



Anti-hygroscopic effect of dextrans in herbal formulations

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ABSTRACT

Equilibrium moisture sorptions of two dried aqueous herbal extracts and their mixtures with dextrans of various molecular weights were investigated as a function of relative humidity at ambient temperature, and the data were analyzed by both the Guggenheim–Anderson–deBoer (GAB) and Brunauer–Emmett–Teller (BET) equations. Glass transition temperatures (T_g) of the samples were measured by differential scanning calorimetry, and their dependence on the moisture contents of the extracts was analyzed by the linear, Fox and expanded Gordon-Taylor mathematical models. All dextran–extract mixtures exhibited single T_g values, indicating that they existed as single homogeneous phases. The BET equation was found adequate for description of the moisture sorption isotherms for all samples. The dextrans appeared to reduce the hygroscopicity of the herbal extracts solely by a dilution effect. The observed increase in T_g and accompanying decrease in tackiness of the herbal extracts in the presence of dextrans may be explained by the ability of dextrans to restrict the molecular mobility of simple sugars and to counteract the plasticizing effect of water in the extracts. The expanded Gordon-Taylor equation has proved useful in predicting the T_g of hygroscopic amorphous herbal mixtures.

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1. Introduction

Dried herbal extracts are complex, amorphous, viscous materials consisting mostly of carbohydrates. Molecular motion within the viscous herbal matrices is limited and crystallization is kinetically hindered. Owing to their high affinity for the surrounding water vapor, these extracts tend to be hygroscopic and tacky, which has posed a major challenge to both formulators and manufacturers in the herbal drug and nutraceutical industries. Not only the manufacturing process but also the quality of the finished products can be adversely affected. To combat these potential problems, various approaches have been attempted including stringent control of relative humidity during production and storage, application of waterproof polymeric coating and the use of moisture-resistant packages (Adhikari et al., 2001).

From a formulation perspective, it is a common practice to circumvent the aforementioned problems by incorporating a non-hygroscopic excipient into the extracts. To this end, safe

food excipients, notably high-molecular-weight carbohydrates (or polysaccharides) such as dextrans, are widely used in herbal and nutraceutical formulations. The present study aimed to elucidate the mechanism of dextrans, a common class of granulating agents, in reducing the hygroscopicity and tackiness of herbal extracts.

In this study, two Chinese herbal medicines, *Radix ophiopogonis* (Mai Dong, MD) and *Rhizoma polygonati* (Huang Jing, HJ), have been selected as model herbs for hygroscopicity characterization. These two herbs have been reputed for their nourishing effects, and have been used clinically to treat persistent, dry cough in mainland China. At ambient conditions, dried aqueous extracts of the two herbs were found to display significant hygroscopicity, stickiness and even deliquescence at high relative humidity (RH > 90%). Preliminary simple sugar analysis by high performance liquid chromatography (HPLC) showed that the dried MD and HJ extracts contained not less than 50% by weight of simple sugars (with 60% fructose in MD and 45.6% fructose, 4.7% glucose in HJ). This observation is consistent with our previous finding that the presence of simple sugars may be primarily responsible for the excessive moisture uptake of most, if not all, herbal extracts (Chu and Chow, 2000). It has been well documented that incorporation of inert substances such as maltodextrins into hygroscopic food materials could significantly alleviate the common anti-caking problem of the latter materials after spray drying (Bhandari et al., 1997).

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However, how such and other similar excipients exert their anti-hygroscopic effect on amorphous food or herbal extracts remains a subject of considerable interest and debate in the herbal and nutraceutical industries. The present study was designed to test whether the anti-hygroscopic effect of dextrans in herbal formulations may be explained by the preferential interaction of the sorbed water with the dextrans.

2. Theoretical background

2.1. Description of moisture sorption isotherm by Brunauer–Emmett–Teller (BET) and Guggenheim–Anderson–deBoer (GAB) equations

Owing to their relative simplicity and ability to provide a mechanistic interpretation of the sorption process, both BET and GAB equations are widely applied in moisture sorption studies of amorphous materials, particularly processed foods.

The BET model describes a phenomenon of localized physical adsorption. The model assumes a fixed number of independent, identical adsorption sites distributed over a material surface (adsorbent). Adsorbate molecules adsorb on these sites in a localized manner without any lateral interactions with the neighboring adsorbed molecules. The first layer of molecules adsorbed on the solid surface (monolayer) is thought to have a much stronger interaction than the second and the following layers of molecules with the surface sites (multilayers). Based on these assumptions, the following BET equation can be derived to describe the adsorption of water molecules on a solid surface as a function of relative pressure or relative humidity (RH):

$$W = \frac{W_m C_B (P/P^0)}{[1 - (P/P^0)][1 - (P/P^0) + C_B (P/P^0)]} \quad (1)$$

where W is the mass of water vapor adsorbed at a particular relative pressure, P/P^0 ; W_m is the theoretical amount of water corresponding to monolayer coverage of the surface; and C_B is an equilibrium constant related to the affinity of sorbate adsorption.

