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Physical Stability of Frozen Eggplant: Emphasis on State Diagram, Sorption, Thermal, Mechanical, and Dielectric Properties

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Physical Stability of Frozen Eggplant: Emphasis on State Diagram, Sorption, Thermal, Mechanical, and Dielectric Properties / Iaccheri, E; Cevoli, C; Ragni, L; Rosa, MD; Fabbri, A. - In: FOOD AND BIOPROCESS TECHNOLOGY. - ISSN 1935-5130. - STAMPA. - 16:7(2023), pp. 1582-1594. [10.1007/s11947-023-03017-0]

This version is available at: <https://hdl.handle.net/11585/942020> since: 2023-09-15

Published:

DOI: <http://doi.org/10.1007/s11947-023-03017-0>

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Iaccheri, E., Cevoli, C., Ragni, L. *et al.* Physical Stability of Frozen Eggplant: Emphasis on State Diagram, Sorption, Thermal, Mechanical, and Dielectric Properties. *Food Bioprocess Technol* **16**, 1582–1594 (2023).

The final published version is available online at:

<https://doi-org.ezproxy.unibo.it/10.1007/s11947-023-03017-0>

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Physical Stability of Frozen Eggplant: Emphasis on State Diagram, Sorption, Thermal, Mechanical, and Dielectric Properties

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Abstract

The frozen eggplant was studied using absorption isotherms, measured by using saturated salt solution in desiccator chamber (DES) and the Dynamic Vapor Sorption (DVS) instrument (~~DVS~~). Melting temperature and glass transition temperature were determined by differential scanning calorimetry (DSC), while mechanical properties were determined by a compression test. In addition, dielectric properties were assessed by means of two instrumental chains to cover a wide frequency range of radiofrequencies. Absorption fitting was able to estimate unfreezeable water content, while the dynamic instrument showed a hysteresis between adsorption and desorption, confirming amorphous materials' presence in the products. Thermograms revealed two phase transition apparent T_g^{III} , and T_g^{II} affected by the plasticizing effect of water. Mechanical properties confirmed the water influence on structures, as Fermi model fitting ($R^2 = 0.984$, $RMSE = 3.9$ N) shown. Dielectric properties were carried out to allow the description of three main dispersion α , β , and γ relaxations. State diagram was developed to show different zones corresponding to possible physical structures.

Keywords: Physical stability, Sorption isotherm, Dielectric properties, Frozen eggplant, Mechanical property, Thermal analysis

Introduction

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Yes, They are.

Food engineers design processes, packaging, or environmental storage conditions. That implies the control of the product and its transformation during production and storage (Rahman, 2009a). Food properties are the result of the nonequilibrium nature of biological systems, dynamics developed through process, or time-dependent changes during storage (Roudaut, 2020). Food properties modification follows the food's physical state, mainly depending on water content, and temperature (Gustavo-Barbosa-Canovas, 2020). Therefore, physical state changes, considering solid constituents' state and their transition, affect structural aspects of foodstuff in terms of water vs glass dynamics; that they can be established to predict functional properties modifications during process and storage by glass transition concept, sorption behavior, and phase diagram development (Addo et al., 2020; Roudaut, 2020; Taylor, 1995).

The widely known change in physical state, from glass to supercooled liquid state (rubbery referred to polymers), called glass transition (T_g) is a compositional dependent behavior of the amorphous system (Roudaut, 2020). T_g is thermodynamically a second-order transition involved in changes in the volume expansion, discontinuity in the thermal expansion coefficient, heat capacity, and changes in mechanical properties in terms of mechanical relaxation time and frequency (Angell et al., 2000). Accordingly, water-solids interactions in foods are relevant around T_g temperature and humidity domains (Roudaut, 2020), particularly considering foodstuffs at high solids concentrations and so with restricted water availability, such as dried or frozen food. The importance of water sorption and glass dynamics effects on food structure involving quality, safety, and stability understanding it gets us familiar mainly by Slade et al. (1993) introducing the food polymer science approach. This approach defines foods as material in a metastable state that underwent time-dependent modifications described by the glass transition T_g (Slade et al., 1993).

