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Glass transitions and state diagrams for typical natural fruits and vegetables

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Abstract

Differential scanning calorimetry (DSC) was used to measure phase transitions and unfreezable water in fresh samples of onion, grape and strawberry after equilibration at different relative humidities. From the DSC trace for each product, the glass transition and melting temperatures, specific heat capacities, latent heats of melting and unfrozen water contents were obtained. It was found that annealing of the sample was necessary to allow devitrification of water and a minimal amount of non-frozen water in the amorphous matrix. The effect of freeze-concentration was observed in an increased glass transition temperature, a gradual disappearance of the ice formation exotherm, and a consequent increase in the ice-melting endotherm. State diagrams for these food samples were defined. The Gordon–Taylor equation was able to predict the glass transition temperature for the water–food systems studied, from the corresponding pure component values.

Keywords: DSC; Fruit; Glass transition; Vegetable

List of symbols

a_w water activity
a,b fitting parameters in Eq. (3)
Δc_p change of specific heat capacity due to glass transition in (J g^{-1} °C^{-1})
ΔH_m latent heat of ice melting in (J g^{-1})

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K empirical parameter in Eqs. (1) and (2)
r correlation coefficient
T_{an} annealing temperature in °C
T_d devitrification temperature in °C
T_g glass transition temperature in °C
T'_g glass transition temperature corresponding to maximally freeze-concentrated material in °C
T_m melting temperature in °C
T'_m melting temperature corresponding to maximally freeze-concentrated material in °C
T_p peak temperature of ice melting in °C
X_i mass percent of component i
X'_g Moisture content corresponding to maximally freeze-concentrated material, wet basis in %

Subscripts

s solid
w water

1. Introduction

Frozen and freeze-dried food materials behave like highly viscous metastable amorphous materials, of low density bulk structure with either "rubber" or "glass" characteristics, depending on the final temperature and moisture content [1]. Several authors have tried to explain this behaviour by considering the material as a water-plasticized food polymer; this is very well documented in a recent, comprehensive review by Slade and Levine [2]. Each material has a particular value of T_g corresponding to the maximally freeze-concentrated amorphous matrix (T'_g). The practical significance of this glass transition temperature as a physicochemical parameter that can govern food processing, product properties, quality, and stability is being increasingly recognized [3].

Franks et al. [4] suggested that all these possible physical states of the material are well described in a temperature vs. concentration state diagram where phase transition curves can be represented for different water contents of the product. Recent literature reports studies resulting in state diagrams and quantitative data for transition temperatures vs. concentration for pure solutions and model systems including low-sugar solutions [2,5–7], starch and related polymers [8–10], and some specific proteins [11]. Roos [1] studied glass transitions in the *Senga Sengana* cultivar of strawberry. However, the phenomena have not been widely studied and discussed for experimental data from natural foods.

The purpose of the present study was to determine phase transitions and associated thermo-physical properties for some fruits and vegetables, either fresh or after freeze-drying and equilibrating at different moisture contents, and so to define the corresponding state diagrams for each material.

2. Materials and methods

2.1. Materials

Three common fresh foods were used in this study: onion, Povoa Red onion (*Allium cepa*), a local cultivar with large reddish bulbs; grape (*Vitis vinifera*), of the Azal white wine-making cultivar; and strawberry (*Fragaria* × *ananassa*), of the Chandler cultivar. All products were supplied by Agricultural Stations from the Portuguese Ministry of Agriculture, Fisheries and Food.

2.2. Sample preparation

All fresh products were washed and dried with paper cloth. Hull and seeds were taken out. Round slices of onion and strawberry, 7 mm thick, were cut perpendicular to their axes and submitted to freezing followed by freeze-drying. Freeze-dried onion and strawberry were powdered and 5–30 mg samples were equilibrated over saturated salt solutions (a_w 0.12–0.90) for three days at room temperature. Moisture uptake was measured by weighing the samples before and after humidification. The same moisture equilibration procedure was used for slices of freeze-dried onion and for fresh non-dried grape. The equilibration time for grape was 15 days. The water activities of the salt solutions and the moisture contents of equilibrated samples are shown in Tables 1 and 2. After humidification, each sample was placed in a 30 μl aluminium DSC pan, sealed and weighed.