It must be noted that the BET model was originally derived with reference to gas adsorption on crystalline surfaces, and as such, would not be applicable to the analysis of the moisture sorption behavior of amorphous food or plant extracts involving plasticization and consequential structural changes by the incorporated water. However, it has been argued that if the analysis can be limited to 40% RH at which significant water absorption into the bulk and dissolution of the material has not yet occurred, the equation may still be valid. Thus most hygroscopicity studies on amorphous food materials employed the BET model for moisture sorption analysis up to this RH limit. However, whether such a restricted analysis can avoid the possible water uptake into the bulk has not yet been verified experimentally. It is possible that significant moisture absorption could still occur in the low RH range for certain highly hygroscopic materials.

Despite the limitation of the BET model for characterizing the moisture sorption of amorphous food materials, the analysis yields parameter estimates for W_m and C_B , which are important for interpretative purposes. As suggested in our previous study, W_m can be equated with the amount of water required to saturate the accessible binding sites both on the surface and in the bulk of the materials, and may therefore be considered as a hygroscopicity indicator (Chu and Chow, 2000). C_B reflects the affinity of water for the hygroscopic material of interest.

The GAB model, an extension of the BET model with one additional parameter, is widely considered to be complementary to the BET model in providing sorption analysis over the entire range of relative pressure. Mathematically, the GAB equation can be

expressed in the following form:

$$W = \frac{W_m C_G K (P/P^0)}{[1 - K(P/P^0)][1 - K(P/P^0) + K C_G (P/P^0)]} \quad (2)$$

where P , P^0 , W and W_m are defined as above; C_G is the affinity constant for the sorbate adsorption based on the GAB model and K is a second equilibrium constant introduced to account for the intermediate state of water adsorption.

Similar to the BET model, the GAB equation was originally formulated for the description of vapor adsorption on crystalline surface. The additional parameter, K , was introduced on thermodynamic grounds to account for the intermediate state of vapor adsorption not accounted for in the BET model. However, since moisture sorption on herbal extracts rarely involves only the surface, and continuous moisture ingress with increasing RH could change the extracts physically, K no longer carries any physical meaning although it may be viewed as a correction factor for the structural changes of the sorbent. The GAB equation reduces to the BET model when K is equal to unity.

While the introduction of K generally can improve the goodness of fit (R^2) and the precision (standard errors) of the parameter estimates, it renders interpretation and comparison of the sorption phenomenon between samples more difficult as K and W_m are self-adjustable constants in model fitting. For comparison purposes, it may be acceptable to employ the BET model empirically for estimating the W_m and C_B values even if the sorbents in question undergo substantial physical changes.

2.2. Dependence of glass transition temperature (T_g) of amorphous materials on water content

A number of mathematical equations relating T_g to water content of amorphous food or herbal materials have been reported. By assuming weight additivity effect at T_g and an absence of specific interaction between the two components of interest, the following equation can be derived:

$$T_{g(\text{mix})} = W_1 T_{g1} + W_2 T_{g2} \quad (3)$$

where $T_{g(\text{mix})}$ is the experimental glass transition temperature of the moist material; T_{g1} and T_{g2} are the glass transition temperatures of water and completely dried material; W_1 and W_2 are weight fractions of water and the dried material.

A variant of Eq. (3) is that according to Fox (Hancock and Zografi, 1994), which assumes weight additivity effect at the reciprocal of T_g of individual components instead, i.e.:

$$\frac{1}{T_{g(\text{mix})}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (4)$$

As Eqs. (3) and (4) are relatively simplistic and may not afford reliable T_g estimates, the Gordon-Taylor equation, which has been widely used to predict the T_g of compatible polymer blends, is more often preferred for T_g estimation. Based on expansion coefficients and the assumption of volume additivity and ideal mixing (Schneider, 1988), the Gordon-Taylor equation differs from Eqs. (3) and (4) in having an additional parameter, C , as follows:

$$T_{g(\text{mix})} = \frac{W_1 T_{g1} + C W_2 T_{g2}}{W_1 + C W_2} \quad (5)$$

where the constant C can be calculated from the densities (ρ) and glass transition temperature (T_g) of the components as follows:

$$C = \frac{T_{g1} \rho_1}{T_{g2} \rho_2} \quad (6)$$

T_{g1} (i.e. glass transition temperature of water; 138 K) can be obtained from literature, and need not be computed by model fitting (Khalloufi et al., 2000).

Since the constant C in the Gordon-Taylor equation can be equated with the ratio of the free volumes of the two components under any given condition, the Gordon-Taylor equation reduces to the Fox equation when there is no density difference between the two components, i.e. water and sorbent.

As the material of interest in the present study may involve up to three components, i.e., water, herbal extract and dextran, Eqs. (3) and (4) can be rewritten for such a ternary system as follows:

$$T_{g(\text{mix})} = W_1 T_{g1} + W_2 T_{g2} + W_3 T_{g3} \quad (7)$$

$$\frac{1}{T_{g(\text{mix})}} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \frac{W_3}{T_{g3}} \quad (8)$$

where W_3 and T_{g3} represent the weight fraction and glass transition temperature of the third component.