Considering the physical stability of frozen food, water is one of the most important factors, being the crystallizing agent (Gustavo-Barbosa-Canovas, 2020), also confirmed by works conducted on de-hydro freezing attempting to reduce water availability (Ben Haj Said et al., 2016). Frozen food is partially characterized by a glass structure formed by cooling a liquid fast enough to avoid crystallization. The fast cooling produces an immobilization of a disordered molecular structure; the structure of the product is formed in time which cannot allow a change in molecular order, as the crystal structure (Debenedetti and Stillinger, 2001). In practice, glass disordered structures are solids but disordered as liquids (Gustavo-Barbosa-Canovas, 2020). Food structure defines also molecular mobility, and in this way, T_g can be also defined as translational

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Yes, They are.

motions called alpha relaxation, and the other two relaxations of less intensity are present in the biological system: beta and gamma relaxations (Angell et al., 2000; Johari and Goldstein, 1971). The T_g recognized as a structural relaxation can be observed by a mechanic or dielectric property, where the last is described by electromagnetic wave interaction with foodstuff (the dielectric), in which water is the main responsible for electromagnetic movements having a large dipolar moment, and it can be described by complex permittivity (ϵ). Complex permittivity mathematical description is composed of a real part and an imaginary part, also known as permittivity (ϵ') and dielectric loss (ϵ''). Permittivity is related to solvent polarity and the ability to solvate ions; not surprisingly, water has a high permittivity (Roudaut, 2020). The high permittivity of water plays an important role in plasticizing effects, because of water's affinity for other molecules enhancing homogeneous mix through a reduction of electrostatic interaction among molecules groups. Dielectric loss is more associated with the efficiency to traduce electromagnetic energy, absorbed in food, into heat (Boyd, 1985; Roudaut, 2020). Dielectric properties can be assessed over a wide frequency range in which different phenomena involve molecules. An alternating electric field gets molecules polarization along the field direction, and the degree of polarization depends on the electromagnetic power and the nature of the product. The measure characterizing low frequency are permittivity and dipole moment values, while at high frequencies products under the electromagnetic field attained equilibrium following the changing field and relax when they cannot chase anymore, in these time lag dispersions takes place (permittivity decreases with frequency increase) (Negi et al., 2019). This gives rise to dielectric relaxations. Particularly, the dispersions can be observed: α - and β -dispersions in the radiofrequency range and γ -dispersion in the microwave range (Traffano-Schiffo et al., 2021). α -Dispersion is related to the orientation of mobile charges, and it is associated with T_g . β -Dispersion is associated to the orientation of charges in macromolecules such as proteins and carbohydrates, and it is before or near T_g (Traffano-Schiffo et al., 2018). γ -Dispersion is attributed to dipolar movements, mainly due to water molecules, typical of the microwave range (Traffano-Schiffo et al., 2021). Foods show a frequency dependent spectrum because of these dispersion mechanisms, involving in dielectric relaxation (Angell et al., 2000; Roudaut, 2020). However, only few papers reported dielectric investigation of foodstuffs about detection of dispersion types and physical modification, also considering frozen products (Tang et al., 2020; Traffano-Schiffo et al., 2021).

Water relations with structural relaxation times provide means to control food processing, food structure, and food performance from manufacturing to digestion (Gustavo-Barbosa-Canovas, 2020). Considering the non-equilibrium nature of food products, the characterization of a matrix is necessary because absorption isotherm, thermal, mechanical, and dielectric properties are unique to each food. Particularly, frozen foods are stable considering microbiological aspects, while they are susceptible to physical modification accounting also for long storage. Frozen foods were stored at the end of the production process in an amorphous state tending as much as possible to a glassy state to improve long-term stability. However, the glassy state may undergo structural changes that worsen when products are stored above the T_g temperature (Roudaut, 2020). Hence, the appropriate description of the physical structures of food systems could be a very useful way for storage management. Accordingly, sorption behavior, glass transition, and mechanical and dielectric properties were assessed. Water sorption isotherms were carried out to evaluate samples in thermodynamic equilibrium for quantification of water and related water activity at various equilibrium conditions and to understand the impact of water sorption on the extent of water plasticization, as also previously reported in the literature (Gustavo-Barbosa-Canovas, 2020).

Accordingly, the physical stability of food cannot be established without sorption isotherm and phase diagram data assessment (Roudaut, 2020). Several studies on state diagrams accounting for different methods to divide maps into micro-macro regions each characterized by a typical physical structure (Rahman, 2009b, 2012) are reported in the literature for several fruit and vegetables, such as onion, grapes, and strawberry (Sá and Sereno, 1994), apple (Figueiredo et al., 1999), pineapple (Telis and Sobral, 2001), apple slices (Melton et al., 2002), abalone (Sablani et al., 2004), date flesh (Rahman, 2004), freeze-dried pineapple (Telis et al., 2006), grapefruit (Fabra et al., 2009), dates (Guizani et al., 2010), raspberry (Syamaladevi et al., 2011), mango (Li et al., 2020; Zhao et al., 2015), broccoli (Suresh et al., 2017), pumpkin (Al-Ghamdi et al., 2020), and parsley (Iaccheri et al., 2021).

