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1 Thermophysical properties of frozen parsley: a state diagram representation

2

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9

10 Abstract

11 Sorption behaviour and glass transition of frozen parsley were investigated in order to study the
12 physical modifications, represented as state diagram to figure out information about product
13 behaviour for storage, and supply chain handling. Frozen products may be located in the state diagram
14 in all the possible freezing temperatures to understand the structure state and study feasible corrective
15 actions mainly focused on temperature and solid content.

16 Parsley was totally dehydrated and equilibrated at selected relative humidity. Sorption behaviour was
17 evaluated by saturated salt slurry method and sorption isotherm fitting, while solid components in
18 terms of mass fraction were investigated by using Differential Scanning Calorimetry. Brunauer-
19 Emmet-Teller (BET) model well fitted with moisture and water activity data ($R^2=0.995$, p -
20 $level<0.05$). The characteristic ranges of stability, in terms of system mobility and physical
21 modification, are the monolayer values (0.240 water activity; 0.052 kg/kg dry basis) and the critical
22 water activity range (0.424 water activity; 0.078 kg/kg dry basis). Glass transition and melting
23 temperature were used to define parsley state diagram. Different zones figure out a specific physical
24 behaviour: depending on solid content and temperature. Unfrozen water was estimated as monolayer
25 BET value 0.84 kg/kg wet basis and extrapolated from state diagram 0.984 kg/kg wet basis.

26

27 **Practical Applications**

28 **Frozen** high-quality product and energy efficiency can be obtained by a correct temperature
29 management. Thermophysical properties of parsley represented in a state diagram are reported in the
30 typical solute and temperature range of freezing process and storage. These data can relate physical
31 structure and temperature, allowing different possible conditions management.

32
33 **Keywords:** frozen parsley; physical properties; state diagram; food chain management

34 35 **1. Introduction**

36 Parsley is worldwide sold as leafy green herb consumed for its own cooking peculiar flavour, but also
37 widely used as ingredient and drugs (Soysal et al., 2006). Because of its high-water content (78–82%,
38 w/w), parsley is ordinarily processed in order to inhibit microorganism growth and prevent
39 degradation (Doymaz et al., 2006). Minimally processed parsley could stay fresh for a period of 23
40 days (Catunescu et al., 2012), but the long-lasting operation induced by freezing produce a peerless
41 shelf lifetime (Tolba et al., 2008).

42 The characterization of biological food tissues is a complicated task, accounting for inhomogeneous
43 arrangement, distribution of cell sizes and shapes, their state and local solute concentrations
44 (Canatella et al., 2004). **Water content and temperature are the most important parameters for physical
45 properties assessment of biological products. The role of water in the physical stability of
46 multicomponent system is critical, particularly regarding mechanical properties (such as crispness,
47 softness, etc.) and structure characteristics (crystallization, collapse, etc.).** Basically, amorphous, and
48 semi-crystalline polymers, that during their industrial processing undergone a fast cooling from
49 environmental temperatures, end up in a **meta-stable** state (Priestley et al., 2005). These modifications
50 over a storage time can show themselves through physical properties changes, such toughness,
51 strength, density, and specific heat (Miles, 1991). Thermophysical properties of foods are mainly
52 dependent on chemical composition, **time**, and temperature. Considering freezing aspects, enthalpy

53 and specific heat capacity of frozen foods are parameters mainly affected by the latent heat of ice
54 fusion (Miles, 1991). Thus, understanding of water/ice equilibrium and phase transition is the basis
55 to understand physical properties of frozen foods. In summary, the whole interpretation of the food
56 frozen system can be simplified and resumed to a two-phase system liquid and dissolved and
57 undissolved solids, with water and dry matter taken as the main components (Fikiin and Fikiin, 1999).
58 Freezing may be subdivided in several stages. The precooling stage, in which the material is cooled
59 from an initial temperature to the initial freezing point, that is the highest temperature at which ice
60 may exist in a food in thermal equilibrium (Miles, 1991). It should be considered that not all the water
61 can be converted into ice at this transition temperature (Roos, 2012), so a phase change period is
62 present as crystallization of the majority part of water required time (Miles, 1991). Finally, a further
63 reduction of temperature is of central importance to freeze water, the so-called tempering stage in
64 which food during time reaches a final established temperature. The quantity of ice increases as a
65 function of decreasing temperature until a plateau, when this phenomenon goes more slowly. Hence,
66 water and ice rate in every foodstuff is highly time dependent (Miles, 1991). Considering the
67 differences between water and ice physical properties, water phase transitions rule frozen food
68 modifications. Thus, the main physical changes occurring during frozen conditions depending on
69 moisture migration and ice recrystallization (Roos, 2012)