Similarly, Eq. (5) can be expanded to yield

$$T_{g(\text{mix})} = \left(\frac{C_{12}W_2}{C_{12}W_2 + W_1} \right) \left[\frac{(1 - W_3)T_{g2} + C_{23}W_3T_{g3}}{1 - W_3 + C_{23}W_3} \right] + \left(\frac{W_1}{C_{12}W_2 + W_1} \right) \left[\frac{(1 - W_3)T_{g1} + C_{13}W_3T_{g3}}{1 - W_3 + C_{13}W_3} \right] \quad (9)$$

where C_{12} , C_{23} , C_{13} correspond to the C -values in the Gordon-Taylor equation for binary mixtures of components 1–2, 2–3 and 1–3, respectively. Eq. (9) is essentially a combined form of three Gordon-Taylor equations for binary mixtures after appropriate simplification, and has been successfully applied to describe the T_g -composition relationship in ternary systems composed of sucrose, glucose and fructose (Truong et al., 2002).

3. Materials and methods

3.1. Materials

Raw *R. ophiopogonis* (Mai Dong) and *R. polygonati* (Huang Jing) herbs, denoted by MD and HJ, were purchased from a local herbal medicine store. AR grade sugar standards (D-glucose, D-fructose and D-sucrose) with purity >99.995% were obtained from Sigma Chemical Co. Ethanol (96% v/v) and the inorganic salts (AR grade) for creating various relative humidities was supplied by BDH Laboratory. Anhydrous phosphorus pentoxide and HPLC grade acetonitrile was obtained respectively from Farco Chemicals Supplies and Lab-Scan Ltd. Dextrans T10 (MW = 10,600), T40 (MW = 37,500), T70 (MW = 69,000) were purchased from Pharmacia Biotech Inc. All water used was double distilled.

3.2. Preparation of aqueous herbal extracts

Aqueous extracts were prepared by boiling 1 kg of each herb in water for 4 h. The resulting mixture was filtered and the filtrate was then made up to 0.5 l. For determination of the water-soluble substance in the filtered extracts, three 1-ml samples were withdrawn and dried to constant weight in an oven at 60 °C.

3.3. Preparation of dried molecular mixtures of herbal extract and dextran

Solutions of known dextran concentrations were mixed with a fixed concentration of aqueous herbal extract. Removal of water was achieved by oven drying at 60 °C for 3 days, followed by storage over phosphorus pentoxide in vacuum desiccators for 7 days. Dried

herbal extracts, with 0%, 25% and 50% (w/w) dextrans (T10, T40 and T70) were obtained.

3.4. HPLC analysis of simple sugars

The contents of three major sugars, fructose, glucose and sucrose, in the extracts were determined by high performance liquid chromatography (HPLC) using a Waters 2695 LC system (Waters Inc., MA, USA) equipped with autosampler, an Alltech Model 500 evaporative light scattering detector (ELSD; Alltech Associates Inc., Deerfield, IL, USA), and an Alltech Alltima amino column (250 mm × 4.6 mm). Two separate mobile phases were employed: (A) 80% acetonitrile and 20% (v/v) water (for fructose and glucose assays) and (B) 90% acetonitrile and 10% water (for sucrose determination). The analysis was conducted isocratically at an eluent flow rate of 1 ml/min and with the following ELSD settings: gas flow rate, 4.02 standard liter per minute (SLPM); gas pressure, 68.6 psig; drift tube temperature, 80.2 °C; exhaust temperature, 44.2 °C; low temperature adaptor (LTA) temperature, 40 °C; baseline value, 56.5 mV. Weighed sample (~500 mg) of each dried extract was allowed to dissolve in 100 ml 80% (v/v) ethanol in water with the aid of sonication for 1 h. The suspension was centrifuged to separate the undissolved material (polysaccharide) from the extract solution. The resulting supernatant was collected after filtration, and diluted with 80% (v/v) ethanol in water to give a final concentration of 1 mg/ml. Twenty microliters of the final solution was injected onto the column. With Mobile Phase A, fructose and glucose were eluted respectively at 16.3 and 20.5 min. The retention time of sucrose with Mobile Phase B was 13.07 min. Calibration plots for standard D-fructose and D-glucose solutions in the concentration range of 0.1–1 mg/ml and 0.02–0.12 mg/ml displayed excellent linearity with an R^2 value of ~0.99. Duplicate measurements were taken. Since no sucrose peak could be detected in the chromatograms of the two herbal extract solutions, quantitative analysis of sucrose was not pursued further.

3.5. Construction of moisture sorption isotherm

Nine different salts, namely, LiCl (10.2% RH), CH_3COOK (22.5% RH), MgCl_2 (33.0% RH), K_2CO_3 (42.8% RH), $\text{Na}_2\text{Cr}_2\text{O}_7$ (54.0% RH), NaNO_2 (65.0% RH), NaCl (75.3% RH), KCl (84.3% RH) and KNO_3 (92.5% RH), were employed to create the desired RH in a closed system. Sorption experiments were conducted in airtight chambers at 25 °C. Equilibrium water content was recorded when three successive weekly weighings differed by not more than 0.1 mg. Potential microbial growth was monitored for all samples throughout the course of the experiment, and was found to be insignificant. All measurements were performed in triplicate. Moisture sorption isotherms were analyzed by both BET and GAB models.

