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Estimation of effective diffusivities and glass transition temperature of polydextrose as a function of moisture content

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Abstract

The glass transition temperature (T_g) of polydextrose was determined by differential scanning calorimetry as a function of moisture content, and was fitted to the Gordon–Taylor equation. T_g decreased with an increase in moisture content, confirming the plasticizing effect of water on polydextrose. The effective diffusivity of water in polydextrose (D), which increased with an increase in storage water activity (a_w), was estimated at room temperature both above and below the glass transition by applying the method of slopes [Effective water diffusivity in starch materials, MS Thesis, Rutgers University (1987); Effect of gelatinization and sugars on the effective moisture diffusivity in starch materials, MS Thesis, Rutgers University (1988)] to the experimental data. D showed a sharp increase in regions close to the glass transition, where polydextrose changed from the glassy to the rubbery state due to increased mobility. D was also correlated to a model [The effect of water activity on moisture diffusivity in soy flour as determined from a free volume based approach (2002)] based on the free volume theory [J. Appl. Polym. Sci. 22 (1978) 2325; AIChE J. 38 (1992) 405], which captured the change in diffusion mechanism as a function of glass transition. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Polydextrose; Glass transition; Diffusivity; Free volume; Gordon–Taylor

1. Introduction

Polydextrose is a bulking agent used to provide body and texture in reduced-calorie foods. It is a non-crystalline powder that can be used to stabilize foods by preventing sugar and polyol crystallization (Staley Mfg. Co., 1997). Polydextrose is a water soluble, randomly bonded bulk polymer with an average degree of polymerization (d.p.) of about 10 glucose residues, obtained by thermal polymerization of D-glucose in the presence of sorbitol and phosphoric acid. Because of this random polymerization process, it can contain almost any possible combination of α and β linkages in its structure. Heating above the glass transition temperature (T_g) leads to a flowable melt that, after cooling, produces a clear glass with a brittle texture (Cultor Food Science, 1998). Other polymers of D-glucose have structures similar to that of polydextrose. For example, maltodextrin, obtained by the hydrolysis of starch, can have the same d.p. and yet have very different physical properties because of its α(1–4) and α(1–6) bonds, as opposed to random bonds in polydextrose.

Several studies related to the phase transitions of small carbohydrate–water systems have been reported in the literature. For example, Slade and Levine (1988) studied the non-equilibrium behavior of small carbohydrate–water systems and reported values of T_g and T_m (temperature of melting) of various polyol sugars. Orford, Parker, and Ring (1990) found that the T_g of a carbohydrate depended strongly on molecular weight and less on its structure. Roos and Karel (1991) studied the effect of molecular weight, water plasticization, and composition on T_g of maltodextrins, maltose, and sucrose. All maltodextrins of different molecular weights were plasticized by water in a similar manner, and the decrease in T_g was linear with respect to water activity (a_w) over the range of 0.11–0.85.

Limited data has been published on the phase transitions of polydextrose and its effect on the stability of foods. Bell and Touma (1996) studied the T_g of polydextrose at two moisture contents using a temperature-cycling differential scanning calorimeter (DSC). Kim, Hansen, and Setser (1986) determined that equivalent concentrations of polydextrose and sucrose had similar effects of increasing the

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onset and peak gelatinization temperatures of starch–water systems.

The diffusion of water in food polymers has been widely studied in the last two decades. The effective diffusivity (D) of water in starch materials was estimated from experimental data using the method of slopes by Marousis (1987) and Karathanos (1988). The same method was used by Vagenas and Karathanos (1991) to estimate D in granular food materials. Parker and Ring (1995) determined diffusion coefficients of maltose–water mixtures at conditions above and below T_g. In 2002, Yildiz and Kokini developed a model for solute diffusion in food polymers based on the free volume theory (FVT) (Vrentas & Duda, 1978; Vrentas & Vrentas, 1994), which will be discussed in detail in Section 2.

The objectives of this study were three-fold: to determine the plasticizing effect of water on polydextrose, to estimate the effective diffusivity of water in polydextrose both above and below T_g, and to correlate it to the modified FVT model developed by Yildiz and Kokini (2002).

