State diagram of apple slices: glass transition and freezing curves

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Abstract

The state diagram of apple flesh was developed by measuring and modeling its freezing points and glass transition temperatures. The freezing curve and glass transition lines were developed using Clausias–Clapeyron and Gordon–Taylor models, respectively. The state diagram of apple pieces developed in this work can be used in determining the stability during frozen storage and in dried conditions as well as in designing drying and freezing processes. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The phase transitions of foods are important in characterizing their quality and in designing efficient processing systems. It has been reported in the literature that foods can be considered very stable at the glassy state, since below glass temperature compounds involved in deterioration reactions take many months or even years to diffuse over molecular distances and approach each other to react (Slade & Levine, 1991). The hypothesis has recently been stated that this transition greatly influences food stability, as the water in the concentrated phase becomes kinetically immobilized and, therefore, does not support or participate in reactions. Formation of a glassy state results in a significant arrest of translational molecular motion, and chemical reactions become very slow (Rahman, 1999). A detailed review on the applications of glass transition on stability of foods and processing are given by Roos (1995), and Rahman (1999). Glass transition is a second-order time-temperature-moisture-dependent transition, which is generally characterized by a discontinuity in physical, mechanical, electrical, thermal, and other properties of a material. Food materials are in an amorphous state

below the glass transition temperature and are rigid and brittle. Glasses are not crystalline with a regular structure, but retain the disorder of the liquid or amorphous state. In kinetic terms, glass temperature is defined as the temperature at which the viscosity of a material reaches 10^{13}–10^{14} Pa s and the molecular diffusion rate is many years.

The state diagram is commonly used to identify different phase boundaries in a material. A state diagram consists of the freezing curve, solubility curve, eutectic point, glass transition line, and conditions of maximal freeze concentration (temperature and solid mass fraction) (Fig. 1). In the state diagram in Fig. 1, the freezing line (AB) and solubility line (BC) are shown in relation to the glass transition line (DEF). The point E $\left(X'_s, T'_g\right)$ lower than T'_m (point B′) is a characteristic transition in the state diagram. The water content at point E is the unfreezeable water.

Differential scanning calorimetry (DSC) is widely used to identify the characteristic changes in the state diagram. The DSC thermogram for the samples having solid content above point E is relatively simple. In this case the samples do not form ice during cooling, the value is a plasticized T_g. A generic DSC thermogram in case of the samples containing ice is shown in Fig. 2 and different phase changes are marked on the diagram. The melting of ice endotherm is shown as D, two glass transitions as A and B, and an overshoot as C. The shift

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Nomenclature

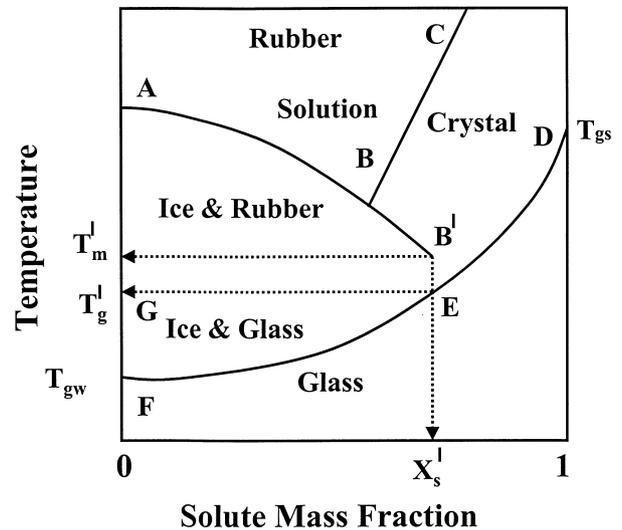|	
E	Molecular weight ratio of water and solids (λ_w/λ_s)
k	Gordon–Taylor parameter
T_f	Freezing point of food (°C)
T_{ge}	End point of glass transition (°C)
T_{gi}	Onset of glass transition (°C)
T_{gm}	Glass transition temperature of mixture (°C)
T_{gs}	Glass transition temperature of solid (°C)
T_{gw}	Glass transition temperature of water (°C)
T_w	Freezing point of water (°C)
T'_g	Maximal freeze concentration temperature (°C)
T'_m	End point of freezing curve (°C)
X_w	Mass fraction of water (wet basis)
X_{wu}	Unfrozen water content
X_s	Mass fraction of solids (wet basis)
X'_s	Solids mass fraction at maximal freeze concentration (wet basis)
β	Molar freezing point constant of water (1860 kg K/kg mol)
λ_w	Molecular weight of water
λ_s	Molecular weight of solids
Δ	Freezing point depression (°C)