The state diagram role for long storage stability is presented in several studies, mainly on dehydrated foodstuffs (Addo et al., 2020; Chen et al., 2017; Enrione et al., 2010; Farroni and del Pilar Buera, 2014; Wang and Zhou, 2013), whereas changes in physical properties, such as mechanical and dielectric relaxation, as a function of different solid contents, affected frozen food processing, properties, safety, and stability have never been

studied before. Even if the evidence of the practical importance to observe the whole behavior of the frozen products, is possible only with a comprehensive work based on different techniques.

In this way, the objective of this research was to study some frozen eggplant physical properties. Particularly, the effects of water on food physical stability were investigated by means of mechanical and dielectric properties measured on conditioned samples at different relative humidity. Dielectric properties were carried out to assess the physical structure assessment and further set up a sensor for storage monitoring. Traditional and dynamic sorption isotherms were stated and combined with thermal properties to build a state diagram of frozen eggplant, created by initial freezing point, and glass transition temperatures.

Material and Methods

Materials

Frozen grilled eggplants were acquired by a local company (Cesena, Italy) within 2 days after production. Five packages (each of 1 kg) were utilized for the research. The ingredients of the final product were eggplant with an addition of sunflower oil (about 7%). The product was immediately thawed at environmental temperature, (22 ± 1 °C), the water content and glass transition were stated at 6.44 ± 0.29 kg/kg dry basis and -30.88 ± 1.46 °C, respectively. Subsequently, the samples were cut with a cork borer (diameter 40 mm), dried in a vacuum oven at 70 °C, until constant weight (about 24 h), and then conditioned into a desiccator containing phosphorus pentoxide (P_2O_5 , UN 1807, Carlo Erba reagents, Val De Reuil Cedex, DASIT Group) for about 30 days to remove all the water and as much as possible to stabilize the samples to the minimum water activity, $a_w < 0.05$. Hereafter, samples were rehydrated as reported in the subsequent subsection.

Sorption Isotherms: DES and DVS Methods

Sorption isotherms were determined by using two methods: traditional saturated salt solution in desiccator chambers (DES), first proposed by Labuza et al. (1972), and a dynamic method exploiting Dynamic Vapor Sorption (DVS) analyzer (DVS).

DES method started with saturated salt solutions preparation by using several salts ($LiCl$, $KC_2H_3O_2$, $MgCl_2$, K_2CO_3 , $NaBr$, $NaCl$, and K_2SO_4) to provide a relative humidity between 11 and 97%. Saturated salt solutions were placed into seven desiccators stored in a chamber with temperature control at 22 ± 1 °C. Ten replicates were employed for each water activity level. The thermodynamic equilibrium was evaluated by weighting samples for three consecutive times to reach a steady weight of $\Delta weight < 0.005$ g. The water

activity of the equilibrated samples was measured by a dewpoint hygrometer, mod. Aqualab (Decagon Devices Inc., Pullman, WA). Moisture content was evaluated by oven method (AOAC 934.06, dry oven at 70 °C until steady weight.). All the analyses were conducted at least in triplicates.

Sorption isotherms were also determined by a Dynamic Vapor Sorption instrument (DVS-Q5000 SA, TA instrument, New Castel, DE). The dynamic method allows the assessment of sorption isotherm by recording the sample mass at different RH automatically, according to previous literature (Bingol et al., 2012; Carter and Schmidt, 2012; Iaccheri et al., 2015). An approximately 10 mg exactly weighted sample piece was loaded onto a quartz DVS pan and automatically introduced into the conditioned chamber. A dry air flow (200 mL/min) was used to maximally dry and rehydrate the sample in the chamber. The equipment kept the same RH in the atmosphere around the sample until a stable mass ($\pm 50 \mu\text{g}$) for 10 consecutive minutes at 23 °C. The water content was acquired for RH steps of 5% (from 10 to 98%). The analysis were conducted in triplicate.

Differential Scanning Calorimetry (DSC)

DSC Q20 (TA Instrument, Germany) was used to determine the glass transition temperature (T_g) and the initial freezing point. The DSC was connected to a cooling unit mod. System90 (TA Instrument, Germany). The same heating rate, used for sample measurement, was applied under a dry nitrogen gas flux of 50 mL/min to perform calibration. The known heat of fusion of Indium (ΔH 28.71 J/g) was measured to calibrate heat flow. Each sample of about 10 mg was evaluated in triplicate and it was weighed in 50 μL hermetic aluminum pans and then loaded into the DSC instrument at room temperature, using an empty pan for reference. Samples were equilibrated at 0 °C for 20 min, and then two cool-heat cycles were applied from -90 to 80 °C at 10 °C/min. Variations of heat flux (W/q), in terms of peak intensity (such as melting peak of ice fusion) and step changes of the baseline (as T_g event figured out), were evaluated by using the automatic tool of the Software TA-Universal analyzer (TA Instrument, Germany).

