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Application of the "Dual Sorption" Model for Water Adsorption of Maltodextrin Various DE

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ABSTRACT

To characterize water sorption of maltodextrin various DE, several physical properties were determined, including molecular weight, glass transition temperature, sorption isotherm and ^{1}H pulsed NMR. The average numbers of molecular weight (M_n) and average weight of molecular weight (M_w) were 1,800,27,000; 900, 7,700; 700, 4,400 and water at monolayer were 5.5296, 4.6753 and 4.4553 g water/100 g dry solid for maltodextrin DE 5, 14 and 18.5 respectively. Sorption isotherms indicated DE 5 and DE 14 to exhibit an "s" shape isotherm while for DE 18.5 a discontinuous isotherm occurred. Maltodextrin DE 5 adsorbed more water than DE 14 and 18.5. Dual Sorption theory was applied for sorption data analysis and the parameter (C'_H) was estimated. The results indicated that maltodextrin DE 5 had higher sorption in "microvoid" than maltodextrin DE 14 and 18.5. This was strongly supported with the results obtained by ^{1}H pulsed NMR, that maltodextrin DE 5 had more mobile proton mobility in the low relative humidity region than maltodextrin DE 18.5.

Key words: maltodextrin, sorption isotherm, dual sorption, ^{1}H NMR, microvoid

INTRODUCTION

The dual sorption theory has been extensively utilized to explain the equilibrium sorption of penetrants in polymers and heterogeneous media (Chandrasekaran *et al*., 1980). Sorption of penetrants in glassy polymers is more complex than in a rubbery state (Koros and Paul, 1978; Chan and Paul, 1980) and exhibits nonlinear concentration dependence (Wang and Kamiya, 1999). The total sorption concentration C consists of two populations or sorption modes. One population C_D held by ordinary dissolution, is described by Henry's law while the second population, C_H sorbed by a fixed number of sites or holes is described by a Langmuir isotherm.

Many investigators have associated the Langmuir capacity of glassy polymers with frozen microvoid nature, believed to be characteristic of these nonequilibrium materials, as a result of small-scale inhomogeneity (Barrer *et al*., 1958). The extreme restriction on the backbone motions of amorphous polymers at temperatures significantly below glass transition temperature (Tg) causing chain relaxation to be very slow with the result that trapped excess free volume which may be sufficiently immobilized over a very long time is important in terms of frozen microvoids (Koros

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and Paul, 1978).

^{1}H pulsed NMR has been used to study the proton mobility in solid system and the pulse was applied to characterize water in polymer solids (Kumagai *et al.*, 2002). The Free induction decay (FID), the signal decay recorded after radio frequency applied at 90° with a permanent magnetic field switched off, contained the important information such as the intensity of the FID signal which was directly proportional to the total number of protons in the sample and the protons in physical or chemical environments decaying at different rates. The observation of FID was a superposition of one (one type of proton) or more individual FIDs, each from different types of proton. Each FID had a characteristic time constant called relaxation time, T_2 (sec). Ruan *et al.* (1999) found that proton mobility of immobile protons of maltodextrin increased when temperature was around glass transition temperature.

The aim of this study was to investigate the effect of DE of maltodextrin on water sorption and "dual sorption theory was used to characterize the sorption behavior of maltodextrin at different DEs which was probably correlated to the retention of flavour.

MATERIALS AND METHODS

Material

Maltodextrin with DEs of 5, 14 and 18.5 (Cerestar, UK) were used in this study.

Molecular weight

A Gel Permeation Chromatograph System PL110 (Polymer laboratories, USA) was used with an Ultralinear hydrogel column set (Waters, USA) to determine the weight average molecular weight (M_w), the number average molecular weight (M_n) and polydispersity of maltodextrin. The sample was prepared by dissolving maltodextrin 1% (w/w) in deionised water and injected at 20 µl using deionised water as mobile phase. The flow rate was 0.6 ml/min at 30°C. RI was used as a detector.

