Glass transitions and state diagrams for fresh and processed apple

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Abstract

Differential scanning calorimetry (DSC) was used to measure phase transitions in samples of *Golden Delicious* apples after freeze-drying and osmotic drying in a sucrose solution. From DSC traces, glass transition (T_g) and melting (T_m) temperatures were obtained and used to plot the state diagrams for the two types of samples. The Gordon–Taylor equation was able to predict the dependence of the glass transition temperature on moisture content. Before calorimetric analysis, dehydrated samples were equilibrated under a wide range of different relative humidities (a_w 0.12–0.93) and sorption isotherms determined. Experimental sorption isotherms agreed with previous results reported in the literature. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A recent trend to explain the behaviour of food materials during processing and storage is based on an interpretation which considers food materials as systems of water plasticised natural polymers [1,2]. This interpretation is believed to provide an enhanced physical characterisation and thus allow the specification of safer storage conditions for each material.

Dehydrated, low-moisture and frozen foods are typically in an amorphous metastable state [3–5] which is very sensitive to changes in moisture content and temperature [6–8]. The most important transition of the amorphous state is a second-order transition where the very viscous amorphous matrix, a ''glass'', changes to a more mobile amorphous structure, a ''rubber'', at a temperature for each material known as ''glass transition temperature'', T_g [1,2].

Franks et al. [9] suggested that all these possible physical states of the material are well described in a phase state diagram where curves showing transition temperatures (e.g. glass transition and melting) are plotted against moisture content. These state diagrams may be experimentally determined by differential scanning calorimetry (DSC). Several food systems have received significant attention during the last 10 years, in particular those with starch and related polymers [10,11] and solutions of carbohydrates [1,12–14].

Water activity and moisture content have been long considered relevant parameters to describe food stability, correlated through sorption isotherms. Several models have been proposed for representing sorption isotherms [15]; their applicability to different types of foods and throughout the entire water activity range is limited. Special attention

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has been given to the three parameter equation proposed by Guggenheim–Anderson–De Boer [16–18] as recommended by the European project "COST 90 on Physical Properties of Foods" [19]. This equation is a generalisation of the BET equation, taking into account the modified properties of the sorbed water in the multilayer regions, which results in the additional parameter K.

As an example of this methodology, sorption isotherms, phase transitions and associated state diagrams of two types of samples of *Golden Delicious* apples were determined:

1. freeze dried (FD) and
2. osmotically dehydrated (OD) in 60% sucrose solution at 22°C for 5 h.

The state diagrams obtained are similar to previously determined for other fruits [20].

2. Materials and methods

2.1. Materials and sample preparation

Fresh *Golden Delicious* apples obtained in the local market were used. For freeze-drying (FD) samples, round slices, 5 mm thick, were cut perpendicular to their axis, blanched and submitted to freezing followed by freeze-drying. For osmotic drying (OD) samples, apple cylinders (11:32 mm; diameter:height) cut parallel to apple axis were blanched and then immersed in 60% sucrose solution at 20°C for 5 h, respectively (samples were dehydrated up to 70% of the initial water content). Immersion in 90°C water for 2 min was used for blanching [21].

Samples of both freeze dried and osmotic dehydrated samples were equilibrated under saturated salt solutions of constant water activities ranging from 0.12 to 0.93 (Table 1).

Four samples from each dehydration treatments were used for each salt solution.

2.2. 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 [22].

Table 1
Water activity of saturated salt solutions at 25°C

Saturated salt solution	a_w
LiCl	0.12
CH_3COOK	0.23
$MgCl_2 \cdot 6H_2O$	0.33
K_2CO_3	0.44
$Mg(NO_3)_2 \cdot 6H_2O$	0.53
NaBr	0.58
$NaNO_2$	0.61
NaCl	0.76
$(NH_4)_2SO_4$	0.81
KCl	0.85
$KCrO_4$	0.87
$BaCl_2 \cdot 2H_2O$	0.90
KNO_3	0.93

2.3. Freeze-drying

Apple samples were frozen at −40°C followed by freeze-drying at 65 Pa in a Telabe LF10 plate freeze-dryer. The dried samples were immediately packed in an aluminium foil and stored in a desiccator over P_2O_5 before use.

2.4. Differential scanning calorimetry

A Shimadzu DSC-50 differential scanning calorimetry fitted with an 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.

