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Glass transition and state diagram for freeze-dried horse mackerel muscle

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ABSTRACT

Glass transition temperatures of freeze-dried horse mackerel muscle conditioned at various water activities at 25 °C were determined by differential scanning calorimetry (DSC). High moisture content (>0.33 g/g, d.b.) samples obtained by adding liquid water into freeze-dried samples, were also analyzed. The state diagram was composed of the freezing curve and the glass transition line, which were fitted according to Clausius–Clapeyron model and Gordon–Taylor model, respectively. The state diagram yielded maximally freeze-concentrated solutes at 0.786 solids with the characteristic temperature of glass formation being −83.1 °C. The state diagram of horse mackerel muscle developed in this work could be used to predict the stability during frozen storage and in dried conditions as well as in designing drying and freezing processes.

1. Introduction

Water activity (a_w) provides a reliable assessment of the microbial growth, lipid oxidation, non-enzymatic and enzymatic activities, and the texture/mouthfeel of foods following manufacturing [1]. Sorption isotherms are employed in process design and control, such as in predicting the end point of drying and optimizing ingredient selection in food formulations [1–5]. Recently, it has been argued that a_w is not sufficient to describe the secondary processes of change-in-state in foodstuffs thus ushering in the concept of glass transition temperature [6]. Glass transition temperature (T_g) is a second-order phase change temperature at which a solid-like "glass" is transformed to a liquid-like "rubber". As the temperature increases above T_g, various changes such as increase in free volume, decrease in viscosity and increase in thermal expansion, are noticed. The most important changes affecting food behaviour are related to the exponential increase in molecular mobility and decrease in viscosity. These factors govern various time-dependent and often viscosity-related structural transformations, such as stickiness, collapse, and crystallization during food processing and storage. The importance of T_g of amorphous food materials for processing and storage stability has been recognized and emphasized by many researchers and a wide range of potential food applications of the glass transition phenomenon have been identified [7–9]. Maximum utility of T_g is made in the state diagram which, in its simplest form, represents the pattern of change in the state of a material as a function of increasing levels of solids [10]. State diagram assists in predicting food stability during storage as well as selecting a suitable condition of temperature and moisture content for processing [11–13].

As the importance of state diagram is better recognized, more studies have been carried out for real foods during recent years. State diagrams have been reported for apple [14–17], grape [18], strawberry [18–20], pineapple [21], mango [22], persimmon [23], kiwifruit [24,25], carrot [26], onion [18], tomato [27,28], garlic [29], date [30], cornstarch [31], tuna muscle [32,33], and abalone [34]. However, based on the authors' knowledge, no data are available for horse mackerel muscle.

There is an ever-increasing demand for fresh and processed fish around the world due to its nutritional value [34]. Horse mackerel (*Trachurus Japonicus*) is a large pelagic fish. It is one of the most important fishery resources in the world. Its productivity is ranked as the third in all the single capture species of the world, with annual landings that exceeded 5–10 million tons in the past ten years [35]. However, due to high content of fat and protein, it is perishable during processing and storage. Preservation is achieved by dehydration or freezing, but it requires data on thermodynamic properties pertaining to a_w and vitrification phenomena. Therefore, the aim of this work was to obtain the state diagram of the freeze-dried horse mackerel muscle and the moisture sorption isotherm in order to optimize freezing, drying or rehydration processes and the stability of the final product during storage.

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2. Materials and methods

2.1. Materials and sample preparation

Whole fresh horse mackerel was purchased from the local market and then delivered to the laboratory on ice. The weight of the individual fish was 95 ± 5 g with an overall length of about 20 ± 1 cm. The whole horse mackerel was washed with tap water and filleted with a sharp knife. The horse mackerel fillets were frozen in a refrigerator at −40 °C for at least 24 h, and then placed into a freeze drier (Model Alpha 1–4LD, Martin Christ Company, Germany). The plate temperature was maintained at −20 °C (samples temperature not controlled) with a vacuum of 5 Pa in the chamber, while condensing plate temperature was kept at −56 °C, and drying continued up to 84 h.