2. Materials and methods

2.1. Sample preparation

Polydextrose Sta-Lite® III (90% pure) was obtained from Staley Manufacturing Co. (Decatur, IL). Polydextrose samples were placed in glass Petri dishes, which conferred the samples a cylindrical shape (9 cm diam. × 1 cm thick.). These samples were equilibrated at different a_w values by storing them in desiccators containing different saturated salt solutions (P_2O_5, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KNO_3), which produced a_w values of 0, 0.33, 0.52, 0.75, and 0.93, respectively, at 24 °C (Nyqvist, 1983).

2.2. Estimation of effective moisture diffusivity

This method assumed that (a) polydextrose samples stored in Petri dishes behaved as infinite slabs, due to their dimensions; and (b) moisture was adsorbed or desorbed only from one face of the samples, due to the physical barrier presented by the Petri dishes. After the samples reached equilibrium at different a_w values, moisture contents were determined by drying in a convection oven at 135 °C for 2 h (American Association of Cereal Chemists, 1986). Moisture gain or loss was plotted with respect to time. The effective diffusivities of water in polydextrose were determined from this plot using the method of slopes (Marousis, 1987; Karathanos, 1988), as described below.

Fick's second law for non-steady state diffusion:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial X}{\partial r}\right) \tag{1}$$

is solved for the initial condition: $X = X_o$ for $t = 0$, and the boundary conditions: $X = X_e$ for $t > 0$ and $r = L$; $dX/dr = 0$ for $t > 0$ and $r = 0$. The solution is given in the form of Eq. (2):

$$W = \frac{X - X_e}{X_o - X_e} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-(2n+1)^2\pi^2\frac{Dt}{4L^2}\right) \tag{2}$$

in which W is the moisture ratio; X the mean moisture content at time t; X_o the initial moisture content at $t = 0$; X_e the equilibrium moisture content after infinite t and L is the slab thickness.

The method of slopes consists of the following calculations:

1. Determining the slope of the theoretical diffusion curve (obtained by plotting Eq. (2)): $(dW/dF_o)_{th}$, where F_o is the Fourier number for diffusion defined as Dt/L^2.
2. Determining the slope of the experimental diffusion curve (obtained from the plot of moisture content vs. time): $(dW/dt)_{exp}$.
3. Comparison of the experimental slope and the theoretical slope:

$$D = L^2\frac{\left(\frac{dW}{dt}\right)_{exp}}{\left(\frac{dW}{dF_o}\right)_{theo}} \tag{3}$$

in which the result is the effective diffusivity, D. This procedure was repeated for all samples stored at different a_w values.

2.3. Correlation of diffusion data using free-volume-based model

From the FVT (Vrentas & Duda, 1978), the following expression for concentration and temperature dependence of a solute diffusion coefficient in a polymer solution has been proposed:

$$D_1 = D_0\exp\left(\frac{-E}{RT}\right)\exp\left(\frac{-\gamma\left(\omega_1\hat{V}_1^* + \omega_2\xi\hat{V}_2^*\right)}{\hat{V}_{FH}}\right) \tag{4}$$

in which D_0 is a pre-exponential factor, E is the activation energy per mole for a molecule to overcome attractive forces holding it to its neighbors, R is the ideal gas constant, T is the absolute temperature, γ is an overlap factor introduced to correct for overlap free volume, ω_i is the mass fraction of component i, $\hat{V}_i^*$ is the specific critical hole free volume of component i required for a diffusive jump, ξ is the jumping unit ratio (which is the ratio of solvent to polymer molecules involved in diffusive jumps), and $\hat{V}_{FH}$ is the specific hole free volume of the system. For small molecules, such as water, jumping unit can be taken as the whole molecule. In the case of polymers, Zielinski and Duda

(1992) showed that for most synthetic polymers, the jumping unit is between 1.5 and 2 monomer units.

