and results in an increase in water sorption (Yuan, 2012, Carter and Schmidt, 2012). The critical water activity of amorphous sucrose obtained was very close to the other result at 0.28 a_w (Decagon, 2014).

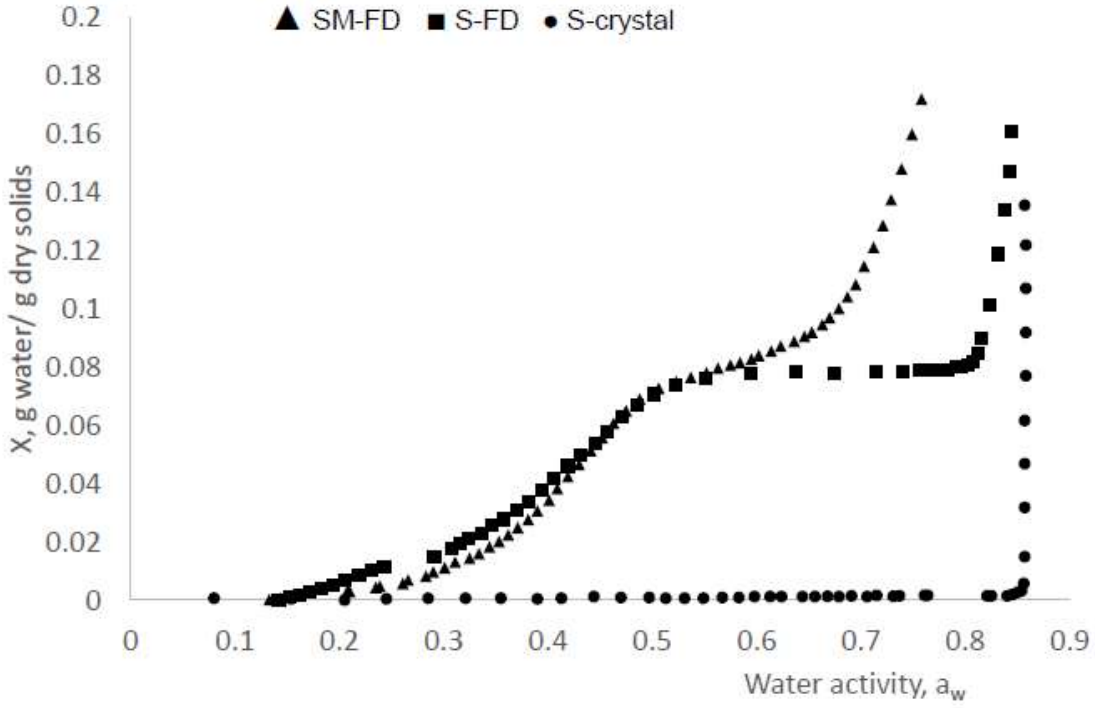


Fig. 3.1. The dynamic water sorption of amorphous sucrose (S-FD) and amorphous sucrose-maltodextrin (SM-FD obtained from freeze-drying and crystalline sucrose (S-crystal).

The adsorption of water by amorphous sucrose and amorphous sucrose-maltodextrin increased after the critical water activity was surpassed. Ghorab et al (20140) stated that the higher water sorption was a result of increased hydrogen bonding as the structure of the material became more flexible. As a consequence, amorphous sucrose in both systems (S-FD and SM-FD) could recrystallize which was shown by the leveling off of water sorption curve above 0.5 a_w. Makower and Dye (1956) reported that amorphous sucrose started to crystallize when stored at 0.28 a_w after 12 days. Crystallization was more rapid at higher relative humidities. For amorphous sucrose-maltodextrin static water sorption, we found that crystallization started after 8 days of storage at 0.65 a_w and was indicated by reduced sample mass due to water loss from the recrystallization of amorphous sucrose in the sample. The crystallization of amorphous components in DDI water sorption was indicated by the leveling off the water sorption curve as shown in Fig. 3.1.

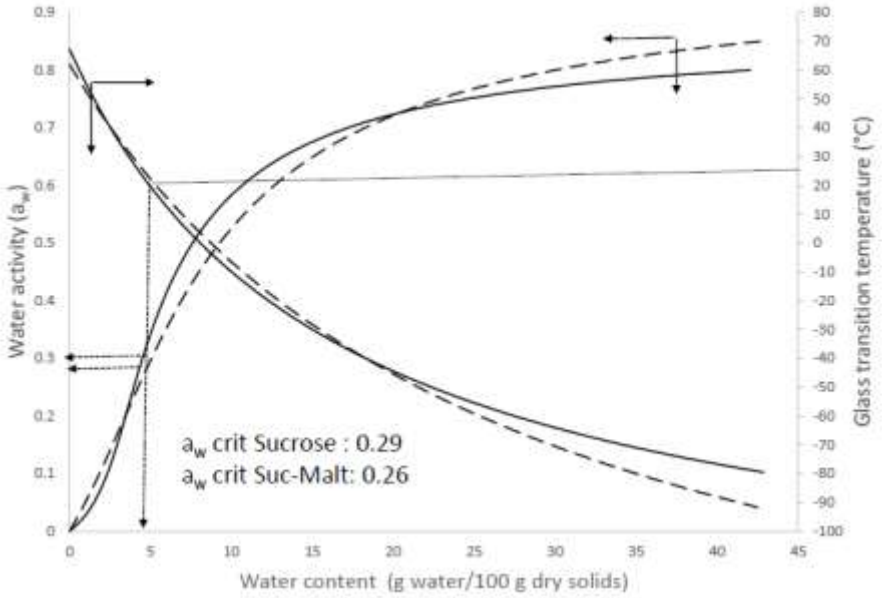
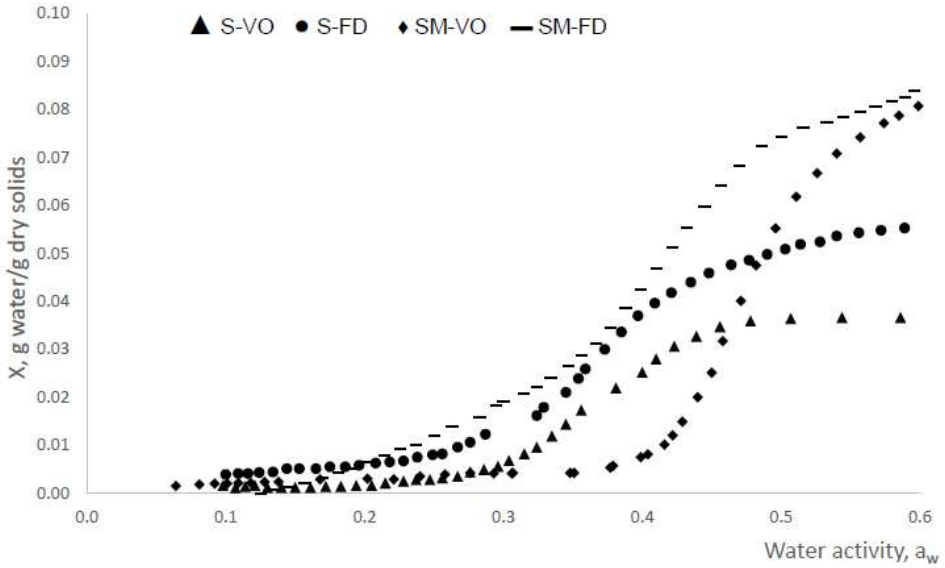


Fig. 3.2. Water Sorption and Water Plasticization behavior of amorphous sucrose (dashed line) and amorphous sucrose-maltodextrin (solid line, 7:3 solid/solid). Data for water sorption of amorphous sucrose was calculated from Makower and Dye (1956) while data for water plasticization of amorphous sucrose was calculated from Roos (1992).

Fig. 3.1 shows that after the water sorption curve leveled off, the adsorption of water increased for the sucrose-maltodextrin system at a lower water activity than was found for sucrose system. The leveling off of the water sorption curve could be explained because crystalline structures adsorb very little water. A sufficient water, crystals will become deliquescent. The RH_o of the sucrose-maltodextrin system was lower than that of sucrose. This finding agreed with Mathlouthi and Roge (2013) who reported that maltodextrin in crystalline sodium chloride lowered the deliquescence point.

Various drying processes might result in a product with different structural properties of dried solids (Vollenbroek et al., 2010). Amorphous sucrose from vacuum oven drying might contain a higher amount of crystalline sucrose component than those from the freeze-drying method. As shown in Fig. 3.3a and 3.3b, amorphous sucrose and amorphous sucrose-maltodextrin powder from vacuum oven drying had lower water sorption at low water activities and peak occurred at higher water activities than those of freeze-drying.

a.



b.

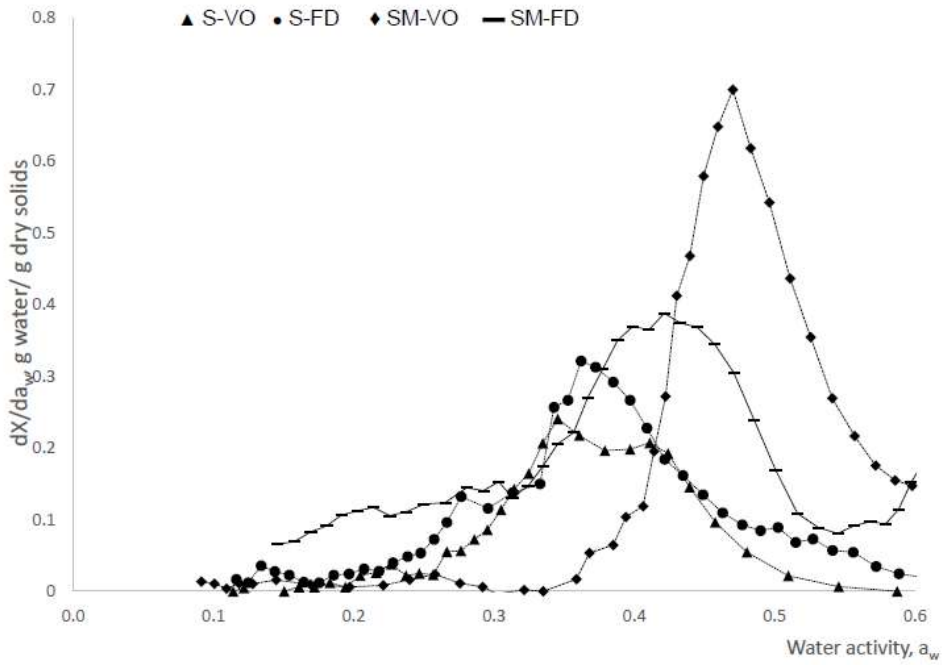


Fig. 3.3. Comparison of sucrose and sucrose-maltodextrin obtained from freeze-drying (FD) and vacuum oven drying (VO). S and SM correspond to Sucrose and Sucrose-Maltodextrin respectively. (a) Dynamic water sorption of freeze-dried and vacuum dried sucrose and sucrose-maltodextrin powder. (b). First derivative of water sorption curve of sucrose and sucrose-maltodextrin powder.

The peak in the first derivate of the water sorption curve (Fig. 3.3b) corresponded to crystallization of amorphous sucrose in both the sucrose and the sucrose-maltodextrin system. As shown in Fig. 3.3b, the rate of water sorption increased started above 0.2 a_w (critical water activity), up to a maximum rate and then decreased to the lowest rate at a_w which corresponded to a_w where leveling off of the water sorption curve occurred. Systems with multiple components showed fractional water sorption (Potes, Kerry, and Roos, 2012, Ghorab et al., 2014). As shown in Fig. 3.3, both samples of amorphous sucrose-maltodextrin (SM-FD and SM-VO) showed higher water sorption at low water activities and higher peak at higher water activities than those of amorphous sucrose (S-FD and S-VO). Maltodextrin in blends with lactose inhibited crystallization of lactose in amorphous sugar-maltodextrin system (Potes, Kerry, and Roos, 2012).

Fig. 3.4 shows the water sorption curve of sucrose and its first derivative curve in one plot. The first derivative curve related to the rate of water sorption per water activity change. The water sorption curve changed significantly when the critical water activity was surpassed (above 0.2 a_w) which corresponded to a glassy to a rubbery state transition. The amorphous structure (in this case sucrose) then changed into a crystalline structure. The water sorption rate increased until reaching maximum around 0.45 a_w. Pazus et al. (2011) showed decreased diffusivity in whole milk powder and skim milk powder after crystallization of lactose (collapse occurred). The area under the first derivative curve of water sorption related to water sorbed by the system before deliquescence occurred (Fig. 3.4). We suggested that the peak related to the turning point where before the peak, the rate of water sorption increase until reaching maximum rates, while after turning point the rate of water sorption decrease related to crystallization process. The area was calculated starting from the critical water activity until the water activity where the water sorption curve leveled off. By calculating the area under the curve by trapezoidal rule, the total water sorbed could be determined.

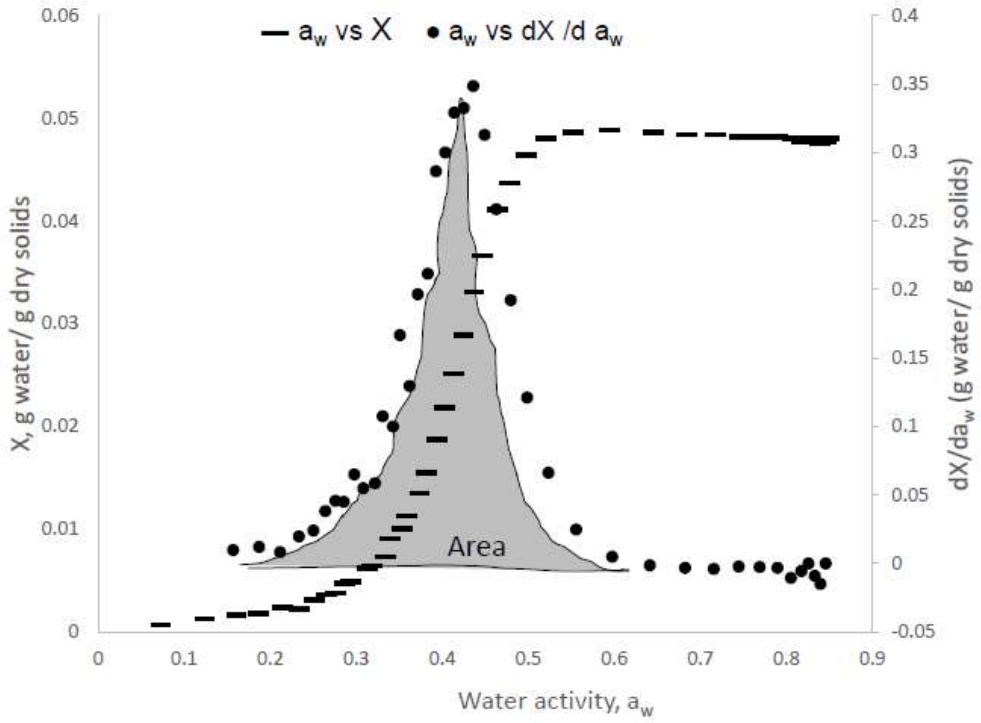
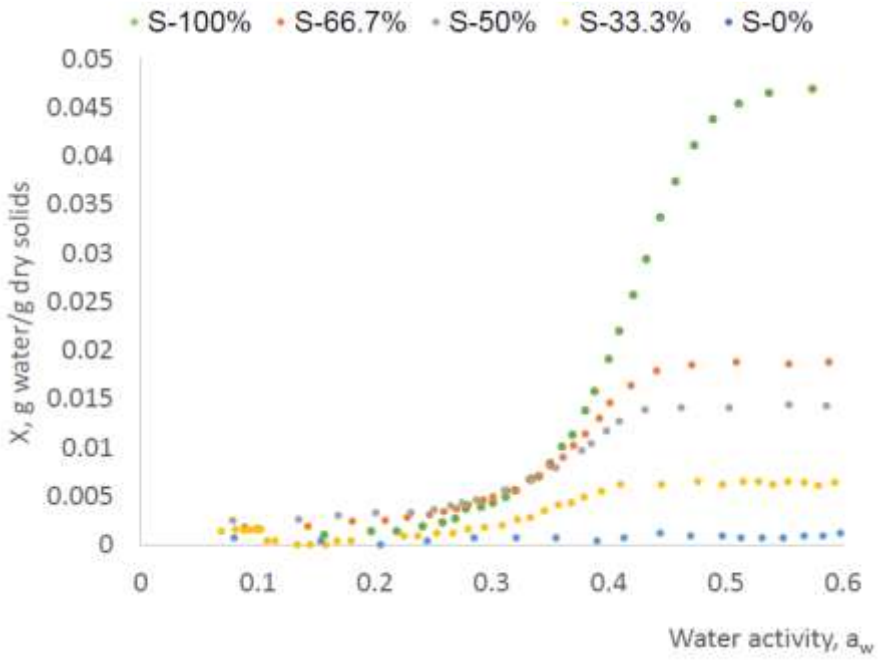


Fig. 3.4. Dynamic water sorption curve and corresponding first derivative of water sorption curve of amorphous sucrose.

3.3.2. Mixture of Amorphous and Crystalline Sucrose-Maltodextrin

Blending crystalline and amorphous sucrose at different ratios were done for both sucrose and sucrose-maltodextrin systems. Blending amorphous and crystalline components were also done by Vollenbroek et al (2010) and Ghorab et al (2014) in their studies. As shown in Fig. 3.5a and 3.6a, systems with a higher amount of amorphous component showed higher water sorption at low water activities which agreed with findings from Bronlund and Peterson (2004). The water sorption curve leveled off at 0.5 a_w which indicated crystallization of amorphous sucrose in both sucrose and sucrose-maltodextrin systems occurred (Fig.s 3.5a and 3.6a). The amount of amorphous component in the systems were proportional to the amount of water adsorbed. The amount of water sorbed by amorphous sucrose in both sucrose and sucrose-maltodextrin systems were calculated by measuring the area under the first derivative of water sorption curves (Fig. 5b and 6b).

a.



b.

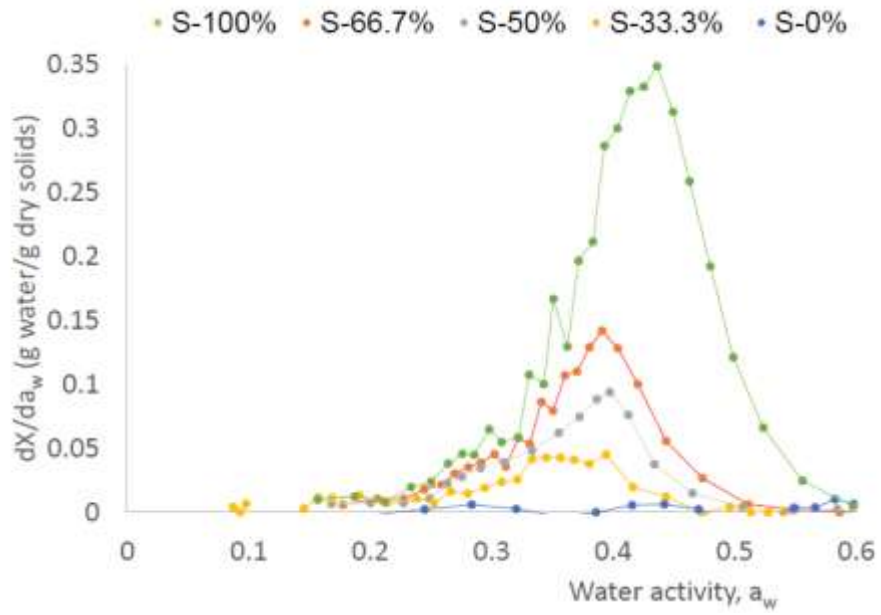
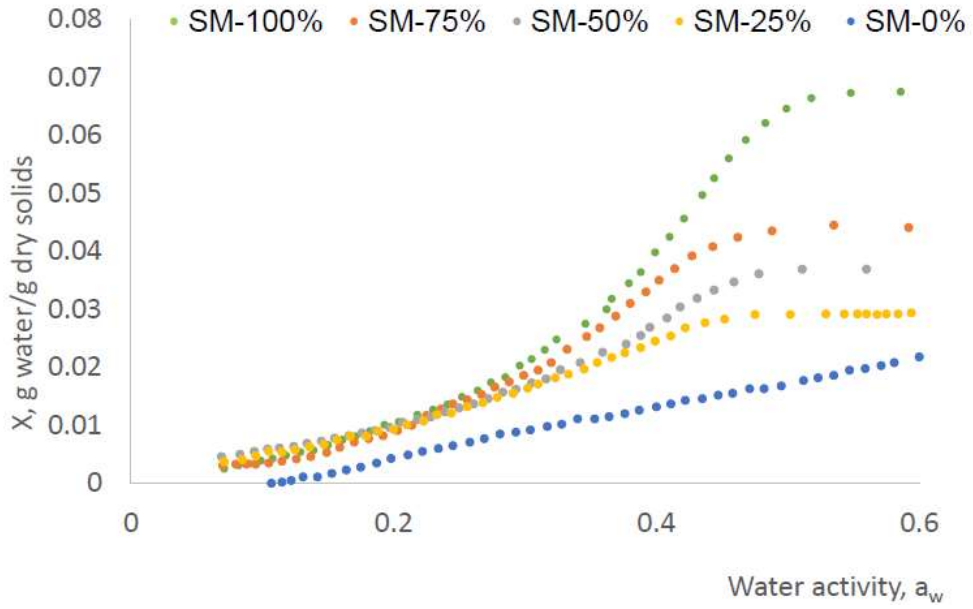


Fig. 3.5. Comparison of sucrose with different ratios of amorphous sucrose to crystalline sucrose (solid/solid). Five amorphous/crystalline systems were made 100 %, 66.7 %, 50 %, 33.3 % and 0 %, namely, S-100, S-66.7%, S-50%, S-33.3% and S-0%, respectively. (a) Dynamic water sorption of sucrose systems (b). First derivative of the dynamic water sorption curve of sucrose systems.

a.



b.