3.6. Powder X-ray diffraction (PXRD)

PXRD patterns were recorded with a Philips powder X-ray diffraction system, Model PW 1830, using a 3 kW Cu anode ($\lambda = 1.540562 \text{ \AA}$) over a 2θ interval of 5.0–40.0°. Step size was 0.05° with a counting time of 2 s.

3.7. Determination of glass transition temperature (T_g)

T_g was determined using a PerkinElmer Pyris 1 differential scanning calorimeter (with Pyris Manager software and sub-ambient accessories). Indium and water were used for routine calibration. Hermetically sealed aluminum pans were used in T_g measurement for all samples except for the completely dried extracts (HJ and MD) and dextrans (T10, T40 and T70) which were analyzed in pin-holed

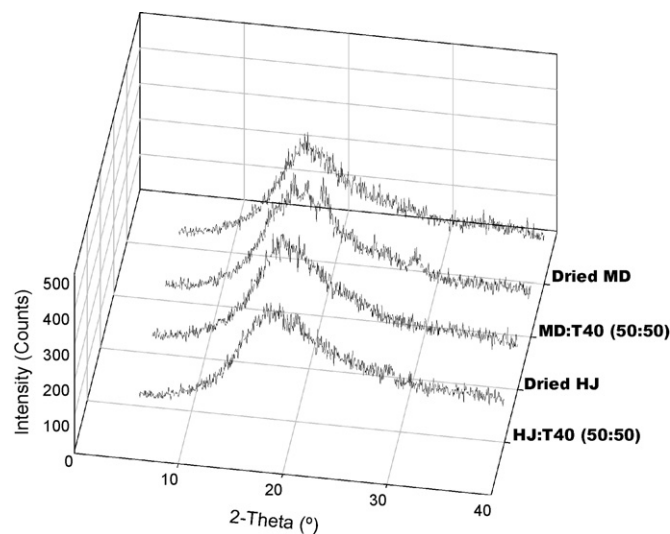


Fig. 1. PXRD patterns of MD, HJ and their 50:50 mixtures with dextran T40.

pan (to remove any residual water that could affect the measurement). Each sample was double-scanned to eliminate its previous thermal history and to confirm its T_g value. The scanning range spanned from 30–40 °C below to 30–40 °C above the observed T_g , and the heating/cooling rate was set at 20 °C/min. T_g was determined from the second scan by the half C_p extrapolation method. All T_g values were the means of at least two independent scans.

4. Results and discussion

4.1. Physicochemical characteristics of herbal extract–dextran formulations

Amorphous forms (reflected by diffused halo PXRD patterns) were confirmed for the two herbal extracts and representative extract–dextran mixtures (Fig. 1). The dried water-soluble matters determined by drying 1-ml aliquots of the aqueous extracts to constant weight were 330.88 ± 0.02 mg/ml for MD and 427.86 ± 0.02 mg/ml for HJ ($n=3$ for each herb). HPLC analysis revealed that both dried MD and HJ extracts possess a high sugar content (>50%, w/w). MD extract contained 60% (w/w) fructose while there were 45.6% (w/w) fructose and 4.72% (w/w) glucose present in the HJ extract.

4.2. Moisture sorption isotherms

Type II isotherms with weak knees were observed for MD and HJ (Fig. 2). The isotherms up to an RH of 84.3% were analyzed by both GAB and BET models. Since the attainment of moisture sorption equilibrium was difficult to ascertain at 92.5% RH, the data obtained at this RH might not be reliable and were, therefore, not used in the analysis. The computed statistics are generally better with the BET model, as shown by the higher R^2 values, lower mean absolute prediction errors (MAPE) and lower standard errors of parameter estimates (Table 1; data for the GAB analysis not shown). In addition, the K values with the GAB model for the extracts with or without dextrans are close to or statistically indistinguishable from unity. All these observations suggest that the BET model is adequate for describing all the moisture sorption isotherms within the RH range employed (Table 1). Consequently, all the quantitative hygroscopicity comparison of the extracts or extract–dextran mixtures was based on the BET- W_m and C_B parameters. As suggested by the statistically insignificant

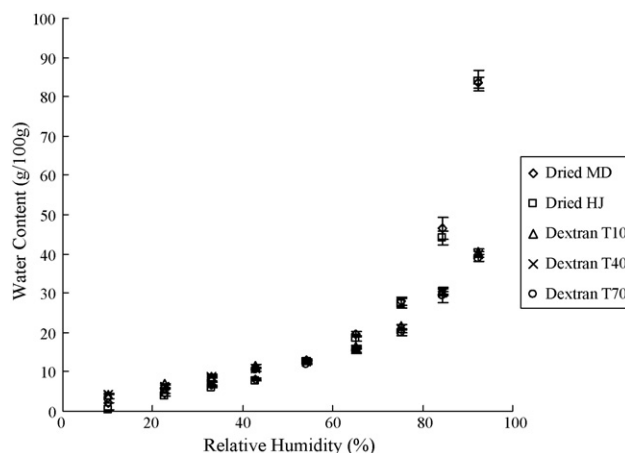


Fig. 2. Moisture sorption isotherms of MD, HJ, and various molecular weights of dextrans (T10, T40 and T70). Error bars depict standard deviations of triplicate determinations.

differences in W_m and C_B estimates between samples (Student's t -test at $p=0.05$; Table 1), MD and HJ were comparable in hygroscopicity. Previous work has demonstrated that the hygroscopicity of dried herbal extracts obtained by water extraction was strongly correlated with their low-molecular-weight carbohydrate contents (Chu and Chow, 2000). In the present study, the observed similarity in moisture sorption between the two herbs is most likely due to their similar sugar contents, as substantiated by the HPLC sugar assay.