All the samples were transformed into powder and further dried in a desiccator over P_2O_5 for 1–3 weeks to obtain completely dried materials [36]. The moisture content and total solids of horse mackerel muscle were measured gravimetrically by drying samples in an air-convection drier (Model DHG-9070A, Shanghai Yiheng Scientific Instrument Co. Ltd., Shanghai, China) at 100–105 °C [37]. The weights of the samples were recorded each hour until they showed variation less than 0.3% [38]. The results were given as an average for three samples.

2.2. Measurement and modelling of a_w

To get samples with a_w from 0.11 to 0.90, powdered freeze-dried horse mackerel muscle samples were put in open weighing bottles and stored in air-sealed glass jars and equilibrated with saturated salt solutions of constant water activities (Table 1) for 1–3 weeks [36]. The jars were placed in a temperature controlled cabinet (Model HSX-160B, Shanghai Fuma Experimental Instrument Co. Ltd., Shanghai, China) and maintained at a constant temperature of 25 °C. After equilibrium was reached (1–3 weeks), samples of about 15–20 mg were taken for DSC analysis and moisture content (d.b.) values were obtained from the weight differences of the samples before and after equilibration.

Freeze-dried samples with moisture contents corresponding to a_w higher than 0.90 were also analyzed. Distilled water was added directly into the freeze-dried powder in weighing bottles (25 mm × 40 mm) and then the bottles were sealed and put in a dry desiccator at 4 °C for 24 h [21] before DSC analyses. The water activities of these samples were determined at 25 °C, with the help of a MS1 water activity meter (Novasina, Novasina Ltd., Switzerland).

The relationship between a_w and moisture content (d.b.) was correlated with the Guggenheim–Anderson-de Boer (GAB) model (Eq. (1)) [38].

$$X_{ws} = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$$

Table 1
Water activity of saturated salt solution at 25 °C (Sa et al. [16], Roos [20]).

Saturated salt solution	a_w^{25}
LiCl	0.11
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
$NaNO_2$	0.62
NaCl	0.76
$(NH_4)_2SO_4$	0.81
KCl	0.85
$KCrO_4$	0.87
$BaCl_2{\cdot}2H_2O$	0.90

where X_{ws} is the moisture content in dry basis (d.b.); a_w is the water activity; X_m is the moisture content at fully occupied active sorption sites with one molecule of water, which is secure moisture content for high quality preservation of freeze-dried food; C and K are the GAB parameters associated with the enthalpies of monolayer and multilayer, respectively.

2.3. Measurement and modelling of glass transition by DSC

The glass transition temperatures of horse mackerel muscle samples at different moisture contents were measured with DSC (DSC-200PC, NETZSCH, Germany). The instrument was calibrated for heat flow and temperature using indium (melting point 156.6 °C, ΔH_m = 28.60 J/g), mercury (melting point −38.8 °C, ΔH_m = 11.44 J/g), and C_6H_{12} (melting point −86.0 °C, ΔH_m = 79.40 J/g). Samples were enclosed in hermetically sealed aluminum pans (1.75 mm height; 6.67 mm internal diameter) just before analysis and then loaded onto the equipment at room temperature. An empty pan was used as reference and nitrogen was used as carrier gas (purge 20–30 mL/min; protective 60–70 mL/min). Liquid nitrogen was used for sample cooling before the runs.

2.3.1. Glass transition of samples containing unfreezable water

Freeze-dried horse mackerel muscle samples (15–20 mg) equilibrated at different a_w were weighted, hermetically sealed in aluminum pans and were cooled from 20 °C to −120 °C at 10 °C/min, and equilibrated for 10 min. After equilibrium it was then scanned from −120 °C to 10 °C at a rate of 10 °C/min, and equilibrated for 10 min. They were then scanned from 10 °C to −120 °C at 10 °C/min, and equilibrated for 10 min. After equilibrium it was then scanned from −120 °C to 20 °C at a rate of 10 °C/min. Each thermogram was analyzed for the onset, mid and end of transition. Three replicates were used for selected samples (a_w/moisture content).