Mechanical Properties

The mechanical properties of samples equilibrated at different RH were evaluated by using a texture analyzer (Zwick/Roell Z2.5) equipped with a 500 N load cell. A parallel plate cylindrical tool (diameter 40 mm) was used as a probe. The speed of the compression test was 1 mm/s and 50% of deformation. Deformation is related to the sample height in which the probe descends, 50% was imposed to overcome possible errors due to the

different heights of samples. At least ten samples for each RH level were analyzed and curves were acquired with 520 data points resolution. The force/distance curves were obtained by carrying out compression tests, and the following parameters were extrapolated: maximum force (N) and distance at yield point (mm).

Dielectric Properties

Dielectric properties were assessed at 22 °C in triplicate in a wide radiofrequency range by means of two instrumental chains, shown in Fig. 1.

Fig. 1. Two instrumental chains applied and related output. 250 MHz to 14 GHz range explored by means of an open-ended coaxial probe (A) and 20 Hz to 1 MHz investigation carrying out with a parallel plate capacitor (B)

The acquisitions from 0.25 to 14 GHz were obtained by using an open-ended coaxial probe (DAKS-3.5 probe, Speag) connected to an R-140 VNA (Vector Network Analyzer, Copper Mountains) and interfaced via USB to a personal computer and operating with dedicated software (DAK Software Installer 2.6.1.7) (Fig. 1-A). The instrumental chain was calibrated by using the parent company calibration kit (Speag DAK-3.5/1.2 Shorting Block, Metallic Strip Sets, and 0.6 lt of Tissue Simulating Liquid) accounting for open, short, and load assessment. The coaxial probe was fixed with a stainless-steel support to avoid possible changes due to cable movements, and samples were kept in contact with the probe by an elevation platform. The instrument allows the acquisition of permittivity (ϵ'), dielectric loss (ϵ''), tangent loss ($\tan(\delta)$), AC-conductivity (σ (S/m)), and reflection coefficient real (Refl.R) and imaginary (Refl.I).

The range, 20 Hz–1 MHz, was explored by using a parallel plate capacitor probe connected to an LCR meter (LCR-8101G, GW-Instek, Good Will Instrument Co., Ltd., Taiwan) interfaced with a personal computer (Fig. 1-B). The capacitor probe was handmade and characterized by two parallel plates of aluminum (diameter 40 mm) and distance between plates of 0.5 mm and allocated in a metal box to avoid external radio electromagnetic interferences. The resulting impedance was the average of 7 subsequent measurements, acquired in series and at 100 mV. The radiofrequency spectra were acquired as impedance complex number (Z , Ω). Impedance is composed of a real part, the resistance (R), and the imaginary part, the reactance (X) related as follows (Eq. 1):

$$Z = R + jX \quad (1)$$

Real and imaginary part of impedance were turn into real and imaginary part of permittivity (Eqs. 2 and 3), as previously reported by Traffano-Schiffo et al. (2017):

$$\epsilon' = \frac{-X}{R^2 + X^2} \frac{1}{2 \pi C_0} \quad (2)$$

$$\epsilon'' = \frac{R}{R^2 + X^2} \frac{1}{2 \pi f C_0} \quad (3)$$

where ϵ' is the permittivity, ϵ'' is the dielectric loss, C_0 is the capacitance in the vacuum, f is the frequency (Hz), and X is the imaginary part of impedance.

Data Analysis

The mathematical model of GAB (Guggenheim, Anderson, & de Boer) (Eq. 1) was used to fit the experimental DES and DVS data, respectively, by using Statistica® 7.0 software (Stat-Soft Inc., USA). GAB is one of the most popular mathematical models that describe the sorption behavior of water in food, due to its strong theoretical basis. This model adequately describes the experimental data for water activity ranges from 0.05 to 0.95 (Gustavo-Barbosa-Canovas, 2020; Yanniotis, 2008).

$$X_w = \frac{V_m C K a_w}{(1 - K a_w)(1 + (C - 1) K a_w)} \quad (4)$$

X_w is the equilibrium moisture content (kg/kg dry basis), V_m is the water content of the monolayer (kg/kg dry basis), and C and K are the constants calculated by the model.

Mechanical parameters at different a_w levels were fit with the modified Peleg-Fermi model (Harris and Peleg, 1996) (Eq. 2) to describe different structural behavior of foodstuff:

$$Y(a_w) = \frac{Y_0 - Y_r}{1 + \exp\left(\frac{a_w - a_{wc}}{b}\right)} + Y_r \quad (5)$$

where $Y(a_w)$ is the estimated mechanical parameter as a function of water activity, Y_0 is the mechanical parameter measured in the dry state, a_{wc} is the critical water activity calculated by the model, it is the characteristic a_w where $Y_0/2$, Y_r is a term which accounts for the residual magnitude of Y at high value of a_w , and b is a constant calculated by the model indicates the rate of loss of texture parameters.