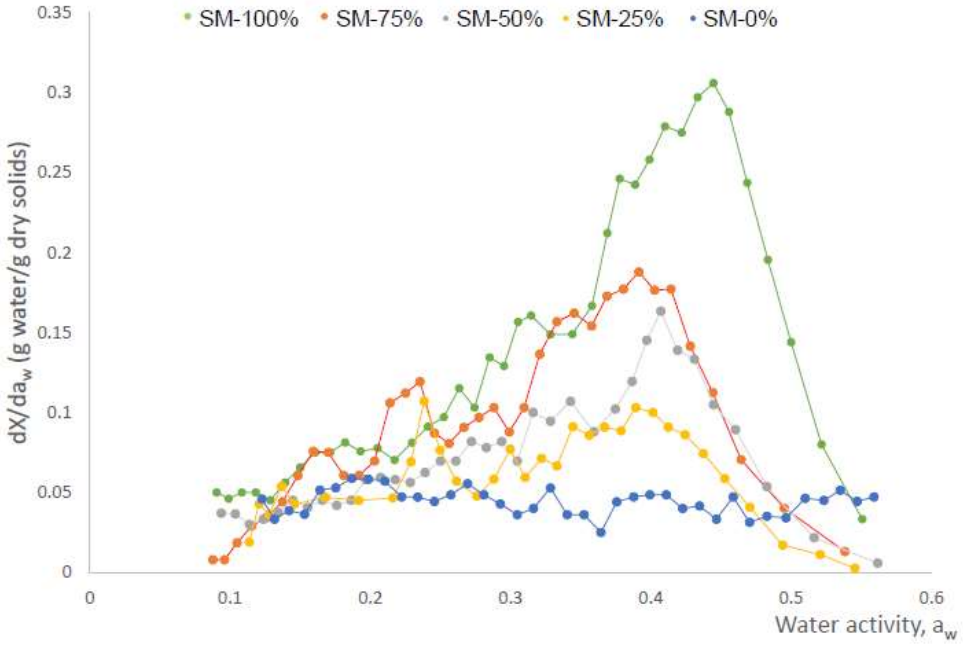


Fig.3.6. Comparison of sucrose-maltodextrin with different ratios of amorphous sucrose to crystalline sucrose (solid/solid, maltodextrin in fix ratio). Five amorphous/crystalline were made 100 %, 75 %, 50 %, 25 % and 0 %, namely, SM-100, SM-75%, SM-50%, SM-25% and SM-0%, respectively. (a) Dynamic water sorption of sucrose-maltodextrin systems. (b). First derivative of the dynamic water sorption curve of sucrose-maltodextrin systems.

Fig. 3.7 shows that the amount of water sorbed by sucrose-maltodextrin was higher than the sucrose system. This is due to an amorphous component in the system containing sucrose and maltodextrin which gave higher water sorption than if it were only sucrose alone. However, if we subtract from the total amount of water adsorbed, the amount of water sorbed by maltodextrin (SM-0%), we get the amount of water sorbed only by amorphous sucrose. These findings were consistent with the result from sucrose system (Inset of Fig. 3.7). The inset (Fig. 7) showed the increasing of water adsorbed as the amorphous content increased.

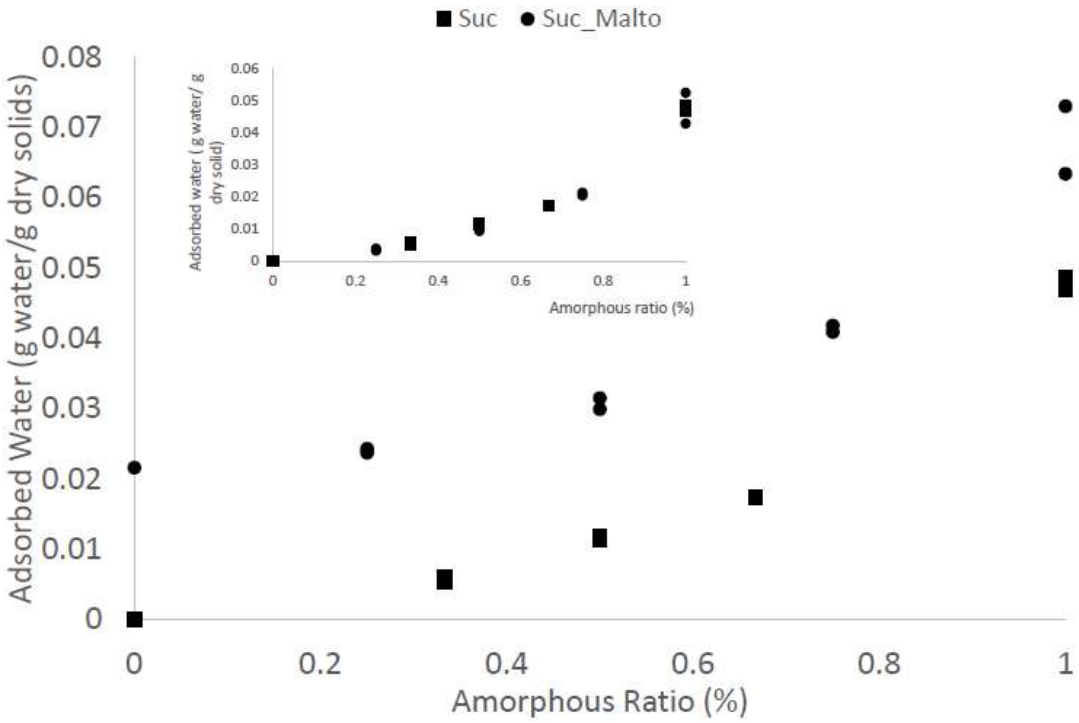
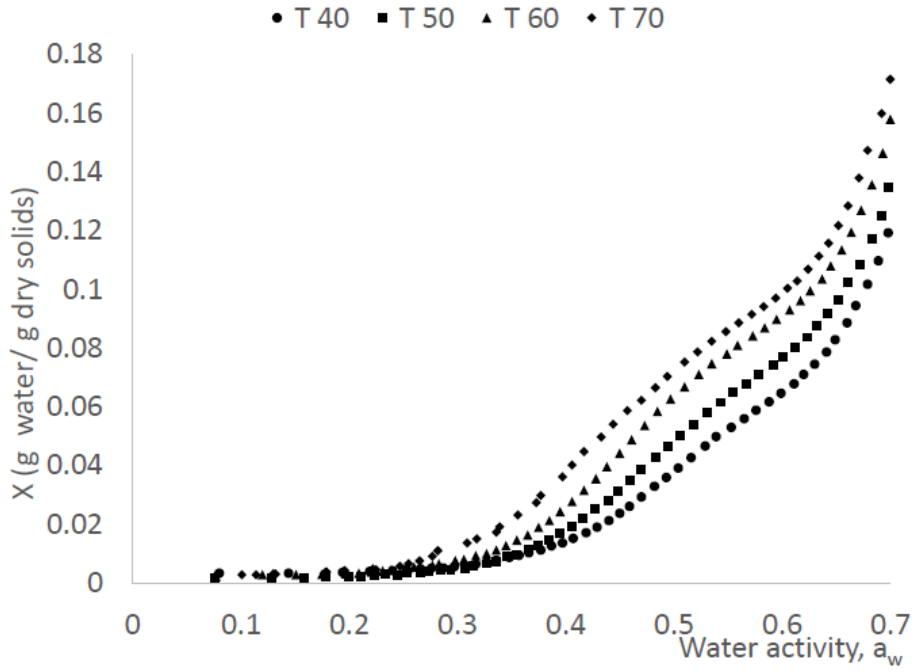


Fig. 3.7. The water sorbed by amorphous sucrose and sucrose-maltodextrin systems. The Inset shows the sorbed water of amorphous sucrose and amorphous sucrose-maltodextrin (where the amount of water sorbed was only by amorphous sucrose) and corresponding amorphous ratio (amorphous sucrose/crystalline sucrose, solid/solid).

3.3.3. Vacuum Dried Honey Powder.

Different temperatures of drying in a vacuum oven were expected to produce honey powders with different amorphous contents. The diffusion of water during the vacuum drying of honey is shown in Table 3.1. It can be seen that the higher the drying temperature, the higher the water diffusion from the system during drying which may affect the formation of amorphous structure of dried samples. Chiou, Langrish and Braham (2008) showed that controlling the inlet temperature of spray drying could affect the amorphous content of product components.

a.



b.

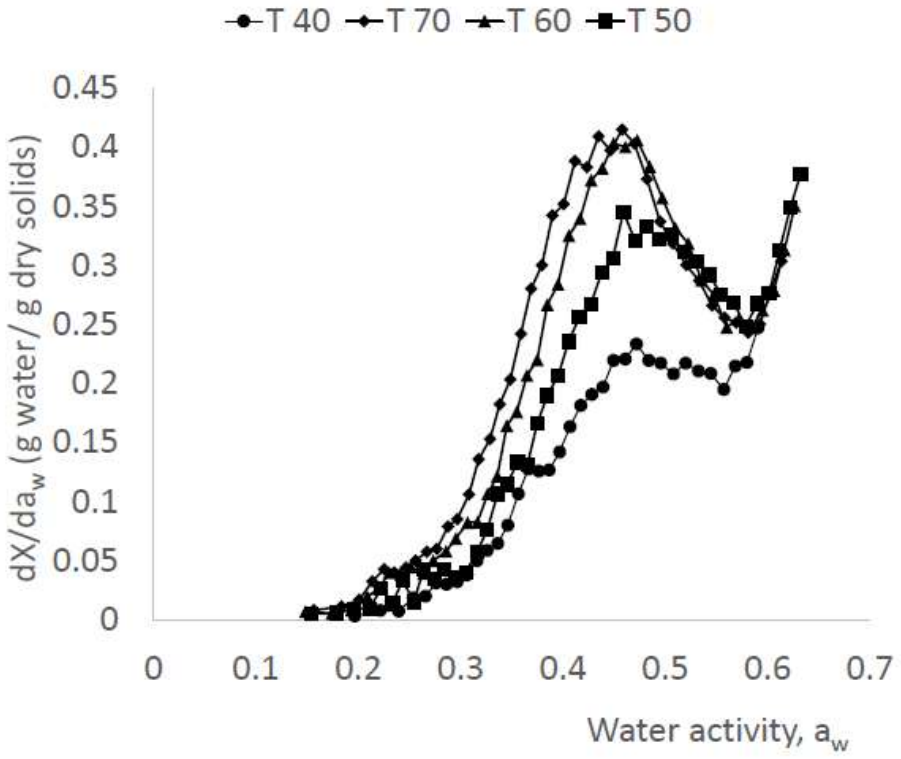


Fig. 3.8. Comparison of Vacuum Dried Honey Powder from Different Drying Temperatures. The drying temperature used were 70, 60, 50 and 40 ℃ (T 70, T 60, T 50, and T 40, respectively). (a) Dynamic water sorption of Vacuum Dried Honey Powder. (b). The first derivative of the dynamic water sorption curve of vacuum dried honey powder.

Fig. 3.8a shows the difference in water sorption of honey powder from different drying temperatures. Honey powder from higher drying temperatures showed higher water sorption than those of lower drying temperatures. The increasing water sorption of vacuum dried honey powder occurred after 0.2 a_w. This finding agrees with Nurhadi and Roos (2016) which showed that the critical water activity of honey powder was 0.2 a_w. From Fig. 8b, the critical water activity occurred around 0.2 a_w and had a peak at 0.45 a_w then the water sorption decreased until 0.6 a_w before increasing again due to dissolution.

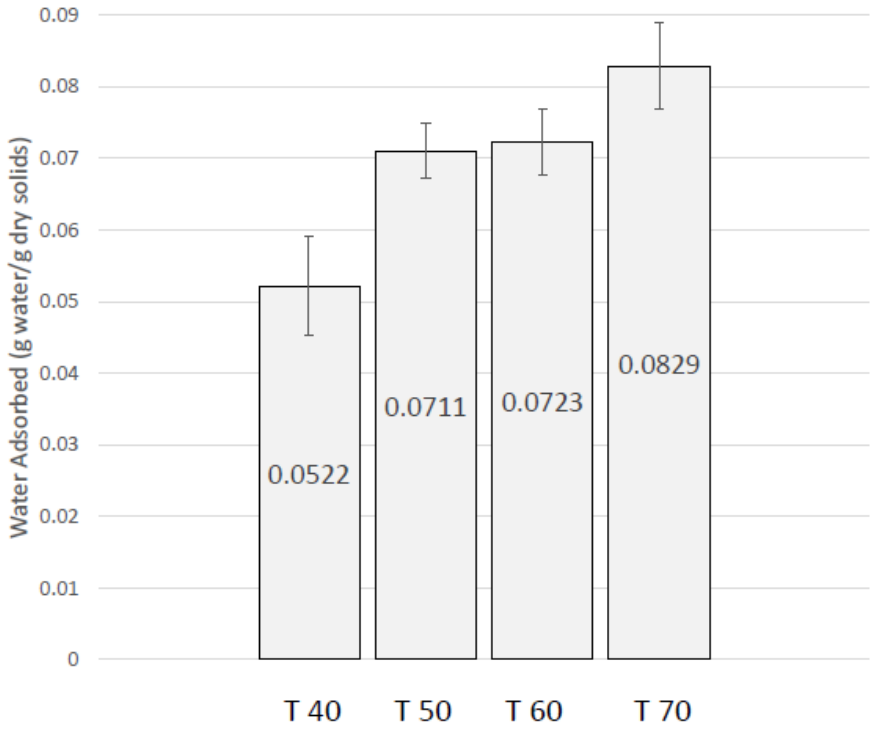


Fig. 3.9. Water sorption of vacuum dried honey powder from different drying temperatures.

As shown in Fig. 3.8b, the higher the drying temperature, the larger the resultant derivative peak. The calculation of water sorbed by honey powder from different temperature is presented in Fig. 3.9. Honey powder from the lowest drying temperature had the smallest amount of water sorbed compared to others. It seemed that the lowest drying temperature resulted in honey powder with the lowest amorphous content. The presence of crystalline structure in vacuum dried honey powder was confirmed by DSC which showed endothermic melting heat (Table 3.1). The endothermic melting peak measured by DSC occurred at a temperature around 73-82 ℃ which agreed very closely with the melting temperature of glucose monohydrate, 83 ℃ (Foster, 2002). As shown in Table 1, the honey powder obtained by higher drying temperature seemed to show lower endothermic melting heat of glucose monohydrate and this finding supported DDI results which showed that higher drying temperatures resulted in higher content of amorphous structure.

Table 3.1. The effective Diffusivity and DSC endothermic melting heat of honey powder from different drying temperature.

Treatment	Effective Diffusivity (1/min)	Endothermic Melting Heat (J/g)
T 40	-0.045 ± 0.0014	1.32 ± 0.17
T 50	-0.051 ± 0.0008	1.38 ± 0.09
T 60	-0.067 ± 0.0023	1.11 ± 0.11
T 70	-0.093 ± 0.0016	1.04 ± 0

3.4. Conclusions

DDI method was used to determine amorphous content by recrystallization principle. The amount of water sorbed during recrystallization process in dynamic water sorption is proportional to the amount of amorphous recrystallizeable component in the powder. The amount of water sorbed by amorphous substances during recrystallization process was calculated from the peak area of first derivative from DDI curve. The DDI method showed good consistency in predicting the amorphous content of pre-known amorphous component of sucrose and sucrose-maltodextrin blend powder. The DDI method predicted qualitatively the amorphous content of vacum dried honey powder from different drying temperature. The result was also backed up with the DSC measurement. It seemed that the higher drying temperature, the higher the amorhous content of the honey powder. Due to its simplicity and quick analysis, the DDI method could be used as an alternative method to determine the amorphous content of a powder whose recrystallizable substances.

CHAPTER IV

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ABSTRACT

Transformation of honey into a dry powder form exhibits difficulties due to its solid composition and liquid properties after drying. The use of high molecular weight materials such as maltodextrins as drying aids in vacuum drying was used to produce honey powder with a high honey content. The present study investigated effects of total solids content of honey maltodextrin systems and the component ratio on water sorption isotherm and water plasticization behavior of the vacuum dried solids. The GAB model fitted well to the water sorption data with monolayer water contents over the range of 4.8 – 6.2 g water/100 g of solids. Water plasticization of the powder followed the Gordon-Taylor equation, with the T_g of dry solids of 30 – 43 ^oC depending on composition. The water content depressing the T_g to ambient temperature was less than the monolayer water content. It appeared that the highest maltodextrin ratio decreased water sensitivity to the highest extent.

Key words: *Honey Powder, Vacuum Drying, Water Sorption, Water Plasticization*

4.1. Introduction

Honey contains up to 65 % (w/w) sugars, primarily fructose (35.7 – 41.7 %, w/w) and glucose (29.7 – 34.9 %, w/w) (Chmielewska, 2004). The ratio of fructose to glucose is in an average 1.2:1 (Chmielewska, 2004). Because of the high glucose content and its lower solubility glucose crystallization is common during storage of honey, and is known as honey granulation. The granulation of honey accelerates with increasing glucose content (Ram, 2014). Honey granulation reduces the sensory acceptability of honey. One alternative to honey liquid with improved shelf life is conversion of honey into honey powder. The production of honey powder could also use crystallization of glucose to stabilize honey powders.

Production of stable solid particles from honey cannot be completed at normal ambient condition because of the low glass transition temperatures, T_g of fructose and glucose, i.e., 5 ^oC and 31 ^oC respectively (Roos, 1993). The water content of fresh honey can exceed 20 % (w/w) and honey is physically a viscous but fluid syrup because of the significant plasticization of the component sugars by water. The reported T_g of honey are low and vary according to several studies: -46 ^oC to -40 ^oC (Sopade et al., 2002), -47 ^oC to -34 ^oC (Lazaridou et al., 2004) and -51 ^oC to -35 ^oC (Ahmed et al., 2007).

Honey powder is commercially produced with drying aids by spray drying and drum drying (Cui et al., 2008). The use of high molecular weight drying aids to enhance dehydration is necessary. Starch, modified starch, maltodextrins and Arabic gum are some of the available filler materials for drying of honey. Nurhadi et al (2012) developed a vacuum oven drying method for honey using starch, pregelatinized starch, maltodextrin and Arabic gum. In vacuum drying, the drying rate was higher compared to conventional drying (cabinet drying). A combination of the high drying rate (low temperature at low absolute pressure) and use of the filler materials enabled the production of powder with a high level of natural solids.

Shi, Fang and Bhandari (2013) and Nurhadi et al. (2012) used water as an aid to enhance homogenous mixing of honey and maltodextrin. The amount of water

added affected total solid content of the liquid (liquid honey mixture). The total solids content of the liquid being dried is an important factor in determining the success of the drying process. In producing honey powder by spray drying, the total solids content of the liquid was set up to 10 % (w/w) (Shi, Fang and Bhandari, 2013) or 25 % (w/w) (Nurhadi et al., 2012). In addition we produced successfully honey powder by freeze-drying at total solids content of 20% (w/w) but freeze-drying was not succeeded at 40 % (w/w) of solids. In vacuum oven drying, different total solids content of honey's mixture, maltodextrin ratio and maltodextrin types might affect the drying process and result in various powder properties of the dried honey. Thus the present study aimed to investigate the effects of water (total solids content), and added maltodextrin type and ratio on dehydration and water sorption and water plasticization behavior of the resultant solids (honey powder) produced using vacuum drying.