DSC scans were evaluated for onset temperature of glass transition (T_g), onset devitrification temperature (T_d), onset and peak temperatures 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), using Shimadzu software.

The samples were cooled with liquid nitrogen to −100°C and scanned at 5°C min^{-1} from −100°C to 30°C to determine their thermal behaviour in the non-annealed state. After isothermal annealing at −58±2°C for FD apple and −50±2°C for OD apple,

the samples were recooled to $-100°C$ at $10°C\ min^{-1}$ and scanned again from $-100°C$ to $30°C$ 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.

At least three independent DSC scans were obtained for each sample processing treatment and moisture content.

2.5. Sorption isotherm model

Parameters for the well-proven GAB model (Eq. (1)) were fitted with the help of a non-linear regression programme, written in FORTRAN 77, and based on the Levenberg–Marquardt method using IMSL's routine ZXSSQ.

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

where X is the moisture content, X_m the moisture content at fully occupied active sorption sites with one molecule of water (monolayer), C and K are the empirical parameters.

2.6. Correlation of glass transition temperatures

Gordon and Taylor [23] empirical equation was used to predict T_g vs. moisture content curve

$$T_g = \frac{x_s T_{g_s} + k x_w T_{g_w}}{x_s + k x_w}, \qquad (2)$$

where T_g, T_{g_s}, and T_{g_w} are glass transition temperatures of the sample, solid matrix and water, respectively, x_s and x_w the corresponding per cent of solid and water contents and k an empirical parameter. Glass transition temperature of pure water was taken as $T_{g_w} = -135°C$ [24].

3. Results and discussion

3.1. Sorption isotherms

Sorption isotherms of FD and OD apple are presented in Figs. 1 and 2 [25–29], respectively, together with similar results obtained from the literature; Fig. 3 shows both the isotherms. Experimental data were fitted to GAB model. GAB parameters and standard deviations between experimental and calculated values of moisture content are presented in Table 2. The two isotherms obtained agree with the expected behaviour of these materials previously reported.

3.2. DSC scans

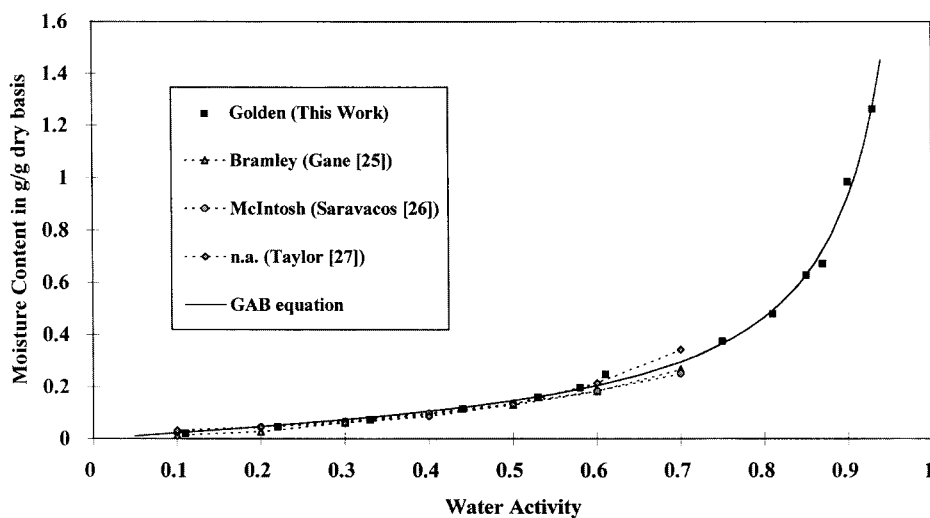Fig. 4 shows typical DSC scans obtained with FD apple samples equilibrated under less than 76%