In the limit of low penetrant concentrations, Eq. (4) is reduced to the following form:

$$D_1 = D_0 \exp\left(\frac{-E}{RT}\right) \exp\left(\frac{-\gamma\xi\hat{V}_2^*}{\hat{V}_{\mathrm{FH}}}\right) \tag{5}$$

Free volume parameters are related to the Williams–Landel–Ferry (WLF) constants, C_1 and C_2 (Williams, Landel, & Ferry, 1955) of the polymer through the following relationships:

$$K_{22} = C_2 \tag{6}$$

$$\gamma\frac{\hat{V}_2^*}{K_{12}} = 2.303C_1C_2 \tag{7}$$

where K_{12} and K_{22} are FVT parameters. Yildiz and Kokini (2002) introduced a useful modification of the FVT, which consisted of incorporation of the Gordon and Taylor (1952) equation into the FVT to account for the a_w-dependence of D_1. The Gordon–Taylor equation has been used to predict the T_g–a_w relationships for many food polymers (Roos, Karel, & Kokini, 1996). In general, for most food polymers with a distribution of hydrophilic groups, an increase in a_w results in a decrease in T_g (Slade & Levine, 1988). The Gordon–Taylor equation is written as:

$$T_g = \frac{x_1T_{g1} + (\Delta C_{p2}/\Delta C_{p1})x_2T_{g2}}{x_1 + (\Delta C_{p2}/\Delta C_{p1})x_2} \tag{8}$$

in which x_i is the weight fraction of the ith-component; T_{gi} is the glass transition temperature of the ith-component; and ΔC_{pi} is the change in heat capacity at T_{gi}.

Finally, the following equation was obtained:

$$D = D_{01} \exp\left(\frac{-(2.303C_1C_2)\xi}{(C_2 + T - T_g)}\right) \tag{9}$$

where D_{01} is a factor that can be approximated as a constant because it is less sensitive to the changes in moisture content than the exponential terms. When the theory is correlated to the data, D_{01} and ξ can be obtained from the slope and intercept of the plot of ln D vs. $\{1/(C_2 + T - T_g)\}$.

2.4. Determination of moisture sorption isotherms

Moisture content of polydextrose samples equilibrated at different a_w values at room temperature was measured using the AACC method 44-19, which consisted of heating in a convection oven at 135 °C for 2 h. The actual a_w of the samples was measured at room temperature using a Hygroscop DT hygrometer (Rotronic, Huntington, NY). Moisture content was plotted vs. a_w to create the isotherm graph.

2.5. Measurement of T_g

A Mettler TA-4000 DSC was used to determine the T_g of polydextrose equilibrated at different a_w values. The instrument was calibrated using indium as a standard. Experiments were run at a rate of 10 °C/min. Re-scans were immediately performed in order to erase the thermal history of the samples and to confirm the existence of T_g (a reversible thermal event). Measurements were performed at least in duplicate and an empty aluminum pan was used as reference. The data were analyzed using a GraphWare TA72 thermal analysis software (Mettler Instrument, Corp., Hightstown, NJ). T_g, a second-order transition, was characterized by a step change of heat flow in the thermograms, as defined by Roos (1995). The midpoint of the change in slope was identified as the T_g of the system.

The dependence of T_g data on moisture content was predicted using Eq. (8). The values used in the present study were the following: $T_{g\text{-water}} = -139$ °C (Kalichevsky & Blanshard, 1993); $\Delta C_{p\text{-water}} = 1.94$ J/g K (Kalichevsky & Blanshard, 1993); $T_{g\text{-polydextrose}} = 94$ °C (determined experimentally); $\Delta C_{p\text{-polydextrose}} = 0.33$ J/g K (estimated by least squares fit, following the procedure used by Kalichevsky and Blanshard (1993) and Jouppila and Roos (1997)).

3. Results and discussion

Fig. 1 shows the dynamics of moisture equilibration for polydextrose at different a_w values ($T = 24$ °C). The data points in the graph represent an average of at least two samples. The lines were drawn by curve-fitting the experimental data to a second-order polynomial. Polydextrose samples had an initial moisture content of 4%, which corresponded to $a_w = 0.31$. Thus, samples equilibrated at a_w values ≥ 0.33 adsorbed moisture, while those equilibrated at $a_w = 0$ lost moisture. Equilibrium was reached after approximately 34 days of storage.