Fig. 1. A typical state diagram for a solution. AB: freezing curve, BC: solubility curve, B: eutectic point, DEF: glass transition line, E: glass transition temperature at maximal freeze concentration, GE: glass transition by slow or equilibrium cooling, T_{gs}: glass transition temperature of solid, T_{gw}: glass transition temperature of water, T_m: end point of freezing curve, T'_g: glass transition for maximal freeze concentration temperature, X'_s: solids mass fraction at maximal freeze concentration (Rahman, 1999).

A $\left(T_g\right)$ is the partial devitrification and B (T'_g and T'_m) is the glass transition for the maximally freeze concentration. The exothermic overshoot as shown as C is due to the devitrification on rewarming and results from crystallization of freezable water trapped in the solid matrix during the fast cooling process (Flink, 1983). This phenomenon can be avoided by isothermal holding (annealing) (Maurice, Asher, & Thomson, 1991; Sereno, Sa, & Figueiredo, 1995). An isothermal hold at temperatures just below the onset of the glass transition followed by subsequent warming through the transition did result in a small overshoot in case of ribose. Standard procedures for using DSC to measure T'_g have not been developed. Brake and Fennema (1999) summarized that the reported procedure differs in cooling rate, warming rate, holding times-temperatures, annealing conditions, and sample size. These parameters can affect the degree to which maximum freeze-concentration is attained. Annealing appeared to be less critical for simple systems than for complex systems and for those samples with limited solubilities (Brake & Fennema). Optimum annealing conditions are required for accurate measurement of maximal freeze concentration (Ablett, Izzard, Lillford, Arvanitoyannis, & Blanshard, 1993; Sereno et al., 1995). Both T_g and T'_g was observed in case of carboxymethyl cellulose, sucrose, and maltodextrin (Lim & Reid, 1991), agarose

(Nishinari, Watase, Williams, & Phillips, 1991), ribose (Maurice et al. 1991). The indication of T_g and T'_g showed two major structural conforms in the case of ribose (Maurice et al.). DSC thermograms of a rice starch exhibiting only a glass transition before the melting endotherms (Biliaderis, 1991). Maurice et al. (1991) identified two glass transitions T_g (partial devitrification), T'_g, and T'_m. The partial devitrification (T_g) was avoided during warming at faster rates > 10°C/min following uniform cooling at 5°C/min (Maurice et al., 1991). Brake and Fennema (1999) defined T'_g as an apparent T'_g when isothermal holding (annealing) is not used during DSC measurement. The T_g shift to a higher value with the increase of heating rate and negligible effect above 20°C/min. The value of T_g shift to T'_g with the increase of annealing time (Ablett et al., 1993; Izzard, Ablett, & Lillford, 1991; Roos, 1992). The DSC method was unable to determine the T_g in some of the more complex samples. In these cases, the results had to be interpreted in terms of the T'_g of the aqueous polymer solution in the sample (Lim & Reid, 1991). It is important to follow specific procedure to get accurate values of T'_m and T'_g. The maximum freeze-concentration of carbohydrate solutions is achieved by annealing at temperature above T'_g but below T'_m (Roos, 1993b; Roos & Karel, 1991a,b; Roos, 1992). Applications of isothermal hold at a temperature of from 1–10°C from the T'_m is necessary to determine accurate T'_g (Roos, 1993b). Maurice et al. (1991) found that T'_g increase sharply with the increase of heating rate, and then
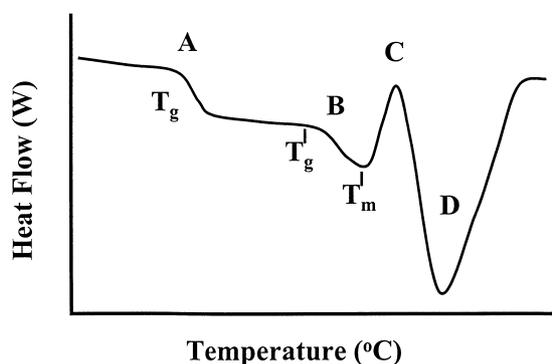
Fig. 2. A generic DSC thermogram in case of the samples containing ice formation. A: partial devitrification, B: glass transition for maximally freeze concentration, C: overshoot, D: melting of ice, T'_m: end point of freezing, T'_g: glass transition for maximal freeze concentration temperature.