2.3.2. Glass transition of samples containing freezable water

Samples of 15–20 mg (moisture content, 0.25–0.60, w.b.) of the powder in a sealed aluminum pan were cooled from 20 °C to −120 °C at 10 °C/min, and equilibrated for 10 min. It was then scanned initially from −120 °C to 20 °C at a rate of 10 °C/min for initial assessment of the thermogram and to locate apparent glass transition temperature, and end point of freezing (i.e. apparent T'_m). In the literature it was mentioned that annealing is necessary in order to achieve maximal-freeze-concentration condition (i.e. real T'_g and T'_m) and eliminate the exothermic peak if present. The procedure was as follows: samples were cooled from 20 °C to −120 °C at 10 °C/min, and equilibrated for 10 min. After equilibrium it was then heated at 10 °C/min to $T'_m - 1$, annealed 30 min at $T'_m - 1$, cooled at 10 °C/min to −120 °C, and equilibrated for 10 min, and scanned from −120 °C to 20 °C at 10 °C/min in order to determine actual T'_g and T'_m. This procedure was similar to Ross [39], and Bai et al. [15]. The average values and standard deviation of three replicates were obtained for selected data point to identify the experimental variability.

The DSC measurement was repeated in triplicate. The results were analyzed with the Proteus Analysis software, which was provided with the DSC instrument. The analysis of the glass transition reported the onset, the mid-point and the end temperatures of the step once the start and stop points of the transition were provided, and the mid-point of the step was taken as glass transition temperature.

The glass transition temperature of foods was modelled by Gordon–Taylor equation (Eq. (2)) [15,16,21].

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

Table 2
Model fitting for sorption experimental data.

GAB parameters	Freeze-dried abalone [34]	Freeze-dried sardines [41]	Freeze-dried tuna meat [42]	Freeze-dried shark [43]	Freeze-dried king fish [44]	Freeze-dried horse mackerel
X_m (g/100 g)	6.8	4.94	6.33	10.4	5.2	3.36
C	10.66	0.0106	9.566	12.7	0.934	73.29
K	0.865	0.7324	0.9139	0.980	0.952	0.992
MRE (%)	15.9	7.4	9.6	3.7	11.2	
Re						0.0086

MRE: mean relative error; Re: residual error.

Where X_s and X_w are the mass fraction of solid and water (w.b.), respectively; T_{gm}, T_{gs} and T_{gw} are the glass transition temperature of the sample, solids and water, respectively. $T_{gw} = -135\,^{\circ}C$ [16]; k is the Gordon–Taylor parameter.

2.4. Measurement and modelling of freezing point by DSC

Rahman [11] reviewed different types of empirical and theoretical models used to predict freezing point of foods. In this work, the theoretical Clausius–Clapeyron equation was used to estimate the freezing point of horse mackerel muscle. The Clausius–Clapeyron equation can be written as:

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

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).

2.5. Statistical analysis

All regressions were made with the help of Matlab software (version 7.0) using the non-linear curve fitting function [40].

3. Results and discussion

3.1. Sorption isotherm

The GAB model was fitted to the sorption experimental data. Moisture sorption isotherm is shown in Fig. 1. On the whole, the GAB model fitted the experimental data well. As expected, the equilibrium moisture content increased with increasing a_w. The empirical parameters and correlation coefficients calculated by non-linear regression are shown in Table 2. These constants can be used to predict moisture sorption isotherms at room temperature. The value of the monolayer moisture content of horse mackerel muscle was 3.36 g/100 g (d.b.) as determined by GAB model. Results were in the range previously reported for abalone (6.8 g/100 g, d.b.), sardines (4.94 g/100 g, d.b.), tuna meat (6.33 g/100 g, d.b.), shark meat (10.4 g/100 g, d.b.), and king fish (5.2 g/100 g, d.b.). The monolayer moisture content X_m is recognized as the moisture content affording the longest time period with minimum quality loss at a given temperature. Below it, rates of deteriorative reactions, except oxidation of unsaturated fats, are minimal. Therefore, at a given temperature, the safest a_w level is that corresponding to X_m or lower.