Table 1
Sorption isotherm data of freeze-dried onion at 25°C (powder and flakes)

Salt solution	Water activity	Equilibrium water content in % [a]			
		Powder		Flakes	
		Wet basis	Dry basis	Wet basis	Dry basis
LiCl	0.12	3.5 ± 0.8	3.7 ± 0.8	2.1 ± 1.5	2.1 ± 1.6
CH_3COOK	0.23	5.5 ± 0.8	5.8 ± 0.9	3.6 ± 0.1	3.7 ± 0.1
$MgCl_2 \cdot 6H_2O$	0.33	7.5 ± 0.4	8.1 ± 0.5	5.9 ± 0.1	6.3 ± 0.1
K_2CO_3	0.44	10.9 ± 0.3	12.2 ± 0.4	9.1 ± 0.1	10.0 ± 0.1
$Mg(NO_3)_2 \cdot 6H_2O$	0.53	14.5 ± 0.8	17.0 ± 1.1	11.5 ± 0.1	13.1 ± 0.2
$NaNO_2$	0.61	18.8 ± 0.1	23.2 ± 0.1	17.2 ± 0.6	20.7 ± 0.8
NaCl	0.76	27.2 ± 0.1	37.4 ± 1.3	23.9 ± 0.5	31.4 ± 0.9
KCl	0.85	37.1 ± 0.6	58.8 ± 1.6	34.1 ± 0.2	51.7 ± 0.5
$BaCl_2 \cdot 2H_2O$	0.90	46.1 ± 1.3	85.6 ± 4.0	44.1 ± 0.6	79.0 ± 1.8
Fresh material	–	90.6 ± 0.5	970 ± 53	90.6 ± 0.5	970 ± 53

[a] The moisture content is an average of four samples ± standard deviation.

Table 2
Sorption isotherm data of grape and freeze-dried strawberry at 25°C

Salt solution	Water activity	Equilibrium water content in % [a]			
		Grape		Strawberry	
		Wet basis	Dry basis	Wet basis	Dry basis
LiCl	0.12	7.1 ± 0.2	7.6 ± 0.2	0.8 ± 0.9	0.8 ± 0.9
CH_3COOK	0.23	7.8 ± 0.2	8.5 ± 0.2	3.4 ± 0.3	3.5 ± 0.4
$MgCl_2 \cdot 6H_2O$	0.33	8.9 ± 0.1	9.7 ± 0.1	5.2 ± 0.5	5.5 ± 0.8
K_2CO_3	0.44	12.9 ± 0.1	14.8 ± 0.1	10.0 ± 1.2	11.1 ± 1.5
$Mg(NO_3)_2 \cdot 6H_2O$	0.53	16.8 ± 0.3	20.2 ± 0.4	14.4 ± 0.6	16.8 ± 0.8
$NaNO_2$	0.61	21.8 ± 0.1	27.9 ± 0.1	–	–
NaCl	0.76	29.0 ± 0.2	40.9 ± 0.4	27.0 ± 0.5	37.1 ± 0.9
KCl	0.85	38.2 ± 0.2	61.8 ± 0.5	38.5 ± 1.3	62.5 ± 4.0
$BaCl_2 \cdot 2H_2O$	0.90	61.4 ± 1.3	160 ± 10	49.1 ± 2.0	96.4 ± 5.3
Fresh material	–	76.5 ± 0.9	327 ± 16	90.6 ± 0.2	962 ± 26

[a] The moisture content is an average of four samples ± standard deviation.

2.3. Freezing and freeze-drying

Strawberry and onion were frozen at −40°C and freeze-dried at 65 Pa in a Telabe LF10 plate freeze-dryer. The dried samples were immediately packed in aluminium foil and stored in a desiccator over silica gel before use.

2.4. Moisture determination

Moisture contents were determined by placing the samples in a vacuum oven at 70°C and 13.3 kPa until consecutive weighings, made at 2 h intervals, gave less than 0.3% variation.

2.5. Differential scanning calorimetry

A Shimadzu DSC-50 differential scanning calorimeter fitted with a LTC-50 cooling unit was used. The instrument was calibrated for heat flow and temperature using *n*-hexane (m.p., −94°C; ΔH_m, 151 J g^{-1}), distilled water (m.p., 0°C; ΔH_m, 333 J g^{-1}) and indium (m.p., 156.5°C; ΔH_m, 28.5 J g^{-1}). Shimadzu hermetically sealable 30 μl aluminium pans were used in all measurements with an empty aluminium pan as reference. Helium at a flow rate of 30 ml min^{-1} was used as carrier gas. At least five traces were obtained for each level of moisture content for each material.