Glass transition temperature

A known amount (8-10 mg) of sample was placed in aluminum sample pan (Perkin Elmer, UK), and was analyzed by DSC 7 (Perkin Elmer, UK). The instrument was calibrated with standard indium and cyclohexane. An empty pan was used as reference. The samples were heated to 160°C at 10°C/min. After heating, the sample was cooled down to -20°C and reheated to 160°C at 10°C/min.

Maltodextrin re-spray drying

Due to the differences in size of maltodextrin various DE, a difference in sorption might occur. To get rid off this problem, re-spray drying was applied. Maltodextrin as received DE 5, 14 and 18.5 20 grams were dissolved in 100 milliliters of distilled water, then spray dried with a spray dryer APV Anhydro, the inlet and outlet temperatures were 200 and 90°C respectively. The spray dried products were kept in a tight plastic box at 5°C for further analysis.

Particle size distribution

Particle size distribution was determined using a Malvern Mastersizer (Malvern Instrument, UK). The volume size average d_{32} was used as particle size distribution parameters. The measurements were performed in duplicate.

Sorption isotherm

Maltodextrin with various DE were dried in a tight container over phosphorous pentaoxide (P_2O_5) for a week and then equilibrated with LiCl, CH_3COOK, K_2CO_3, $Na_2Cr_2O_7$, NaBr, $CuCl_2$, NaCl, KCl and K_2SO_4 saturated salt solution for equilibrium relative humidity of 11.3, 22.5, 35.2, 54.8, 59.5, 67.7, 75.5, 85.1 and 97.0% respectively, for 3 weeks and heated by oven at 105°C for 6 hours or until constant weights were reached. The calculated moisture contents as a dry basis were

plotted to show the relationship between moisture content and %RH as sorption isotherm (Laaksonen and Roos, 2000). The sorption data was fit with BET model. The monolayer parameter was calculated.

Proton relaxation by ^{1}H Pulsed NMR.

Maran 33 spectrophotometer was used and operated at 23 MHz. Samples were sealed in an 8 mm internal diameter NMR tube. Proton free induction decays (FID) were measured between 0-100°C. The signal decay after radio frequency applied at 90° with a permanent magnetic field switched off was recorded. Spin-Spin Relaxation Time (T_{2m}) was calculated. The measurements were performed in duplicate.

RESULTS AND DISCUSSION

Molecular weight

The average weight of molecular weight (M_w), the average number of molecular weight (M_n) and the polydispersity of maltodextrin DE 5, 14 and 18.5 are shown in Table 1. When DE increased, M_n and M_w decreased. Hydrolysis of starches cut large molecules down into small fractions. DE 5 had a higher polydispersity than the others. It had a wide range of molecular distribution which could affect the mechanical properties of final product such as its film forming properties.

Glass transition temperature (Tg)

The results are shown in Table 2. The %RH affected glass transition temperature. When %RH increased, Tg decreased. Water played a role as a plasticizer (Roos, 1995). As the water content increased, Tg decreased monotonically, because the average molecular weight of maltodextrin-water decreased which led to increased intermolecular space or free volume. Maltodextrin low DE had higher Tg than high DE. This indicated that low molecular weight molecules had higher molecular mobility than high molecular weight molecules. From the results shown in Table 2, maltodextrin DE 5 and 14 had higher Tg than the temperature used in the sorption experiment while DE 18.5 at 75%RH had lower Tg than the temperature in the sorption experiment. This indicated that sorption experiments especially at low relative humidity region were done in the glassy state.

Table 1 M_n, M_w and Polydispersity of maltodextrin DE 5, 14 and 18.5.

DE	M_n	M_w	Polydispersity
5	1,800	27,000	14.84
14	900	7,700	8.48
18.5	700	4,400	6.09

Table 2 Glass transition temperature (°C) of maltodextrin DE 5, 14 and 18.5 at various relative humidity.