Applying similar data analysis to the moisture sorption isotherms of the various molecular weight grades of dextrans, it could be seen that the dextrans were all comparable in moisture uptake at various RHs, irrespective of their molecular weights, and were considerably less hygroscopic than MD and HJ at RH above 54% (Fig. 2). The observed water uptakes of dextrans T10 and T40 are consistent with those reported by Zhang and Zografi (2000). Although the BET- W_m values tend to decrease with increasing molecular weight of the dextrans, the changes are not statistically significant (Table 1). This is perhaps not unexpected, since the number of water binding sites (i.e., hydroxyl groups) and hence the equilibrium water content on a per gram basis should be similar among dextrans of different molecular chain lengths.

Both MD and HJ displayed similar moisture sorption tendency with all dextrans studied (T10, T40, T70), as reflected by the similarity in BET- W_m value among the various extract–dextran mixtures (Table 1). Increasing the mass fraction of the dextrans depressed the moisture sorption isotherms of the herbal extracts progressively with a concomitant reduction of the BET- W_m values (Table 1). Such reduction of moisture uptake into the extracts in the presence of dextrans was most apparent at RH above 65%, as illustrated by MD and dextran T40 in Fig. 3. Linear correlation analysis revealed a strong association between the BET- W_m values and the dextran concentrations ($R^2=0.966$ – 0.998) for all mixtures of MD/HJ and dextrans, suggesting that the dextrans may simply serve to provide more accessible binding sites for water molecules, and their apparent anti-hygroscopic effect may be solely ascribed to their weight percentage contribution. To test this hypothesis, the predicted equilibrium water contents were computed using Eq. (10) below and correlated with the observed water contents at various RHs.

$$\text{Predicted values} = W_1 \times P_1 + W_2 \times P_2 \quad (10)$$

where W_1 and W_2 are the weight fractions of the herbal extract and dextran, respectively; P_1 and P_2 are respectively the equilibrium

Table 1
BET analysis of moisture sorption isotherms of MD- and HJ-dextran mixtures up to 84.3% RH at 25 °C

Crude drug	Dextran	Herbal extract (%)	Dextran (%)	W_m (g/100g)	C_B -value	MAPE	R^2
MD	T10	100	0	7.823 (0.160)	2.626 (0.400)	0.330	0.992
		75	25	7.140 (0.134)	5.605 (1.199)	0.390	0.989
		50	50	6.592 (0.111)	13.96 (4.52)	0.470	0.987
		0	100	5.178 (0.132)	423.7 (2536)	1.467	0.953
MD	T40	100	0	7.823 (0.160)	2.626 (0.400)	0.330	0.992
		75	25	7.371 (0.122)	3.896 (0.600)	0.494	0.993
		50	50	6.575 (0.137)	10.25 (3.473)	0.921	0.982
		0	100	5.060 (0.117)	318.7 (1413)	1.265	0.962
MD	T70	100	0	7.823 (0.160)	2.626 (0.400)	0.330	0.992
		75	25	7.288 (0.170)	5.144 (1.288)	0.727	0.984
		50	50	6.496 (0.113)	8.530 (2.137)	0.265	0.989
		0	100	4.914 (0.123)	42.07 (45.89)	1.137	0.961
HJ	T10	100	0	7.552 (0.150)	2.391 (0.338)	0.577	0.993
		75	25	6.573 (0.163)	7.362 (2.381)	1.092	0.979
		50	50	6.316 (0.176)	16.14 (9.529)	1.434	0.962
		0	100	5.178 (0.132)	423.7 (2536)	1.467	0.953
HJ	T40	100	0	7.552 (0.150)	2.391 (0.338)	0.577	0.993
		75	25	7.146 (0.156)	5.860 (1.493)	0.624	0.985
		50	50	6.431 (0.129)	16.23 (6.790)	0.902	0.981
		0	100	5.060 (0.117)	318.7 (1413)	1.265	0.962
HJ	T70	100	0	7.552 (0.150)	2.391 (0.338)	0.577	0.993
		75	25	6.639 (0.171)	6.844 (2.226)	1.137	0.978
		50	50	5.895 (0.162)	11.62 (5.562)	1.204	0.968
		0	100	4.914 (0.123)	42.07 (45.89)	1.137	0.961

Note: $MAPE = \left(\sum_{i=1}^N |Y_{oi} - Y_{pi}| \right) / N$, where Y_{oi} and Y_{pi} are the observed and predicted values, respectively; N is the number of data points. Values in parentheses depict standard deviations of triplicate measurements.

water contents of 100% extract and 100% dextran at the RH of interest.