Fig. 2 shows the effective diffusivity of water in polydextrose as a function of a_w at 24 °C, estimated by the method of slopes. Its value increased with a_w, similar to the increase in water sorption rate with increasing environmental relative humidity in low moisture food materials reported by Slade and Levine (1988). The values of D had orders of magnitude between 10^{-13} and 10^{-11} m^2/s, values that agree with those reported in the literature for other food materials such as flour ($D_{25\,°\mathrm{C}} = 4 \times 10^{-12}$ m^2/s), potato starch gel ($D_{25\,°\mathrm{C}} = 2.4 \times 10^{-11}$ m^2/s), and others (Okos, Narsimhan, Singh, & Weitnauer, 1992).

In order to correlate the effective diffusivity data to the modified FVT developed by Yildiz and Kokini (2002), Eqs. (8) and (9) were used. The so-called 'universal' WLF constants, $C_1 = 17$ K and $C_2 = 51$ K, were utilized to obtain the free volume parameters. Several studies (Morales-Diaz & Kokini, 1998; Yildiz & Kokini, 2001) showed

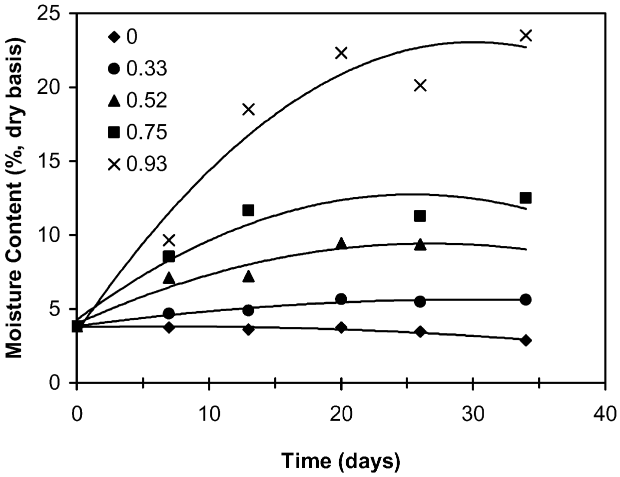

Fig. 1. Dynamics of moisture equilibration of polydextrose at different a_w values (24 °C).

that the WLF constants for food polymers are remarkably different than the universal constants. However, for simple sugars such as glucose, the universal constants have been applied successfully (Soesanto & Williams, 1981). Therefore, in the absence of experimental data, the universal constants were used to approximate molecular behavior of polydextrose, which is a relatively small molecule composed of glucose units. Adjustable parameters were calculated based on experimental T_g data at different a_w values. Assuming that the water mass fraction was small enough, experimental diffusion data were fitted to Eq. (9), which was linearized in order to obtain the parameters D_{01} and ξ from the slope and intercept, respectively. The calculated values corresponded to $D_{01} = 3.4 \times 10^{-11} \mathrm{m}^2/\mathrm{s}$ and $\xi = 0.052$. The calculated value of ξ suggests, based on molar volumes of water and polydextrose, that polydextrose jumping unit consists of approximately 2–3 glucose monomers assuming that water jumps as a whole molecule. Therefore, the trend obtained here is in agreement with the available data on synthetic polymers (Zielinski & Duda, 1992). One additional parameter, lambda (λ) was introduced in order to extend the correlation below T_g. This parameter was included in the FVT to account for the difficulty in volumetric contractions below T_g (Vrentas and Duda, 1978). In this work, the value of λ which best fitted data below T_g corresponded to $\lambda = 0.4$. The correlation between the experimental data and the FVT as a function of a_w is shown in Fig. 3. A correlation coefficient of $R^2 = 0.99$ between data and FVT model indicated a good fit. Diffusivity curves above and below T_g intersected at $a_w = 0.50$, and the magnitude of the diffusivity at this point as predicted from the model was 4.0×10^{-12} m^2/s.