reached a plateau at 10°C/min, while concentration varying from 5 to 30% had no significant change of T'_g. The values of T'_g shifted in the order of 0.6°C if isothermal hold is 120 min in case of ribose (Maurice et al., 1991). Actual T'_g after isothermal annealed is found to be independent of the initial concentration before freezing in case of maximally freeze concentration (Roos, 1993b). Roos (1993b) found optimum annealing time for 15 min at $T'_m - 1$ allowed ice formation and maximum freeze concentration of low molecular carbohydrate solutes. Kwon et al. (1999) used 30 min annealing time for maltogenic amylase.

In the literature, glass transitions of pure components are more commonly reported than the real foods, which are complex multi-components mixtures (Roos, 1993a). Van den Berg (1991) concluded that the behavior of multi-component glasses can not be simply predicted from the theory valid for binary systems. Furthermore, with regard to non-carbohydrate food components present in many food systems (proteins, lipids, salts ect.), less is presently known about their glassy state. Recently Rahman (1995) compiled glass transition and freezing points data of pure components as well as foods. In the present study the glass transition line and the freezing curve of apple slices were measured to develop state diagram for apple slices. The state diagram has important applications in determining product stability during storage and in optimizing drying conditions.

2. Material and methods

2.1. Sample preparation

Pacific Rose apples, purchased from a local supermarket in Auckland, were stored less than one week at 1°C before being used for experiments. The apples were taken out from the cool room and fruit cylinders of 60 mm diameter were cut using a corer. The cylinders were then cut into 10 mm thick slices and 25 mm center cores were removed to form rings. The rings were then placed on a wire mesh tray and dried in a heat pump drier (Perera & Rahman, 1997; Rahman, Perera, & Thebaud, 1998) at 45–50°C and 20–25% relative humidity. The air velocity was at 1.5 m/s. Samples were taken out from the drier at different time intervals (0–24 h) and kept at 1°C for more than 24 h in air sealed polyethylene bags to equilibrate the moisture profile. If the measurement was delayed by more than one day (24 h), the samples were stored at −20°C. The samples dried in the heat pump were then dried further in a vacuum drier to reduce the moisture content to zero. The water content of apple was measured gravimetrically by using a vacuum oven method at 70°C for at least 18 h of drying. The moisture content in wet and dry basis mean kg water/kg sample and kg water/kg solids, respectively.