Fig. 4 reveals an excellent linear correlation ($R^2 = 0.9964$; $n = 108$) between the experimental and predicted (based on weight percentage contribution) equilibrium water contents with a mean absolute prediction error (MAPE) of 1.406. In addition, the slope (1.016 ± 0.006) was close to unity and the intercept (0.798 ± 0.169) tended to zero, indicating that the predicted values were virtually identical to the observed values. However, owing to the remarkably good linear fit of data and the small standard errors of the computed slopes and intercepts, the regression line still exhibited a statistically significant ($p < 0.05$), albeit small, deviation from the line of identity (broken line in Fig. 4; slope = 1 and intercept = 0).

All the dextran–extract mixtures exhibited a single T_g (Tables 2 and 3), indicating that they existed as single homogeneous molecular dispersions rather than as separate heterogeneous phases. All these observations strongly support the hypothesis that

the dextrans reduce the hygroscopicity of the extracts purely by a dilution effect. Accordingly, the incorporated dextrans exhibit no preferential binding with water relative to the host extracts, and water binds to both components with equal probability. Similar finding was reported by Shamblin and Zograf (1999) who demonstrated that the water vapor sorption of the sucrose–PVP and sucrose–PVP/VA systems could be quantitatively described by the weighted contributions of individual components in the mixtures.

As can be seen from Tables 2 and 3, dried MD and HJ extracts display T_g of 287 and 296 K, respectively that fall within the range of the reported T_g values of their major sugar components ($T_g = 278$ – 291 and 295 – 311 K for fructose and glucose, respectively) (Truong et al., 2004; Liu et al., 2006; Simperler et al., 2006), possibly reflecting the dominant effect of these simple sugars on the overall T_g of the extracts. Consistent with the moisture uptake, the T_g values of all samples were observed to decrease as a function of RH (Fig. 5) and each sample showed only a single T_g , suggesting

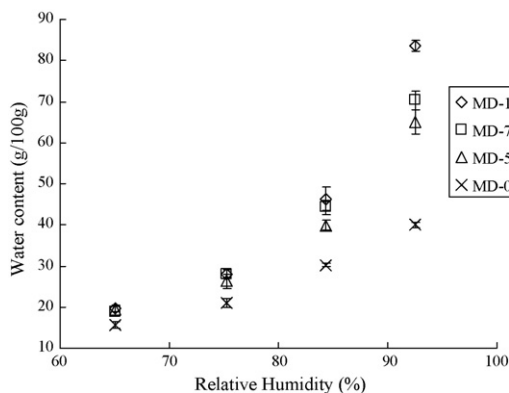


Fig. 3. Moisture sorption isotherms beyond 60% RH for MD incorporated with different mass fractions of dextran T40. Error bars depict standard deviations of triplicate determinations.

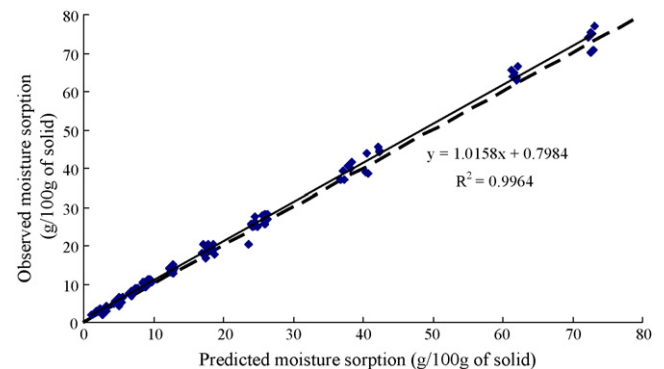


Fig. 4. Correlation between the observed and predicted equilibrium water contents. The solid and broken lines represent the regression line and the line of identity (slope = 1; intercept = 0), respectively.

Table 2
 T_g (K) values, determined by half C_p extrapolation, of MD and MD–dextran mixtures as a function of relative humidity

RH (% at 25 °C)	MD	MD:T10, 75:25	MD:T10, 50:50	MD:T40, 75:25	MD:T40, 50:50	MD:T70, 75:25	MD:T70, 50:50
0.0	287.04 (0.18)	310.61 (0.61)	343.07 (1.74)	327.72 (1.55)	361.33 (1.81)	343.76 (2.35)	371.01 (1.84)
10.2	283.18 (0.23)	305.66 (0.31)	315.87 (0.46)	315.48 (1.22)	321.12 (0.85)	322.92 (0.86)	328.67 (1.38)
22.5	280.48 (0.60)	302.34 (0.94)	313.22 (0.92)	313.27 (1.10)	315.88 (1.14)	317.35 (0.51)	325.81 (0.53)
33.0	270.92 (1.07)	286.96 (0.62)	311.08 (0.08)	295.26 (1.02)	316.87 (0.21)	314.80 (0.52)	323.67 (1.33)
42.8	257.94 (0.41)	277.15 (1.34)	307.89 (1.15)	281.06 (0.37)	307.57 (1.19)	284.29 (0.99)	322.82 (1.25)
54.0	240.08 (0.53)	256.03 (1.02)	285.81 (1.30)	258.51 (1.07)	286.89 (1.49)	261.25 (1.28)	286.70 (0.86)
65.0	225.82 (0.50)	243.57 (0.64)	252.41 (0.66)	243.73 (1.23)	258.06 (0.61)	246.00 (1.04)	258.67 (1.19)
75.3	210.38 (0.95)	223.51 (0.60)	230.15 (1.00)	220.37 (1.60)	233.24 (1.31)	218.69 (0.24)	236.73 (1.07)
84.3	191.09 (0.08)	201.10 (0.04)	205.82 (0.21)	199.41 (1.57)	211.70 (0.79)	201.70 (0.19)	213.83 (1.38)

Note: Values in parentheses depict standard deviations of triplicate measurements.