4.2. Materials and Methods

4.2.1. Materials*, Processing and Treatments*

Honey Boyne Valley Honey (500 g) was purchased from a local supermarket in Cork, Ireland. Maltodextrins with various dextrin equivalent values; M 150 (DE 15), M 100(DE 10) and M 40 (DE 4)) were from Grain Processing Corp, IA, USA. The water content of honey and maltodextrins was determined by vacuum drying (P_{abs} < 100 mbar) at 70 ^{o}C for about 6 hours (Park and Bell, 2004).

Honey powder was prepared using formulation given in Table 1 by dissolving maltodextrin in water using a stirrer at 40 ^{o}C until a clear solution was obtained and then finally mixed with honey and stirred for about 10 min until the mixture was homogenous. Samples of 10 g honey mixture were then prepared on petri dishes which were closed with a cover (the cover was perforated to allow water evaporation). The solution was dried using a vacuum oven (P_{abs} < 10 mbar, T = 60 ^{o}C) for three hours. After 3 hours of drying, the material was cooled in a desiccator with

P_2O_5 to room temperature (about 30 min), the dried solids were grinded using mortar and pestle, and filled into a vial for storage in a desiccator with P_2O_5 until further analysis. The experimental setup had 7 solid compositions listed in Table 4.1.

Table 4.1. Solids compositions of honey powder formulations.

Formulation		Description		
No.	Description*	% Maltodextrin per total solid (w/w)	% total solids per total weight (w/w)	DE
1	H:M:W=6:4:0, DE 10	44	87	10
2	H:M:W=6:4:5, DE 10	44	58	10
3	H:M:W=6:4:10, DE 10	44	43	10
4	H:M:W=6:4:10, DE 4	44	43	4
5	H:M:W=6:4:10, DE 15	44	43	15
6	H:M:W=7:3:10, DE 10	33	43	10
7	H:M:W=5:5:10, DE 10	54	43	10

Note: *H = Honey, M = Maltodextrin, W = water

4.2.2. Water sorption isotherm

The water sorption isotherm data were obtained from gravimetric water content measurements of steady state water contents at various water activities. Samples of 1 g of honey powder were prepared in glass vials and stored in vacuum desiccators over various saturated salt solutions. (LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $NaNO_2$ and NaCl gave water activities, 0.11, 0.23, 0.33, 0.44, 0.66 and 0.76 respectively). The samples were weighed at 24-hours intervals for 14 days (for aw 0.11, 0.23, 0.33, 0.44) and for 21 days for samples stored at a_w 0.66 and 0.76. The original water contents of the honey powder were determined by dehydration in vacuum oven at 100 ^oC for 6 h. The equilibrium water content of each sample at

various water activity was taken from the weight showing less than 0.001 g difference of consecutive measurements (Sablani, Kasapis and Rahman, 2007). Analyses were carried out in triplicate. The relationship of water activity and the corresponding equilibrium water content was modeled using the BET (eq. 1) and GAB relationships (eq. 2).

$$X = \frac{X_m C a_w}{(1-a_w)(1+(C-1)a_w)} \qquad (1)$$

$$X = \frac{X_m C K a_w}{(1-Ka_w)(1+(C-1)Ka_w)} \qquad (2)$$

Where,

X = water content (g water/ g dry solid)

a_w = water activity

X_m = monolayer water content

X_m, C and K are constants

The goodness of fit of the models was evaluated with the relative percentage square (% RMS) (eq. 3), where the value less than 10 % indicated very good fit (Rizvi, 2005).

$$\%RMS = 100\left[\frac{\sum_{i=1}^{N}\left\{\frac{\left(X_i - X_i^*\right)}{X_i}\right\}^2}{N}\right]^{\frac{1}{2}} \qquad (3)$$

$X_i = Experimental\ water\ content\ (g\ water\ /\ g\ dry\ solid)$

$X_i^* = Calculated\ water\ content\ (g\ water\ /\ g\ dry\ solid)$

$N = number\ of\ data$

4.2.3. Glass transition temperature

The glass transition temperature was measured with differential scanning calorimetry (DSC, Mettler Toledo Schwerzenbach, and Switzerland). Honey powder, 10 -20 mg of was prepared in a standard 40 µl aluminum pan and equilibrated at desiccators over various saturated salt solutions (with various water activity of 0.11, 0.23, 0.33 and 0.44) for 1 weeks and then hermetically sealed and analyzed with DSC. Samples were first analyzed from -40 to 70 ^{o}C at a heating rate of 5 ^{o}C/min, cooled from 70 to -40 ^{o}C at 10 ^{o}C/min and reheated from -40 to 70 ^{o}C at 5 ^{o}C/min. The glass transition temperature was determined using the STAR^{e} software version 8.10 (Mettler Toledo Schwerzenbach, Switzerland). The first heating scan was intended to erase thermal history effect that might affect the T_g determination (Liu, Bhandari and Zhou, 2006). The second heating scan was used for T_g analysis. The relationship between water content and glass transition was modelled with Gordon-Taylor equation (4).

$$T_g = \frac{(1-X)T_{g1} + k_{G-T}XT_{g2}}{(1-X) + k_{G-T}X} \qquad (4)$$

T_{g1} = glass transition temperature of dry solid honey powder

T_{g2} = glass transition temperature of water

X = fraction of water

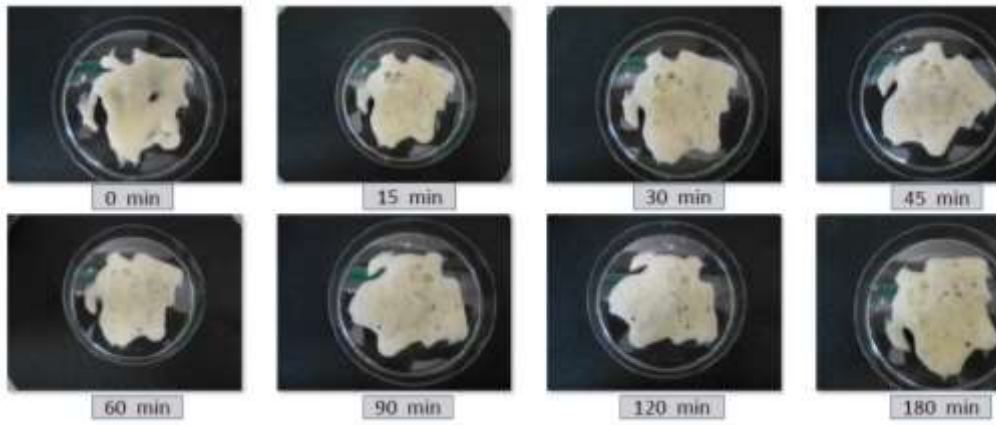
K_{G-T} = constant

4.3. Results and Discussion

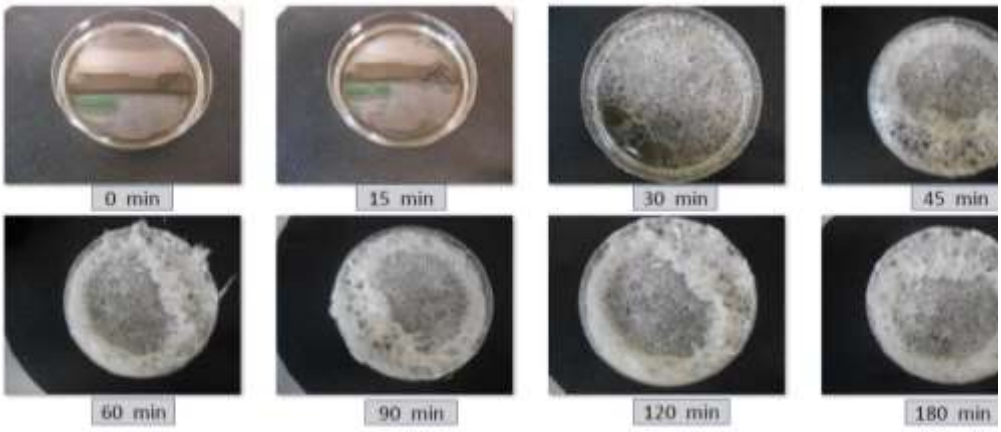
4.3.1. *Vacuum Drying*

All formulations could be used to produce honey powder successfully. Contrast to honey powder production by spray drying which needs total solids content of honey mixture of 10-25 % (w/w) and ratio honey's solid to total solid less than 50 % (w/w) (Nurhadi et al., 2012 and Shi, Fang and Bhandari, 2013), the vacuum drying was more effective. Formulations with total solids contents up to 87 % (w/w) or formulations with maltodextrin ratio to total solid up to 33 % (w/w) could produce honey powder successfully. Honey cannot be dehydrated into powder without addition of other materials (filler materials of a high glass transition temperature). The glass transition temperatures were from -47 ^{o}C to -34 ^{o}C (Lazaridou et al., 2004), or -51^{o}C to -34 ^{o}C (Ahmed et al., 2007) and its value was dependent on the water content and composition. The main factor that enabled dehydration of honey by vacuum drying was the addition of a filler material such as maltodextrin and the use of vacuum. The addition of maltodextrin provided a solids composition with a higher glass transition temperature which could form a solid structure at room temperature (Roos, 1995 and Adhikari et al., 2009). The second main factor was the use of a low pressure. At low pressure, water could evaporate at low temperature. The present study used an oven temperature of 60 ^{o}C and pressure $\leq$ 100 mbar. The vapor pressure of water at 60 ^{o}C was 199.2 mbar (Toledo, 2007), which enhanced evaporation water from honey.

Evaporation of water from honey in the vacuum oven produced a foam (Fig. 4.1.b) and an increase of the evaporation surface. All materials except the formulations H:M:W 6:4:0 with the highest solid fraction (87 %, w/w) did not produce foam-like appearance (Fig. 4.1.a). From Fig. 4.1.b., it can be seen that foaming stopped after 15 minutes of drying. The vigorous boiling of water and bubbling made accelerated the drying process. As a result, a mixture of amorphous and crystalline states of sugars coexisted in the powder.



a.

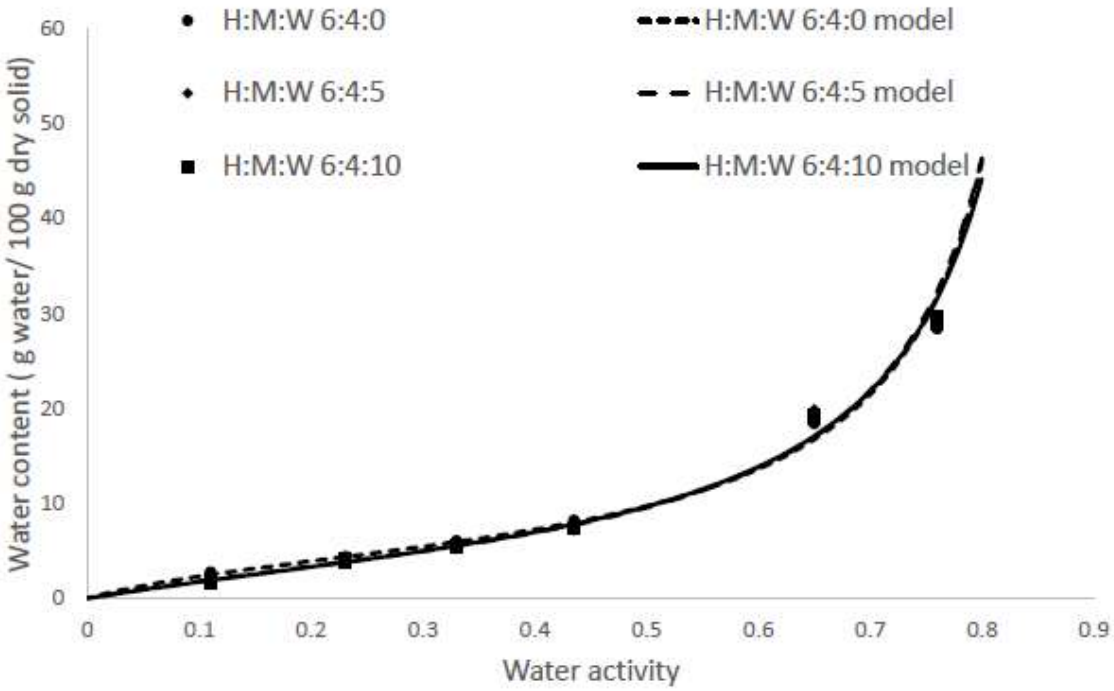


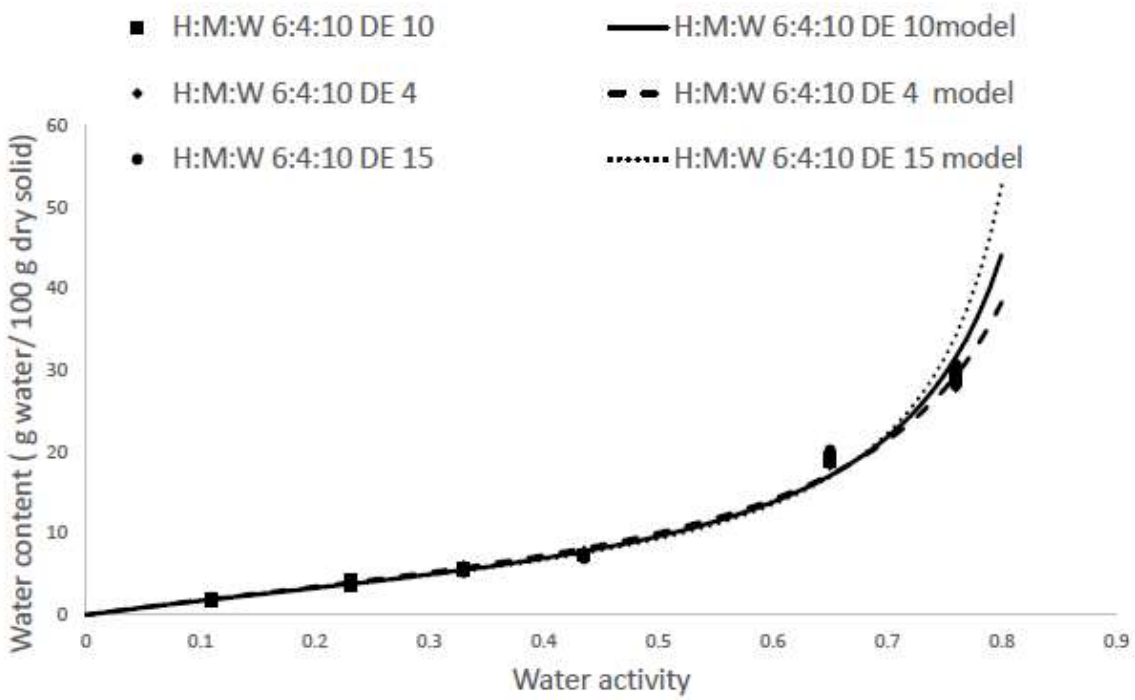
b.

Fig. 4.1. The honey mixture appearance during drying by vacuum oven, (a.)The formulation of H:M:W 6:4:0, (b.) the formulation of H:M:W 6:4:10.

4.3.2. Water Sorption Isotherm

The water content of honey powder stabilized at different times in a series of water activity experiments. It was found that at a lower water activity (up to 0.44), the water content of the honey powder stabilized in less than 2 weeks, while at higher water activities it took almost 3 weeks (data not shown).


H:M:W 6:4:0
H:M:W 6:4:0 model
H:M:W 6:4:5
H:M:W 6:4:5 model
H:M:W 6:4:10
H:M:W 6:4:10 model
Water content (g water/ 100 g dry solid)
Water activity
0
10
20
30
40
50
60
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9


H:M:W 6:4:10 DE 10
H:M:W 6:4:10 DE 10model
H:M:W 6:4:10 DE 4
H:M:W 6:4:10 DE 4 model
H:M:W 6:4:10 DE 15
H:M:W 6:4:10 DE 15 model
Water content (g water/ 100 g dry solid)
Water activity
0
10
20
30
40
50
60
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

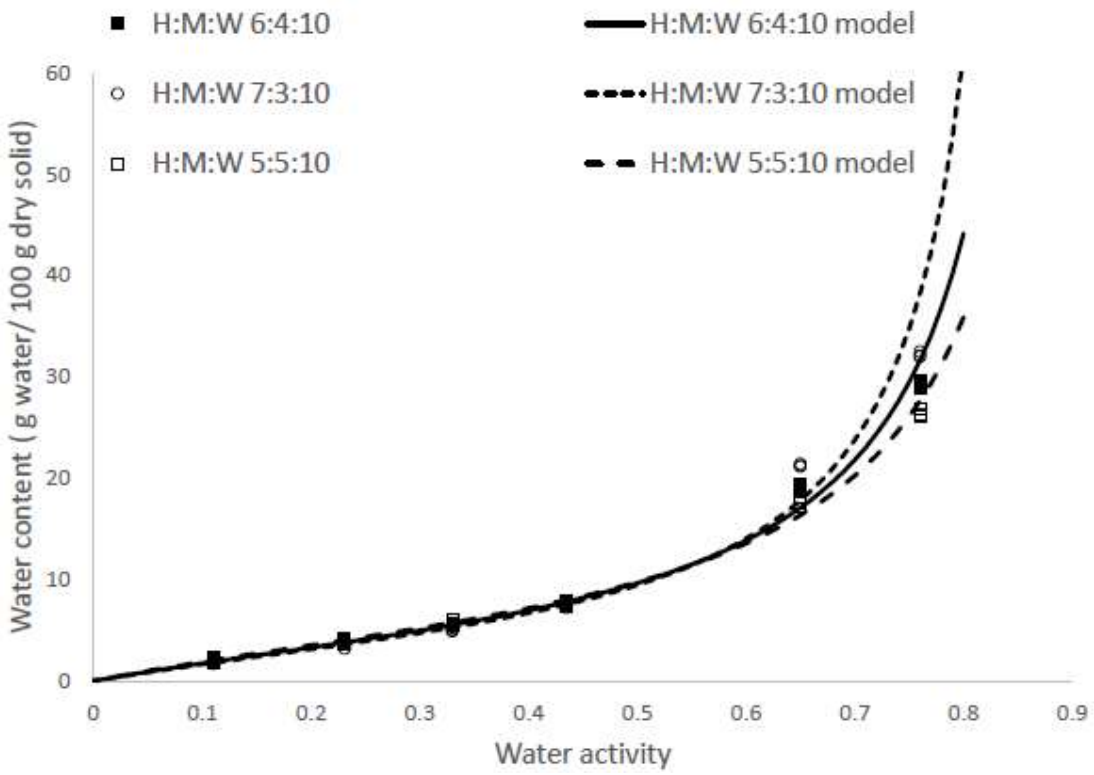


Fig.4.2. Water activity and experimental and GAB calculated water content of honey powder; Top: at different total solid content of honey mixture; Middle: at different DE value of Maltodextrin; below: at different Maltodextrin Ratio.

The BET and GAB models are the main fundamental models relating water content and water activity (Rahman, 2006 and Labuza and Altunakar, 2007). The BET model is backed up by strong theoretical basis for the use in determining stability (Rahman, 2006), but the model is used over more narrow range water activities (0 – 0.5) (Labuza and Altunakar, 2007). The weakness of BET model is overcome by GAB model which could fit to experimental data over a wider range of water activities (0 – 0.95) (Labuza and Altunakar, 2007). The fitness of model was analyzed by the % RMS value (rather than R square value), where a value less than 10 %, showed a good fit to water sorption data (Rizvi, 2005). As presented in Table 4.2, the GAB model showed much lower % RMS than the BET model. The GAB model gave a better fit than BET to

water sorption data of honey powder. Based on the value of C of the BET model (Table 4.2), all the sorption isotherms of honey powder followed the type II of Brunauer water sorption isotherm classification with value between 2-50 (Rizvi, 2005 and Labuza and Altunakar, 2007). However the sorption isotherm shape was less sigmoidal and this phenomenon is common for materials with high sugar contents (Guizani et al., 2010). This type II water sorption of honey powders was similar to other foods with high sugar contents, such as strawberry (Moraga, Martinez and Chiralt, 2004) and raspberry (Syamaladevi et al., 2009).