2.2. Differential scanning calorimetry (DSC)

The freezing point and glass transitions of the dried samples at different moisture content were measured by differential scanning calorimetry (DSC). The heat flow curves for freezing points and glass transition temperatures were determined in triplicate using a "Rheometric model DSC-SP" at the University of Auckland. The instrument was calibrated using indium. Cut samples of 15–20 mg from the fresh and dried apple slices placed in a sealed aluminum pan were cooled to −100°C at 10°C/min, and scanned from −100 to 20°C at a rate of 10°C/min. Each thermogram was analyzed for the onset of melting from the endotherm. The freezing point is considered as the intersection of the tangent and base line to the left side of the melting peak (Fig. 3). The average values of triplicate measurements were obtained. Standard deviation was used to identify the variability or error in the experimental measurements in case of freezing point as well as glass transition temperature.
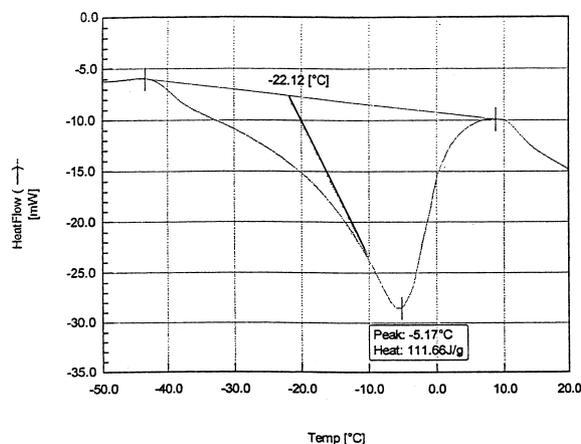

Fig. 3. A typical DSC thermogram to determine the freezing point of apple slices.

Glass transition temperature for the samples containing unfrozen water was as follows. Cut samples of 15–20 mg from the dried slice placed in a sealed aluminum pan were cooled to −100°C at 10°C/min, and scanned from −100 to 20°C at a rate of 10°C/min in case of heat pump dried samples up to 24 h. Samples dried in vacuum drier were scanned from −50 to 60°C at a rate of 10°C/min. The onset temperature of the glass-transition region, and end of glass transition temperature were identified from the DSC thermogram (Fig. 4). The glass-transition midpoint value was obtained as an average of the onset and end values. The T_g values reported are averages and standard deviation of triplicate measurements.

Glass transition and ice formation in samples containing freeze-able water was as follows. Cut samples of 15–20 mg (moisture content 85.5, 73.3, 58.3%) from the dried slice placed in a sealed aluminum pan were cooled to −100°C at 10°C/min, and scanned initially from −100 to 20°C in order to locate T_g, apparent T'_g and T'_m. Since T'_g and T'_m were independent of the initial concentrations, the average value for apple without annealing was estimated as −59.7°C±1.7 and −53.2°C ±0.8 for T'_g and T'_m, respectively (total number of measurements). In the literature it was mentioned that annealing is necessary in order to achieve maximum freeze-concentration and eliminate the devitrification (Roos, 1993a; Roos & Karel, 1991a,b). In this experiment, annealing was done for the sample at moisture content 85.5%. The sample was cooled to −100°C at 10°C/min, heated at 10°C/min to −56°C [T'_m−2.8°C], annealed for 15–30 min at −56°C, cooled at 10°C/min to −100°C, and scanned from −100 to 20°C for the determination of actual T'_g and T'_m. This procedure was similar to Roos (1993b).

2.3. Models for freezing point and glass transition

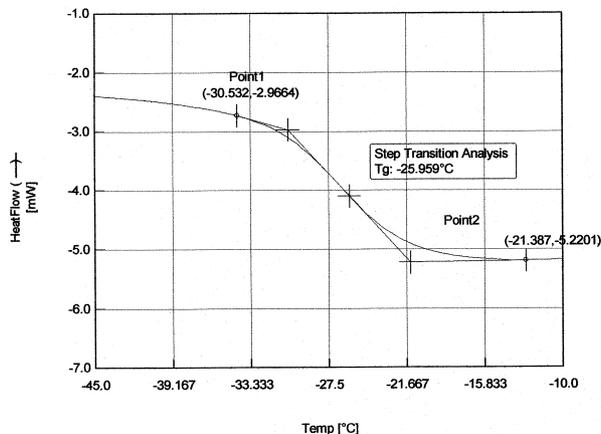Rahman (1995) reviewed different types of empirical and theoretical models used to predict freezing points of foods. In this work, the theoretical Clausias–Clapeyron was used to estimate the freezing point of apple. The Clausias–Clapeyron equation can be written as:

$$\Delta = -\frac{\beta}{\lambda_w}\ln\left[\frac{1 - X_s}{1 - X_s + EX_s}\right] \quad (1)$$

where Δ is the freezing point depression ($T_w - T_f$), T_f is the freezing point of food (°C), T_w is the freezing point of water (°C), β is the molar freezing point constant of water (1860 kg K/kg mol), λ_w is the molecular weight of water, X_s is the solids mass fraction, and E is the molecular weight ratio of water and solids (λ_w/λ_s).

The glass transition temperature of foods and biological materials is commonly modeled by the following equation proposed by Gordon and Taylor (1952):

$$T_{gm} = \frac{X_s(T_{gs}) + kX_w(T_{gw})}{X_s + kX_w} \quad (2)$$

where T_{gm}, T_{gs} and T_{gw} are the glass transition temperature of mixture, solids, and water, respectively, and k is the Gordon–Taylor parameter.

3. Results and discussion

The transition temperatures for freezing were determined as the onset of the observed melting in the heat flow curves as shown in Fig. 3. The freezing points of fresh and dried as a function of moisture content apple are given in Table 1. The result showed that freezing point decreased with the increase of solids content. The prediction model of freezing point was developed using SAS non-linear regression as:

$$\Delta = -\frac{1860}{\lambda_w}\ln\left[\frac{1 - X_s}{1 - X_s + 0.238X_s}\right] \quad (3)$$

Fig. 4. A typical DSC thermogram to determine the glass transition of apple slices for plasticized sample.

Table 1
Freezing point and glass transition temperature of apple as a function of moisture content

X_w	X_s	T_f(°C)	T'_g(°C)	T'_m (°C)
0.856[b]	0.144	−4.7 (0.4)[a]	−61.6 (0.8)	−53.6 (0.7)
0.732[b]	0.268	−8.0 (1.7)	−58.4 (1.0)	−52.3 (1.0)
0.583[b]	0.417	−22.0 (1.2)	−59.2 (1.0)	−53.7 (0.9)
0.856[c]	0.144	−4.6 (0.5)	−57.8 (0.4)	−50.3 (0.2)

[a] Note: values in the parenthesese are standard deviation of 3 samples.
[b] Without annealing (average values for all samples: T'_g = −59.7°C±1.7, and T'_m = − 53.2°C±0.8).
[c] Glass transition at maximal freeze concentration (15 min annealing at −56°C)

From the above equation, the effective molecular weight of the solids was 75.6. The values of T'_m (i.e. $-50.3°C$) was considered the end point of freezing point (Table 1). More details of T'_m are discussed in one of the next section.

A DSC thermogram of sample containing no freeze-able water (plasticized sample) is shown in Fig. 4. The glass transition temperature, T_g was determined from the DSC heat flow curves as shown in Fig. 4. The onset T_{gi} and final T_{ge} points of transitions were obtained by extrapolating the side and base lines. The T_g was estimated from the midpoint of the onset and final points (Fig. 4). All the thermograms for samples at and above moisture content 28.5% showed only one transition and no formation of ice. As expected T_g value increased

Table 2
Glass transition temperature of apple as a function of moisture content (when there is no formation of ice)

X_w	X_s	$T_g(°C)$
0.285	0.716	−57.0 (1.6)
0.146	0.854	−33.8
0.130	0.871	−26.3 (1.1)
0.061	0.940	−22.7 (1.2)
0.000	1.000	36.7 (1.0)

with increasing solids content as shown in Table 2. The glass transition data of plasticized apple was fitted in Gordon–Taylor equation and the values of T_{gs}, T_{gw}, and k were estimated as $41.3°C$, $-134.8°C$, and 3.59. The glass transition of pure water was considered $-135°C$ for the non-linear regression (Johari et al., 1987). The predicted values for apple ($k = 3.59$) are similar to the literature values as of k of 4.7 for strawberries and 5.3 for horseradish (Roos, 1993a).