Using Shimadzu software, the traces were evaluated for onset, midpoint and endpoint temperatures of the glass transition (T_{g1}, T_{gm}, T_{g2}), onset devitrification temperature (T_d), onset and peak temperature of ice melting (T_m, T_p), change of specific heat capacity across the glass transition (Δc_p) and latent heat of ice melting (ΔH_m).

The samples were cooled with liquid nitrogen and scanned at 5°C min^{-1} from −120 to 100°C to determine their thermal behaviour in the non-annealed state. After isothermal annealing at -50 ± 2°C for grape and strawberry and -52 ± 2°C for onion, the samples were recooled to −120°C at 10°C min^{-1} and scanned again from −120°C to 20°C at 5°C min^{-1}. The latent heat of ice melting (ΔH_m) was obtained by integration of the melting endotherm of the annealed samples.

2.6. Prediction of glass transition temperatures

Glass transition temperatures of binary compatible polymer [12] mixtures can be predicted via the empirical equation proposed by Gordon and Taylor [12]. The same equation was recommended to predict glass transition temperature of water–food systems [13]

$$T_g = \frac{X_s T_{gs} + K X_w T_{gw}}{X_s + K X_w} \quad (1)$$

where T_g, T_{gs} and T_{gw} are the glass transition temperatures (°C) of the mixture, solid and water, respectively, X_s and X_w are the percent content of solid and water, respectively, and K an empirical parameter.

Because the T_{gs} value for dry grape was not measured, Eq. (1) was rearranged for the simultaneous evaluation of T_{gs} and K with a linear regression routine

$$T_g = T_{gs} + K \frac{X_w}{X_s} (T_{gw} - T_g) \quad (2)$$

A T_{gw} value of −135°C was used for pure water [14].

2.7. Calculation of unfreezable water content

Unfreezable water content (X'_g) corresponding to the maximally freeze-concentrated material was calculated from the linear relationship (Eq. 3) between the latent heat of melting (ΔH_m) of annealed samples and moisture content (X_w), by extrapolation to $\Delta H_m = 0$

$$\Delta H_m = a X_w + b \quad (3)$$

where ΔH_m is the latent heat of ice melting in the sample (J g^{-1}) and a, b are fitting parameters.

This X'_g corresponds to the lowest T_g values, T'_g, that can be determined from the DSC trace of the annealed sample (Fig. 3) and evaluated using Eq. (1).

3. Results and discussion

3.1. Thermal behaviour of non-annealed samples

Figs. 1 and 2 show DSC traces obtained for grape; similar plots were obtained for onion and strawberry. Analysis of such plots indicated that samples equilibrated