The monolayer water content (X_m) was considered as an indicator of stability of low moisture foods (Rizvi, 2005). A food with a higher monolayer water content is considered as more stable in storage than a food with lower monolayer water content especially in term of microbial deterioration (Sablani, Kasapis and Rahman, 2007). As given in Table 4.2, the monolayer water content (X_m) of both models showed similar trend for each treatment and showed no significant differences in agreement with Rizvi (2005), who stated that the monolayer water content of BET and GAB model were not significantly different. A comparison of formulations 1, 2 and 3, showed that the addition of water to lower total solids content might increase the monolayer water content. The addition of water made foam formed more easily as a result the drying rate is getting faster and amorphous component was formed preferably instead of crystalline component. Vallenbroek et al (2010) showed that the amorphous ratio of lactose was proportional to the monolayer water content of the mixture of amorphous and crystalline lactose.

Maltodextrin is a hydrolysis product of starch and the extent of hydrolysis is given by the dextrose equivalent (DE) value. The higher the DE value of maltodextrin, the lower is the average molecular weight of the maltodextrin resulting in a lower the glass transition temperature. Maltodextrin is added to honey to increase its glass transition temperature to enable honey solids formed to remain stable at room temperature. Thus the addition of maltodextrin gave positive impact to the stability

of honey powder. According to Table 4.2, the lower the DE value of maltodextrin and the higher ratio of maltodextrin used, the higher was the monolayer water content resulting in more stable honey powder formed.

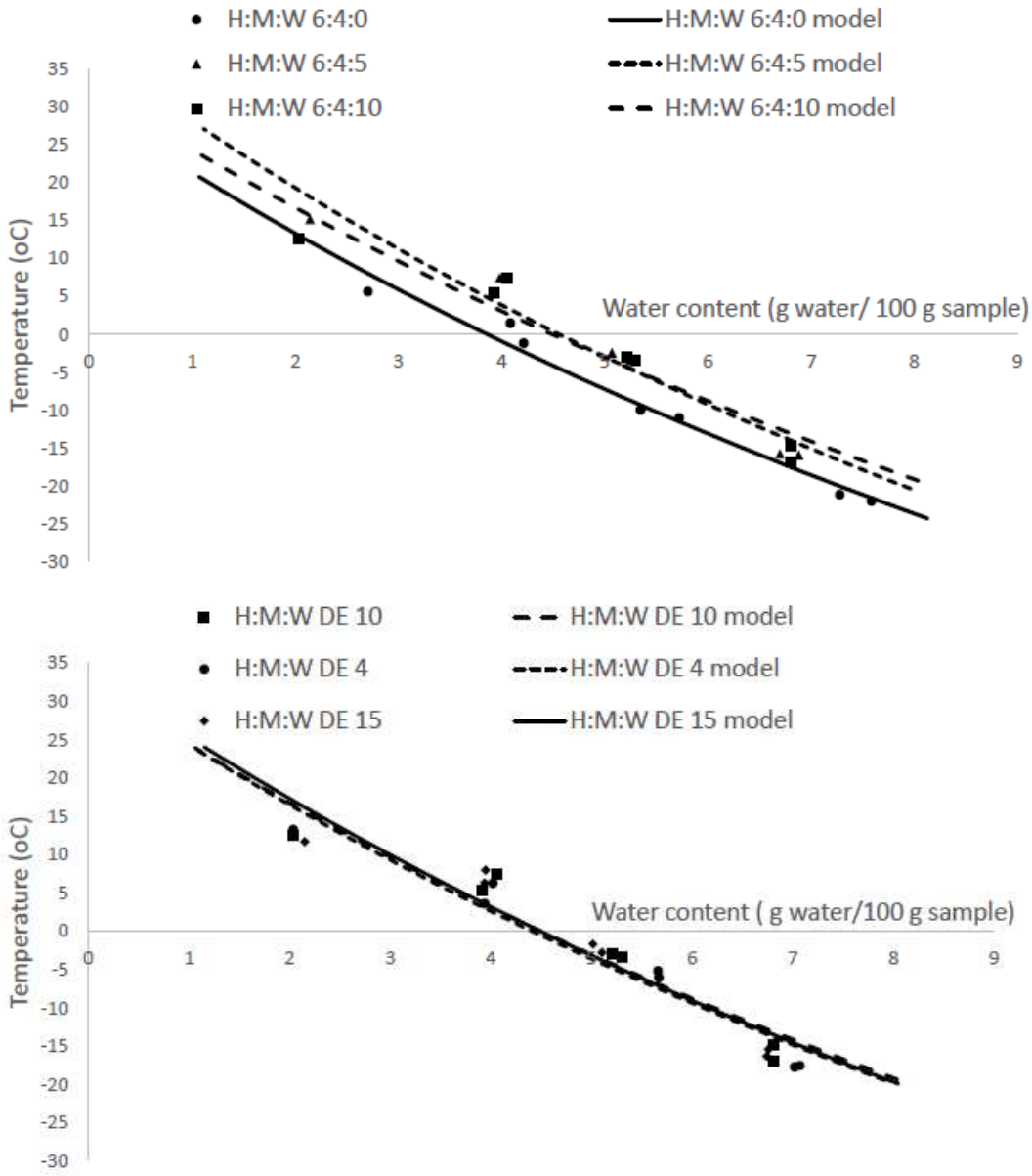
Table 4.2. The BET and GAB model parameters of Honey Powder and Its Corresponding Fit Parameter.

Treatment		BET Model				GAB Model				
No.	Description	X_m	C	R^2	%RSM	X_m	C	K	R^2	%RSM
1	H:M:W=6:4:0, DE 10	5.5	5.3	0.95	80.4	4.8	5.8	1.1	0.93	7.7
2	H:M:W=6:4:5, DE 10	5.6	3.7	0.94	73.8	5.2	3.5	1.1	0.93	8.4
3	H:M:W=6:4:10, DE 10	5.8	3.4	0.93	71.4	5.5	3.2	1.1	0.94	7.7
4	H:M:W=6:4:10, DE 4	6.3	3.2	0.94	68.9	6.2	3.0	1.1	0.96	5.4
5	H:M:W=6:4:10, DE 15	5.3	4.2	0.97	76.8	4.8	4.0	1.1	0.94	9.1
6	H:M:W=7:3:10, DE 10	5.9	3.0	0.88	68.6	4.9	3.2	1.2	0.94	11.2
7	H:M:W=5:5:10, DE 10	6.1	3.4	0.91	70.0	5.8	3.4	1.1	0.93	5.8

X_m = monolayer water content (g water/ 100 dry solid)

4.3.3. *Water Plasticization Behavior*

The honey powder produced by vacuum oven drying gave a mixed structured powder with amorphous and less portion of crystalline components. The crystalline fraction might be glucose monohydrate which showed a melting endotherm peak at 71-78 ^oC (data not shown) which was very close with melting temperature of glucose monohydrate 83 ^oC (Foster, 2014). Water is the main plasticizer in food solids. The function of water as a plasticizer is related to complex mechanism that involved hydrogen bond formation between water and food component and change of the matrix free volume (Mrad et al., 2012). The effect of water as plasticizer in the honey powder would reduce its glass transition temperature (Fig. 4.3).


H:M:W 6:4:0
H:M:W 6:4:0 model
H:M:W 6:4:5
H:M:W 6:4:5 model
H:M:W 6:4:10
H:M:W 6:4:10 model
Temperature (oC)
Water content (g water/ 100 g sample)
H:M:W DE 10
H:M:W DE 10 model
H:M:W DE 4
H:M:W DE 4 model
H:M:W DE 15
H:M:W DE 15 model
Temperature (oC)
Water content (g water/100 g sample)

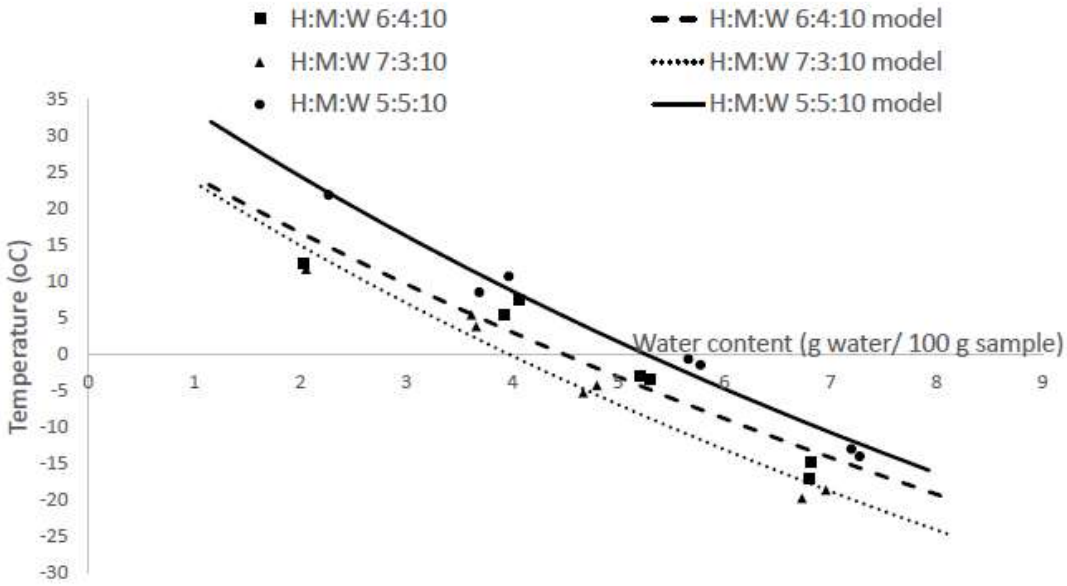


Fig. 4.3. Water content and Glass Transition Temperature of vacuum dried honey powder; Top: at different total solid content of honey mixture; Middle : at different DE value of Maltodextrin; Below: at different Maltodextrin Ratio.

Honey powder from highest total solid fraction of the honey mixture (H:M:W 6:4:0) had the lowest glass transition at each water content, followed by two other formulations of lower total solid fraction H:M:W 6:4:5 and H:M:W 6:4:10, respectively. The honey powder from highest total solid fraction of mixture might contain more crystalline components and this result was backed up by the result that Honey powder produced from highest total solid content (H:M:W 6:4:0) which had the lowest ΔC_p value then followed by honey powder H:M:W 6:4:5 and H:M:W 6:4:10 (Table 4.3). This result complied with Lehto et al. (2006) finding that the amorphous content (amorphicity) is proportional to the value of ΔC_p of DSC analysis. From Fig. 4.3, it can be seen that the honey powder from highest solid fraction formulation had lowest temperature. It can be understood that the decrease in amorphous phase in honey powder with high solid content (H:M:W 6:4:0) affected the increasing water ratio to amorphous phase, thus it decreased the glass transition temperature. The glass transition of honey powder increased as the ratio of maltodextrin increase from

33 % to 44 % and 54 %. However different DE values of maltodextrin had minor effects on the glass transition temperature of the honey powders (Fig. 4.3).

The Gordon-Taylor model is often used to relate the water content and glass transition temperature of amorphous solid. The equation contains two constants (T_{g1} or dry solid glass transition temperature) and a constant, K value, while the T_g of water of -135 ^oC may be used. The Gordon-Taylor model related well the water content and glass transition temperature data of honey powders with R^2 value more than 0.9 (Table 4.3). The value of glass temperature of dry solids of honey powder was in the range of 30 to 38 ^oC being very close to the onset glass transition temperature of amorphous glucose (Roos, 1995). The significantly highest value of the glass transition of honey powder dry solid was obtained for formulation with the highest maltodextrin ratio (H:M:W 5:5:10). It was suggested that the solid ratio of maltodextrin to total solid 54 % (or honey to total solid 46 %) affected significantly the glass transition temperature of the system. It complied with Roos (1995), who stated that the minimum amount ratio of maltodextrin to sugar more than 50 % would increase the glass transition temperature of the mixture significantly.

Table 4.3. The Gordon-Taylor Model Parameters Based on Data of Onset, Midpoint and Endpoint Glass Transition Temperature and the Average of ΔC_p Values and Standard Deviations.

Treatment		Onset			Midpoint			Endpoint			ΔC_p	
No.	Description	T_{g1} (°C)	K_{G-T}	R^2	T_{g1} (°C)	K_{G-T}	R^2	T_{g1} (°C)	K_{G-T}	R^2	avg	Stdev
1	H:M:W=6:4:0, DE 10	30	5.6	0.98	42	6.0	0.98	50	6.0	0.97	0.6	0.05
2	H:M:W=6:4:5, DE 10	38	5.9	0.96	45	5.6	0.97	50	5.2	0.97	0.7	0.03
3	H:M:W=6:4:10, DE 10	33	5.2	0.92	42	5.2	0.95	49	5.1	0.95	0.7	0.05
4	H:M:W=6:4:10, DE 4	33	5.3	0.95	40	5.2	0.97	47	5.1	0.98	0.7	0.02
5	H:M:W=6:4:10, DE 15	34	5.3	0.91	41	5.0	0.96	48	4.8	0.98	0.7	0.06
6	H:M:W=7:3:10, DE 10	33	5.9	0.97	41	5.8	0.98	48	5.6	0.99	0.8	0.05
7	H:M:W=5:5:10, DE 10	43	5.8	0.98	52	5.6	0.98	60	5.3	0.99	0.6	0.02

4.3.4. Water *Sorption and Water Plasticization Relationship*

Along with water activity, glass transition temperature is used as an indicator for predicting food stability. It is suggested that a product stored at a temperature lower than its glass transition temperature, will be stable better because all chemical and physical change occurred slowly below the glass transition temperature (Roos, 1995). The correlation between water sorption isotherm and water plasticization of honey powder can be found in Table 4.4. The storage temperature chosen was 25 ^{o}C and the water content and its corresponding water activity of honey with glass transition temperature at 25 ^{o}C is called critical water content and critical water activity, respectively (Roos, 1995).

The critical water content and critical water activity of honey powder based on the onset, midpoint and endpoint glass transition temperature were lower than the monolayer water content and its corresponding water activity. The same result was obtained for products with high sugar contents such as strawberry (Moraga, Martinez and Chiralt, 2004), kiwifruit (Moraga, Martinez and Chiralt, 2006), raspberry (Syamaladevi et al., 2009) and Grapefruit (Fabra et al., 2009). Sablani, Kasapis and Rahman (2007) explained that for high sugar food, the effect of water in depressing glass transition temperature is more significant than the effect of sugar in reducing the water activity. Thus critical water content and corresponding water activity of honey powder is more appropriate to use as a parameter of stability than the monolayer water contents. As presented in Table 4.4, honey powder with the highest ratio of maltodextrin (formulation 7) gave significantly the highest critical water content and water activity to other honey powders. It was suggested that the ratio maltodextrin higher than 50 % played more significant effect on honey powder's stability than the treatment of DE value and solid content.

Table 4.4. The Critical Water Content and Water Activity of Honey Powder Based on the Onset, Midpoint, Endpoint Glass Transition Temperature and Monolayer Water Content and Corresponding Water Activity.

Treatment		Sorption Isotherm		$T_{g(onset)}$		$T_{g(midpoint)}$		$T_{g(endpoint)}$	
No.	Description	X_{m*}	$a_{w\ (x=xm)}$	X_{crit}	a_{wcrit}	X_{crit}	a_{wcrit}	X_{crit}	a_{wcrit}
1	H:M:W=6:4:0, DE 10	4.6	0.3	0.6	0.0	1.8	0.1	2.5	0.1
2	H:M:W=6:4:5, DE 10	4.9	0.3	1.4	0.1	2.2	0.1	3.0	0.2
3	H:M:W=6:4:10, DE 10	5.2	0.3	0.9	0.1	2.0	0.1	2.9	0.2
4	H:M:W=6:4:10, DE 4	5.8	0.4	0.9	0.1	1.8	0.1	2.7	0.2
5	H:M:W=6:4:10, DE 15	4.6	0.3	1.0	0.1	2.0	0.1	2.9	0.2
6	H:M:W=7:3:10, DE 10	4.7	0.3	0.9	0.1	1.8	0.1	2.5	0.2
7	H:M:W=5:5:10, DE 10	5.5	0.3	1.9	0.1	3.0	0.2	3.9	0.2

X_{m*} and $X_{critical}$ in g water/100 g sample

4.4. Conclusions

The treatments of solid content and DE value less significantly affected the water sorption isotherm and water plasticization behavior of the resulted honey powder. However the treatment of maltodextrin ratio affected more significantly the properties of honey powder. The honey powder from maltodextrin ratio more than 50 % had the highest critical water content and critical water activity at storage temperature of 25 ^{o}C. The critical water content of honey powder at 25 ^{o}C was lower than that of their monolayer water content, thus the critical water content was more appropriate as an indication of honey powder stability during storage

CHAPTER V

Influence of Anti-Caking Agent on the Water Sorption Isotherm and Flow-ability Properties of Vacuum Dried Honey Powder

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ABSTRACT

Honey powder is a hygroscopic powder due to its composition and structure. The addition of anti-caking agent was aimed to increase the stability of honey powder. The present study aimed to study the influence of anti-caking agent on the water sorption isotherm and flow-ability properties of vacuum dried honey powder. Anti-caking agents, calcium silicate and calcium stearate, were added in honey powder. The addition of anti-caking agent influenced water sorption and flow-ability properties of honey powder. Calcium silicate addition seemed not to affect water sorption isotherm properties of honey powder, however, calcium stearate showed inhibiting effect of recrystallization and collapse of structure of amorphous honey powder. Addition of anti-caking agent to honey powder increase flow-ability of honey powder and calcium stearate seemed to increase flow-ability better than calcium silicate.

Key Words: *Honey powder, calcium silicate, calcium stearate, flow-ability, water sorption isotherm*

5.1. Introduction

Honey powder is a hygroscopic powder due to its composition and structure. The two main sugars found in honey solids, fructose, and glucose, have very low glass transition temperatures making honey powder hygroscopic (Bhandari and Howes, 1999). Nurhadi and Roos (2016b) reported the production of honey powder by using vacuum drying technique and drying aid materials (filler), maltodextrin. Anhydrous honey powder glass transition temperature was reported over 30 to 43 °C depending on drying aid material type and composition (Nurhadi and Roos, 2016b). Critical water content of honey powder was also very low, less than 2 % (g water/100 g sample) (Nurhadi and Roos, 2016b). Honey powder might be in purely amorphous or partially amorphous structure depending on process used (Nurhadi and Roos, 2016a). When water is sorbed by honey powder during storage, water acts as a plasticizer. Reduced glass transition temperature of honey powder to lower than ambient temperature, results significant changes of macroscopic properties of honey powder, i.e. collapse which includes phenomena such as stickiness, caking and shrinkage (Roos, 1995; Bhandari and Howes, 1999). The rate of changes was dependent on the difference of ambient temperature to glass transition temperature ($T-T_g$), the higher the difference was the faster was the rate at which the macroscopic properties changed (Roos, 1995; Foster, Bronlund, Paterson, 2006; Roos and Drusch, 2015). The change would reduce quality of honey powder and the powder is becoming difficult to handle or difficult to flow.

Method to keep honey powder stable during storage is by storing it at a temperature below its glass transition temperature or below its Ca_w. Additionally, anti-caking agent could be used to maintain stability of sugar-rich powder such as honey powder (Welti-Chanes et al., 2007). Anti-caking agent (or flow conditioner or free flowing agent) is the ingredient added at low quantity to increase stability and maintain free flowing properties of host material (in this case honey powder) (Barbosa-Canovas et al., 2005). Anti-caking agent mechanism is different for

amorphous and crystalline materials (Msagati, 2013). The mechanism of anti-caking agent might be by competing for water with host material, acting as a water barrier, eliminating surface friction and inhibiting crystal growth (Barbosa-Canovas et al., 2005 and Lipasek et al., 2012). Anti-caking agent is classified as natural (such as kaolin, talc, and bentonite/silicate material) or synthetic when manufactured from raw materials such as silicon dioxide (Msagati, 2013). Lipasek et al (2012) reported the use of silicon dioxide, calcium silicate and calcium stearate up to 2 % as anti-caking agent in host powder of crystalline material. The addition of anti-caking agent might affect water sorption and flowing properties of host powder. The addition of anti-caking agent into crystalline material did not change the shape of water sorption and some anti-caking agent showed delaying deliquescence of crystalline material (Lipasek, Taylor and Mauer, 2011 and Lipasek et al., 2012).