The moisture sorption isotherm for polydextrose at 24 °C is shown in Fig. 4. The data were fitted to the Guggenheim, Anderson and deBoer (GAB) model:

$$\frac{w}{w_m} = \frac{Cka_w}{(1 - ka_w)(1 - ka_w + Cka_w)} \tag{10}$$

in which w corresponds to the equilibrium moisture content, fraction dry basis; w_m is the monolayer moisture content, fraction dry basis, which has been shown to correspond to the moisture content at which the rates of quality loss due to chemical reactions in foods are negligible (Bell & Labuza, 2000); C, the Guggenheim constant, is a correction factor for the sorption properties of the first layer with respect to the bulk liquid; and k is a correction factor for the properties of the multilayer with respect to the bulk liquid (Singh & Heldman, 1993; Bell & Labuza, 2000). Eq. (10) is represented in Fig. 4 as a line with sigmoid shape, behavior that is typical for sorption isotherms of food materials (Roos, 1995). The values for w_m, C, and k were calculated and corresponded to 4.33%, 2.75 and 0.984, respectively, values comparable to those found in the literature (Singh & Singh, 1996; Bell & Labuza, 2000). The monolayer moisture value was very similar to that of the initial moisture content of polydextrose and to values reported for other glassy food materials by Singh and Singh (1996).

Fig. 5(a)–(e) correspond to DSC thermograms for

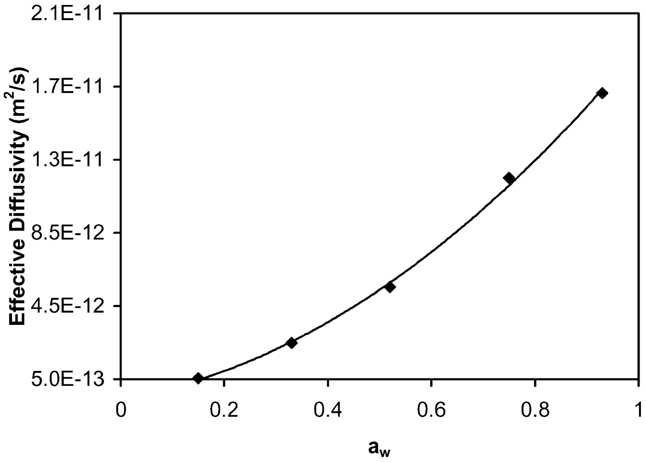

Fig. 2. Estimated effective diffusivity of water in polydextrose as a function of a_w (24 °C).

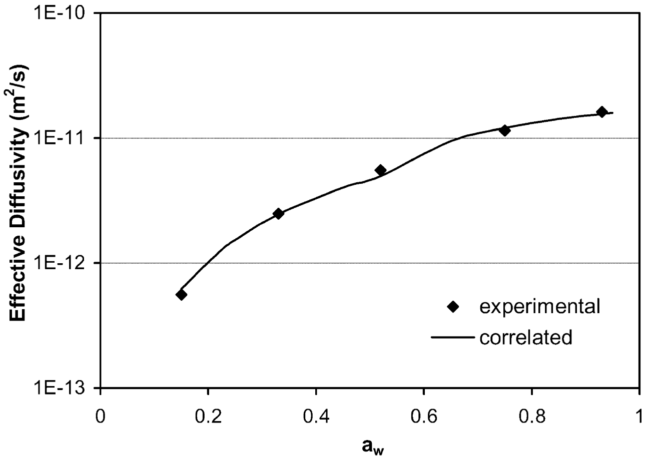

Fig. 3. Correlation of experimental effective diffusivity data using the modified FVT model.

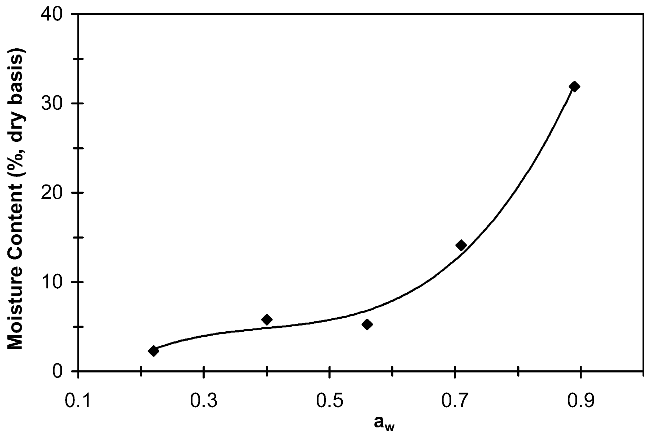

Fig. 4. Moisture sorption isotherm of polydextrose at 24 °C. Data points are compared to the GAB model (represented by a line).