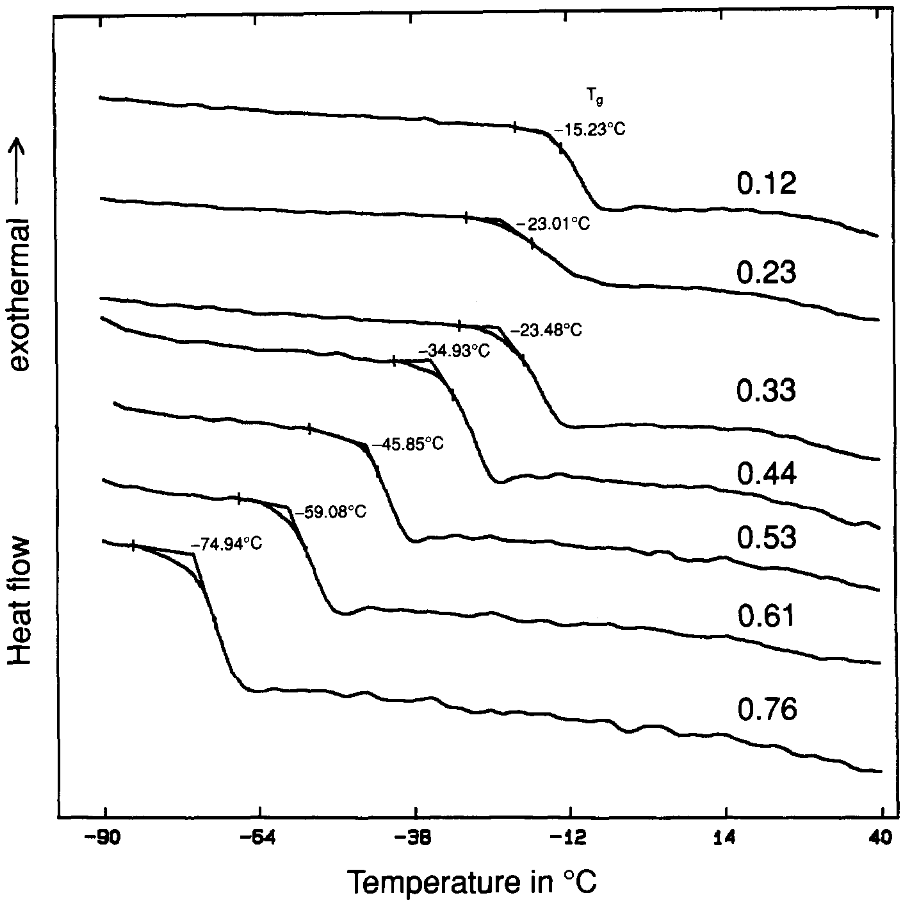

Fig. 1. Glass transitions of grape previously equilibrated at different water activities (see traces) at 25°C.

at less than 85% relative humidity showed no ice formation on freezing, and on rewarming only one glass transition was observed, decreasing the value of T_g with increasing moisture content. Onset and endpoint glass transition temperatures, T_{g1} and T_{g2}, for the products studied are given in Tables 3 and 4.

Ice melting was found in samples equilibrated at 85% relative humidity or above, for all products. With these samples an exothermal peak after the glass transition and before the melting endotherm was determined, with onset temperatures, $T_d = -71.9$°C, -58.8°C and -50.6°C for onion, grape and strawberry, respectively. This exothermic behaviour is due, according to Flink [15], to the devitrification on rewarming. Devitrification results from crystallization of freezable water that had remained unfrozen in the solid matrix owing to hindered crystallization during the fast cooling process.

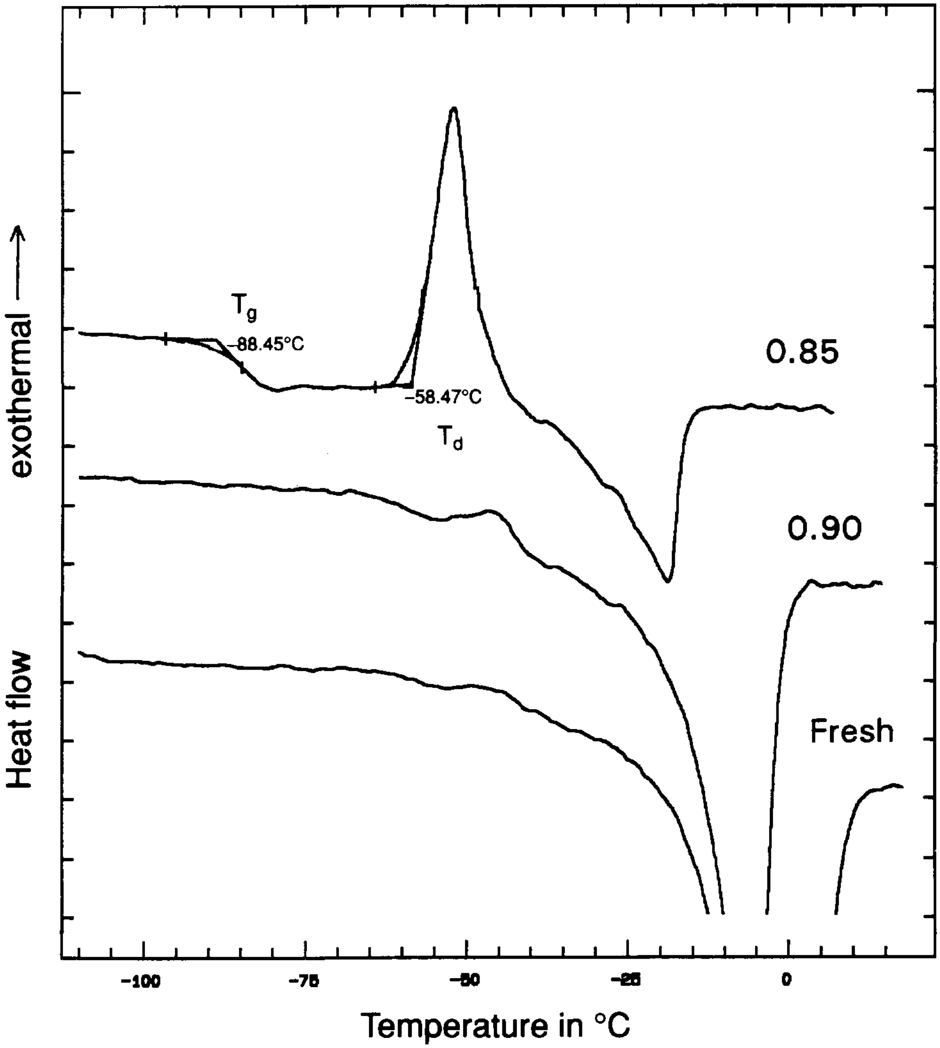

Fig. 2. Melting of ice in grape samples previously equilibrated at different water activities (see traces) at 25°C.