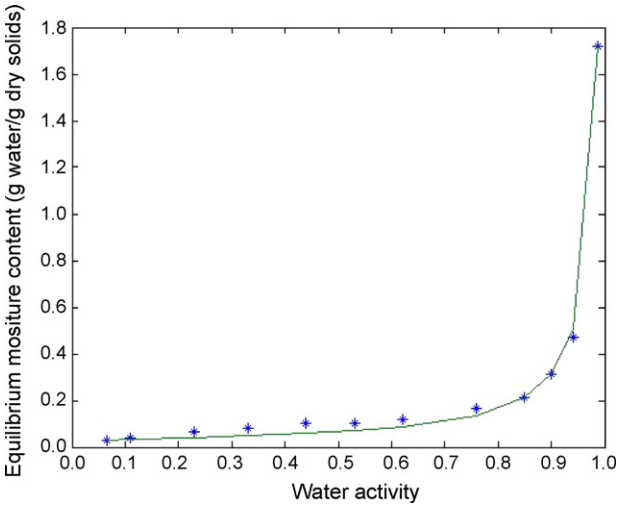

Fig. 1. Sorption isotherm of horse mackerel muscle (*experimental data; —GAB model).

3.2. Thermal transitions by DSC

3.2.1. Samples containing unfreezable water

The glass transition temperature was determined from the DSC heat flow curves with professional software (Proteus Analysis, NETZSCH, Germany), as shown in Fig. 2. The onset T_{gi} and final T_{ge} points of transitions were obtained by extrapolating the side and base lines [15,30]. The T_{gm} was estimated from the midpoint of the onset and final points (Fig. 2).

The samples with different a_w behaved differently during DSC tests. Since much of the water was linked to the solid matrix, samples with low moisture content (X_w 0.238) only showed up the glass transition. As expected T_g decreased with increasing moisture content, as shown in Table 3. T_{gm} decreased from −21.0 °C to −80.1 °C when the moisture content increased from 0.031 to 0.238 (g/g, w.b.) (Table 3).

Gordon–Taylor equation was fitted to the glass transition data of plasticized horse mackerel muscle and the values of T_{gs} and K were found to be −12.3 °C and 5.01, respectively. The predicted value of k = 5.01 for horse mackerel muscle is similar to the literature values of 2.89 for tuna meat [33]. The variation was

Table 3
Glass transition temperature of horse mackerel muscle when there is no formation of ice.

Moisture content X_w (g/g, w.b.)	a_w	T_{gi} (°C)	T_{gm} (°C)	T_{ge} (°C)
0.031	0.065	−21.7 (2.2)[a]	−21.0 (2.4)	−20.4 (2.7)
0.039	0.11	−33.0 (0.9)	−32.2 (0.5)	−31.2 (0.3)
0.064	0.23	−43.7 (4.3)	−43.0 (4.0)	−42.4 (3.7)
0.075	0.33	−46.1 (4.1)	−44.6 (3.6)	−43.0 (3.2)
0.094	0.44	−58.3 (2.5)	−57.4 (1.9)	−56.5 (1.5)
0.095	0.53	−62.7 (2.9)	−61.9 (2.9)	−61.2 (2.9)
0.108	0.62	−69.0 (2.2)	−68.0 (2.5)	−66.8 (2.7)
0.143	0.76	−75.2 (2.1)	−74.0 (2.3)	−72.8 (2.4)
0.156	0.81	−73.5 (1.1)	−72.7 (1.2)	−71.9 (1.3)
0.175	0.85	−77.9 (1.9)	−76.8 (1.4)	−75.5 (1.3)
0.202	0.87	−80.1 (2.7)	−79.1 (2.9)	−78.0 (3.0)
0.238	0.90	−81.8 (1.1)	−80.1 (2.1)	−78.1 (3.1)

[a] *Note*: values in the parentheses are standard deviation of three samples.