Powder flow-ability is more complex than fluid (Xanthakis et al., 2015). Powder flow-ability is affected by material properties and stress history of material during processing (Koynov, Glasser, Muzzio, 2015). Powder flow-ability is affected by internal factor such as particle size and distribution and external factor such as air humidity and temperature (Barbosa-Canovas et al., 2005). Powder flow-ability is one of powder bulk properties (Barbosa-Canovas et al., 2005). Powder would flow if the load acting on the powder is bigger than the powder strength (or the bulk structure of powder failed) (Barbosa-Canovas et al., 2005). Barbosa-Canovas et al (2005) considered powder flow-ability as a failure phenomenon. Two main properties used to describe the flow-ability of powder are failure function and effective angle of internal fraction. Failure function correlates with major principal consolidation stress (MPS) and unconfined failure strength (UFS) to deduce the value of flow index. The correlation between MPS and UFS is linear and the inverse slope of the best fit linear line equals to the flow index (Barbosa-Canovas et al., 2005, Koynov, Glasser and Muzzio, 2015). The slope describes the change of stress needed to induce the powder flow. The lower is the slope, the more free flowing properties of the powder exist. The

effective angle of internal friction is a property that describes the inter particle interaction (Barbosa-Canovas et al., 2005) and powder with a low value of effective angle is considered as a free flowing powder. The current study was aimed to investigate the influence of anti-caking agents on water sorption and flow-ability properties of anhydrous vacuum-dried honey powder.

5.2. Materials and Methods

5.2.1. Honey Powder

Honey was bought from local supermarket (Boyne valley Honey Brand). Deionized water was used from KB scientific (Cork, Ireland) and maltodextrin DE 10 (M100) was obtained from Grain processing corporation (IA, USA). Honey-maltodextrin solutions (total solid 43 %, ratio honey: maltodextrin = 6:4 (40 %) and 4:6 (60%), solid ratio) were prepared on petri dishes sealed using perforated covers for drying in vacuum oven (WTB Binder, Germany) at temperature 60 °C for 3 hours. The dried samples were grinded and stored in P_2O_5 (Sigma-Aldrich) for further analysis.

5.2.2. Mixing Honey Powder and Anti-Caking Agent

Anti-caking agents, calcium silicate and calcium stearate (Sigma-Aldrich), were used. Anti-caking agents in Erlenmeyer flask and honey powder were added gradually based on geometric mixing principle to obtain an even distribution. Each addition of honey powder was followed by mixing with spatula.

5.2.3. Water Sorption Isotherm

5.2.3.1. *Static water sorption*

The static water sorption followed the same procedure presented in section 2.2.2 (Chapter 2).

5.2.3.2. **Dynamic *water sorption (Dynamic Dew point Isotherm/DD*I)**

The DDI water sorption followed the same procedures presented in section 3.2.2.4 (Chapter 3).

5.2.4. Tapped Density

Honey powder sample was poured in 25 ml measuring cylinder until fully covered the volume stated. The measuring cylinder with honey powder inside then was put in tapped density meter (J. Engelsmann AG, Germany) and tapping was done for 100 times. The end volume was then recorded. Hausner Ratio (H_R) was calculated as followed (Barbosa-Canovas et al., 2005):

$$H_R = \frac{\rho_\infty}{\rho_o}$$

Where:

ρ_∞ = tapped density (bulk density of powder after tapping)

ρ_o = initial loose bulk density

5.2.5. Powder Flow-ability

Flow-ability of honey powder was measured using Powder Flow tester (Brookfield, USA). Sample of honey powder was put in trough with an annular shape and flattened with inner catch tray. The trough had a volume of 38 cc and the initial weight of trough and after sample addition were recorded. The vane lid was then moved down to cover the trough. The vane lid had a diameter of 12.7 cm and a curved profile. Standard flow test was set to run the experiment. The trough then rotated while powder was consolidated/compressed. Five consolidation stresses and 3 stresses for each stress were set up. Five consolidation stresses used were 0.795, 1.607, 3.246, 6.559 and 13.252 kPa. As an example at consolidation stress of 0.795 kPa, the 3 stresses used were 0.795 kPa and the other two stresses lower than 0.795 kPa, 0.265 and 0.536 kPa (Fig. 5.1). The trough rotated until steady flow was reached and then the shear stress and normal stress were recorded. Data of normal stress and

shear stress were recorded for each consolidation stress. From Fig. 5.1., major principal consolidation stress (MPS) and unconfined failure strength (UFS) were determined for each consolidation stress with the use of powder flow pro. V1.2 Build 19 software (Brookfield, USA). The best fit line of normal stress and shear stress was called as yield locus and Mohr's semi-circle was used to determined MPS and UFS (Barbosa-Canovas et al., 2005 and Koynov, Glasser, Muzzio, 2015). UFS was determined with the use of Mohr's semi-circle which passing through origin point and tangent to the yield locus while MPS was determined with the use of Mohr's semi-circle which was passing through pre shear consolidation stress (0.536 KPa) and tangent to the yield locus. MPS and UFS represented the condition for the critical state and critical failure respectively (Koynov, Glasser, Muzzio, 2015). Xanthakis, Ommen, Ahrne (2015) added that UFS is strength that developed during powder compaction to make powder flow. Effective yield locus was determined based on the line which passing through origin and tangent to bigger Mohr's semi-circle and the angle between x-axes (normal stress axes) and effective yield locus was called as effective angle of internal friction (Barbosa-Canovas et al., 2005). The data between MPS and UFS for every consolidation stress was then correlated to determined flow index. Flow index was the inverse of slope of best fit linear line between MPS and UFS.

Based on the value of flow index (ff), flow-ability of a powder can be classified as (Barbosa-Canovas et al., 2005).

Ff < 1 non flowing

1 < ff <2 very cohesive

2 < ff < 4 cohesive

4 < ff < 10 easy flowing

ff > 10 free flowing

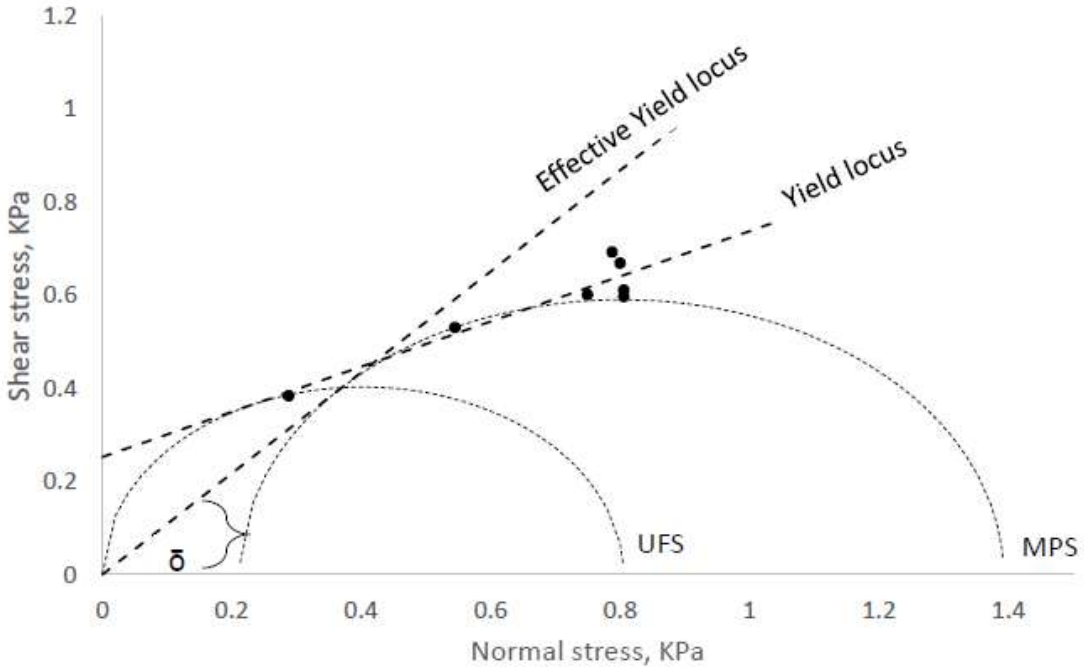


Fig. 5.1. Yield Locus, effective yield locus, and Mohr's stress semi-circle from an example of honey powder flow-ability measurement by powder flow tester at 0.795 kPa consolidation stress.

Loose and consolidated density of honey powder at each consolidated stress were also obtained.

5.3. Results and Discussion

5.3.1. Water Sorption Isotherm

Water sorption isotherm of honey powder was done by using static/conventional and dynamic method (DDI method). Even though the data from dynamic water sorption could not be compared with data obtained from conventional method in calculating water sorption model (such as GAB and BET model) (Schmidt and Lee, 2012), the DDI data could be used to study the properties changes during water sorption experiment (Romani et al., 2016) such as critical water activity determination (Yuan, Carter and Schmidt, 2011; Carter and Schmidt, 2012), deliquescent point (Ghorab et al., 2014) and amorphous content (Nurhadi and Roos, 2016a). From Fig. 2, it can be seen that addition of anti-caking agent (2%) to host powder of honey powder did not change shape of WSI and the WSI were classified as type II of Brunaeur water sorption isotherm classification. Nurhadi and Roos (2016b) also reported that honey powder had type II of Brunaeur water sorption isotherm. Thus addition of anti-caking agent did not change WSI shape of honey powder. As shown in Fig. 5.2, anti-caking agent addition to honey powder also did not change its corresponding monolayer water content. The result agreed with those reported by Lipasek, Taylor and Mauer (2011) that the anti-caking agent did not change the shape of deliquescent material WSI.

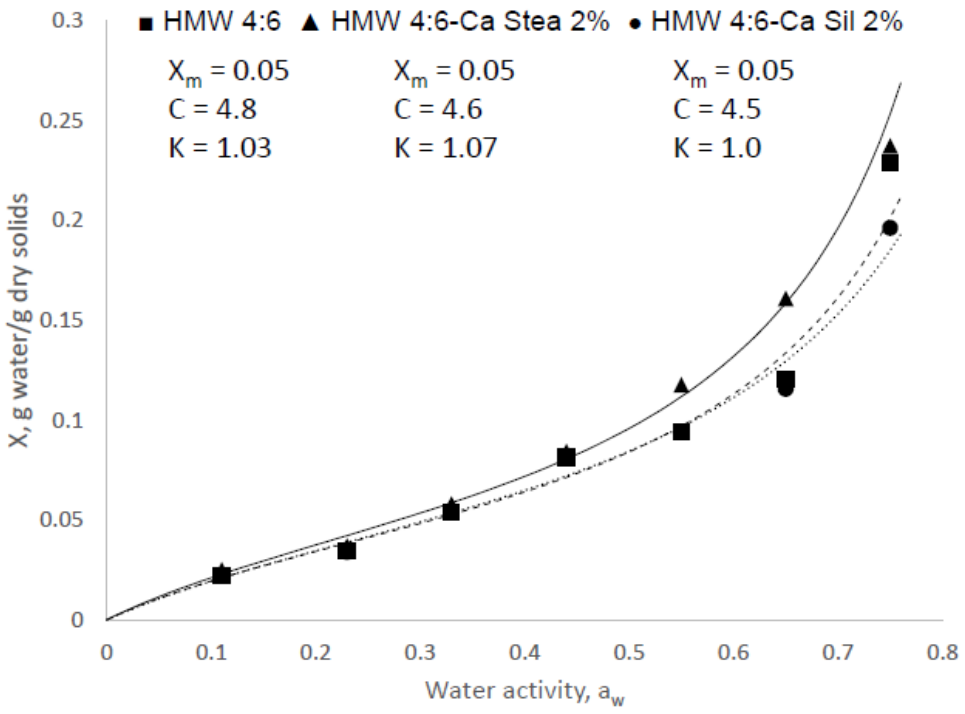
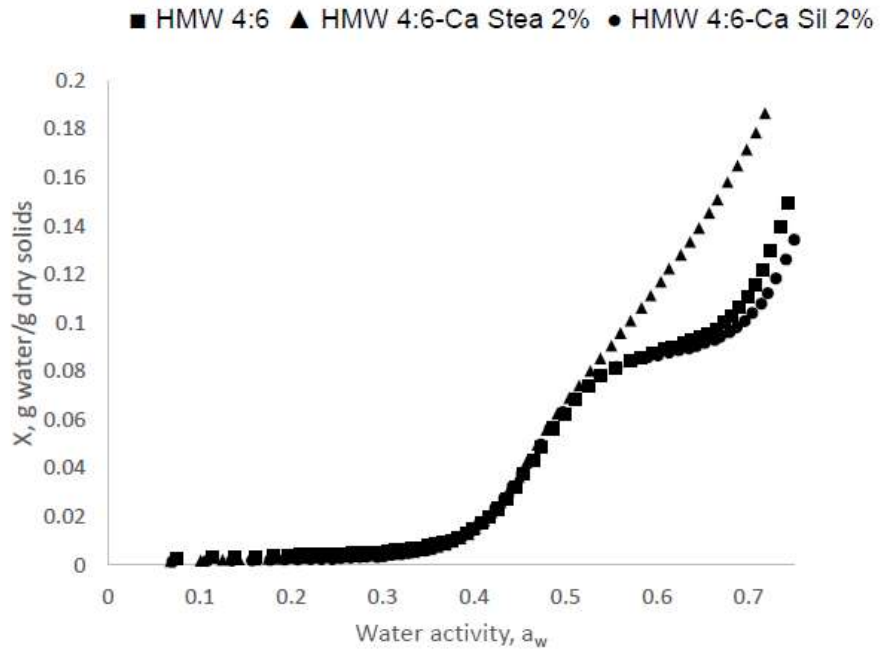


Fig. 5.2. Static water sorption isotherm of honey powder and honey powder with addition of anti-caking agent and GAB parameter for each treatment.

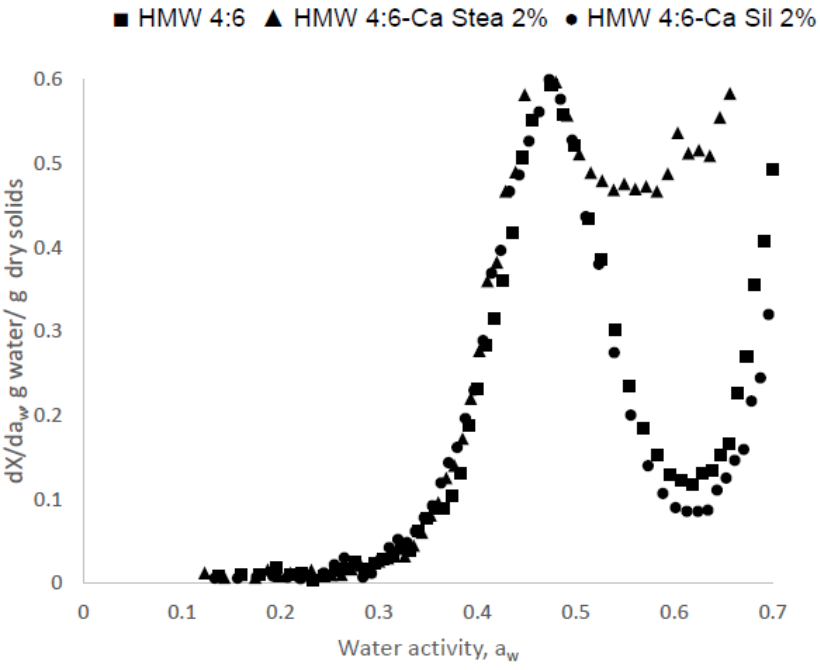
Honey powder (maltodextrin ratio of 60 % per total solid) with calcium stearate addition (2%) had higher water sorption than other two treatments of honey powder over water activity (a_w) range of 0.44-0.76. As shown by Fig. 5.3a, the significant increase of water sorption of honey powder occurred above a critical water activity (around 0.35 a_w). The critical value obtained by DDI method is much affected by the flow rate of air over the sample during the measurement. The higher is the air flow rate, the higher is the critical water activity obtained (Yuan, Carter and Schmidt, 2011). The Ca_w from normal method (DSC and WSI method) would be equal to the Ca_w obtained from DDI method by extrapolating the Ca_w at zero flow rate (Yuan, Carter and Schmidt, 2011). It could be seen that anti-caking addition seemed not to change the critical water activity of honey powder. The critical water activity was correlated with the significant increase of water sorption due to transition from glassy structure to rubbery structure of amorphous component (Yuan, Carter and Schmidt, 2011;

Carter and Schmidt, 2012). After critical water activity surpassed, the macroscopic properties such as crystallization of amorphous components and caking increased significantly (Nurhadi and Roos, 2016a). As shown in Fig. 5.3a, there was a difference in water sorption after 0.5 a_w between honey powder with calcium stearate and other two honey powders (honey powder and honey powder with calcium silicate). The equilibrium water content for both calcium stearate and calcium silicate were very low, (based on DDI WSI) in the range of 0.1-0.8 a_w. The water content range 0.2 % - 0.5% and 1.8 % - 6.0 % corresponded to calcium stearate and calcium silicate, respectively. The low water sorption of both calcium stearate and calcium silicate were also reported by Lipasek et al. (2012).

The clearer differences of water sorption behavior between honey powders are shown in Fig. 5.3b. Nurhadi and Roos (2016a) used first derivative of WSI curve to show crystallization of amorphous components during water sorption which appeared as a peak and the area of peak correlated to the extent of crystallization occurred. It seemed that the crystallization of amorphous components of honey powder occurred, however, the inhibition of crystallization was apparent in honey powder with addition of calcium stearate. Honey powder without anti-caking agent and honey powder with calcium silicate had more complete peak than the honey powder with calcium stearate (Fig. 3b).



a.



b.

Fig. 5.3. Dynamic water sorption of honey powder and honey powder with the addition of anti-caking agent (a), first derivative curve of dynamic water sorption of honey powder and honey powder with the addition of anti-caking agent.

From static WSI experiment, the collapsed structure of honey powder appeared in honey powder without anti-caking agent and honey powder with calcium silicate starting at 0.44 a_w while collapse did not occur in honey powder with calcium stearate (Fig. 5.4). However at higher a_w, honey powder with Calcium stearate addition also showed stickiness and lump phenomena (0.65 and 0.75 a_w) and need tapping several time to the vial to move out the powder from the vial. Calcium stearate act as a barrier and due to its hydrophobic properties to repel water from ambient air to the host particle (honey powder) that prevent crystallization of amorphous sugar (maintaining structural integrity) and collapse. Lipasek et al. (2012) explained the ability of calcium stearate as moisture barrier between particles that might interrupt bridging mechanism as an initial step of collapse occurred. Murrieta et al. (2011) stated the collapsed structure of milk powder was triggered by recrystallization of amorphous lactose in milk powder. The collapse phenomena occurred when Ca_w surpassed and caused physical and chemical changes such as non-enzymatic browning reaction (Roos, 1995, Roos and Drusch, 2015). Thus it could be shown that the addition of anti-caking agent (Calcium stearate) into honey powder could inhibit crystallization and collapse of amorphous structure of honey powder during water sorption experiment. That explained the phenomena occurring in static WSI of honey powder (Fig. 5.2) where honey powder with calcium stearate had higher water sorption than the other two honey powders due to recrystallization inhibition of amorphous sugar in honey powder. The addition of anti-caking agent, calcium silicate and calcium stearate at 1% in honey powder showed the same result as those with 2% (data not shown).The disadvantages of calcium stearate addition are related to its taste and solubility. Honey powder with addition calcium stearate at 1 % (w/w) still showed bitter taste (Chalk taste) and did not dissolved in water.

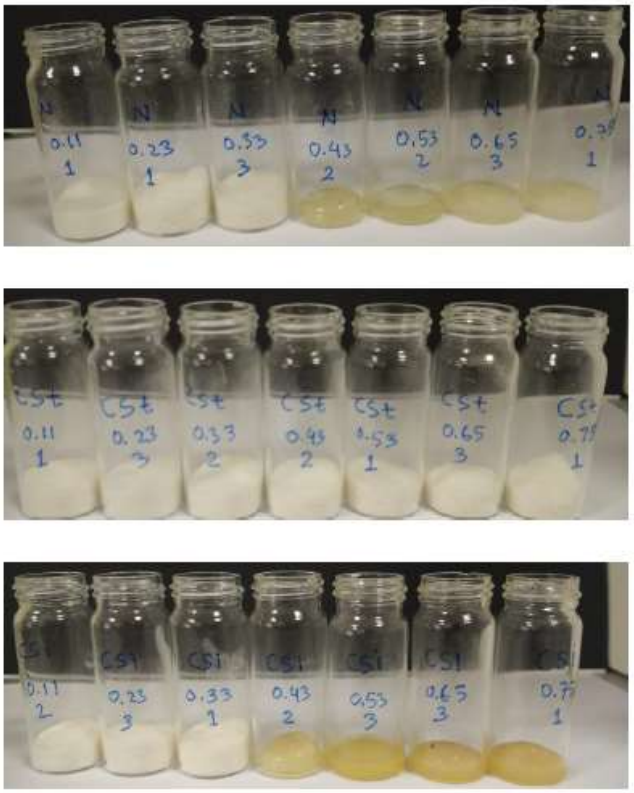


Fig. 5.4. Honey powder and honey powder with addition of anti-caking agent after reaching equilibrium at various water activity, from top to bottom correspond to honey powder, honey powder + 2 % calcium stearate and honey powder + 2 % calcium silicate, respectively.