The dependence of the onset glass transition (T_{g1}) on water activity was adequately described by a linear relationship: $T_{g1} = -149.9a_w + 50.3$ ($r = 0.995$) and $T_{g1} = -138.0a_w + 36.6$ ($r = 0.987$) for onion flakes and powder, respectively; $T_{g1} = -101.1a_w + 3.7$ ($r = 0.979$) for grape; and $T_{g1} = -150.0a_w + 39.3$ ($r = 0.999$) for strawberry.

3.2. Thermal behaviour of annealed samples

Optimum annealing conditions are obtained when the sample is held at T'_g for a considerable period of time, allowing a maximum amount of ice to be formed, and

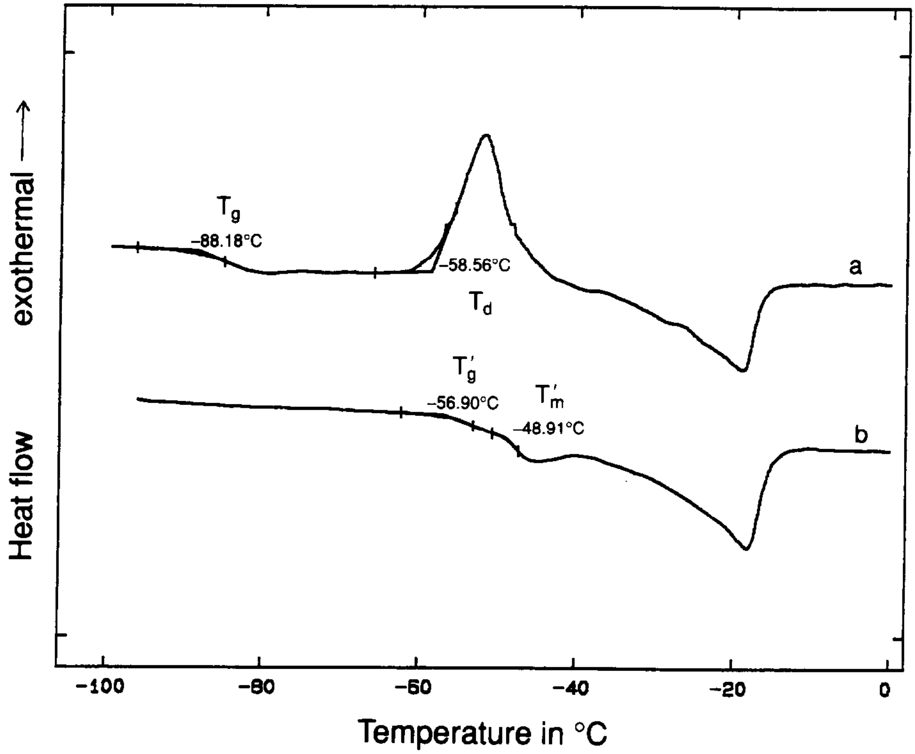

Fig. 3. Thermal behaviour of grape equilibrated at 85% relative humidity observed in (a) non-annealed and (b) annealed samples.

Table 3
Glass transition temperatures (T_{g1} and T_{g2}) of freeze-dried onion (powder and flakes) equilibrated at different water activities

Water activity	Glass transition temperature in °C [a]			
	Powder		Flakes	
	Onset (T_{g1})	End (T_{g2})	Onset (T_{g1})	End (T_{g2})
0.12	15.0 ± 2.3	26.5 ± 2.7	30.8 ± 1.1	46.8 ± 1.1
0.23	–	–	14.8 ± 2.0	25.0 ± 2.1
0.33	−11.0 ± 4.7	−1.5 ± 4.5	−1.5 ± 1.4	10.8 ± 1.3
0.44	−21.1 ± 2.9	−8.7 ± 1.4	−12.0 ± 0.9	−0.5 ± 1.0
0.53	−26.1 ± 0.6	−15.4 ± 2.3	−26.5 ± 1.3	−13.4 ± 0.4
0.61	−46.6 ± 0.5	−34.7 ± 1.1	−40.0 ± 5.0	−23.9 ± 4.8
0.76	−68.8 ± 0.5	−57.6 ± 1.4	−59.3 ± 4.6	−45.9 ± 4.9
0.85	−87.5 ± 4.9	−78.0 ± 4.5	−83.9 ± 4.0	−69.5 ± 4.5

[a] The glass transition temperature is an average of five determinations ± standard deviation.