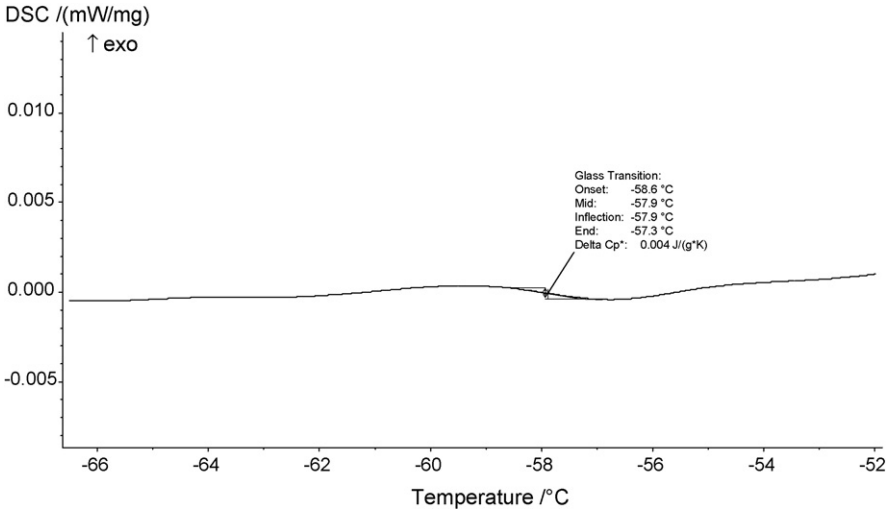

Fig. 2. A typical DSC thermogram to determine the glass transition of horse mackerel muscle for plasticized sample (a_w 0.53, X_w 0.095 g/g, w.b.).

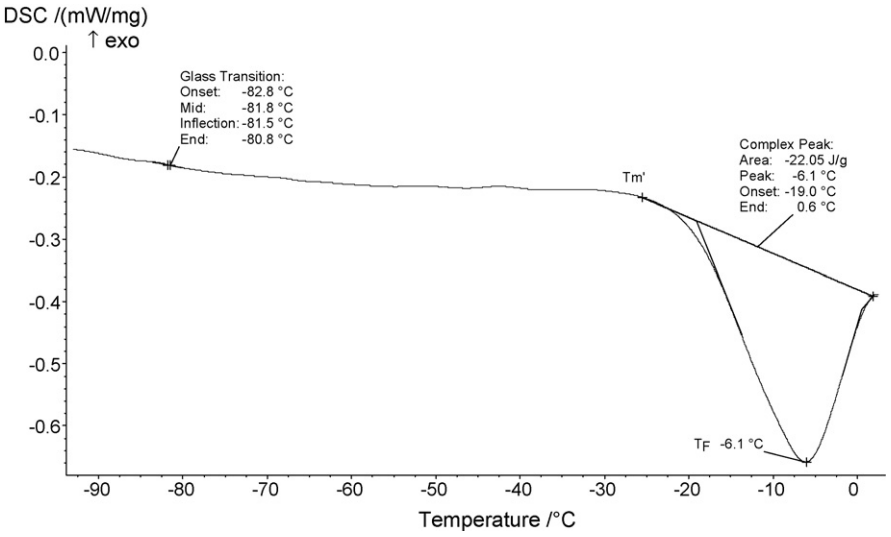

Fig. 3. A typical DSC thermogram for horse mackerel muscle for non-annealed sample (a_w 0.98, X_w 0.640 g/g, w.b.).

expected due to the differences in chemical compositions of fish muscle.

3.2.2. Samples containing freezable water

A typical DSC thermogram of sample having freezeable water without annealing is shown in Fig. 3. It showed freezing point (T_F), apparent glass transition (T'_{ga}), and end point of freezing (T'_m). Since T'_m were independent of the initial concentrations, the average values for horse mackerel muscle without annealing were −83.8 °C and −35.7 °C for T'_{ga} and T'_m, respectively (Table 4). The value of T'_m (i.e.−35.7 °C) was considered as the end point of freezing. Optimum annealing condition was obtained when the samples were held at $T'_m - 2.3$ °C (−38 °C) for 30 min, leading to a maximum amount of ice to be formed. A typical DSC thermogram of annealed sample is shown in Fig. 4. As expected annealing led to increasing of T'_g values and elimination of little devitrification exotherm. A well-visible devitrification peak appeared after T_g and before T_m. This phenomenon occurred because rapid cooling resulted only in partial freeze-concentration of the solution, during rewarming the increase in a_w caused crystallization of trapped amorphous water [13,45,46]. As expected, T_g of annealed samples was higher than that of the non-annealed ones (Table 4), due to the greater fraction of ice formed and consequent concentration of the amorphous glassy matrix [18,21].