T_g and solid contents (water content expressed on dry basis) were related by means of the Gordon and Taylor equation able to describes the composition dependence of the transition temperature of amorphous components (Eq. 6) (Gordon and Taylor, 1952):

$$T_g = \frac{T_{gs} X_s + k T_{gw} X_w}{X_s + k X_w} \quad (6)$$

T_g , T_{gs} , and T_{gw} are the glass transition temperatures of the sample, solid and water, respectively; X_s and X_w are the solid and water content of sample, and k is an equation parameter. T_{gw} was taken as -135°C , according to literature data (Roos and Karel, 1991).

Permittivity for the whole frequency range was fitted with an adaptation of the modified Gompertz model (Eq. 7) and permittivity values for each dispersion were calculated by using Eqs. 8, 9, and 10, as previously reported by Traffano-Schiffo et al. (2018).

$$\epsilon' = \epsilon'_\infty + \sum_{n=1}^3 \frac{\Delta\epsilon'_n}{1 + e^{(\log^2 \omega - \log^2 \omega_n) \alpha_n}} \quad (7)$$

where ϵ' is the permittivity, ϵ'_∞ is the permittivity at high frequencies, $\Delta\epsilon'_n$ is the dielectric strength, \log is the decimal logarithm of the angular velocity (rad/s), $\log \omega_n$ is the decimal logarithm of the angular velocity for each dispersion n , and α_n are the dispersion slopes.

$$\epsilon'_\alpha = 10^{\left(\log \epsilon'_\infty + \Delta \log \epsilon'_\gamma + \Delta \log \epsilon'_\beta + \frac{\Delta \log \epsilon'_\alpha}{2} \right)} \quad (8)$$

$$\epsilon'_\beta = 10^{\left(\log \epsilon'_\infty + \Delta \log \epsilon'_\gamma + \frac{\Delta \log \epsilon'_\beta}{2} \right)} \quad (9)$$

$$\epsilon'_\gamma = 10^{\left(\log \epsilon'_\infty + \frac{\Delta \log \epsilon'_\gamma}{2} \right)} \quad (10)$$

α , β , and γ are the three dispersions.

The determination coefficient (R^2) and the associated root mean square error (RMSE) values were employed to evaluate all models' performances.

Significant differences between means of different physical properties affected by water activity levels were analyzed using ANOVA, the assumption of normality and homoscedasticity were previously verified by using Shapiro-Wilk and Levene tests, respectively (analysis of variance, p -level < 0.05, post-hoc Tukey, Statistica® 7.0 software-Stat-Soft Inc., USA).

Results and Discussion

The absorption isotherm of thawed eggplant was obtained by fitting water content and water activity for each hydration level with the GAB equation (Figure 2).

Fig. 2. Absorption isotherm with DES method and glass transition temperature fitted with linear model. Standard deviations were displayed for X_{dry} , water activity, and mean T_g values (V_m , monolayer value, C , constant of sorption heat, k constant, and standard error values of the parameters are in brackets p -level < 0.05)

A good coefficient of determination ($R^2 = 0.996$, $RMSE = 0.01$, p -level < 0.05) confirms the ability of the model to well described the moisture sorption profile. The three GAB parameters were typical of the food matrix where V_m is the monolayer moisture value, C is from 1 to 20, and K is from 0.7 to 1. The resultant shape of the sorption isotherm is type III, confirmed by the value of C parameter higher than 2 (Yanniotis, 2008). Food systems represented by III type are composed principally by small molecules with good water affinity and crystalline components in which moisture gain is very low up to the deliquescent point (generally around 0.8 a_w). The V_m , monolayer value, is 0.052 kg H₂O/kg solids with a correspondent a_w value of 0.297. The monolayer is also called unfreezable water, an important value contributing to the frozen product metastability definition (Rahman, 2009b). K is 0.963, describing structures with molecules tending to behave like a liquid, according to Quirijns et al. (2005).

Sorption profile was also assessed with dynamic method to define adsorption and desorption behavior (Figure 3).