5.3.2. Flow-ability

In order to work optimally as anti-caking agent, there should be interaction or surface affinity between anti-caking agent and host powder (Barbosa-Canovas et al., 2005). The interaction is indicated by the increase of bulk density of host powder after addition of an anti-caking agent (Barbosa-Canovas et al., 2005). As shown in Table 5.1, the addition of anti-caking agent (calcium stearate and calcium silicate) increased bulk density from 0.59 to 0.64-0.66 (g/cm^3). The increase of bulk density showed the high surface affinity between anti-caking and host particle and if it is not, anti-caking agent could fill the void between host particles powder and no increase of bulk density may occur (Barbosa-Canovas et al., 2005).

Table 5.1. Parameters of honey powder obtained from powder flow tester and tapped density tester.

Treatment	Powder flow-ability tester				Tapped Density (g/cm^3)		
	Flow index, ff	Density (g/cm^3)					
		Initial	After Consolidation 6.5 kPa	Relative Increase	ρ_o	ρ_t	H_R
HMW 6:4	3.04 ± 0.26	0.49 ± 0.03	0.72 ± 0.02	1.49 ± 0.03	0.58 ± 0.01	0.75 ± 0.00	1.3 ± 0.03
HMW 4:6	7.64 ± 0.43	0.59 ± 0.01	0.91 ± 0.03	1.57 ± 0.06	0.67 ± 0.01	0.81 ± 0.01	1.21 ± 0.00
HMW 4:6-Ca Stea 2 %	11.91 ± 2.55	0.66 ± 0.03	1.05 ± 0.12	1.49 ± 0.11	0.70 ± 0.01	0.85 ± 0.02	1.22 ± 0.00
HMW 4:6-Ca Sil 2 %	13.44 ± 0.38	0.64 ± 0.01	0.90 ± 0.02	1.39 ± 0.03	0.70 ± 0.00	0.81 ± 0.00	1.16 ± 0.00

Flow-ability of honey powder with higher maltodextrin ratio was better than the lower ratio. As given in Table 5.1 and Fig. 5.5, the flow-ability index of honey powder increased from cohesive to easy flowing when the ratio of maltodextrin to honey increased from 40 % to 60 % (solid ratio). Honey powder with lower maltodextrin ratio had lower glass transition temperature (Nurhadi and Roos, 2016b) and tended to be more hygroscopic. The DDI critical water activity of honey powder increased (from around 0.3 a_w to 0.35 a_w) when the maltodextrin ratio to honey increased from 40 % to 60 % (per total solid) (Fig. 5.6). Barbosa-Canovas et al (2005) explained that flow-ability of powder was influenced significantly by external conditions such as air relative humidity. Water acted as a plasticizer and reduced glass transition temperature to below ambient temperature (Roos and Drusch, 2015) and honey powder became more sticky and difficult to flow.

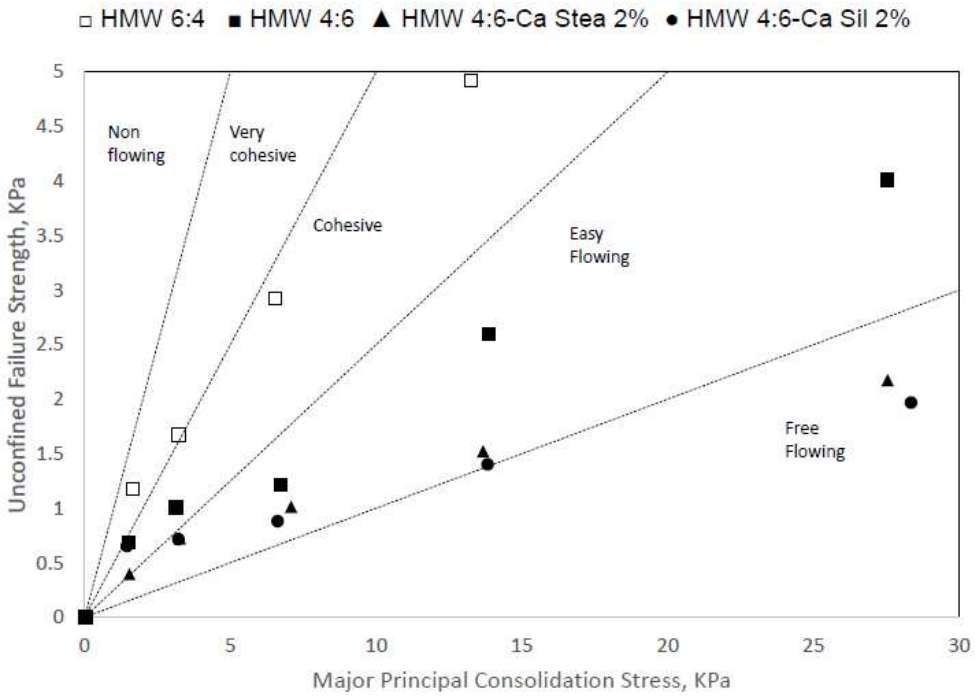


Fig. 5.5. The flow-ability characteristic of honey powder and honey powder with addition of anti-caking agent.

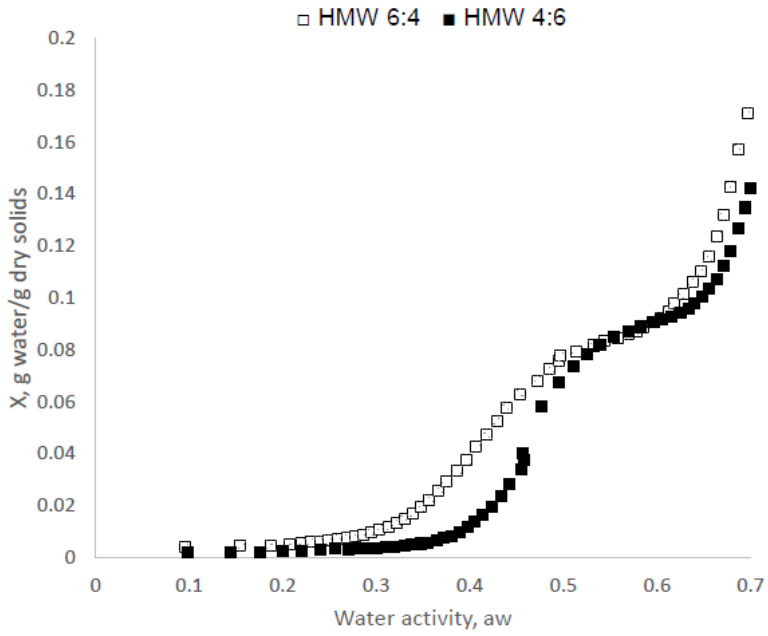


Fig.5.6. Dynamic water sorption of honey powder at different ratio of maltodextrin DE 10

Instead of increasing the ratio of maltodextrin as a drying aid material, anti-caking agent might be used to improve the flow-ability of honey powder. As can be seen in Table 5.1 and Fig. 5.5, the addition of anti-caking agent 2 % (both calcium stearate and calcium silicate) could increase the flow-ability properties of honey powder from an easy flowing to a free flowing powder. Density properties were also used as an indication of powder flow-ability (Barbosa-Canovas et al., 2005 and Xanthakis, Ommen and Ahrne, 2015). Relative decrease of bulk density after compaction or tapping of powder was an indicator that the powder had good flow-ability properties (Barbosa-Canovas et al., 2005). From Table 5.1, based on the value of Hausner ratio (H_R), the honey powders (excluding honey powder with lower maltodextrin ratio, HMW 6:4) were classified as a medium flowing powder while HMW 6:4 was classified as a difficult flowing powder. The increasing bulk density value after compaction in powder flow-ability tester of honey powder with anti-caking agent were smaller than honey powder with anti-caking agent and the result was comparable to flow index results. However, the inconsistent result based on density measurement was found in honey powder with different maltodextrin ratio. The inconsistent flow-ability measurement based on density properties was also reported by Xanthakis, Ommen, and Ahrne (2015).

Flow-ability of powder was determined as a failure function in term of flow index as explained in Barbosa-Canovas et al (2005). In addition to flow index, the effective angel of internal friction can also be used to determine the flow-ability properties of honey powder. The lower the value of effective angle of internal friction, the more free flowing properties the powder has (Barbosa-Canovas et al., 2005). As shown in Fig. 5.7, honey powder with calcium stearate had the lowest effective angle of internal friction followed by both honey powder and honey powder with calcium silicate and honey powder with lower maltodextrin ratio (HMW 6:4). The effective angle of internal friction was a propertiy that described inter-particle interaction of

powder. The lower value of the angle indicated a smoother surface interaction between particles in the powder. Compared to calcium silicate, calcium stearate has smaller size and had ability to coat the surface more extensively. Lipasek et al (2012) also reported calcium stearate as the best anti-caking agent in reducing effective angle of internal friction of sucrose.

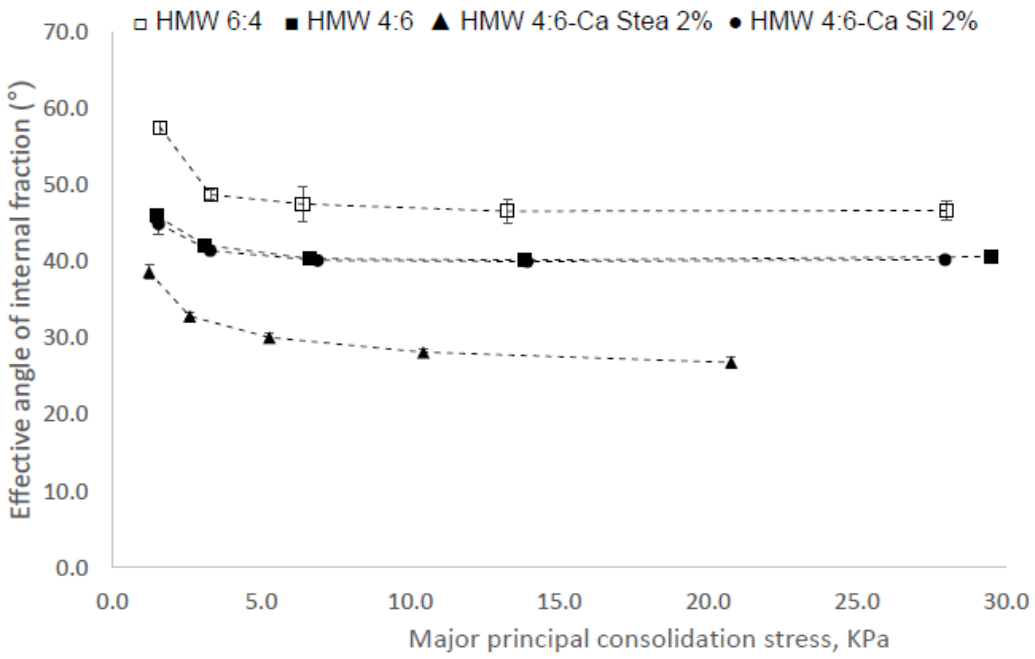


Fig. 5.7. Effective angle of internal friction of honey powder and honey powder with addition of anti-caking agent.

5.4. Conclusion

Anti-caking agent calcium silicate and calcium stearate were added into honey powder. The addition of anti-caking agent influenced water sorption and flow-ability properties of honey powder. Calcium silicate addition seemed not to affect water sorption isotherm properties of honey powder, however calcium stearate showed inhibiting effect of recrystallization and collapse of structure of amorphous components of honey powder. Addition of anti-caking agent to honey powder increase flow-ability of honey powder and calcium stearate seemed to increase flow-ability better than calcium silicate. Addition of anti-caking agent increased flow-ability of honey powder from an easy flowing to a free flowing powder and calcium stearate showed significant reduction of internal friction between particles of honey powder that contributed the powder becoming more free flowing.

CHAPTER VI

GENERAL DISCUSSION

6.1. Vacuum-Dried Honey Powder: Ingredient Properties

Honey has high sugar content with more than 85 % of total solids being fructose and glucose although fructose of higher amount than glucose (Table 1.4). The pH of honey is low over the range of 3.8 – 5.0 (Ahmed et al., 2007, Nurhadi et al., 2012). Citric acid and gluconic acids are the main acids (Chmielewska, 2004). The T_g of honey is very low from -51.14 to -33.64 depending on solids composition and water content (Kantor, Pitsi and Thoen, 1999, Ahmed et al., 2007, Venir, Spaziani and Maltini, 2010, Nurhadi et al., 2012, Shi, Fang and Bhandari, 2013).

The solid composition of honey makes honey difficult to dry due to stickiness problem. Based on the main sugar composition of honey, it could be predicted that anhydrous solids T_g of honey should be between that of T_g of fructose (5 °C) and glucose (31 °C) (Table 1.4.). Lazaridou et al. (2004) used Gordon-Taylor equation to determine anhydrous T_g of honey solids and obtained the value of 15 °C. Shi, Fang and Bhandari (2013) reported that the T_g of freeze-dried honey powder was 12.5 °C (with water content of 3.2 g water/100 g samples). Thus it is impossible to dry honey to an anhydrous glassy solid at normal ambient temperature of 25 °C and drying aids or fillers with high molecular weights (high T_g) should be added to increase the T_g of honey. Fillers or drying aids are also needed to reduce stickiness problems and maintain stability during storage (Roos, 1995, Roos and Drusch, 2015).

Maltodextrin is a starch hydrolysis product and the products are differentiated by their molecular weight which indicates their dextrose equivalent (DE value) (Linden and Lorient, 1999). The higher the DE of maltodextrin, the lower the molecular weight of maltodextrin or the lower the (Linden and Lorient, 1999). The water sorption and water plasticization properties of maltodextrin DE 10 complied with the previous results (Nurhadi et al., 2016). The maltodextrin showed type II WSI of Brunauer classification with sigmoid WSI curve and was plasticized by water following Gordon-Taylor equation (Nurhadi et al., 2016). Maltodextrin DE 10 had high T_g and showed high critical water activity (Nurhadi et al., 2016). The properties of drying aid should

have higher critical water activity than water activity at equilibrium with water content equal to monolayer water content (Sablani, Kasapis and Rahman, 2007).

In addition to glass transition, enthalpy relaxation is another important property related to the stability of materials in their glassy state. Enthalpy relaxation might result in more compact molecular organization and as a result increasing rigidity and brittleness and decreasing density and transport properties (Kim et al., 2003). Enthalpy relaxation of maltodextrin DE 10 was studied where maltodextrin was stored at various a_w below its critical water activity (water annealing method, a_w 0.68) at the same temperature, 25 °C (Nurhadi et al., 2016). Maltodextrins stored at low a_w showed longer relaxation times which meant more stable glass (Nurhadi et al., 2016). At the same T_g-T, maltodextrin had enthalpy relaxation lower than lower molecular weight sugars such as trehalose (Nurhadi et al., 2016). Kawai et al. (2005) showed at the same T_g-T, the lower the Tg of sugar the higher the value of enthalpy relaxation was. Enthalpy relaxation time was temperature dependent and it could be modelled by Arrhenius equation (Kawai et al., 2005; Liu, Bhandari and Zhou, 2006; Nurhadi et al., 2016). The activation energy of maltodextrin was found higher than that of trehalose and other sugars which meant maltodextrin was more stable glass among the sugars (Nurhadi et al., 2016).

The study of enthalpy relaxation of the mixture of drying aids (amorphous tapioca starch with DE value 39-42) and sucrose was investigated by Liu, Bhandari and Zhou (2007). Theoretically the lower the sugar addition to the mixture, the longer the relaxation time was. However some deviation was found in the system containing amorphous tapioca starch and sucrose and the deviation might be due to the true composition of amorphous tapioca starch (Liu, Bhandari and Zhou, 2007). The system containing amorphous tapioca starch and sucrose was similar to the mixture of maltodextrin and honey. The situation might be more complex for the mixture of honey and maltodextrin due to the complex composition of both maltodextrin and

honey. Maltodextrin with the same DE value might have different compositions (Linden and Lorient, 1999).

6.2. Vacuum-Dried Honey Powder: Processing Aspect

Rapid evaporation of water during drying process is needed to produce amorphous glassy solids (Roos, 1995, Roos and Drusch, 2015). In spray drying process, the rapid evaporation of water is due to combined effect of a very small size of sample droplets (20-250 μm) and high temperature (Bhandari, Patel and Chen, 2008). In freeze-drying, slow sublimation takes place as combination of very low temperature (below freezing point) and very low pressure condition (less than 0.1 kPa or 100 Pa) (Ratti, 2008, Ratti, 2013). Vacuum drying refers to drying process at low temperature (above freezing point) and at pressure lower than ambient pressure (Land, 2012).

The pressure used in vacuum drying process of the present study was less than 2 kPa. As shown in Fig. 6.1., at pressure of 2 kPa, water boils at a temperature below than 20 °C (17.5 °C, Toledo, 2007). The drying process in vacuum drying method is depicted by reducing the pressure (process a) and increasing temperature (process b) (**Fig. 6.1.**). The drying temperature used was over the range of 40 – 70 °C which was higher than the corresponding boiling temperature of water at pressure less than 2 kPa and excess boiling occurred during the drying process. The excess boiling gave a foaming/frothy structural appearance and as a result an increasing drying rate or water evaporating rapidly from the samples (Nurhadi and Roos, 2016b). Most of dried honey could be recovered and only little was left in a sealer and the recovery seem giving a yield of more than 80 % (per total solid feed mixture) as reported by Nurhadi et al. (2012). Grinding should be done as quickly as possible to avoid plasticization due to temperature increasing during grinding and water sorption. Grinding might result in amorphization of crystalline material in the system (Vidovic et al., 2014).

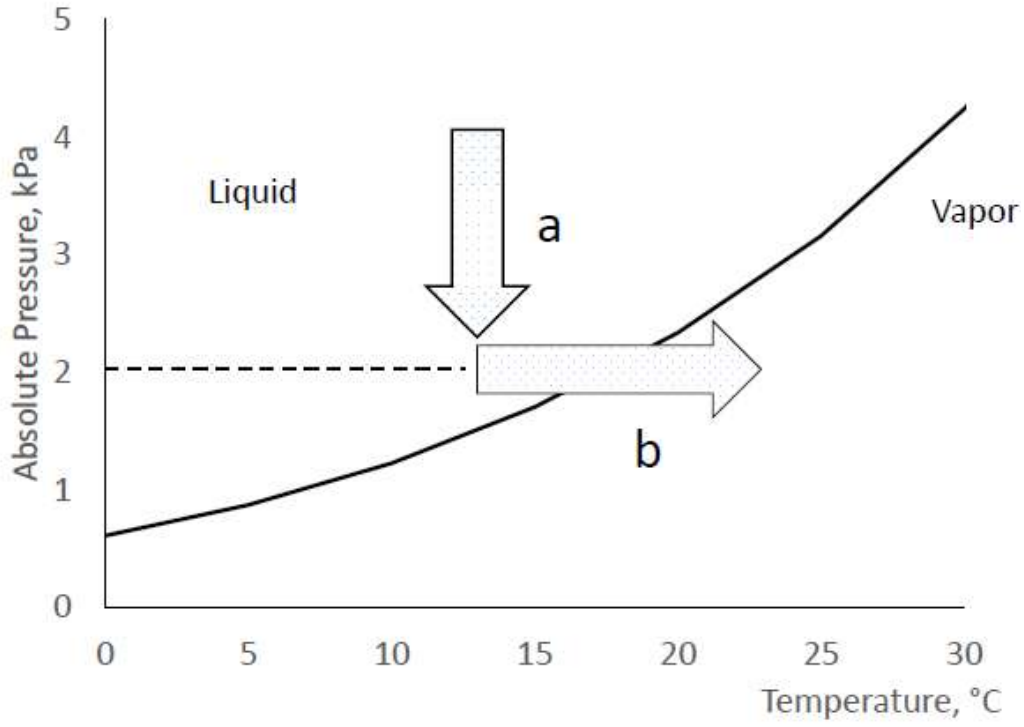


Fig. 6.1. Schematic Vacuum Drying Process

6.2.1. Temperature Effect

Drying temperature affected the amorphous content of lactose powder obtained by spray drying process (Chiou, Langrish and Braham, 2008, Islam, Langrish and Chiou, 2010). Nurhadi and Roos (2016a) investigated the effect of temperature on the amorphous content of the resultant honey powder. The higher the drying temperature during vacuum drying process, the higher the drying rate is and as a result might not be enough time for amorphous sugar in honey mixture to crystallize during drying.