In the higher moisture content range (X_s 0.431), T_g appeared less visible just before the ice melting and remained practically constant (Table 4). Because the heat effect involved in glass transition is prac-

Table 4
Glass transition temperature and freezing point of horse mackerel muscle when there is freezable water.

Moisture content X_w (g/g, w.b.)	a_w	T_F (°C)	T_{gm} (°C)	T'_m(°C)
0.246[a]	0.905		−85.9	−35.4
0.270[a]	0.930		−85.3	−35.6
0.319[a]	0.941		−81.6	−35.0
0.605[a]	0.984		−82.5	−36.6
0.370[b]	0.953	−19.5	−86.1	
0.431[b]	0.971	−17.4	−86.0	
0.567[b]	0.982	−8.7	−82.2	
0.632[b]	0.988	−6.7	−84.4	
0.246[b]	0.905	−30.3	−82.7	
0.270[b]	0.930	−25.3	−84.5	

[a] Without annealing (averages values for all samples: $T'_m = -35.7$ °C ± 0.6 °C, and $T'_{ga} = -83.8$ °C ± 1.8 °C).
[b] Glass transition temperature for annealed samples (30 min annealing at −38 °C).

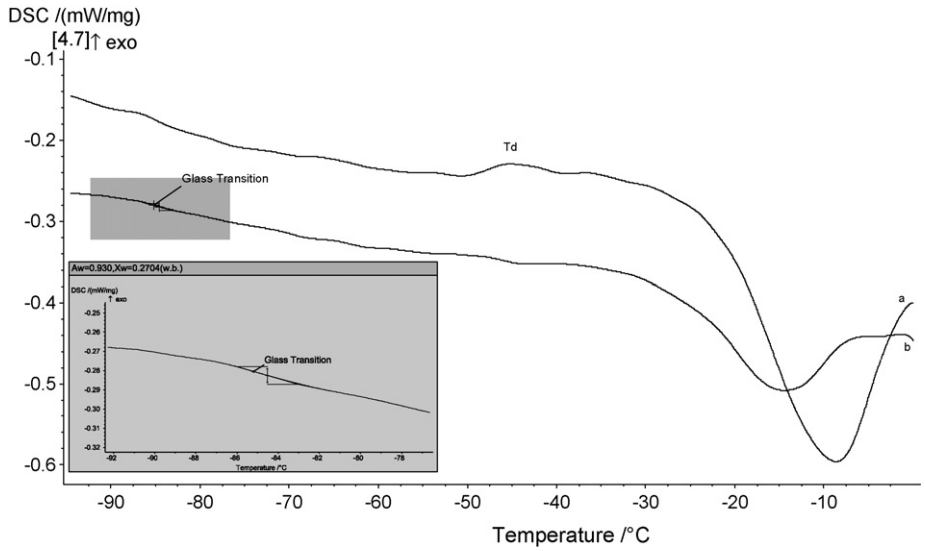

Fig. 4. A typical DSC thermogram for horse mackerel muscle for 30 min annealed sample (a_w 0.93, X_w 0.270 g/g, w.b.); (a) without annealing, and (b) annealed for 30 min.

tically negligible in comparison with the latent heat of melting. The results were similar to those obtained by Roos and Karel [36] with diluted sucrose solutions, Sá and Sereno [18] with fresh grape samples, Sobral et al. [23] with persimmon, Telis and Sobral [21,28] with pineapple and tomato.