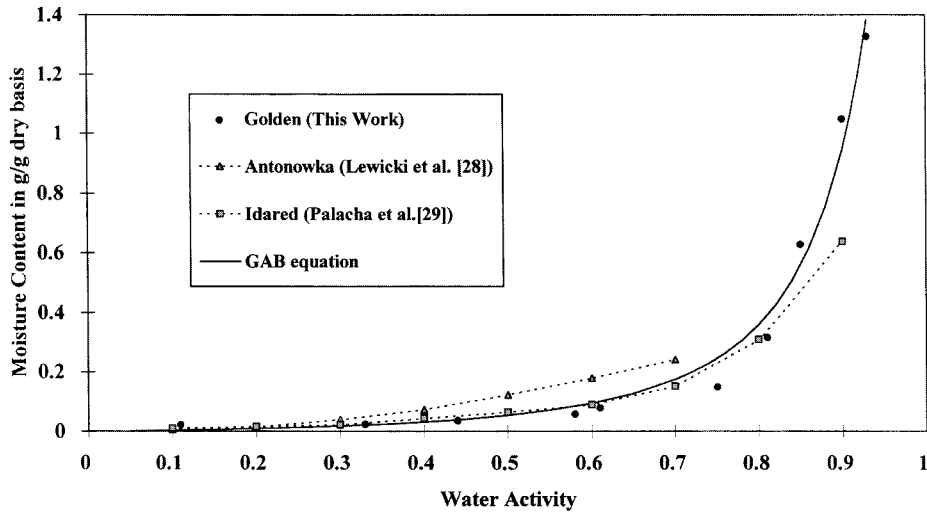Fig. 1. Sorption isotherms of freeze dried (FD) apple.

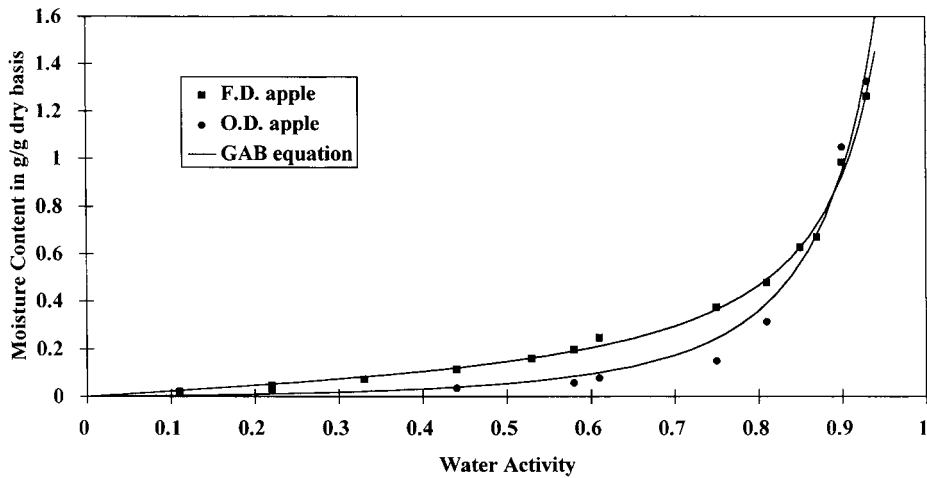Fig. 2. Sorption isotherms of osmotic dehydrated (OD) apple.

Fig. 3. Sorption isotherms for FD and OD apple.

Table 2
GAB parameters for FD and OD apple

GAB parameters	FD	OD
X_m	0.112	0.081
C	2.093	1.371
K	0.985	1.013
s	0.025	0.060

s – standard deviation in moisture content.

relative humidity, where the water is linked to the solid matrix and only the glass transition shows up. As expected T_g uniformly decreases with increasing moisture content.