Fig. 3 Ad-desorption isotherm of frozen eggplant obtained by DVS method (V_m , monolayer value, C , constant of sorption heat, k constant, p -level < 0.05)

The dynamic data were fitted with GAB model too, obtaining a good coefficient of determination 0.990 ($RMSE = 0.02$, p -level < 0.05). The sorption profile obtained gives additional information than that of DES reported, such as desorption profile. The dynamic DVS data compared to the static DES

data bring the same sorption profile (type III), but they are quite different (with different shapes). This behavior has been already observed in literature and it can be explained by differences in moisture sorption methods: static and dynamic, in which two intermolecular forces are prevalent. Processes involving electrostatic interactions are referred to as physical adsorption or physisorption. Physisorption of water is reversible and physically adsorbed water may be desorbed from a solid by increasing the temperature and/or reducing the vapor pressure (or relative humidity), and this is the process exploited by DVS, whereas the DES method involves chemical adsorption or chemisorption occurs, as well as reported by several authors (Gustavo-Barbosa-Canovas, 2020; Roudaut, 2020; Voelker et al., 2020) where the water molecules are linked by chemical bonding and hence chemisorption is irreversible.

Figure 3 shows the obtained results, in which the visible hysteresis clearly indicates amorphous material in the product. The amount of amorphous is solid in which water is moving into and it acts as plasticizer reducing T_g . The important point is that the T_g of an amorphous solid is in between the T_g of a dry solid and water, and the smaller solids have the lower T_g (Voelker et al., 2020). Accordingly, solids structures can be studied with their transition, particularly the T_g also considering the presence of multiple events due to different solid structures present in the matrix. In this way, DSC was conducted to estimate the thermal behavior of the eggplant equilibrated at different a_w . The thermal events evidenced in the equilibrated samples were shown in Figure 4.

Fig. 4 Example of thermograms (II cycle) of thawed eggplant evidencing first- (apparent T_m' , melting temperature) and second-order (T_g^{II} , apparent T_g^{III}) transition event

A clear first-order transition around 0 °C can be attributed to ice melting, but also different second-order transitions are detected. Two glass transition apparent T_g^{III} and T_g^{II} are observed in different temperature range and entities confirming the hypothesis of several solid structures. The detection of

two T_g was previously reported on fruit and vegetables (Iaccheri et al., 2020; Katekawa and Silva, 2008; Kurozawa et al., 2012; Telis and Sobral, 2002, 2001). Generally, the first T_g is the event of higher intensity, and it is mainly attributed to sugars, organic acids, and a small number of amino acids while the second T_g is a lower enthalpic step taking place on macromolecules, such as weight starch, fibers, and small amount of proteins (Fan & Roos, 2017). In addition, an energy release before glass transition event is observed and generally referred to molecular amorphous substance's rearrangement, recognized as β relaxation (Johari and Goldstein, 1971). According to Johari and Goldstein (1971), physical ageing is driven by polarization movements enhanced by free volume at particle interfaces observed as β relaxation. Considering frozen food storage, in which the matrix persists for a long time close to a glassy state, physical ageing could be an interesting phenomenon to follow to understand the origin of quality modifications.

Apparent T_g^{III} , T_g^{II} , area of ice melting averaged values (μ) and related standard deviation (σ), for different water activities, were reported in Table 1.

Table 1 Glass transition temperature ($^{\circ}\text{C}$) and area of ice melting (J/g) of ice fusion

Water activity	T_g^{III} ($^{\circ}\text{C}$)	T_g^{II} ($^{\circ}\text{C}$)	Area of ice melting (J/g)
0.11	-8.69 ^a (1.45)	53.38 ^a (1.38)	16.46 ^a (0.60)
0.22	-12.56 ^b (0.87)	52.22 ^a (2.18)	17.06 ^a (0.04)
0.33	-13.65 ^b (0.73)	42.73 ^b (1.22)	17.97 ^a (0.30)
0.43	-16.28 ^c (1.16)	42.39 ^b (1.30)	29.04 ^b (1.04)

0.57	17.76 ^c	(0.29)	38.97 ^c	(1.82)	30.41 ^b	(1.05)
0.75	20.74 ^d	(2.14)	36.80 ^{cd}	(2.01)	32.29 ^b	(1.83)
0.97	29.43 ^e	(0.19)	34.73 ^d	(0.35)	106.8 ^c	(3.03)

Averaged values and standard deviations in brackets. Different letters in the same column indicates statistical differences (p -level < 0.05)

Table 1 reports the effect of water in decreasing T_g values, both in the first and the second transition. As expected from sorption isotherms results, also T_g confirms structural differences among the product analyzed, and a different physical behavior is expected.

Area of ice melting revealed an underestimation of ice fusion, also previously reported and related to enthalpy of ice melting dependence on temperature. The enthalpy of ice is underestimated and measured below 0 °C (Bantle, 2017).

Furthermore, the area of ice melting increases as a function of water availability according to increase of ice crystals, as shown in Figure 5.