Table 3
 T_g (K) values, determined by half C_p extrapolation, of HJ and HJ–dextran mixtures as a function of relative humidity

RH (% at 25 °C)	HJ	HJ:T10, 75:25	HJ:T10, 50:50	HJ:T40, 75:25	HJ:T40, 50:50	HJ:T70, 75:25	HJ:T70, 50:50
0.0	296.13 (0.43)	319.77 (0.47)	324.13 (0.85)	323.03 (1.25)	325.44 (1.07)	329.41 (1.63)	342.13 (1.82)
10.2	287.57 (0.74)	297.00 (0.15)	307.88 (1.55)	315.23 (0.24)	319.32 (0.53)	317.02 (0.76)	326.91 (2.88)
22.5	286.46 (0.27)	297.87 (1.40)	307.93 (1.00)	311.59 (0.78)	317.88 (0.99)	312.94 (0.52)	319.17 (1.24)
33.0	268.13 (0.19)	286.03 (0.46)	294.21 (1.90)	274.14 (1.72)	298.57 (1.22)	286.55 (1.24)	316.11 (0.55)
42.8	256.64 (0.18)	259.84 (0.98)	275.77 (0.00)	263.80 (0.32)	287.37 (1.37)	266.56 (0.76)	289.97 (0.25)
54.0	239.45 (0.48)	246.82 (0.42)	256.78 (1.27)	246.11 (0.04)	257.96 (0.44)	246.52 (1.75)	257.30 (2.08)
65.0	225.29 (0.13)	229.40 (0.45)	238.23 (0.63)	229.82 (0.09)	240.81 (0.38)	231.47 (0.23)	244.96 (0.11)
75.3	209.60 (0.96)	210.84 (0.17)	218.91 (0.87)	214.14 (0.16)	219.81 (1.08)	213.78 (0.93)	231.04 (0.34)
84.3	191.38 (1.34)	192.74 (0.75)	198.31 (0.12)	194.30 (0.80)	203.78 (0.72)	195.13 (0.40)	205.54 (1.30)

Note: Values in parentheses depict standard deviations of triplicate measurements.

that water was incorporated into the herbal extracts at all RHs and the general assumption of negligible water absorption at RH below 40% might not hold. This further reinforces the fact that the use of the BET model in moisture sorption analysis of hygroscopic amorphous materials may be purely empirical even in the low RH range (i.e., below 40% RH).

As indicated in Tables 2 and 3, an increase in dextran concentration brought about an increase in T_g of the extracts at all RHs studied, probably through the anti-plasticizing effect of the polymer. Dextrans of higher molecular weight also afforded higher T_g for the extracts. Similar MW- T_g trend was observed for pure anhydrous dextrans ($T_g = 482.4 \pm 0.2$ K, 494.0 ± 0.4 K, 495.8 ± 0.0 K for dextrans T10, T40, and T70, respectively with $n=3$). The T_g data of maltodextrins reported in a previous study also showed similar MW-dependence (Roos and Karel, 1991). T_g has been recognized as a fundamental parameter for explaining and controlling the stickiness of amorphous foods, particularly for low molecular weight

carbohydrates (Adhikari et al., 2001; Bhandari and Howes, 1999). Amorphous substances with higher T_g values are usually less tacky. Such a generalized phenomenon has also been observed qualitatively for the dextran–extract mixtures in the present study, and may be explained by a reduction of molecular mobility of simple sugars in the presence of high molecular weight polymers.

4.3. Influence of moisture sorption and incorporated dextrans on the glass transition temperatures of herbal extracts

The T_g -composition relationships of the herbal extracts were analyzed by the various models depicted by Eqs. (7)–(9). Employing the linear and Fox equations, predicted T_g of each mixture was calculated based on known or measured T_g values of individual components (water, dextran and herbal extract) and correlated with the observed value. However, for the expanded Gordon-Taylor model, predicted T_g values cannot be directly computed

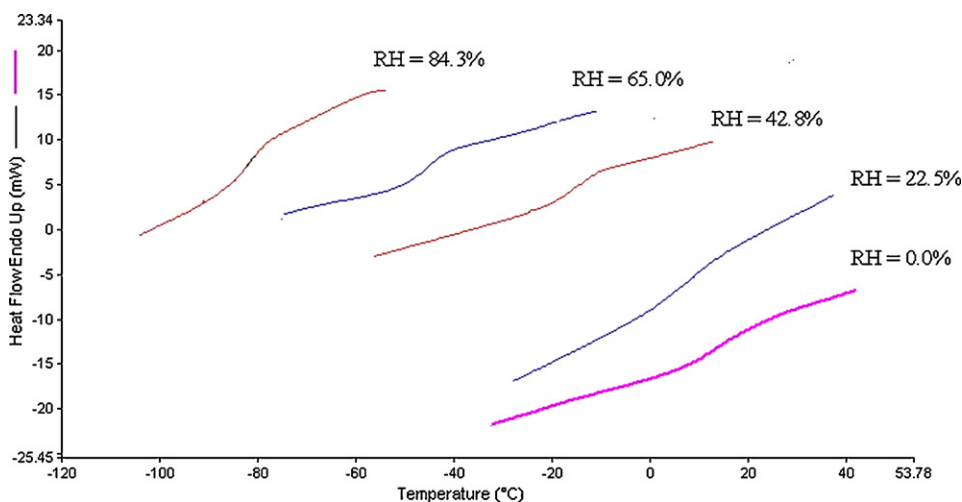


Fig. 5. Glass transition curves from the second DSC scan of MD equilibrated at different relative humidities.