70 An easy way to show these phases, correspondent to different physical properties of a frozen food, is
71 depicting a stability map able to describe relations among water in the amorphous and crystalline
72 phase, solute freeze concentration and the residual unfrozen water, highlighting the critical zones. In
73 this way, different states of a food as a function of soluble solids and temperature of state transition
74 were displayed to build up a state diagram. In literature, food stability has been formerly reported as
75 a function of thermo physical modifications due to a second order thermodynamic transition, such as
76 glass transition, in which the material undergoes a change in phase but not in state (Roos, 1991)
77 Particularly, the concept of food state diagram based on glass transition and freezing curve has been
78 proposed in the '90s by Roos and Karel, and since then by several other authors (Roos, 1991; Sá and

79 sereno, 1994; Figueiredo et al., 1999; Rantanen et al., 2000; Melton et al., 2002; Rahman, 2004;
80 Rahman, 2006 Rahman, 2009; Guizani et al., 2010; Rahman, 2012; Zhao et al., 2015; Suresh et al.,
81 2017).

82 Frozen products could be located in the state diagram as a function of solids content and temperature.
83 Based on the location in a defined zone it is possible to estimate the stability of the foodstuff and
84 develop strategies for storage design and management. The objective of this work is to explore the
85 concepts of state diagram and glass transition to figure out the thermophysical properties of frozen
86 parsley.

87

88 **2. Material and methods**

89

90 *2.1 Samples preparation*

91 Frozen parsley was purchased in a commercial supermarket in Cesena, Italy. Frozen parsley was
92 chosen to investigate the humidity influence and physical properties of a disintegrated cellular
93 structure, in order to well evaluate the possible behaviour of products under storage and distribution
94 conditions. Three packages were employed, and the ingredients of the final product were parsley and
95 sunflower oil (maximum 3%, for preservation purposes). Short time after purchasing, the products
96 was de-frozen at environmental temperature, $22^{\circ}\text{C} \pm 1$, then water content and glass transition for de-
97 frozen parsley was stated at 4.57 kg/kg dry basis and -48.64°C , respectively.

98 All the samples were then conditioned for about 30 days into a desiccator containing phosphorus
99 pentoxide (P_2O_5) in order to dehydrate and stabilize the samples to the minimum water activity, about
100 0. Hereafter samples were rehydrated as reported in the following subsection.

101

102 *2.2 Sorption isotherm*

103 Traditional saturated salt slurry method (DES) was carried out for sorption isotherms assessment.
104 DES method consists in the achievement of a defined hydration level of samples, imposed by salt

105 solution saturation. The salt solution produces a relative humidity of the closed environment, and
 106 time is required to the samples to reach a thermodynamic equilibrium with the surrounding
 107 atmosphere. Dehydrated parsley samples were positioned inside a hermetically closed desiccator
 108 containing, on the bottom, different saturated salt solutions (LiCl, $\text{KC}_2\text{H}_3\text{O}_2$, MgCl_2 , K_2CO_3 , NaBr,
 109 and NaCl). The thermodynamic equilibrium was evaluated by weighting samples three consecutive
 110 times, considering a steadiness at $\Delta_{\text{weight}} < 0.0005$.

111 Water activity of the equilibrated samples was measured by a dewpoint hygrometer, mod. Aqualab
 112 (Decagon Devices Inc., Pullman, WA). Moisture was evaluated by oven method (AOAC 934.06, dry
 113 oven at 70°C until steady weight) and hereafter expressed as water content on dry basis for moisture
 114 sorption isotherms and as solid content on wet basis for state diagram representation. All the analyses
 115 were conducted at least in triplicates. BET equation was chosen to fit experimental data of water
 116 content and water activity:

$$118 \quad X = \frac{V_m C a_w}{(1-a_w)(1+(C-1)a_w)} \quad (1)$$

119
 120 X is the water content (kg/kg dry basis), V_m is the water content of the monolayer (kg/kg dry basis)
 121 and C is the constant related to monolayer sorption heat. According to the literature, BET equation is
 122 the best ways to determine the sorption behaviour in mid-low water activity range, particularly it well
 123 estimates monolayer moisture content, fundamental parameter for product stability defining the
 124 quantity of water un-available for physical structure modifications (Ross, 1991).