A DSC thermogram of sample having freeze-able water is shown in Fig. 5 without annealing. It shows melting endotherm (T_f), T'_g, and T'_m, and the values are given in Table 1. Since T'_g and T'_m were independent of the initial concentrations, the average values for apple without annealing are $-59.7°C\pm1.7$ and $-53.2°C \pm0.8$ for T'_g and T'_m, respectively (total number of measurements) (Table 1). There is little overshoot just at the beginning of the melting endotherm and no partial devitrification (T_g) was observed in the case of apple. Optimum annealing condition was obtained when the sample is held at $T'_m-2.8°C$ $[-56°C]$ for a considerable period of time, allowing a maximum amount of ice to be formed, and leading to a maximally concentrated solid matrix of moisture content equal to X'_s. A DSC thermogram of annealed sample is shown in Fig. 6. As expected isothermal annealing led to increased T'_g
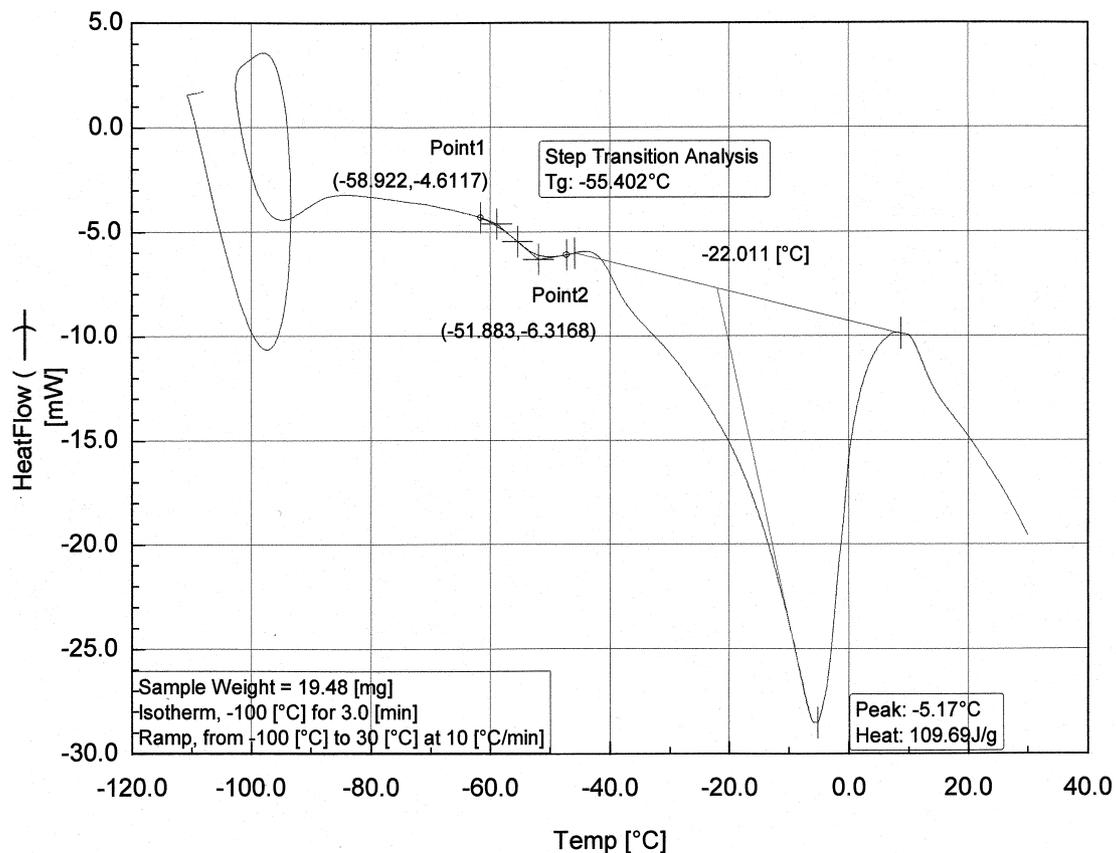