Fig. 5 Area of ice fusion (J/g) and apparent T_g^{III} trend for the different water activity levels

Area of ice melting and apparent T_g^{III} values were reported in the same figure to evidence that significative crystal growing corresponds to physical modification range and apparent T_g^{III} progressively decrease, confirming the importance of water glass/supercooled liquid dynamics. According to sorption isotherms, above 0.8 of the a_w system is affine to crystalline components and it overcomes the deliquescent point, also confirmed by the huge increase of ice area produces by the high mobility of water.

Mechanical properties were assessed in order to measure moisture influences on structures.

Mechanical modification as a function of hydration level were-is shown in Fig.ure 6.

Fig. 6 Mechanical properties at different water activity levels and maximum force (N , Y_{aw}) fitted with modified Fermi equation (Eq. 5, $p\text{-level} \leq 0.05$)

Maximum force at yield point (N) and yield modulus calculated as maximum force at yield point divided by the deformation at yield point (N/mm) shown a depletion of both parameters as a function of water activity raise evidencing the plasticizing effect of water as the main phenomena affecting mechanical properties. Considering the yield modulus, passing from water activity level, 0.11 to 0.22 this condition is not verified, showing a resistance to collapse, previously reported as anti-plasticizing effect of water (Castagnini et al., 2020; Job, 2018; Pittia and Sacchetti, 2008).

A good coefficient of determination was obtained by applying Fermi equation, R^2 0.984 (RMSE 3.9 N) used to describe the influence of water activity level on mechanical properties. The calculated a_{wc} and b parameters are 0.268 (± 0.01 , $p\text{-level} \leq 0.05$) and 0.10 (± 0.01 , $p\text{-level} \leq 0.05$), respectively. a_{wc} is the critical water activity calculated by the model and it is in the inflection point of the curve, where $Y_0/2$ as reported by literature (Arimi et al., 2010; Wollny and Peleg, 1994), while b is similar to those reported for food with restricted water availability, such as loss of crispness in cake bread (0.09–0.018) and cornflakes (0.11) (Arimi et al., 2010; Gondek et al., 2006).

Dielectric properties were also measured in a huge frequency range, from extremely low frequencies to microwaves. Permittivity (ϵ'), at different water activity levels on angular frequency (calculated on frequency, rad/s), is shown in Fig.ure 7.

Fig. 7 Dielectric spectrum from ELF to microwave evidencing the electromagnetic waveform, through the regions of different dispersion as dielectric theory defined. Note: values of permittivity < 1 can be attributed to experimental limits in the measurements for very low permittivity at high frequency

As can be possible to observe from Figure 7, permittivity (ϵ') changes as a function of equilibrium moisture content and related water activities. At high frequencies and low water content, permittivity reaches very low values (< 1) because of experimental limit. The decrease of ϵ' for all samples analyzed at high frequencies could be attributed to the inability of the dipoles to follow the electromagnetic field changes. Foods are hygroscopic materials in which the amount of water is the main parameter affecting dielectric properties, due to their polarization movement (Ryynänen, 1995). At higher frequencies, and after relaxation, the dipolar rotations are restricted, as the lowest ϵ' values describe, and the main contribution could be determined by solids components, as previously reported by literature (Bergo et al., 2012, 2013).

The modified Gompertz model adapted by Traffano-Schiffo et al. (2021) was applied to model the sigmoidal data. α , β , and γ dispersions are clearly visible and related R^2 , RMSE, and ϵ' were reported in Table 2.

Table 2. R^2 and RMSE of the modified Gompertz model (p -level < 0.05), α , β , and γ dispersion and related standard errors for the different water activity levels. Note: values < 1 from Eqs. 8, 9, and 10 (permittivity) can be attributed to the experimental limits in the measurements for very low permittivity

a_w		0.11	0.22	0.33	0.43	0.57	0.75	0.97
Modified Gompertz (Eq. 7)	R^2	0.993	0.977	0.993	0.965	0.970	0.929	0.985
	RMSE	0.192	0.342	0.384	0.474	0.218	0.737	0.410
(Eqs. 8, 9, 10)	α	2.7 (0.1)	2.9 (0.1)	3.1 (0.1)	3.3 (0.1)	3.5 (0.2)	4.3 (0.3)	6.4 (0.2)
	β	0.4 (0.0)	0.5 (0.0)	0.6 (0.0)	0.8 (0.1)	1.1 (0.0)	1.9 (0.1)	3.2 (0.1)
	γ	0.1 (0.1)	0.2 (0.1)	0.1 (0.2)	0.3 (0.2)	0.3 (0.1)	0.4 (0.2)	0.9 (0.4)

Commented [VJ3]: LE: Table 2 contains entries in italics but without significance. If deemed to have significance, please provide their significance in the form of a table footnote; otherwise, please set them upright.