126 2.3 Differential Scanning Calorimetry

127 The glass transition temperature (T_g) and the initial freezing point were evaluated in triplicate by
 128 using a DSC mod. Q20 (TA Instrument, Germany). The DSC was connected to a low-temperature
 129 cooling unit mod. System90 (TA Instrument, Germany). For calibration, the same heating rate used

for sample measurement was applied under a dry nitrogen gas flux of 50 mL/min. Heat flow was calibrated using the heat of fusion of indium (ΔH 28.71 J/g). Each sample (about 1 mg) was weighed in 50 μ l hermetic aluminium pans and then loaded into the DSC instrument at room temperature, using an empty pan for reference. Samples were equilibrated at -35°C for 10 min, and then two heat-cool cycles were applied from -90 to 80°C at 5°C/min. Variations of heat flux (V), displayed as thermogram base line deviations in terms of peak and step changes of the baseline, were evaluated by using the automatic tool of the Software TA-Universal analyser (TA Instrument, Germany).

137

2.4 Glass transition fitting

The Gordon and Taylor model (eq. 2) was applied to experimental data:

140

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

142

T_g , T_{gs} and T_{gw} are the glass transition temperatures of the sample, solid and water, respectively, instead X_s and X_w are the percentage of solid and water content in the sample, and k is the calculated parameter. The T_{gw} was taken as -135°C, according to average value of the literature data (Roos, 1995). Gordon and Taylor equation describes the composition dependence of the transition temperature of amorphous components, and it is usually used for T_g prediction (Gordon and Taylor, 1952).

149

3. Results and discussion

The influence of water on molecular mobility is pronounced on system where moisture content is restricted, such as frozen parsley. Prediction of the physical state was based on water mobility assessment in temperature and humidity domains, and also on modelling water plasticization, thus T_g

depression with increasing water content. Sorption data and T_g determination allow the description of changes in physical state that may occur during processing and storage conditions.

Thermal properties of parsley were obtained by using DSC. The annealing conditions selected, holding samples at -35°C , allowed the maximum ice formation leading to a maximum solid part concentration since water solidified alone creating a soluble solid amorphous concentrated phase. Two examples of parsley thermograms are shown in figure 1.

Thermogram of sample equilibrated at 69% of relative humidity (RH) (Fig. 1a) showed ice formation on freezing and rewarming. Ice formation is a first order state transition of water, the passage from liquid to solid and vice versa, it is detected by maximum value of peak correspondent to melting temperature (T_m) and crystallization temperature (T_c). Sample equilibrated at 17% of RH (Fig. 1b) reported no ice formation. Ice melting was found for samples equilibrated at RH higher than 24%.

No ice formation means unfrozen water presence, water unavailable to solidified alone. Un-freezable water is the amount of water remaining unfrozen as un-crystallized free water or bound to the solid matrix even at low temperature (Raman et al. 2006). Different state of water could be measured in several way, such as sorption isotherms with monolayer, multilayer concepts or unfreezeable water estimated by DSC (Raman et al. 2006). Several authors estimated un-freezable water content comparing DSC endotherms of samples having freezable water from the plot of melting enthalpy (Roos, 1991). This procedure was used for crackers (Given, 1991), strawberry (Roos, 1987), dates (Rahman, 2004), sucrose (Ablett et al., 1992), cabbage (Paakkonen & Plit 1991) and garlic (Rahman et al., 2005a).

In table 1 the averaged value of temperature for both glass transition and melting point of water in parsley at each a_w levels are reported.

T_g ranges from -5.02 to -46.71°C and, as expected, T_g decrease with water content increase. Melting point at $0.172 a_w$ was not detected, due to water unavailability according to literature (Duckworth & Smith, 1963).

179 Linear relation between T_g and a_w can be calculated in addition to sorption isotherm to build a stability
180 map useful for predicting T_g of materials stored at various conditions (figure 2).