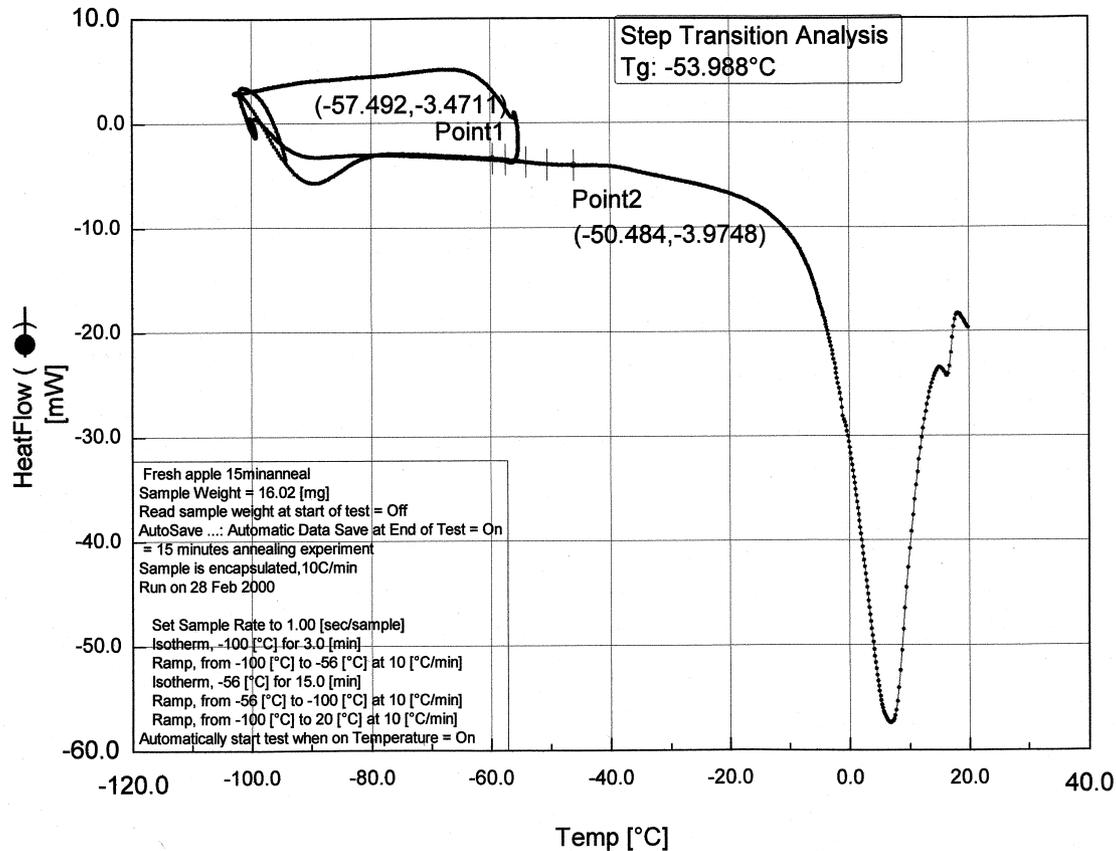Fig. 5. A typical DSC thermogram for apple slices for non-annealed sample.