polydextrose samples at the actual a_w values of 0.08, 0.37, 0.55, 0.75, and 0.92, respectively. Both the first scan and re-scan are shown. The data were normalized by dividing the heat flow by the sample weight. The thermal history of the samples was erased during the first scan. On the re-scan, T_g was identified as a change in the baseline corresponding to a change in the heat capacity of the samples. The presence of T_g on the rescan confirmed its reversibility. The ΔC_p values for polydextrose at different a_w values varied between 0.38 and 0.67 J/g K. Although the transition occurred within an interval of 20 °C, T_g was identified at the midpoint of the transition.

Fig. 5(e) shows a melting endotherm ranging approximately from − 10 to 5 °C, which corresponded to ice melting; at a_w close to 0.9 the moisture content of the samples corresponded to approximately 32%, and it is well-known that phase separation of water exists at moisture contents above 20%, facilitating the formation of ice (Orford et al., 1990). Polydextrose is a non-crystalline substance that did not show the typical DSC thermogram of freeze–dried amorphous sugars, in which T_g is followed by a crystallization exotherm and the crystals formed melt at elevated temperatures and produce a melting endotherm at the typical melting temperature of the material (Roos, 1995). A similar non-crystalline behavior is presented by aqueous solutions of fructose, which are known to be almost impossible to crystallize without pre-seeding or precipitation with a non-solvent (Slade & Levine, 1988).

Fig. 6 shows the relationship between T_g of polydextrose and moisture content. The data points represent the average of at least two experimental T_g values at each moisture content. Water plasticized polydextrose, indicated by a decrease in T_g of the samples with an increase in moisture content. Experimental data were compared to predictions made with the Gordon–Taylor equation, represented as a solid line in the figure, which predicted well the data. This equation has been proven to be a reliable predictor of T_g of various food components at different water contents (Roos et al., 1996).

Bell and Touma (1996) reported T_g values for polydextrose of 34 °C at 4% w.b. and 3 °C at 9.4% w.b., which were