Table 4
Glass transition temperatures (T_{g1} and T_{g2}) of grape and freeze-dried strawberry equilibrated at different water activities

Water activity	Glass transition temperature in °C [a]			
	Grape		Strawberry	
	Onset (T_{g1})	End (T_{g2})	Onset (T_{g1})	End (T_{g2})
0.12	-15.8 ± 1.4	-7.0 ± 1.8	20.1 ± 2.3	25.1 ± 3.7
0.23	-22.3 ± 3.9	-9.0 ± 1.9	–	–
0.33	-22.6 ± 2.8	-14.8 ± 2.6	-11.5 ± 2.1	0.0 ± 1.9
0.44	-35.2 ± 1.0	-26.4 ± 1.3	-24.7 ± 0.7	-14.7 ± 0.4
0.53	-44.5 ± 1.2	-37.1 ± 1.9	-38.3 ± 0.8	-26.8 ± 0.3
0.61	-59.3 ± 0.6	-51.7 ± 0.5	–	–
0.76	-75.5 ± 0.7	-67.7 ± 0.9	-73.6 ± 0.8	-64.7 ± 0.5
0.85	-86.3 ± 0.8	-80.9 ± 0.4	-90.8 ± 0.5	-83.0 ± 0.4

[a] The glass transition temperature is an average of five determinations ± standard deviation.

leading to a maximally concentrated solid matrix with moisture content equal to X'_g [16]. As T'_g is not known exactly in advance, an annealing temperature between T'_g and T'_m was used ($T_{an} = -50 \pm 2$°C for grape and strawberry and -52 ± 2°C for onion). As expected, isothermal annealing led to increased T_g values, the elimination of the devitrification exotherm, a decrease in the melting temperature and an increase in the size of the melting endotherm (Fig. 3). The annealing period was gradually increased until the values of T'_g and T'_m, and the size of the melting endotherm showed no apparent variation. The crystallization of water in samples equilibrated at 0.85 relative humidity was substantially delayed. These samples were maximally freeze-concentrated after four hours at the annealing temperature. For fresh products and products equilibrated at 0.90 relative humidity, a shorter period of annealing was necessary.

3.3. State diagrams and prediction of glass transition temperatures

State diagrams for the materials studied are plotted in Figs. 4, 5 and 6. In Fig. 6, T_g values obtained by Roos [1] are compared with the present results. Values for the empirical parameter K in Eqs. (1) and (2) are shown in the same plots. The Gordon–Taylor equation is equivalent to the Couchman–Karasz equation [17] where $K = \Delta c_{pw}/\Delta c_{ps}$, Δc_{pw} and Δc_{ps} being the changes in the specific heat across the glass transition for water and solid, respectively.

The Δc_p values determined for dried onion and dried strawberry were 0.5 and 0.9 J g^{-1} °C^{-1}, respectively. A Δc_p value for dried grape was not determined, but for the humidified samples it varied between 0.84 and 1.1. The Δc_p value of amorphous water has been reported in the range of 0.1 to 1.94 J g^{-1} °C^{-1} [18,19], leading to K values from 0.20 to 3.88 for onion, 0.09 to 2.31 for grape and 0.11 to 2.15 for

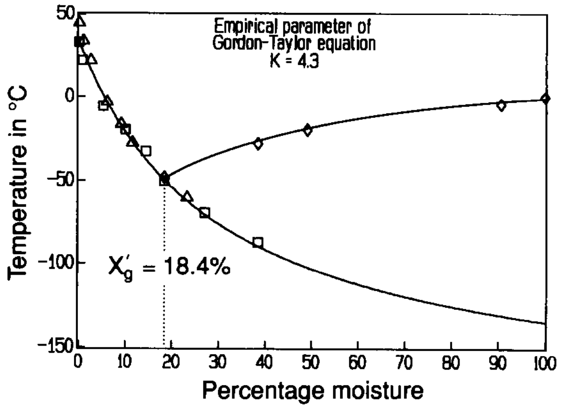

Fig. 4. State diagram for onion (□, Teflon flakes; △, Teflon powder; ◇, melting temperature).