Footnote: values < 1 are provide in italics.

Good coefficients of determination were obtained ranging from 0.929 to 0.993 confirming the modified Gompertz model able to describe the sigmoidal trend of the dielectric real part. As

previously mentioned, the experimental limit produces very low numerical values of permittivity (<1) for sample with low water content. Nevertheless, permittivity data allow to show a trend between relaxation and water availability. β_2 and γ relaxations, even if indicative, increase as a function of water availability, confirming the huge influence that this molecule acts in foodstuff.

The aforementioned analysis proof physical modifications and the importance of controlling them and estimates technological performances. Accordingly, the data herein presented are organized in a map, the state diagram (Fig. 8), able to depict several regions in which different physical structures are present.

Fig. 8 State diagram of frozen eggplant. T_{gw} , glass transition of water (black dot on y axes), T_{gs} glass transition of solid (black dot on the vertical line correspondent to 1 of solid content), T_{mw} melting of water (grey dot on y axes), T_{ms} , melting point of dry solid (grey dot on the vertical line correspondent to 1 of solid content), T_{mw}^I , end melting point of water (dark grey dot on y axes) and T_{ms}^I , end melting point of solid (dark grey dot on the vertical line correspondent to 1 of solid content)

It is immediate to figure out the stability of the product at a selected temperature and solid content. Starting from temperature ($^{\circ}\text{C}$) and solid content data (X_s), the state diagram was carried out. Glass transition of water (T_{gw} , -135°C literature data (Roos, 2012)) and glass transition of dried eggplant T_{gs} represent the ends of the T_g range. In the mid part, the glass transitions of the product at different solid contents are reported (black dots), and fitted with Gordon-Taylor equation (Eq. 6, black dashed line). The Gordon and Taylor model shows a good ability to interpolate data ($R^2 = 0.978$, $\text{RMSE} = 3.65^{\circ}\text{C}$, $p\text{-level} < 0.05$). The value of the calculated k parameter is 1.03, comparable to literature k values of foodstuff, from 0.20 to 3.88 for onion, 0.09 to 2.31 for grape, and 0.11 to 2.15 for strawberry (Sá and Sereno, 1994). Values between T_{mw}^I and T_m end represent the freezing curve of the product. B is the T_m at the end freezing point, and the straight vertical line from B to the T_g curve is the point. A is the unfreezeable water (the solid content extrapolated is 0.97 kg/kg dry basis). As expected,

expressed on wet basis, the unfreezeable water content is 0.03 kg/kg in accordance with 0.052 of absorption isotherms calculated V_m . Rahman reported that monolayer solid content values calculated by traditional sorption isotherms models, such as GAB, are higher than that of the unfreezeable water of state diagram, confirming the obtained results (Rahman, 2009b, 2009a). P is the line defining a typical product at the end of the production process, characterized by 0.84 kg/kg dry basis of solid content, with prevalence of supercooled liquid state, hence not totally stable at typical storage temperature of -26°C .

Conclusions

The frozen grilled eggplant examined resulted in thermodynamic non-equilibrium involving time-dependent structural properties changes, being water an important physical factor affecting: glass-liquid supercooled transition, and mechanical and dielectric properties.

Frozen eggplants, characterized by 0.84 kg/kg dry basis of solid content, seem to be not totally stable at the usual storage temperatures of -26°C , in accordance with the state diagrams presented. Unfreezeable water content was estimated at is 0.03 kg/kg from the state diagram, comparable with unfreezeable water of 0.052 calculated from absorption isotherms. Mechanical properties showed to well described structural modification as a function of water, in terms of plasticization and anti-plasticization effect. Thermal properties revealed different phase transitions T_g^{III} and T_g^{II} . Dielectric properties confirmed an energy availability of the food system for physical modifications, such as α , β , and γ relaxations. The α , β , and γ relaxations increase as a function of water availability, confirming the huge influence that water acts on the food system. The state diagram built based on the experimental data is useful to figure out all the possible physical structures in a wide temperature and solid content range that other techniques evidence.

In conclusion, the obtained results could be useful to improve the frozen food structure understanding and manage the storage stability of frozen eggplant. With further study, dielectric properties could also be exploited for the development of sensors able to monitor physical structures.

Author Contribution

Eleonora Iaccheri: conceptualization, data curation, formal analysis, investigation, methodology, writing—original draft, review, and editing; **Chiara Cevoli**: data curation, validation, review, and editing, supervision; **Luigi Ragni**: supervision, review, and editing; **Mareo Dalla Rosa**: supervision, review, and editing; **Angelo Fabbri**: supervision, review, and editing.

Data Availability

No data availability.

Declarations

Conflict of Interest

The authors declare no competing interests.

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