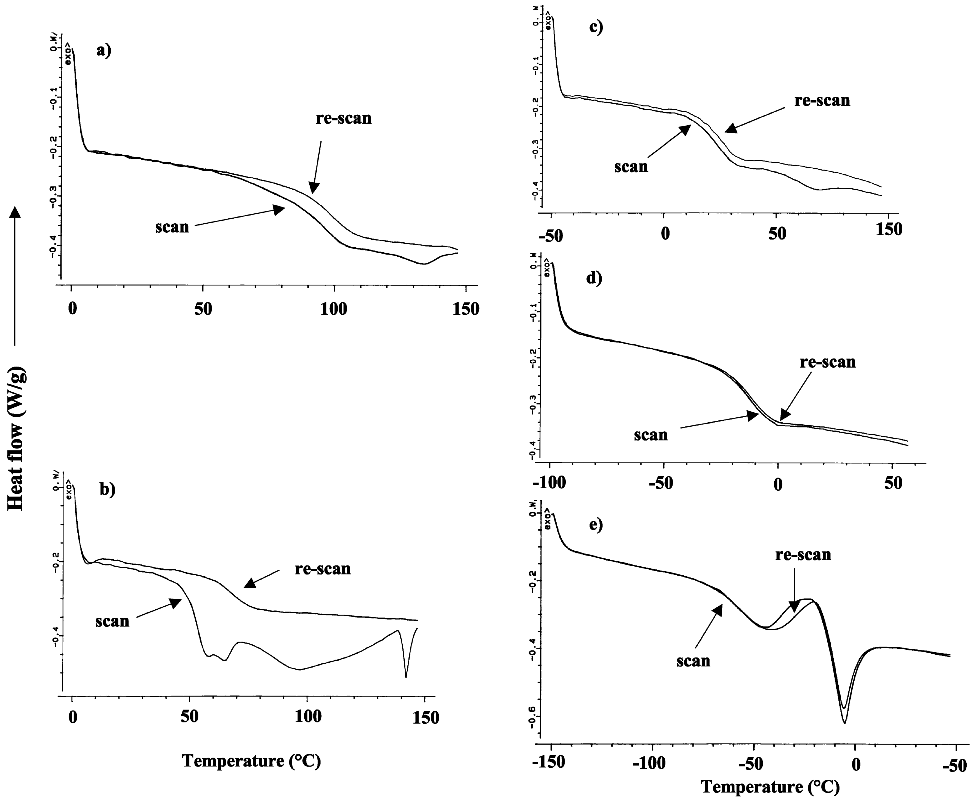

Fig. 5. DSC thermograms for polydextrose at a_w values of (a) 0.08; (b) 0.37; (c) 0.55; (d) 0.75 and (e) 0.92.

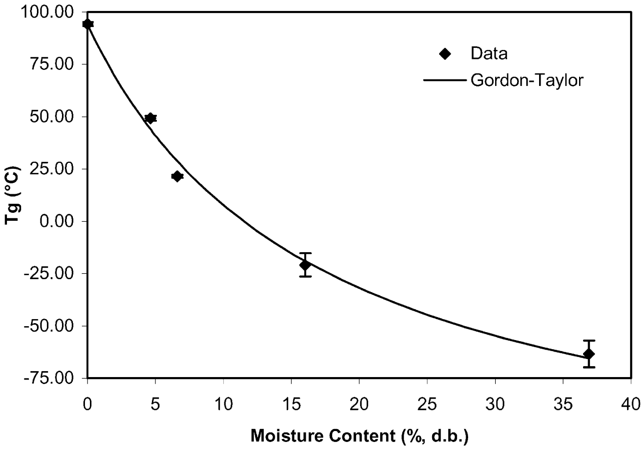

Fig. 6. T_g of polydextrose as a function of moisture content, compared to the Gordon–Taylor equation.

different from our experimental results of 53 and 9 °C, respectively. Bell and Touma (1996) identified T_g as the onset of the transition as opposed to identifying T_g at the midpoint of the transition, as done in the present study. Different methodologies were also used to measure T_g, since in their study, Bell and Touma (1996) utilized a temperature-cycling DSC and a heating rate of 5 °C/min, while in the present study a heating rate of 10 °C/min was used. It has been demonstrated that T_g increases as a function of heating rate (Kalichevsky, Blanshard, & Marsh, 1993).

In 1990, Orford et al. suggested that a carbohydrate's T_g depended strongly on molecular weight and less on its structure. Thus, according to this hypothesis, the T_g of maltodextrin with a d.p. of 10 would have a similar T_g than that of polydextrose at any specific value of moisture content (or a_w). In Fig. 7, the T_g of polydextrose is compared to data obtained by Roos and Karel (1991) for maltodextrin with a d.p. of 10. T_g vs. a_w followed a linear relationship, as found elsewhere in the literature. The two data sets were not comparable, especially at high a_w values. It should be noted that in their study, Roos and Karel (1991) used the onset of the transition to determine the T_g, while T_g was identified at the midpoint of the transition in the present study. If this were the only cause of discrepancy, maltodextrin's T_g should have been lower than that of polydextrose, which was not true in the present case. Roos and Karel (1991) used a heating rate of 5 °C/min, while in the present study a rate of 10 °C/min was used; if this were the only cause of the difference, maltodextrin's T_g should have been lower than that of polydextrose, which was not true either in the present case. Thus, additional factors may have had an effect. Among these, crystallinity is known to cause an increase in T_g (Mizuno, Mitsuiki, & Motoki, 1998). As can be observed, at high a_w values (above 0.5), the difference between T_g of maltodextrin and polydextrose grows with increasing a_w. Polydextrose does not recrystallize, but some degree of crystallinity in maltodextrin could have caused an increase on its T_g at high a_w values, since amorphous materials are likely to undergo recrystallization, and thus, become semi-crystalline at high relative humidity environments (Zimeri & Kokini, 2002). The influence of other structural differences between both compounds, such as different types of linkages, on T_g needs to be investigated further.