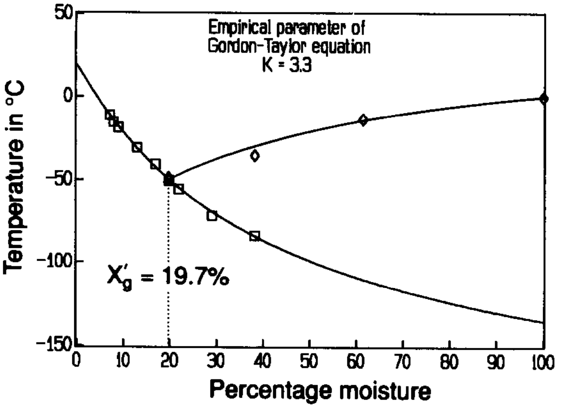

Fig. 5. State diagram for grape (□, glass transition temperature; ◇, melting temperature).

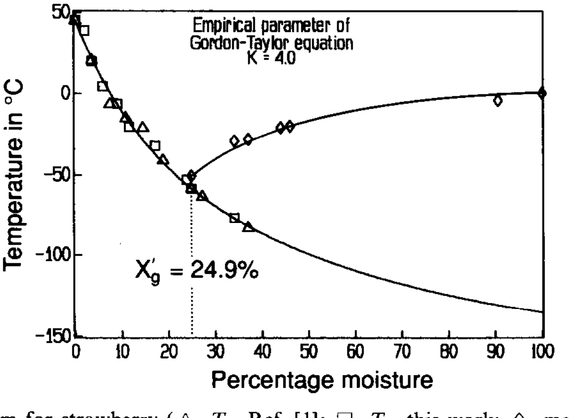

Fig. 6. State diagram for strawberry (△, T_g, Ref. [1]; □, T_g, this work; ◇, melting temperature).

strawberry which differ from those calculated with the observed data. Similar poor correlation between empirical K values and changes in the specific heats of carbohydrate solutions were determined by Roos and Karel [7].

3.4. Unfreezable water content

For fresh and partially dehydrated samples the latent heat of melting (Table 5) was found to be a linear function of the moisture content. Regression equations found were $\Delta H_m = 4.40X_w - 109.2$ (correlation coefficient, $r = 0.992$) for onion, $\Delta H_m = 3.39X_w - 66.9$ ($r = 0.996$) for grape, and $\Delta H_m = 3.67X_w - 67.7$ ($r = 0.999$) for strawberry. The T'_g values calculated through regression of ΔH_m vs. moisture contents were, in general, higher than the experimental values obtained from the thermograms of annealed samples (Fig. 3). Values of X'_g and T'_g obtained via Eqs. (2) and (3) are presented in Table 6.

4. Conclusions

In this study it was possible to determine reproducibly the glass transition temperatures and associated phase diagrams for three natural fresh and partially dehydrated foods. Such diagrams show the same general trends as those previously reported for pure solutions and model food systems.

The empirical Gordon–Taylor equation was able to predict the dependence of T_g on moisture content, with K parameters determined by least-squares regression. A

Table 5
Onset melting temperature (°C) and latent heat of melting (J g^{-1}) for onion, grape and strawberry at different water activities

a_w	Onion (powder)		Grape		Strawberry	
	T_m	ΔH_m	T_m	ΔH_m	T_m	ΔH_m
0.85	−28.0 ± 0.2	−61 ± 2	−35.5 ± 0.8	−65 ± 2	−28.0 ± 0.5	−73 ± 2
0.90	−20.2 ± 0.2	−110 ± 3	−13.7 ± 0.5	−130 ± 3	−19.8 ± 0.6	−113 ± 3
Fresh	−4.3 ± 0.3	−288 ± 6	−10.5 ± 0.2	−197 ± 5	−4.4 ± 0.3	−265 ± 7

Table 6
Values of T'_g and X'_g corresponding to maximally freeze-concentrated material

Product	X'_g in %	T'_g in °C
Onion	24.9	−58.3
Grape	19.7	−50.3
Strawberry	18.4	−50.1

single T_g line valid for both powdered and flaked onion, having distinct sorption isotherms, provides new evidence of the shortcomings of the a_w concept to describe water management in foods.

Annealing was necessary to achieve maximum ice formation and to obtain meaningful values of T'_g and X'_g corresponding to maximally freeze-concentrated material.

As expected, the total heat of ice melting varied linearly with moisture content of the sample. T'_g values obtained through regression of ΔH_m vs. moisture content were higher than the values obtained from direct experimental data on annealed samples; this may suggest that the annealing time was not long enough.