DDI method was developed to determine amorphous content of sucrose and sucrose-maltodextrin systems with pre-known amorphous sucrose content (Nurhadi and Roos, 2016a). DDI method is a simple method and generate a high number of data which could be used also to determine critical water activity (Li, 2010, Carter and Schmidt, 2012) and deliquescent point (Ghorab et al., 2014, Lipasek, Taylor and

Mauer, 2011, Lipasek et al., 2012). The principle of amorphous content determination by DDI method is based on different WSI properties between amorphous and crystalline material and recrystallization of amorphous material in the system. Crystallization of amorphous sugar during water sorption started after its critical water activity surpassed. The peak formed in the first derivative DDI curve is related to crystallization of amorphous sugar in the system and the area under the peak is equal to the amount of water needed during recrystallization process (Nurhadi and Roos, 2016a). The a_w correlated with the peak called as turning point where below its value, the rate of water sorption increase until reaching maximum rate and then after that the rate of water sorption start to decrease. DDI method showed good result in predicting the amorphous content from pre-known amorphous sucrose content of sucrose and sucrose-maltodextrin system (Nurhadi and Roos, 2016a).

DDI method was used to compare qualitatively the amorphous content of vacuum-dried honey powder from different temperature (Nurhadi and Roos, 2016a). The honey powder obtained from higher temperature had higher amorphous content than the powder obtained from lower temperatures and the finding was also backed up by DSC results of endothermic melting heat (Nurhadi and Roos, 2016a). The melting point obtained was over the range of 73 – 82 °C which was very close to the melting point of glucose monohydrate, 83 °C (Foster, 2002).

6.2.2. Formulation Effect

The effect of total solid content, DE value and maltodextrin ratio on WSI and water plasticization properties was investigated by Nurhadi and Roos (2016b). All treatments produced honey powder successfully with high powder recovery (more than 80 %) while in spray drying process, the successful drying is indicated by powder recovery of more than 50 % (Bhandari, Patel and Chen, 2008). It seemed that despite the same formulation, higher powder recovery might be obtained by vacuum drying process than by spray drying.

In spray drying process, the total solid concentration may be limited to maximum of 50 % (per total solid feed solution) (Bhandari, Patel and Chen, 2008). The total solid concentration of honey mixture (honey + maltodextrin) was varied from 10 % (Shi, Fang and Bhandari, 2013) and 20 % (Nurhadi et al., 2012). Much higher total solid concentration could be used in producing honey powder by vacuum drying method. Total solid concentration up to 87 % was reported successfully in producing honey powder by vacuum drying process (Nurhadi and Roos, 2016b). The mixture of honey and maltodextrin without water addition would produce total solid concentration around 87 %. However without water addition, the mixture of honey with maltodextrin was difficult to obtain (uniform mixing) and maltodextrin needed to be added gradually until the desired level of maltodextrin was added. The water addition would make the mixing process easier and give benefit to the drying process. Nurhadi and Roos (2016b) reported that the addition of water at 40 – 60 % would improve foaming and give structural appearance during drying that could increase the drying rate (Fig. 4.1.).

Maltodextrin with different DE values (DE of 4, 10 and 15) showed a good solubility and produced mixtures of honey and maltodextrin uniformly (Nurhadi and Roos, 2016b). Stickiness was the main problem during drying of honey by spray drying method and maltodextrin concentration up to 50 % (Nurhadi et al., 2012) or 60 % (Shi, Fang and Bhandari, 2013) was needed to obtain honey powder with powder recovery more than 50 %. In vacuum drying, stickiness was not the main concern and maltodextrin just needed to increase the T_g of dried honey to above ambient temperature. Low maltodextrin concentration up to 33 % still could produce honey powder successfully by using vacuum drying process (Nurhadi and Roos, 2016b). in summary, vacuum drying method gave some advantages over spray drying method in producing of honey powder in term of high initial total solid feed concentration, lower maltodextrin ratio used and higher powder recovery.

6.3. Vacuum-Dried Honey Powder: Stability

Stability of vacuum-dried honey powder is disturbed when amorphous glassy solid in the powder is plasticized by temperature and water sorption. The T_g of anhydrous honey solid was over the range of 30 – 43 °C and the effect of water on T_g of honey was modelled by Gordon-Taylor equation (Nurhadi and Roos, 2016b). Similar to other sugar-rich foods, the vacuum-dried honey powder had critical water activity lower than a_w where equilibrium water content was equal to monolayer water content (Nurhadi and Roos, 2016b).

The effect of maltodextrin ratio seemed more significant to increase critical water activity than other treatments of DE value, total solid concentration and drying temperature (Nurhadi and Roos, 2016a, Nurhadi and Roos, 2016b). DDI water sorption showed critical water activity increased significantly when maltodextrin concentration increased from 40 % (per total solid) to 60 % (Fig. 5.6). Temperature affected amorphous content of vacuum-dried honey powder, however the critical water activity seemed not to differ significantly (Fig. 3.8). This might be due to the amorphous material found on the surface of the powder that easily sorbed water from surroundings (Mackin et al., 2002; Adhikari et al., 2009). When the critical water activity of honey powder was surpassed, collapse and non-enzymatic browning occurred.

The stability of honey powder could be maintained by storing at temperature below T_g and using packageing material that has a low water vapor permeability and adding of anti-caking agent (Welti-Chanes et al., 2007). Addition of anti-caking agent (Calcium stearate and Calcium silicate) to honey powder was done to maintain honey powder stability and increase flow-ability. At low maltodextrin concentration of 40 %, the powder according to flow-ability was classified as a cohesive powder and flow-ability increased to an easy flowing powder when maltodextrin concentration was increased up to 60 % (Fig. 5.5). Addition of anti-caking agent (2%) either calcium stearate or calcium silicate increased the flow-ability of honey powder from an easy-

flowing powder to a free-flowing powder (Fig. 5.5.). Anti-caking agent of honey seemed not to change critical water activity. Calcium stearate also showed inhibition of honey powder collapse that might be related by crystallization of amorphous sugar in honey powder during WSI experiment. The finding was also backed up by the result of static and dynamic WSI (**Fig. 5.2.** and **Fig. 5.3.**).

6.4. Application of the Research Outcomes

The result is important in understanding glass transition approach to produce honey powder by simple vacuum drying method and using water sorption isotherm and water plasticization approaches for assessing the stability of honey powder. The vacuum technology is a simple applied technology and has been known in Indonesia. Indonesia is a developing country with a huge potential of honey and until now the processing of honey is still limited to honey liquid. Hopefully this technology could be applied to diversify honey products and finally could increase the added value of honey.

6.5. Overall Conclusions

The present study investigated the processing and stability of honey powder by vacuum drying method. Variation of drying temperature and formulation were tested in producing honey powder and the stability was correlated to their water sorption isotherm and water plasticization behavior. The research also investigated the effect of anti-caking agent on stability and flow-ability of honey powder. The overall conclusion could be stated as follow.

- Maltodextrin provide stable glass compared to lower molecular weight sugars.
- DDI data could be used to determine amorphous content of a system. Two principle should be followed: firstly different water sorption properties between amorphous and crystalline materials; and secondly amorphous component in the system should be able to crystallize during water sorption experiment. The area

under the first derivative curve from DDI curve is equal to the amount of water needed by amorphous material to crystallize.

- The drying temperature affected the amorphous content of vacuum-dried honey powder. The higher temperature seemed to result in honey powder with more amorphous component.
- The ratio of maltodextrin affected more significantly the stability of honey powder compared to the treatments of total solids concentration, DE value and drying temperature.
- The critical water activity of honey powder was lower than water activity of the equilibrium water content corresponding to BET monolayer water content.
- Addition of anti-caking agent increased stability and flow-ability of honey powder. Addition of Calcium stearate could inhibit collapse of the honey powder during storage.

BIBLIOGRAPHY

Adhikari, B., T. Howes, B.R. Bhandari and T.A.G. Langrish. 2009. Effect of addition of proteins on the production of amorphous sucrose powder through spray drying. *Journal of Food Engineering 94: 144-153*.

Adhikari, B. P., and B.R. Bhandari. 2009. Sticky and Collapse temperature: measurements, data and predictions. In Food Properties Handbook. 2nd Edition. M.S. Rahman (ed). CRC Press. Boca Raton.

Ahmed, J., S.T. Prabhu, G.S.V. Raghaven, M. Ngadi. 2007. Physico-chemical, Rheological, Calorimetric and Dielectric Behaviour of Selected Indian Honey. *Journal of Food Engineering 79: 1207-1213.*

Allan, M. and L.J. Mauer. 2015. Comparison of Method for Determining the Deliquescence Points of Single Crystalline Ingredients and Blends. *Food Chemistry 195: 29-38.*

Anandharamakrishnan, C., and P. Ishwarya S. 2015. Spray drying techniques for food ingredient encapsulation. John wiley and Sons, Ltd. West Sussex.

Anzai, M., T. Hagiwara, M. Watanabe, J. Komiyana and T. Suzuki. 2011. Relationship between Enthalpy Relaxation and Water Sorption of Ball-Milled Potato Starch. *Journal of Food Engineering 104: 43-48.*

Arslan, N and H. Togrul. 2005. Modelling of water sorption isotherm of macaroni stored in chamber under controlled humidity and thermodynamic approach. *Journal of Food Engineering 69: 133-145.*

Bellik, Y. and M. Iguerouda. 2014. Honey in the food industry. In Honey in traditional and medicine. L. Boukraa (ed). CRC Press. Boca Raton.

Bhandari, B.R. and T. Howes. 1999. Implication of Glass Transition for the Drying and Stability of Dried Foods. *Journal of Food Engineering 40: 71-79*.

Bhandari, B.R., and B.P. Adhikari. 2008. Water activity in food processing and preservation. In Drying Technologies in Food Processing. X.D. Chen and A.S.

Mujumdar (eds). Blackwell Publishing ltd. West Sussex.

Bhandari, B.R., K.C. Patel and X.D. Chen. 2008. Spray Drying of Food Materials-Process and and Product Characteristic. In Drying Technologies in Food Processing. X.D. Chen and A.S. Mujumdar (eds). Blackwell Publishing ltd. West Sussex.

Bhandari and Roos. 2012. Food material science and engineering : an overview in Food Material Science and Engineering. Bhandari, B., and Roos, Y.H. (eds). Blackwell Publishing ltd. West Sussex.

Bhandari, B. 2013. Introduction to food powders in handbook of food powder. Processing and properties. B. Bhandari, N.Bansal, M. Zhang and P. Schuck (Eds.). Woodhead Publ. Limited. Oxford.

Borde, B., H. Bizot, G. Vigier and A. Buleon. 2002. Calorimetric Analysis of the Structural Relaxation in Partially Hydrated Amorphous Polysaccharides. I. Glass Transition and Fragility. *Carbohydrate Polymers. 48: 83-96.*

Borde, B., H. Bizot, G. Vigier and A. Buleon. 2002. Calorimetric Analysis of the Structural Relaxation in Partially Hydrated Amorphous Polysaccharides. II. *Phenomenological Study of Physical Ageing.* Carbohydrate Polymers. 48: 111-123.

Bronlund, J. and T. Paterson. 2004. Moisture sorption isotherm for crystalline, amorphous and predominantly crystalline lactose powders. *International Dairy Journal 14:247-254.*

Burnett, D., Malde, N., Williams, D., 2009. Characterizing amorphous material with gravimetric vapor sorption technique. *Pharm. Tech. Eur. 123-133*.

Cabrera, M.A.R., and S.J. Schmidt. 2015. Determination of glass transition temperature during cooling and heating of low-moisture amorphous sugar mixtures. *Journal of food engineering 146: 36-43.*

Canovas, G.V.B., E.O. Rivas, P. Juliano and H. Yan. 2005. Food Powders. Physical Properties, Processing, and Functionality. Kluwer Academic/Plenum Publisher. New York.

Canovas, G.V.B., and P. Juliano. 2007. Desorption phenomena in food dehydration process. In Water Activity in Foods. Fundamentals and Applications. Canovas, G.V.B., A.F. Fontana Jr., S.J. Schmidt, T.P. Labuza (eds). IFT Press. Iowa.

Carter, B.P., and S.J. Schmidt. 2012. Developments in glass transition determination in foods using moisture sorption isotherms. *Food Chemistry 132: 1693-1698.*

Chanes, J.W., E. Perez, J.A.G. Beltran, S.M. Alzamora and F.V. Balderas. 2007. Application of water activity management in the food industry. In Water Activity in Foods. Fundamentals and Applications. Canovas, G.V.B., A.F. Fontana Jr., S.J. Schmidt, T.P. Labuza (eds). IFT Press. Iowa.

Chiou, D., T.A.G. Langrish and R. Braham. 2008. The effect of temperature on the crystallinity of lactose powders produced by spray drying*. Journal of Food Engineering 86: 288-293.*

Chirife, J., and J. Fontana. 2007. Introduction: Historical highlights of water activity research. In Water Activity in Foods. Fundamentals and Applications. Canovas, G.V.B., A.F. Fontana Jr., S.J. Schmidt, T.P. Labuza (eds). IFT Press. Iowa.

Chmielewska, H.R. 2004. Honey. in Chemical and Fuctional Properties of Food Saccharides. Tomasik, P. (ed.). CRC Press. Boca Raton.

Cui, Zheng-Wei, Li Juan Sun, Wei Chen and Da Wen Sun. 2008. Preparation of Dry Honey by Microwave-Vacuum Drying. *Journal of Food Engineering 84: 582-590*.

Decagon, 2014. Fundamental of Moisture Sorption Isotherm. Application Note. Available at http://www.aqualab.com/assets/Uploads/13947-04-AN-Fundamentals-of-Moisture-Sorption-Isotherms.pdf. [Accessed on November 11th, 2015].

Descamps, N., S. Palzer and U. Zuercher. 2009. The Amorphous State of Spray-Dried Maltodextrin: Sub-Sub Tg Enthalpy Relaxation and Impact of Temperature and Water Annealing. *Carbohydrate Research 344: 85-90.*

Descamps, N., S. Palzer, Y.H. Roos and J.J. Fitzpatrick. 2013. Glass Transition and Flowability/Caking Behaviour of Maltodextrin DE 21. *Journal of Food Engineering 119: 809-813.*

Fabra, M.J. P.Tolens, G. Moraga and N. Martinez-Navarrete. 2009. Sorption Isotherm and State Diagram of Grape Fruit as A Tool to Improve Product Processing and Stability. *Journal of Food Engineering (93): 52-58.*

Fang, Z. and B.Bhandari. 2012. Comparing the Efficiency of Protein and Maltodextrin on Spray Drying of Bayberry Juice. *Food Research International 48: 478-483.*

Farnish, R.V. and R. Berry. 2013. Handling of Food Powders: Flow Patterns and Storage Design. In handbook of food powder. Processing and properties. B. Bhandari, N.Bansal, M. Zhang and P. Schuck (Eds.). Woodhead Publ. Limited. Oxford.

Favre, A., G. Niquet, M. Maglione, J. Farnazero, J.F. Jal and L. David. 1999. Dynamic of Sorbitol and Maltitol over a Wide Time-Temperature Range. *The European Physical Journal 10: 277-286.*

Figura, L.O., and A.A. Teixeira. 2007. Food Physic physical properties measurement and application. Springer. Berlin.

Foster, K.D. 2002. The Prediction of Sticking in Dairy Powders. Thesis in Massey University. New Zealand. Available at http://mro.massey.ac.nz/bitstream/handle/10179/1782/02_whole.pdf?sequence=1. [Accessed on August 12, 2014].

Foster, K. D., Bronlund, J. E., & Paterson, a. H. J. (T). (2006). Glass transition related cohesion of amorphous sugar powders. *Journal of Food Engineering*, *77*(4), 997–1006.

Ghorab, M.K., K. Marrs, L.S. Taylor and L.J. Mauer. 2014. Water-solid interaction between amorphous maltodextrin and crystalline sodium chloride. *Food Chemistry 144: 26-35.*

Gleiter, R.A., H. Horn and H.D. Isengard. 2006. Influence of type and state of crystallization on the water activity of honey. *Food Chemistry 96: 441-445.*

Gorsel, H.V., C.Li., E.L. kerbel., M. Smits and A.A. Kader. 1992. Compositional characterization of prune juice. J. Agric. Food Chem. 40: 784-789.

Guizani, N., G.S. Al-Sardi, M.S. Rahman, S. Barnaz and A.A. Al-Alawi. 2010. State Diagram of Dates: Glass Transition, Freezing Curve and Maximal-Freeze-Concentration Condition. Journal of Food Engineering (99): 92-97.

Hancock, B.C., S.L. Shamblin and G. Zografi. 1995. Molecular Mobility of Amorphous Pharmaceutical Solids below Their Glass Transition Temperature. *Pharmaceutical Research 12(6): 799-806.*

Haque, M.K., and Y.H. Roos. 2005. Crystallization and x-ray diffraction of spray-dried and freeze-dried amorphous lactose. *Carbohydrate Research 340: 293-301*.

Haque, M.K., Kawai, K., and Suzuki, T. 2006. Glass Transition and Enthalpy Relaxation of Amorphous Lactose Glass. *Carbohydrate Research. 341(11): 1884-1889.*

Haque, E., A.K. Whittaker, M.J. Gidley, H.C. Deeth, K. Fibrianto and B. Bhandari. 2012. Kinetics of Enthalpy Relaxation of Milk Protein Concentrate Powder upon Ageing and Its Effect on Solubility. *Food Chemistry 134: 1368-1373.*

Hartmann, M. and S. Palzer. 2011. Caking of Amorphous Powders-Material Aspects, Modelling and Applications. *Journal* of *Powder Technology (206): 112-121.*

Hedegaard, R.V. and L.H. Skibsted. 2013. Shelf-Life of Food Powders. In handbook of food powder. Processing and properties. B. Bhandari, N.Bansal, M. Zhang and P. Schuck (Eds.). Woodhead Publ. Limited. Oxford.

Hobbs, L. 2009. Sweeteners from Starch. In Starch. Chemistry and Technology, 3rd edition. J.B. Miller and R. Whistler (eds). Academic Press. Amsterdam.

Intipunya, P., and B.R. Bhandari, B.R. 2010. Chemical deterioration and physical instability of food powders. In Chemical deterioration and physical instability of food powders. L.H. Skibsted, J. Ribo and M.L. Andersen (eds). CRC Press. Boca Raton.

Islam, M.I.U. and L.D. Chiou. 2010. Particle crystallization during spray drying in humid air. *Journal of Food Engineering 99: 55-62.*

Jaya, S. and H. Das. 2004. Effect of maltodextrin, glycerol mono stearate and tricalcium phosphate on vacuum dried mango properties. *Journal of Food Engineering 63: 125-134.*

Jayasundera, M., B. Adhikari, R. Adhikari and P. Aldred. 2011. The effect of protein and low molecular weight surfactants and spray drying of model sugar-rich foods: Powder production and characterization. *Journal of Food Engineering 104: 259-271.*

Jiang, H. and M. Zhang. 2013. Fruit and Vegetable Powder. In handbook of food powder. Processing and properties. B. Bhandari, N.Bansal, M. Zhang and P. Schuck (Eds.). Woodhead Publ. Limited. Oxford.

Kantor, Z., G. Pitsi and J. Thoen. 1999. Glass transition temperature of honey as a function of water content determined by differential scanning calorimetry. *J. Agric. Food Chem. 47: 2327-2330.*

Kawai, K, T. Hagiwara, R. Takai and T. Suzuki. 2005. Comparative Investigation by Two Analytical Approaches of Enthalpy Relaxation for Glassy Glucose, Sucrose, Maltose and Trehalose. *Pharmaceutical Research 22 (3): 490-495.*

Karadeniz, F. and A. Eksi. 2002. Sugar Composition of Apple Juice. Eur. Food Res. Technol. 215: 145-148.