181 The sorption isotherm of parsley at 22°C was fitted with BET model with a good determination
182 coefficient ($R^2=0.995$, $RMSE=0.02$, $p\text{-level}<0.05$) confirming that the model well described the low
183 moisture region of sorption profiles. The calculated monolayer value X_m corresponded to an a_w of
184 0.24 and a water content of 0.052 kg/kg dry basis. BET monolayer was previously reported as un-
185 freezable water and contributed to metastability of frozen product evaluation (Labuza et al., 1972;
186 Rahman, 2009; Ross, 2012). The monolayer value is the limit under which water is strictly bound to
187 the matrix, hence represent the most stable zone in terms of moisture mobility.

188 The linear relation created by using experimental data of T_g and a_w was used to calculate the critical
189 a_w value. This critical value was calculated by using the used storage temperature of frozen product
190 (-26°C) and correspond to a water activity of 0.424. According to sorption isotherm the corresponding
191 water content expressed on dry basis is 0.079 kg/kg. Above this critical value physical modifications
192 begin, such as loss of crispness, stickiness of powder and hard candies, recrystallization of amorphous
193 sugars causing caking, mechanical modification including collapse phenomena, loss of porosity as
194 well as diffusion (Gordon and Taylor, 1952; Labuza et al., 1972; Ross, 2012).

195 Actually, this map can give important indications about product stability. Despite this, equilibrium
196 freezing conditions influenced by the amount of ice formed on temperature and composition are
197 missing information. Freezing curve and glass transition data were implemented in a state diagram to
198 draw several regions with different physical states, as previously reported in literature (Raman 2004,
199 Raman et al. 2006).

200 State diagram of parsley is shown in figure 3. The state diagram was built starting from temperature
201 and solid content data. T_{gw} and T_{gs} are glass transition of water and totally dried product, respectively.
202 Glass transition of the product at different solid contents are reported, with grey dot, in between and
203 fitted with Gordon Taylor equation (eq. 2). The Gordon and Taylor model show good coefficient of

determination value ($R^2=0.958$, $RMSE=0.17$, $p\text{-level}<0.05$). The value of the calculated k parameter is 3.78, comparable to literature k values of foodstuff (Sá and Sereno, 1994).

The melting temperatures of onset and end point were added to figure out different zone of solute, solution, and solid presence. The freezing curve is created from T_{mw}^I and T_m^{end} of the product at the higher hydration level (a_w 0.693). B is the melting temperature at the end freezing point. The intersection of vertical interpolation from B to the T_g curve is the point A. The point A is known as unfrozen water. The extrapolated solid content is 0.84 kg/kg wet basis. Similar solid contents were reported in literature for date flesh and garlic (Rahman, 2006, 2005), even if attention to wet or dry basis should be paid to avoid misinterpretation. The calculated solid content of monolayer X_m of the BET equation, other expression of unfrozen water is 0.948 kg/kg wet basis, as expected in agree with state diagram. BET-monolayer solid content value is used as un-freezable water quantification and it can be determined by using different methods. As several works reported (Rahman 2006, 2009, 2012), parsley un-freezable water calculated with BET-monolayer value is higher than that of the extrapolated from the state diagram. These stability values are of utmost importance for process and storage management, as parameters influencing product stability. Several authors (Roos and Karel, 1991; Sá and Sereno, 1994), reports the temperature storage dependence on product degradation. Particularly, it suggests a simple index based on $T_{storage}-T_g$. In this way if T_g correspond to storage temperature no degradation occurs. For frozen food stored at about -26°C this corresponds roughly to the moisture content of the critical water activity, well under the typical frozen product. As guess, frozen vegetables are not totally stable, with time dependent chemical-physical modifications.

224

225 Conclusions

226 The present study maps the phase modification of liquid, rubbery, glassy, and crystal components of
227 parsley by means of a stability map and a state diagram as a function of water content, solid content,
228 and temperature.

229 The sorption profile of parsley was assessed and integrated with glass transition temperature to draw
230 a stability map. Thermophysical properties of parsley, such as glass transition and melting point, were
231 measured. The temperature ranges from 20 to -135 allowing an easily visualization of the typical
232 process and storage temperatures of freezing. Different zone delineated in the state diagram are
233 characterized by different physical structures of parsley characterized as a function of water and
234 temperature. Considering the supply cold chain of frozen products, the state diagram could provide
235 useful data in terms of critical temperature strictly related to the product physical modification and
236 hence the final quality.

237 Further work should be done to extend the solid content range and implement the state diagram with
238 deliquescent point data, to provide information also referring to the [drying](#) process.

239

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244

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