Recent reports [20] suggest that food degradation depends on $(T_{storage} - T_g)$. This leads to the immediate conclusion that if T_g equals $T_{storage}$ there would be no degradation. For the food materials studied stored at 20°C, this corresponds roughly to the moisture content obtained in the freeze-dried product.

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References

[1] Y. Roos, Effect of moisture on the thermal behaviour of strawberries studied using differential scanning calorimetry, J. Food Sci., 52 (1987) 146–149.

[2] L. Slade and H. Levine, Beyond water activity: recent advances based on an alternative approach to the assessment of food quality and safety, in F.M. Clydesdale (Ed.), Critical Reviews in Food Science and Nutrition, CRC Press, Boston, 1991, pp. 115–360.

[3] H. Levine and L. Slade, Cryostabilization technology: thermoanalytical evaluation of food ingredients and systems, in V.R. Harwalkar and C.-Y. Ma (Eds.), Thermal Analysis of Foods, Elsevier Applied Science Publishers, London, 1990, pp. 221–305.

[4] F. Franks, M.H. Asquith, C.C. Hammond, H.B. Skaer and P. Echlin, Polymeric cryoprotectants in the preservation of biological ultrastructure. I. Low temperature states of aqueous solutions of hydrophilic polymers, J. Microsc., 110 (1977) 223.

[5] L. Slade and H. Levine, Non-equilibrium behaviour of small carbohydrate–water systems, Pure Appl. Chem., 60 (1988) 1841–1864.

[6] Y. Roos and M. Karel, Phase transitions of amorphous sucrose and frozen sucrose solutions, J. Food Sci., 56 (1991) 266–267.

[7] Y. Roos and M. Karel, Amorphous state and delayed ice formation in sucrose solutions, Int. J. Food Sci. Technol., 26 (1991) 553–556.

[8] C. van den Berg, Water activity, in D. MacCarthy (Ed.), Concentration and Drying of Foods, Elsevier Applied Science, London, 1986, pp. 11–36.

[9] J.M.V. Blanshard, Starch granule structure and function: physicochemical approach, in T. Galliard (Ed.), Starch: Properties and Potential, John Wiley, New York, 1987, pp. 16–54.

[10] M.T. Kalichevsky, E.M. Jaroskiewicz, S. Ablett, J.M.V. Blanshard and P.J. Lillford, The glass transition of amylopectin measured by DSC, DMTA and NMR, Carbohydr. Polym., 18 (1992) 77–88.

[11] S.R. Kakivaya and C.A.J. Hoeve, The glass transition of elastin, Proc. Natl. Acad. Sci. USA, 72 (1975) 3505–3507.

[12] M. Gordon and J.S. Taylor, Ideal copolymers and the second-order transitions of synthetic rubbers. I. Non-crystalline copolymers, J. Appl. Chem., 2 (1952) 493–500.

[13] P.D. Orford, R. Parker, S.G. Ring and A.C. Smith, Effect of water as a diluent on the glass transition behaviour of malto-oligosaccharides, amylose and amylopectin, Int. J. Bio. Macromol., 11 (1989) 91–96.

[14] G.P. Johari, A. Halbrucker and E. Mayer, The glass–liquid transition of hyperquenched water, Nature, 330 (1987) 552–553.

[15] J.M. Flink, Structure and structure transitions in dried carbohydrate materials, in M. Peleg and E.B. Bagley (Eds.), Physical Properties of Foods, Vol. 17, AVI Pub. Co., Inc. Westportt, Conn., 1983, pp. 473–521.

[16] S. Ablett, M.J. Izzard and P.J. Lillford, Differential scanning calorimetric study of frozen sucrose and glycerol solutions, J. Chem. Soc. Faraday Trans., 88(6) (1992) 789–794.

[17] P.R. Couchman and F.E. Karasz, A classical thermodynamic discussion of the effect of composition on glass transition temperatures, Macromolecules, 11 (1978) 117–119.

[18] A. Halbrucker, E. Mayer and G.P. Johari, Glass transition in pressure-amorphized hexagonal ice. A comparison with amorphous forms made from the vapor and the liquid. J. Phys. Chem., 93 (1989) 7751–7752.

[19] M. Sugisaki, H. Suga and S. Seki, Calorimetric study of the glassy state. IV. Heat capacities of glassy water and cubic ice, Bull. Chem. Soc. Jpn., 41 (1968) 2591–2599.

[20] Y. Roos and K. Jouppila, Glass transitions and physical state of dehydrated milk products, presented at ICEF6—6th International Conference on Engineering and Food, Kyoto, Japan, 1993.