3.3. Freezing point

The freezing points of horse mackerel muscle as a function of moisture content are given in Table 4. The results showed that freezing point decreased with increasing of solid content. The model parameter E was estimated using Matlab 7.0 software non-linear curve fitting method and found to be 0.112 for horse mackerel muscle. From the values of E, the effective molecular weight of solids was160.7. The values of E for tuna meat and squid mantle meat were found to be 0.071 and 0.082, respectively [33,47]. The solids content (X'_s) at the T'_m was estimated as 0.786 (X'_w 0.214) by extrapolating the freezing curve up to T'_m of −35.7 °C.

3.4. State diagram

State diagram of horse mackerel muscle is shown in Fig. 5. AB represents the equilibrium between the solution and the solids (ice) formed and can be designated the freezing curves (Eq. (3)). DF represents the glass transition curves. Point C is the maximal-freeze-concentration point, at which the freezing temperature T'_m equals −35.7 °C, and the solid content is 0.786 (g/g, w.b.). This part of water is considered as unfreezable [29]. The intersection of the vertical extrapolation of the point C on the glass transition curve at $X'_s = 0.786$ (point E in Fig. 5) is identified as maximal-freeze-concentration glass transition point (T'_g), its temperature equals −83.1 °C and its solid content is the same as X'_s at point C.

With understanding of the state diagram, the best storing condition for products could be proposed. For example, for horse mackerel muscle dried to moisture content of 0.25 (g/g, w.b.), it had better to be stored below its glass transition point, −89.0 °C. For products that have to be stored above the glass transition temperature, Williams–Landel–Ferry (WLF) equation [13] could be employed to estimate their shelf life. WLF equation was given as follows:

$$\log\frac{\tau}{\tau_g} = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (4)$$

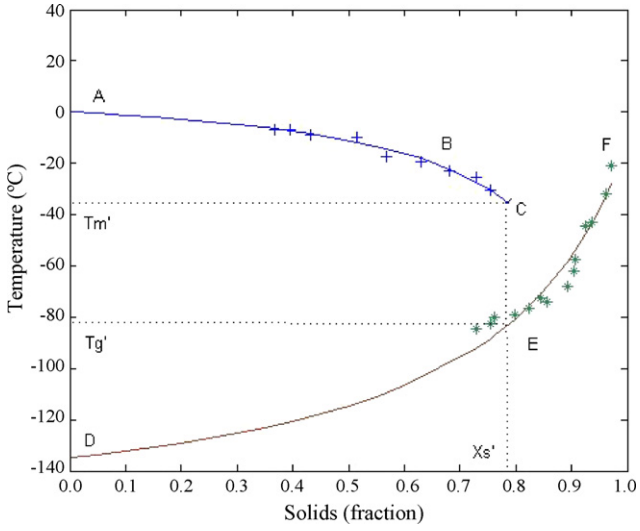

Fig. 5. State diagram of horse mackerel muscle (AB: freezing curves; DF: glass transition line; E: glass transition point of maximal freeze-concentration).

where τ_g and τ_s are time constants for crystallization at T_g and T, respectively; C_1 and C_2 are general constants. According to Sun [48], for the system which has a freezing point much higher than its glass transition point, $C_1 = 20$ and $C_2 = 155$. The storage period under glass state, τ_g, is estimated as follows: since the growth rate of ice crystal under glass state is estimated as 1 mm per 10^3 years [49], typical diameters for fish cells are about 10–100 μm [50] (suppose diameter for horse mackerel muscle cell is 20 μm), it will take 20 years for a trivial crystal to grow big enough to destroy the horse mackerel cells, therefore τ_g equals 20 years. As an example, lets consider dried horse mackerel with moisture content $X_w = 0.10$ (g/g, w.b.), its glass transition temperature can be found from the diagram to be −56.2 °C. According to Eq. (4), the shelf life of this product at 20 °C can then be calculated to be 10.0 days. It is easy to make similar estimation for products with other water contents and stored at other temperatures.

4. Conclusions

The state diagram developed for horse mackerel muscle 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. The state diagram provided an estimate of maximally freeze-concentrated solutes at 0.786 (g/g, w.b.) with the characteristic temperature of end point of freezing (T'_m) being −35.7 °C and glass formation (T'_g) being −83.1 °C.

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