Kim, Y.J., T. Hagiwara, K. Kawai, T. Suzuki and R. Takai. 2003. Kinetics Process of Enthalpy Relaxation of Glassy Starch and Effect of Physical Ageing upon Its Water Vapor Permeability Properties. *Carbohydrate Polymers 53: 289-296.*

Kiranoudis, C.T., Z.B. Maroulis, E. Tsami and D.M. Kouris. 1993. Equilibrium moisture content and heat of desorption of some vegetables. *Journal of Food Engineering 20: 55-74.*

Kolayli, S., O. Yildiz, H. Sahin and R. Aliyazicioglu. 2014. Biochemistry and physicochemical properties of honey. In Honey in traditional and medicine. L. Boukraa (ed). CRC Press. Boca Raton.

Koynov, S., Glasser, B., & Muzzio, F. (2015). Comparison of three rotational shear cell

testers: Powder flowability and bulk density. *Journal of Powder Technology*, *283*, 103–112.

Labuza, T.P., Kaanane, A., and Chen. J.Y. 1985. Effect of temperature on the moisture sorption isotherms and water activity of two dehydrated foods. J. Food Sci (50): 385-391.

Labuza, T.P., and B. Altunakar. 2007. Water Activity Prediction and Moisture Sorption Isothermal. In Water Activity in Foods: Fundamentals and Applications. Canovas, G.V.B., A.F. Fontana Jr., S.J. Schmidt, T.P. Labuza (eds). IFT Press. Iowa.

Lazaridou, A., G.G. Biliaderis, N. Bacandritsos and A.G. Sabatini. 2004. Composition, Thermal and Rheological Behaviour of Selected Greek Honeys. *Journal of Food Engineering (64):9-21.*

Land, C.M.V. 2012. Drying in the Process Industry. John Wiley and Sons. New Jersey.

Lehto, V.P., M. Tenho, K.V. Heikkila, P. Harjunen, M. Peallysho, J. Valissari, P. Niemela and K. Jarvinem. 2006. The Comparison of Seven Different Methods to Quantify the Amorphous Content of Spray Dried Lactose. *Journal of Powder Technology (167): 85-93.*

Linden, G. and D. Lorient. 1999. New Ingredients in Food Processing: Biochemistry and Agriculture. CRC Press, Boca Raton.

Liu, Y., B. Bhandari and W. Zhou. 2006. Glass Transition and Enthalpy Relaxation of Amorphous Food Saccharides: A Review. *Journal of Agricultural and Food Chemistry 54: 5701-5717.*

Liu, Y., B. Bhandari and W. Zhou. 2007. Study of Glass Transition and Enthalpy Relaxation of Mixtures of Amorphous Sucrose and Amorphous Tapioca Starch Syrup Solid by Differential Scanning Calorimetry (DSC). *Journal of Food Engineering 81: 599-610.*

Li, Q. 2010. Investigating the glassy to rubbery transition of polydextose and corn flakes using automatic water vapor sorption instruments, DSC and texture

analysis. Thesis of University of Illinois at Urbana-Champaign. Available at https://www.google.ie/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0CCUQFjAAahUKEwjNuL-6oJ7HAhWioNsKHaRsAIk&url=https%3A%2F%2Fwww.ideals.illinois.edu%2Fbitstream%2Fhandle%2F2142%2F16711%2F2_li_qingruisi.pdf%3Fsequence%3D4&ei=yXXIVY2wNqLB7gak2YHICA&usg=AFQjCNE30qb69irA_CaPIPHPDdJJwZBX_A&sig2=dZxhwjMrQ_EffVh8dHohDw [Accessed on August, 20th 2015].

Lehto, V.P., M. Tenho, K.V. Heikkila, P. Harjunen, M. Peallysho, J. Valissari, P. Niemela and K. Jarvinem. 2006. The Comparison of Seven Different Methods to Quantify the Amorphous Content of Spray Dried Lactose. *Journal of Powder Technology (167): 85-93.*

Lipasek, R. A., Taylor, L. S., & Mauer, L. J. (2011). Effects of Anticaking Agents and Relative Humidity on the Physical and Chemical Stability of Powdered Vitamin C. *Journal of Food Science*, *76*(7), 1062–1074.

Lipasek, R.A., J.C. Ortiz, L.S. Taylor and L.J. Mauer. 2012. Effects of anti-caking agents and storage conditions on the moisture sorption, caking, and flowability of deliquescent ingredients. *Food Research International 45: 369-380*.

Lourdin, D., P. Colonna, G.J. Brownsey, T.R. Noel and S.G. Ring. 2002. Structural Relaxation and Physical Ageing of Starchy Materials. *Carbohydrate Research 337: 827-833.*

Lupano, C. 1997. DCS study of honey granulation stored at various temperatures. *Food Research International 30: 683-688.*

Mackin, L., R. Zanon, J.M. Park, K. Foster, H. Opalenik and M. Demonte. 2002. Quantification of low level (< 10%) of amorphous content in micronized active batches using dynamic vapor sorption and isothermal micro calorimetry. *International Journal of Pharmaceutics 231: 227-236.*

Makower, B., and W.B. Dye. 1956. Equilibrium moisture content and crystallization of amorphous sucrose and glucose. *Agricultural and Food Chemistry 4: 72-77.*

Mathlouthi, M. 2001. Water content, water activity, water structure and the stability of food stuffs. *Food Control 12: 409-417.*

Mathlouthi, M. and B. Roge. 2003. Water Vapor Sorption Isotherms and the Caking of Food Powders. *Food Chemistry 82: 61-71.*

Meste, M.L., D. Champion, G. Roudaut, G. Blond and D. Samatos. 2002. Glass Transition and Food Technology: A Critical Appraisal*. Journal of Food Science 67(7): 2444-2458.*

Mosquera, L.H., G. Moraga and N.M. Navarreta. 2012. Critical Water Activity and Critical Water Content of Freeze-Dried Strawberry Powder as Affected by Maltodexrin and Arabic Gum. *Food Research International 47: 201-206.*

Moraga, G., N. Martinez and A. Chiralt. 2006. Water Sorption Isotherms and Phase Transitions in Kiwi Fruit. *Journal of Food Engineering (72): 147-156.*

Moraga, G., N. Martinez-Novarrete and A. Chiralt. 2004. Water Sorption Isotherm and Glass Transition in Strawberies: Influence of Pretreatment. *Journal of Food Engineering (62): 315-321.*

Mrad, N.D., C. Bonazzi, N. Boudhrioua, N. Kechaou and F. Curtois. 2012. Influence of Sugar Composition on Water Sorption Isotherms and On Glass Transition in Apricots. *Journal of Food Engineering (111):403-411.*

Msagati, T.A. 2013. Chemistry of food additives and preservatives. Wiley-Blackwell. West Sussex.

Muhtaseb, A.H., W.A.M. Mc Minn and T.R.A. Magee. 2002. Moisture sorption isotherm characteristics of food products: A Review. *TransIchem 80. Part C.*

Murrieta-Pazos, I., Gaiani, C., Galet, L., Cuq, B., Desobry, S., & Scher, J. (2011). Comparative study of particle structure evolution during water sorption: Skim and whole milk powders. *Colloids and Surfaces B: Biointerfaces*, *87*(1), 1–10.

NIST/SEMATECH. 2012. e-handbook of statistical method. Available at http://www.itl.nist.gov/div898/handbook. [Accessed on August, 20th 2015].

Noel, T.R., R. Parker and S. G. Ring. 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.*

Nurhadi, B., Andoyo, R., Mahani and Indiarto, R. 2012. Study The Properties of Honey Powder Produced From Spray Drying and Vacuum Drying Method. *International Food Research Journal: 19(3): 849-854.*

Nurhadi, B., & Roos, Y.H. 2016 a. Dynamic Water Sorption for the Study of Amorphous Content of vacuum dried honey powder. *Journal of Powder Technology 301: 981-988.*

Nurhadi, B., & Roos, Y. H. 2016 b. Water Sorption and Water Plasticization Behavior of Vacuum Dried Honey. *International Journal of Food Properties* 19: 1370-1380.

Nurhadi, B., Roos, Y. H., & Maidannyk, V. 2016. Physical Properties of Maltodextrin DE 10: Water Sorption, Water Plasticization and Enthalpy Relaxation. *Journal of Food Engineering*, *174*, 68–74.

Okos, M.R., O. Camponella, G. Narsimhan, R.K. Singh and A.C. Weitnauer. 2007. Food Dehydration in Handbook of Food Engineering 2nd Edition. Heldman, D.R. and D.B. Lund (eds.). CRC Press. Boca Raton.

Park, Y.W., and L.N. Bell. 2004. Determination of Moisture and Ash Content of Foods. In Handbook of Food Analysis 2nd edition. Nollet, L.M.L (ed). Marcel Dekker, Inc., New York.

Pazos, I, M., C. Gaiani, L. Galet, B. Cuq, S. Desobry and J. Scher. 2011. Comparative study of particle structure evolution during water sorption. Skim milk and whole milk powders. Review. *Colloids and Surfaces B: Interfocus 87:1-10*.

Potes, N., J.P. Kerry and Y.H. Roos. 2012. Additivity of water sorption, alpha relaxation and crystallization inhibition in lactose-maltodextrin system. *Carbohydrate Polymers 89: 1050-1059.*

Rahman, M.S. 2009. Glass Transition Data and Models of Foods. In Food Properties Handbook 2nd Edition. Rahman, M.S. (ed). CRC Press. Boca Raton.

Rahman, M.S. 2006. State Diagram of Foods: Its Potential Use in Food Processing and Product Stability. *Trends in Food Science and Technology 17:129-141.*

Ram, A.K. 2011. Production of Spray Dried Honey Powder and Its Application in Bread. A Thesis in Louisiana State University and Agricultural and Mechanical College, USA. Available at http://etd.lsu.edu/docs/available/etd-07052011-085925/unrestricted/kasalRam_Thesis.pdf. [Accessed August, 12 2014].

Ratti, C. 2008. Freeze-drying and Vacuum Drying of Foods. In Drying Technologies in Food Processing. X.D. Chen and A.S. Mujumdar (eds). Blackwell Publishing ltd. West Sussex.

Ratti, C. 2013. Freeze-drying for food powder production in handbook of food powder. Processing and properties. B. Bhandari, N.Bansal, M. Zhang and P. Schuck (Eds.). Woodhead Publ. Limited. Oxford.

Rays, S., U. Raychaudhuri and R. Chacraborty. 2015. An Overview of encapsulation of active compounds used in food products by drying technology. *Food Bioscience 13: 77-83.*

Reis, F.R. 2014. Studies on Conventional Vacuum Drying of Foods. In Vacuum Drying for Extending Food Shelf-life. F.R. Reis (ed). Springer. New York.

Rizvi, S.S.H. 2005. Thermodynamic Properties of Foods in Dehydration. In Engineering Properties of Foods 3rd edtion. Rao, M.A., Rizvi, S.S.H. and Datta, A.K.(eds). CRC Press. Boca Raton.

Romani, S., P. Rocculi, S. Tappi and M.D. Rosa. 2015. Moisture Adsorption Behavior of Biscuit during Storage Investigated by Using a New Dyanamic Dew Point Method. *Food Chemistry 195: 97-103.*

Roos, Y.H. and M. Karel. 1991. Phase Transition of Mixture of Amorphous Polysaccharides and Sugars. *Biotechnological Progress 7: 49-53.*

Roos,Y.H. 1992. Phase transition and transformation in food system. In handbook of food engineering. D.R. Heldman and D.B. Lund (eds). Marcel Dekker, New York.

Roos, Y.H. 1993. Melting and Glass Transition of Low Molecular Weight Carbohydrates. *Carbohydrate. Research (238): 39-48.*

Roos, Y.H. Phase Transition in Foods. 1995. Academic Press, California.

Roos, Y.H., K. Roininen, K. Jouppila and H. Tuorila. 1998. Glass transition and water plasticization effects on crispness of a snack food extrudate. *International Journal of Food Properties 1(2): 163-180.*

Roos, Y.H. 2002. Importance of glass transition and water activity to spray drying and stability of dairy powders. *Lait 82: 475-484.*

Roos, Y.H. 2007. Phase transitions and transformation in food systems. In Handbook of food engineering 2nd edition. D.R. Heldman and D.B. Lund (eds). CRC Press, Boca Raton.

Roos, Y.H. 2010. Glass transition temperature and its relevance in food processing. *Annu. Rev. Food Sci. Technol. 1: 469-96*.

Roos, Y.H. and N. Potes. 2015. Quantification of Protein Hydration, Glass Transitions, and Structural Relaxations of Aqueous Protein and Carbohydrate-Protein Systems. *Physical Chemistry B 119: 7077-7086.*

Roudaut, G., D. Samatos, D.Champion, E. Conteras-Lopez and M.L. Mester. 2004. Molecular Mobility around the Glass Transition Temperature: A Mini Review. *Innovation Food Science and Emerging Technologies 5: 127-134.*

Roos, Y.H. and S. Drusch. 2016. Phase transition in foods second edition. Academic Press. Oxford.

Sablani, S.S., S. Kasapis and M.S. Rahman. 2007. Evaluating Water Activity and Glass Transition Concept for Food Stability. *Journal of Food Engineering 78: 266-271.*

Sahu, J.K. 2008. The effect of additives on vacuum dried honey properties. *International Journal of Food Engineering. Volume 4 (8).*

Schmidt, S. J., & Lee, J. W. (2012). Comparison between Water Vapor Sorption Isotherms Obtained Using the New Dynamic Dewpoint Isotherm Method and Those Obtained Using the Standard Saturated Salt Slurry Method. *International Journal of Food Properties*, *15*(1-2), 236–248.

Shamblin, S.L., X. Tang, L. Chang, B.C. Hancock and M.J. Pikal. 1999. Characterization of the Time Scales of Molecular Motion in Pharmaceutically Important Glasses. J. *Phys. Chem B 103: 4113-4121.*

Shi, Q., Z. Fang and B. Bhandari. 2013. Effect of Addition of Whey Protein Isolate on Spray Drying Behaviour of Honey with Maltodextrin as a Carrier Material. *Drying Technology (31): 1681-1692.*

Slade, L., and H. Levine. 1991. Beyond water activity: Recent advances based on an alternative approach to the assessment of food qualtiy and safety. *Critical Review in Food Science and Nutrition 30: 115-360.*

Sopade, P.A., P. Haley, B. Bhandari, B. D'Archy, C. Doebler and N. Coffin. 2002. Application of the Williams-Landel-Ferry Model to the Viscosity-Temperature Relationship of Australian Honeys. *Journal of Food Engineering (56): 67-75.*

Soutari, N., A.B.M. Buanz, M.O. Gul, C. Tuleu and S. Garford. 2012. Quantification crystallization rates of amorphous pharmaceuticals with dynamic mechanical analysis (DMA). *International Journal of Pharmaceutics 42: 335-340.*

Stoklosa, A. M., Lipasek, R. A., Taylor, L. S., & Mauer, L. J. (2012). Effects of storage conditions, formulation, and particle size on moisture sorption and flowability of powders: A study of deliquescent ingredient blends. *Food Research International*, *49*(2), 783–791.

Syamaladevi, R.M., S.S. Sablani, J. Tang, J. Powers and B.G. Swanson. 2009. State Diagram and Water Adsorption Isotherm of Raspberry (Rubus idaeus). *Journal of Food Engineering (91): 460-467.*

Syamaladevi, R.M., S.S. Sablani and B.G. Swanson. 2010. Ageing of ampropRaspberry Powder: Enthalpy Relaxation and Fragility. *Journal of Food Engineering 101:32-40.*

Syamaladevi, R.M., G.V. Barbosa-Canovas, S.J. Schmidt, S.S. Sablani. 2012. Influence of Molecular Weight on Enthalpy Relaxation and Fragility of Amorphous Carbohydrates. *Carbohydrate Polymers. 88:223-231.*

Timmermann, E.O., Chirife, J., abd H.A. Iglesias. 2001. Water sorption isotherms of foods and foodstuffs: BET or GAB parameters? Journal of Food Engineering 48: 19-31.

Toledo, R.T. 2007. Fundamental of Food Process Engineering 3rd Edition. Springer. New York.

Tong, Q. , X. Zhang, F. Wu, J. Tong, P. Zhang and J. Zhang. 2010. Effect of honey powder on dough rheology and bread quality. Food Research International 43:2284-2288.

Venir, E., M. Spaziani and E. Maltini. 2010. Crystallization in Tarassaco Italian honey studied by DSC. *Food Chemistry 122: 410-415.*

Vidonic, S.S., J.Z. Vladic, Z.G. Vastog, Z.P. Zehovic and L.M. Papovic. 2014. Maltodextrin as a carrier of health benefit compounds in *satureja montana* dry powder extract by spray drying technique. *Journal of Powder Technology 258: 209-215.*

Vollenbroek, J., G.A. Hebbink, S. Ziffels and H. Steckel. 2010. Determination of low level of amorphous content in inhalation grade lactose by moisture sorption isotherms. *International Journal of Pharmaceutics 395: 62-70.*

Wang, S., and T. Langrish. 2009. A Review of process simulations and the use of additives in spray drying. *Food Research International 42: 13-25.*

Wang, W. and W. Zhou. 2012. Characterization of spray dried soy sauce powder using maltodextrin as carrier. *Journal of Food Engineering 109: 399-405.*

Willart, J. F., Dujardin, N., Dudognon, E., Danède, F., & Descamps, M. (2010).

Amorphization of sugar hydrates upon milling. *Carbohydrate Research*, *345*(11), 1613–1616.

Wingtanagorn, R. and S.J. Schmidt. 2001. Phenomenological Study of Enthalpy Relaxation of Amorphous Glucose, Fructose and Their Mixture. *Thermochemica Acta 369: 95-116.*

Wolf, W., W.E.L. Spiess, G. Jung, H. Weisser and H. Bizot. 1984. The water-vapor sorption isotherms of micro crystalline cellulose (MCC) and of purified potato starch. Result of collaborative study. Journal of Food Engineering 3: 51-73.

Woo, M.W. and B.R. Bhandari. 2013. Spray drying for food powder production. In handbook of food powder. Processing and properties. B. Bhandari, N.Bansal, M. Zhang and P. Schuck (Eds.). Woodhead Publ. Limited. Oxford.

Xanthakis, E., Ruud van Ommen, J., & Ahrné, L. (2015). Flowability characterization of nanopowders. *Journal of Powder Technology*, *286*, 156–163.

Yuan, X., B.P. Carter and S.J. Schmidt. 2011. Determining the critical relative humidity at which the glassy to rubbery transition occurs in polydextrose using an automatic water vapor sorption instruments. *Food Science 76: 78-89.*

Yu, X., A.R. Schmidts, L.A.B. Perez and S.J. Schmidt. 2008. Determination of the bulk moisture diffusion coefficient for corn starch using an automated water sorption instrument. *Journal of Agricultural and Food Chemistry 56: 50-58.*

Zamora, M.C., and J. Chriffe. 2006. Determination of water activity change due to crystallization in honey from Argentina. Food Control 17: 59-64.

APPENDIX

LIST OF PUBLICATIONS

Nurhadi, B., & Roos, Y. H. (2016). Water Sorption and Water Plasticization Behavior of Vacuum Dried Honey. *International Journal of Food Properties* 19: 1370-1380.

Nurhadi, B., Roos, Y. H., & Maidannyk, V. (2016). Physical Properties of Maltodextrin DE 10: Water Sorption, Water Plasticization and Enthalpy Relaxation. *Journal of Food Engineering*, *174*, 68–74.

Nurhadi, B., & Roos, Y.H. 2016. Dynamic Water Sorption for the Study of Amorphous Content of vacuum dried honey powder. *Journal of Powder Technology 301: 981-988.*

Nurhadi, B., & Roos, Y.H. Influence of Anti-Caking Agent on the Water Sorption Isotherm and Flow-ability Properties of Vacuum Dried Honey Powder (Manuscript to be submitted).

APPENDIX

LIST OF CONFERENCES

Oral Presentation

Nurhadi, B., and Roos, Y.H. Dynamic Water Sorption for the Study of Amorphous Content of vacuum dried honey powder. 2nd International Conference on Food Properties (iCFP2016) Anantara Riverside Bangkok Resort, Thailand, May 31-June 2, 2016.

Poster Presentation

Nurhadi, B., and Roos, Y.H. Dynamic Water Sorption for the Study of Amorphous Content of vacuum dried honey powder. The 18th World Congress of Food Science and Technology. The International Union of Food Science and Technology (IUFoST). Dublin, Ireland. August, 21st -25th, 2016.