In the case of samples equilibrated under higher relative humidity ($0.81 \leq a_w < 0.90$), an exothermic recrystallisation (devitrification) peak of unfrozen water, retained in the solid matrix due to a very quick cooling of the sample during the freezing process [30],
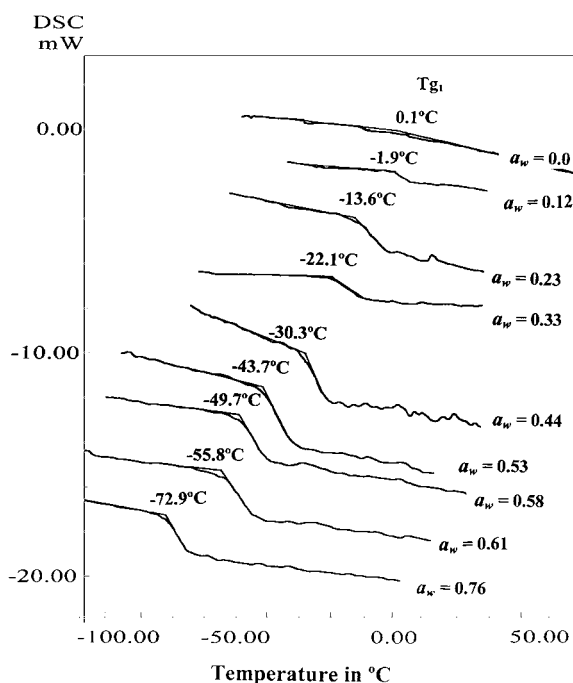
Fig. 4. Typical DSC scans of FD apple equilibrated under different a_w (low range).
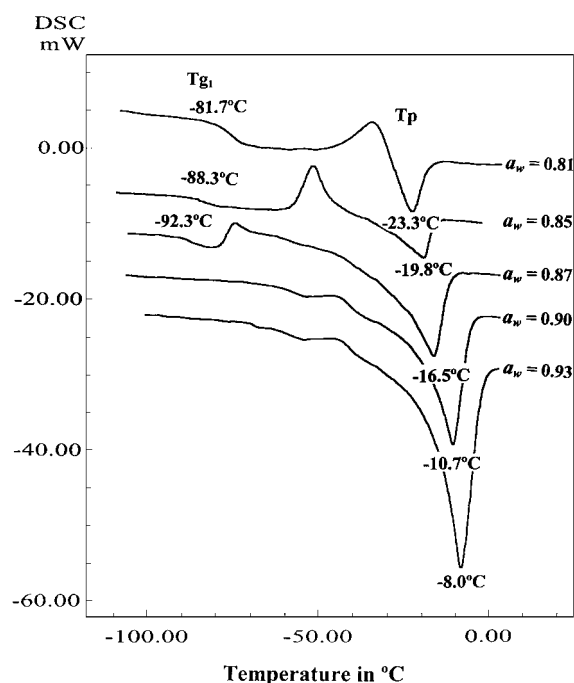

Fig. 5. Typical DSC scans of FD apple equilibrated under different a_w (high range).

is observed in Fig. 5. This phenomenon was elimi-
nated by annealing the sample [31]. 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
melting endotherm. The annealing period was gradu-
ally increased until the values of T_g and T_m and the size
of the melting endotherm showed no further apparent
variation, as shown by Sá and Sereno [20]; these
values of T_g and T_m correspond to the maximally
freeze-concentrated material and are denoted by T'_g
and T'_m, respectively.

Using the methodology previously reported by Sá
and Sereno [20], values of T'_g of 71.1°C and −61.5°C
were calculated for FD and OD apple, respectively.

Samples equilibrated above 90% relative humidity
have shown a behaviour similar to the annealed sam-
ples. For those samples, the cooling process is not fast
enough to hinder ice formation, due to its high mole-
cular mobility. In this case values of T_g and T_m
obtained are an estimate of T'_g and T'_m as is evidenced
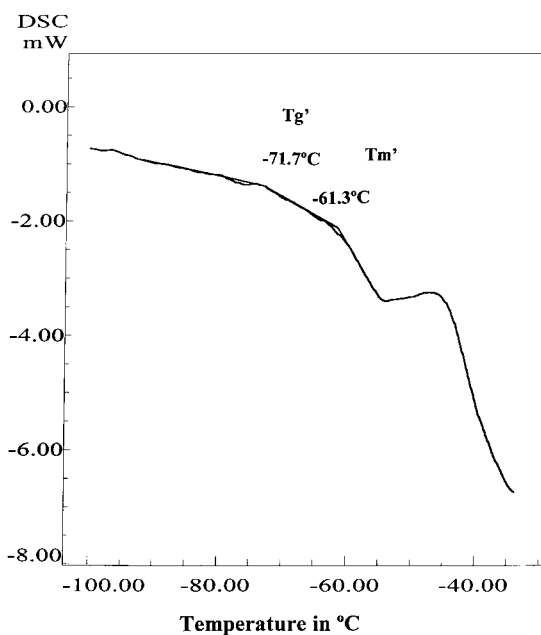in Fig. 6.