Table 4

Fitted C -parameters from the expanded Gordon-Taylor equation, coefficients of determination (R^2), mean absolute prediction errors (MAPE), and regression slopes and intercepts from the linear correlation between the observed and predicted T_g values

	MD extract	HJ extract
Dextran T10		
$C_{\text{extract-dextran}}$	0.559 (0.085)	0.317 (0.065)
$C_{\text{dextran-water}}$	4.770 (0.993)	5.213 (1.659)
$C_{\text{extract-water}}$	3.288 (0.353)	4.256 (0.406)
R^2	0.951	0.951
MAPE	7.77	7.09
Slope	1.053 (0.048)	1.060 (0.048)
Intercept	-13.8 (12.9)	-15.5 (12.6)
Dextran T40		
$C_{\text{extract-dextran}}$	0.654 (0.086)	0.379 (0.077)
$C_{\text{dextran-water}}$	5.360 (0.930)	5.713 (1.687)
$C_{\text{extract-water}}$	3.297 (0.361)	4.155 (0.452)
R^2	0.956	0.941
MAPE	7.75	7.13
Slope	1.035 (0.044)	1.053 (0.053)
Intercept	-8.8 (12.1)	-13.6 (14.0)
Dextran T70		
$C_{\text{extract-dextran}}$	0.949 (0.152)	0.503 (0.081)
$C_{\text{dextran-water}}$	6.266 (1.050)	6.813 (1.434)
$C_{\text{extract-water}}$	3.219 (0.459)	4.214 (0.426)
R^2	0.937	0.955
MAPE	9.27	7.41
Slope	1.018 (0.053)	1.041 (0.045)
Intercept	-4.3 (14.7)	-10.7 (12.2)

Note: Values in parentheses depict standard errors of parameter estimates.

from known T_g values of individual components because the C parameters in the equation are not known quantities. In the latter case, the data were first fitted to the equation through an iterative computer-fitting process using Sigmapstat Version 3.1 software, and the computed C parameter estimates were then used to calculate the predicted T_g for each sample. The coefficients of determination (R^2) together with the C parameter estimates and associated standard errors for the Gordon-Taylor model are presented in Table 4.

As reflected by its higher R^2 and lower MAPE values for all samples, the Fox equation ($R^2 = 0.827\text{--}0.916$; MAPE = 14.9–29.4) afforded better predictability and prediction accuracy than the linear model ($R^2 = 0.376\text{--}0.556$; MAPE = 42.1–62.7). However, the slopes for the correlation between the predicted and observed T_g values with both models exhibited significant departure from unity, particularly with the linear model (data not shown). In addition, the associated intercept values were fairly large and deviated substantially from zero in virtually all cases (data not shown). All these statistics suggest that neither model is satisfactory for T_g prediction here.

In contrast, the expanded Gordon-Taylor equation was superior to either the linear or Fox model in terms of predictability ($R^2 = 0.937\text{--}0.956$) and prediction accuracy (MAPE = 7.09–9.27) (Table 4). In addition, there was good agreement between the experimental T_g data and those predicted by the model, as reflected by the correlation slopes and intercepts being statistically indistinguishable from unity and zero, respectively (Table 4). The observed R^2 value of ~0.95 indicates that about 95% of the variation in T_g is accountable by the predictor variables, which is considered remarkably good for such complex material systems.

As shown in Table 4, the $C_{\text{extract-water}}$ values of MD or HJ obtained with all three dextrans were essentially identical, irrespective of the

dextran involved. Similarly, for a given molecular weight of dextran, the $C_{\text{dextran-water}}$ estimates were comparable within their standard errors for the two herbs, indicative of their independence of the herb tested. These observations together with the good R^2 values lend support to the utility of the model equation for T_g prediction and the validity of the assumption involved. The results may also reflect the non-preferential nature of water binding to either dextran or herbal extract, an assumption implicit in our hypothesis that the anti-hygroscopic effect of each dextran is solely accountable by its weighted contribution in the extracts.

5. Conclusion

All three different molecular weight grades of dextrans have been shown to reduce the hygroscopicity of the amorphous herbal extracts purely by a dilution effect. The observed increase in T_g and concomitant decrease in tackiness of the herbal extracts in the presence of dextrans may be explained by the ability of dextrans to restrict the molecular mobility of simple sugars (major constituents) and to counteract the plasticizing effect of water in the extracts. The expanded Gordon-Taylor equation has proved useful in predicting the T_g of hygroscopic amorphous herbal mixtures.

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