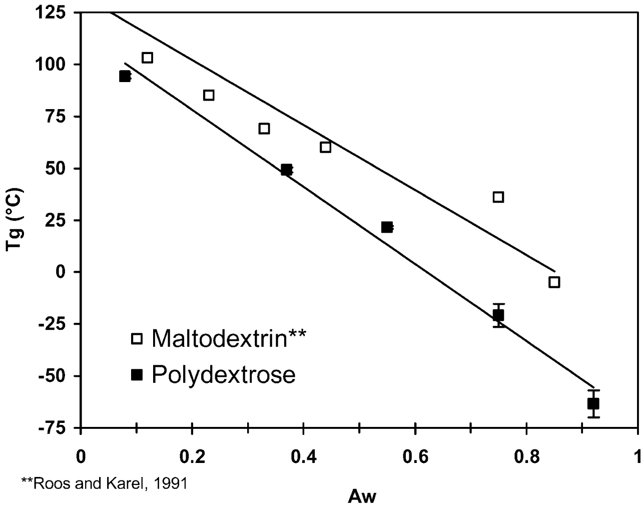

Fig. 7. Comparison between T_g profile of maltodextrin (d.p. = 10) and polydextrose vs. a_w.

Fig. 8 shows the dependence of T_g (represented by the Gordon–Taylor equation, solid line) and effective diffusivity (represented by the FVT correlation, dashed line) on moisture content. The moisture content at which the samples underwent a change from the glassy to the rubbery state, at room temperature (24 °C), was identified as the critical moisture content (C_g), and it was predicted to be 7.1% (d.b.) using the Gordon–Taylor equation. At this critical moisture content, a_w of samples was 0.57 and the corresponding critical moisture diffusivity, D_g, was 7×10^{-12} m^2/s (represented in the figure by arrows). As mentioned above, at the intersection of the diffusivity curves determined using the modified FVT above and below T_g, the predicted moisture diffusivity was

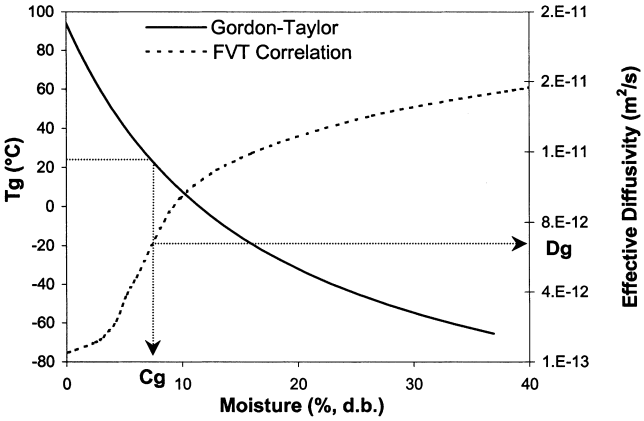

Fig. 8. Dependence of T_g (Gordon–Taylor equation) and D (FVT model) on moisture content. C_g, critical moisture content at glass transition (24 °C); D_g, critical effective diffusivity at C_g (24 °C).

4.0×10^{-12} m^2/s. The location of this value corresponded to a_w of 0.50, which was very close to a_w at C_g (0.57). Thus, results from two independent experiments suggest that the sharp increase in the magnitude of D (from 10^{-13} to 10^{-11} m^2/s) is due to the glass transition. The knowledge of T_g, C_g and D_g is very important in food stability because they define the point at which stability dynamics and, as a result, diffusion mechanisms change. The modified FVT was able to relate moisture diffusivity to physical properties of the matrix (such as T_g) and capture the change in diffusion mechanism as a function of a_w (and moisture content). Thus, the proposed model can be used to improve product stability in foods where moisture diffusivity is a critical parameter.

4. Conclusions

The Gordon–Taylor equation predicted well the plasticization effects of water on polydextrose. Effective diffusivity of moisture in polydextrose was estimated as a function of moisture content using the method of slopes, and was correlated to a model based on the FVT. Effective diffusivity increased sharply as polydextrose changed from the glassy to the rubbery state, due to an increase in mobility facilitated by an increase in moisture content, behavior that was captured by the modified FVT. These results contribute to building a database on physical properties of food materials, knowledge that is important in designing foods with better texture and stability.

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