	%RH		
DE	11.3	54.5	75.5
5	152.38	82.41	49.01
14	118.87	56.62	38.24
18.5	98.34	45.19	6.51

Sorption isotherm

The adsorption isotherms of commercial maltodextrins of various DE are shown in Figure 1. The particle sizes of maltodextrin DE 5, 14 and 18.5 were not significantly different (Table 4). The effect of particle size was minimal. Maltodextrin DE 5 absorbed more water than those with DE 14 and 18.5 at the same relative humidity (RH). Maltodextrin DE 5 and DE 14 exhibited "S" shape (type II) sorption isotherms indicating a noncrystallizing system character. McMinn and Magee (1997) tested the sorption isotherm of potato starch gel and potato starch

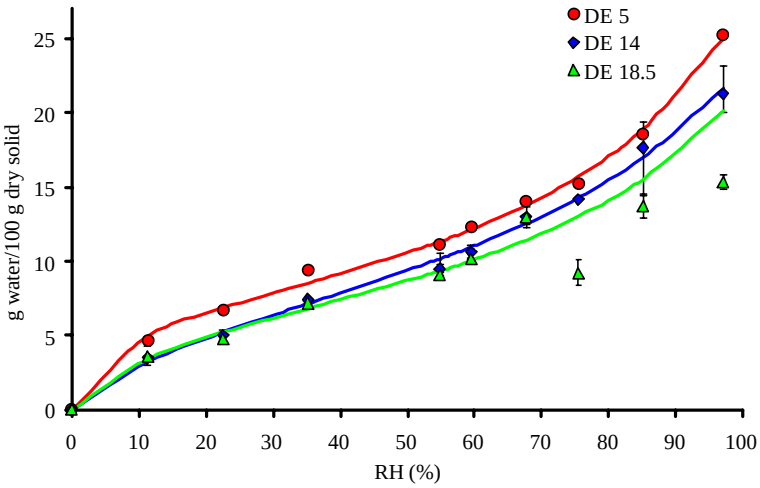

Figure 1 Water sorption isotherm of maltodextrin DE 5, 14 and 18.5 at 25°C. The solid line is the "BET" fitted curve.

with 25, 50 and 75% glucose. Sorption isotherms of starch with increasing glucose content had relatively low moisture contents in the low water activity region. Moates *et al.* (1997) tested sorption isotherm of maltooligomers at 20°C. At low a_w, the maltooligomers which had higher molecular weight adsorbed more water than the low molecular one. Maltodextrin DE 18.5 exhibited a discontinuity in the sorption isotherm at RH higher than 67.7% and absorbed less water than maltodextrin DE 5 and 14 at RH 67.7-97%. The discontinuity in the sorption isotherm and less water absorption indicated that crystallisation or molecular entanglement might occur. Discontinuity in the sorption isotherm indicated that crystallization might occur which led to a decrease in the solubility of maltodextrin due to molecules trying to rearrange themselves to more tightly packed which could not hold water as much as before (Saltmarch and Labuza, 1980). Non-crystallizing system adsorbed more water due to more space between molecules, while tightly packed molecules adsorbed only on the outside of the surface.

Water at monolayer

Water at the monolayer was calculated by fitting the experiment data with the BET Model results shown in Figure 1. The BET Model plotted for maltodextrin exhibited that it fitted with the experiment data for maltodextrin DE 5 and 14 while DE 18.5 fitted just only up to %RH less than 0.75. Crystallization might play an important role in the deviation from that model fitting (Saltmarch and Labuza, 1980). The calculated water at the monolayer is shown in table 3. M_m refers to the "BET-monolayer limit" for water vapor absorption which represents the maximum number of hydrophilic binding sites of water on material (Zhang and Zografi, 2000). When DE increased, the water at the monolayer decreased. High DE maltodextrin had low molecular weight and was

Table 3 Water at monolayer (M_m) of maltodextrin DE 5, 14 and 18.5.