Fig. 6. DSC scan obtained for a sample equilibrated at 90%
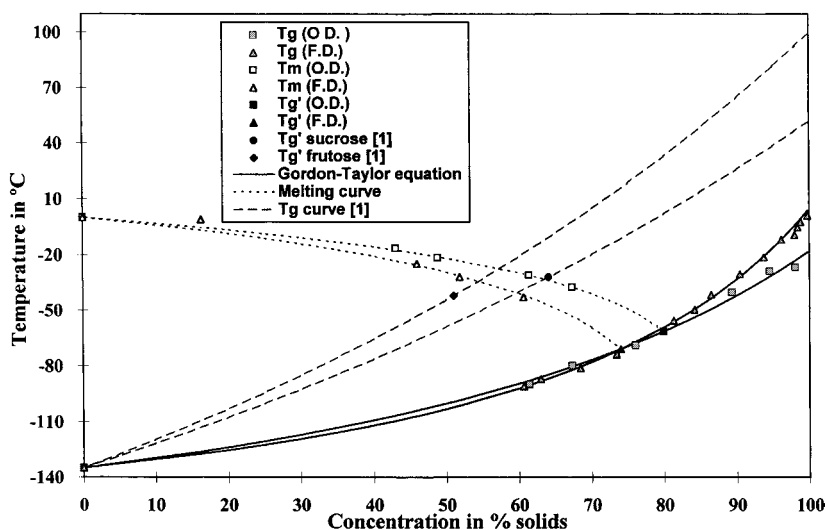relative humidity in the temperature range from −90°C to −40°C.

Fig. 7. State diagrams for FD and OD apple.

Ice melting was observed for samples equilibrated over 81% relative humidity. Since food materials melt in a relatively broad temperature range, several characteristic temperatures can be determined to characterise such a transition. Among those characteristic points the onset temperature (T_m) has been widely used as recommended by Rey [32], and was taken for the melting curve in the state diagram. The onset melting temperature is defined by the intersection of the tangent to first part of DSC melting peak and the extrapolated baseline before melting.

The small endothermic peak observed for high moisture contents immediately before fusion is known as antemelting [33–37] and has been observed during phase transitions of biological products. This phenomenon has been the subject of intense discussion; Rasmussen and Luyet [34] and later Mackenzie [35] suggested that it is due to molecular layers of liquid which form in the surface of the crystals; for Moreira and Simatos [36] it is the fusion of small crystals of ice formed during devitrification; Couach et al. [37] using X-ray diffraction and paramagnetic electronic resonance confirmed the initial fusion of crystalline structures of ice during antemelting. Another explanation for antemelting endothermic peak could be the formation of limited region of an eutectic mixture, melting at lower temperatures.

3.3. State diagrams

State diagrams obtained for apple samples are plotted in Fig. 7. Gordon–Taylor equation was fitted to the experimental values of T_g, by least squares regression, leading to values of 3.4 (FD) and 2.4 (OD) for empirical K parameter. Experimental values of onset melting temperature were fitted to a second-order empirical equation based on the results of Chang and Tao [38]. Glass transition temperatures for sucrose and fructose obtained by Slade and Levine [1] are represented in the same diagram. Sucrose and fructose T_g data may suggest an explanation for the relative position of T_g curves measured for OD and FD apple samples. During the osmotic treatment there is always a leaching of solutes from the solid sample and its impregnation with solutes from the solution. In this case it is expected an increase of the relative amount of sucrose with the corresponding shift of T_g curve and T_g' for OD apples samples.

4. Conclusions

Measured sorption isotherms agree with similar curves obtained from the literature.

Results show that glass transition temperatures and associated phase characteristics may be reproducibly

determined by DSC and from this information state diagrams for those materials can be plotted. Such diagrams have the same general characteristics as those previously reported for similar fruits and vegetables [20].

In the case of samples equilibrated under high relative humidities, sample stabilisation (annealing) was required to promote devitrification of entrapped water. Empirical Gordon–Taylor equation was able to predict the dependence of T_g on moisture content with k parameter determined by least squares regression.

T_g results obtained for the osmotic dehydrated samples as compared to freeze dried may be explained by partial replacement of fructose with sucrose during OD treatment.

5. Nomenclature

a_w	water activity
C	GAB constant
ΔH_m	latent heat of melting (J g^{-1})
k	empirical parameter of Gordon–Taylor equation (Eq. (2))
K	GAB constant
T_g	glass transition temperature (°C)
T_g'	glass transition temperature corresponding to maximally freeze-concentrated material (°C)
T_m	melting temperature (°C)
x_i	mass per cent of component i
X	moisture content in g g^{-1} dry basis
X_m	monolayer moisture content in g g^{-1} dry basis

Subscript

s	solid matrix
w	water

Acknowledgements

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