Fig. 6. A typical DSC thermogram for apple slices for 15 min annealed sample.

values and the elimination of little devitrification exotherm, the increase of melting temperature, and an increase of the size of the melting endotherm. The annealing time was varied from 15 to 30 min and the size of melting endotherm showed no significant variation, thus 15 min was used as the optimum annealing time at $T'_m - 2.8°C$ ($-56°C$). The actual values of T'_g and T'_m with 15–30 min annealing were -57.8 and $-50.3°C$, respectively (Table 1).

State diagram of apple is shown in Fig. 7. Curve AB represents equilibria between the solution and the solid (ice) formed and can be designated the freezing curve [Eq. (3)]. Line AB has a negative slope showing the expected decrease in freezing point with increasing solids concentration. The maximal freeze concentration shows a characteristic transition temperature (point E) lower than the T'_m ($-50.3°C$), and the water content at point E is the unfreezeable water. The glass transition temperature above point E decreases from the T_{gs} of pure amorphous material to a theoretical T_{gw} of pure water [Eq. (2)]. The value of X'_s was estimated as 0.736 from Eq. (2) using T'_g as $-57.8°C$. At point E, T'_g and X'_s are two parameters, which reflect the physical state of the noncrystallizing solute. X'_s is the composition of solutes at T'_g. The values of unfrozen water content can be estimated from X'_s as $X_{wu} = 1 - X'_s$. The unfrozen water content [X_{wu}] in apple was estimated 26.4% (wet
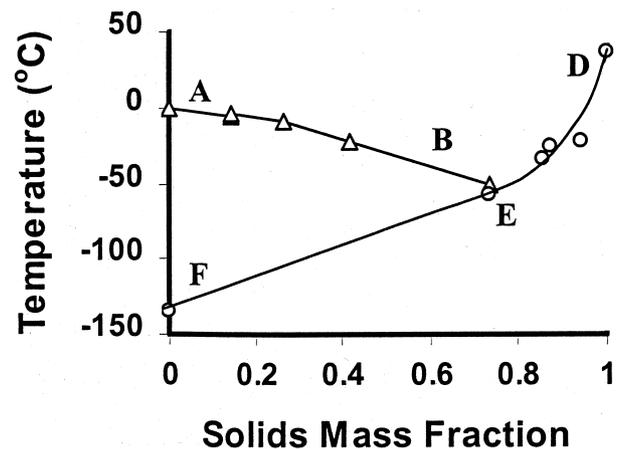

Fig. 7. The state diagram of heat pump dried apple. AB: freezing curve, DEF: glass transition line, E: glass transition temperature at maximal freeze concentration.

basis). The unfrozen water content of sucrose and fructose are 20 and 21% (wet basis), respectively (Ablett et al., 1993; Roos & Karel, 1991a). Similarly, the unfrozen water contents were 21.4% for strawberry (Roos, 1987), and for cabbage 26.3 to 30.4% (Paakkonen & Plit, 1991), respectively.

The state diagram developed here can be a valuable tool in determining the stability of dried foods during

storage. An example can be provided. If we want to know what should be the moisture content of a dried apple for most stability during storage at 20°C? Based on glass stability of dried apple, the sample should be dried below 3.69% (wet basis) water content. This value was estimated from Eq. (2) using $T_{gm} = 20°C$ when other parameters are known ($T_{gs} = 41.3°C$, $T_{gw} = -134.8°C$ and $k = 3.59$) for apple slices

4. Conclusion

The freezing curve and glass transition lines were developed using Clausias–Clapeyron and Gordon–Taylor models. The effective molecular weight of solids in apple was 75.6. The values of T_{gs}, and k were 41.3°C and 3.59, respectively. The values of T'_g, T'_m, and X'_s were found $-57.8°C$, $-50.3°C$, and 0.736, respectively from the maximal freeze-concentration.

Acknowledgements

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