DE	M_m
5	5.5296^{a}
14	4.6753^{b}
18.5	4.4553^{bc}

In a column, means with the same letters are not significantly different at $p<0.05$

supposed to have more hydroxyl end groups due to more hydrolysis during maltodextrin production. As the molecular weight decreased, the number of chain ends per unit weight increased. That mean adsorption sites were newly produced when the molecular weight decreased. This controversial results showed that high DE had less water adsorption than low DE maltodextrin. This might indicate a different structure of maltodextrin at low molecular weight (high DE maltodextrin) which probably had a tights structure than that with a high molecular weight (low DE maltodextrin).

Dual-mode sorption

In general, sorption equilibria in glassy polymers are more complex than in rubbers (Koros and Paul, 1978). The dual-mode sorption model has provided a useful explanation of the data for many gas-glassy polymer systems. The sorption data of maltodextrin of various DE fits with eq.2. The parameter C'_H obtained is shown in Table 5. C'_H value decreased when DE increased. When the molecular weight decreased (more short chain molecules, high DE), molecules had more mobility than long chain molecules (low DE) and packed more tightly which reduced space between molecules and then reduced water adsorption. This result conformed to the sorption isotherm result as mentioned earlier. Barrer *et al*. (1958) and many investigators associated the Langmuir capacity of glassy polymers with frozen microvoids. Chan and Paul (1980) studied solubility of CO_2 in annealed Polycarbonate at 35° C. The result showed that C'_H decreased considerably as the duration of annealing increased. During annealing at sub Tg (temperature below Tg), molecular mobility and rearrangement to reach equilibrium was expected. Barrie *et al*. (1980) studied sorption of hydrocarbon vapors in glassy polymer at different temperature and found that C'_H decreased as the temperature increased. Koros and Paul (1978) conducted a sorption experiment of CO_2 in Poly (ethylene Terephthalate) above and below Tg. The results indicated that C'_H decreased as the temperature increased and disappeared when temperature reached Tg.

Table 4 Mean particle size (μm) of maltodextrin.

DE	Mean particle size (μm)
5	31.92±2.4
14	39.58±5.9
18.5	32.49±1.5

Proton relaxation time (Spin-Spin Relaxation)

The results above showed that C'_H value obtained from dual sorption at low relative humidity region, decreased when DE of maltodextrin increased. The study of proton relaxation behavior according to water by maltodextrin should support the dual sorption scenario. Free Induction Decay from ^1H NMR of maltodextrin DE 5 and 18.5storage at 25°C, %RH = 11.3, 54.5 and 75.5 were determined. The experiment data was fitted with following equation (Van den Dries *et al*., 1998):

$$F(t) = A \exp\left[\frac{-a^2t^2}{2}\right]\frac{\sin\ bt}{bt} + B \exp\left[\frac{-t}{T_{2m}}\right]$$

A = contributions of the immobile proton in the sample.

B = contributions of the mobile proton in the sample.

Table 5 "Langmuir saturation" constant (C'_H) of maltodextrin DE 5, 14 and 18.5.

DE	C'_H
5	$3.0874^{a} \pm 0.4021$
14	$1.5996^{b} \pm 1.0710$
18.5	$1.5636^{bc} \pm 0.2982$

In a column, means with the same letters are not significantly different at $p<0.05$

a = Gaussian line shape with standard deviation.

b = total width rectangular line shape of immobile proton fraction.

T_{2m} = Spin-Spin relaxation time of mobile proton fraction.

The effect of DE and %RH on T_{2m} of maltodextrin is shown in Figure 2. At low %RH (less than monolayer level, Table 4), maltodextrin all DE had very low T_{2m}, which was 10^5-10^6 time (for DE 5 and 18.5) smaller than the value of free water (~3s). Hills *et al*. (1999) mentioned that at low water contents, where structural water played an important role, relaxation was very short. Rugraff *et al*. (1996) stated that at low water content (<5 g water/ 100 g dry solid) of wheat starch, all water proton present had a "solid like" behavior. This indicated that the water molecules were strongly bound by maltodextrin matrix, probably via hydrogen bond to the hydroxyl groups of the maltodextrin molecules (Hills *et al*., 1999). T_{2m} increased with increasing moisture content. When water increased, there were more hydrogen bonds forming between water molecules, which lead to increased mobility and longer T_{2m} (Van den Dries *et al*., 1998). DE 5, at water content 4.01%, there were 4.01 water molecules per maltodextrin molecule. It was less probable that the water molecule was next to the other. Increasing the water content to 10.7%, there were 10.7 water molecules per maltodextrin molecule. The probability of hydrogen bonds between the water molecules increased and led to an increase of mobility. Hemminga *et al*.(1999) stated that the less concentrated the system, the less rigid the hydrogen bond net work. Maltodextrin DE 18.5 had the same trend but had less T_{2m} than DE 5 due to less water molecule per maltodextrin molecule.

The intensity of an NMR signal was directly proportional to the number of protons contributing to it. It could be concluded that maltodextrin DE 5 absorbed more water than maltodextrin DE 18.5 at a low relative humidity region. It is probable that the low DE of maltodextrin had more free water to be adsorbed to free space between molecules than high DE. High DE also had less space between molecules which resulted in strong hydrogen bonds between the hydroxyl group of maltodextrin and water (Saltmarch and Labuza, 1980 ; Bell and Labuza, 2000). This strongly supported the existence of microvoids.

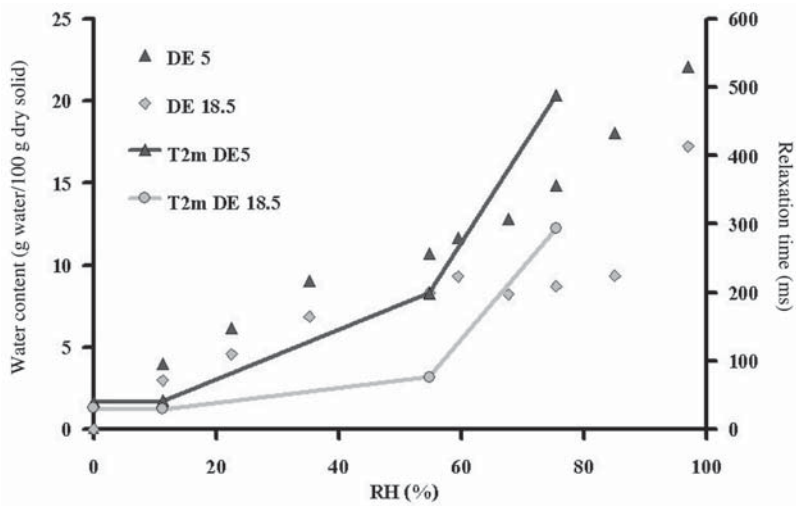

Figure 2 Comparison of sorption isotherms and relaxation times (T_{2m}) at 20°C of maltodextrin DE 5 and 18.5, storaged at various a_w at 25°C.

CONCLUSION

Sorption isotherms clearly showed that maltodextrin Low DE adsorbed more water at a low relative humidity region. Dual-mode sorption theory was applied for the sorption data analysed. It was found that maltodextrin low DE had high microvoid compared to high DE ones. This scenario was strongly supported by T_{2m} relaxation of mobile proton that maltodextrin DE 5 had more mobile proton mobility than DE 18.5. This could be explained by the molecular weight of maltodextrin that low DE had higher molecular weight and resulted in higher Tg which lowers molecular mobility.

From those results it implied that when rubbery maltodextrin cooled down or water evaporated during spray drying, it moved from rubbery to glassy state. Molecules stoped moving, and unrelaxed molecules created microvoids. Low DE maltodextrin created more microvoids which allowed penetrant molecules to diffuse through. Because of this, low DE maltodextrin as a flavour encapsulation carrier retained less flavour components after spray drying compared to high DE.

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