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New insights into the glass transition of dried fruits and vegetables and the effect of pulsed electric field treatment

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Innovative Food Science and Emerging Technologies

New insights into the glass transition of dried fruits and vegetables and the effect of pulsed electric field treatment

--Manuscript Draft--

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Keywords:	Pulsed electric fields; Glass transitions; Dried Fruits and vegetables; Air-drying; Water sorption isotherm
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Abstract:	<p>Pulsed Electric Field (PEF) pre-treatment has been recently studied to be applied to fresh apple, carrot, and potato tissue as novel food technology to improve the drying performances and the quality of final products. Although the modification induced by PEF and the related reactions have been studied as a function of many parameters and related to several quality aspects, no relationship has been investigated with glass transition temperature (T_g) modification of solid products. This study aims to evaluate the effect of PEF treatment on the T_g of different vegetable tissues. Obtained thermograms revealed the existence of two T_g (T_{Ilg}, and T_{IIg}), the first one mainly dependent from the presence of small molecules, such as sugars, organic acids and small amount of amino acids, while high molecular weight starch, fibers and small amount of proteins are associated to higher temperature values of T_{IIg}. PEF treated samples of dried apple, carrot, and potato compared to the untreated ones showed a T_{IIg} shift at 0.22 a w to a lower temperature, from 45.12 to 43.37, from 45.15 to 31.04 and from 90.23 to 85.81°C for apple, carrot and potato respectively. The T_{IIg} shift confirmed the mobility raise of the system promoted by PEF treatment, creating a less stable matrix.</p>
Response to Reviewers:	<p>Editor and Reviewer comments:</p> <p>Reviewer #1: The authors have substantially improved the manuscript and all the suggestions have been considered. However, I would be very careful with the statements about starch modification with such low intensities of PEF. I would suggest making a slight modification in line 274-278. --> In this direction, the effect of PEF on detected in our study was reasonably caused by changes in the interaction of starch with water and other surrounding molecules.</p> <p>According to reviewer suggestion, the sentence has been corrected (line 276-278 of the revised version)</p>

Facultad de Ciencias de la Alimentación
Universidad Nacional de Entre Ríos
Concordia, Entre Ríos, Argentina
Wednesday, July 8th, 2020

D. Knorr
Innovative Food Science and Emerging Technologies

Dear Editor:

Please find enclosed a manuscript entitled: "New insights into the glass transition of dried fruits and vegetables and effect of pulsed electric field treatment" which I am submitting for exclusive consideration of publication as a research article in the Journal of Food Engineering.

Since no relationship has been studied between the glass transition temperature modification on solid products pretreated with Pulsed Electric Fields, this article aims to investigate the effect of this innovative technology into different fruit and vegetable tissues (apple, carrot and potatoes) by mean of sorption isotherms and differential scanning calorimetry. The most important result is the finding of two glass transitions temperatures, the T_g^I is probably mainly dependent from the presence of sugars, organic acids and a low concentration of amino acids while high molecular weight starch, fibres and proteins are associated to the T_g^{II} . Another event visible for apple and carrot was an overshoot area around T_g , linked to molecular rearrangement, reasonably ascribable to β relaxation phenomenon.

Further experiments are necessary in order to deeply understand the different structure modification inducing glass transition and system mobility change, using optical techniques. β relaxation phenomenon has to be confirmed by dielectric techniques and mechanical measurements, to effort results and gives additional information on product metastability.

Thank you for your consideration of my work. Please address all correspondence concerning this manuscript to me at Facultad de Ciencias de la Alimentación, Universidad Nacional de Entre Ríos, and feel free to correspond with me by e-mail (jmcastagnini@gmail.com).

Sincerely,
Juan Manuel Castagnini

Editor and Reviewer comments:

Reviewer #1: The authors have substantially improved the manuscript and all the suggestions have been considered. However, I would be very careful with the statements about starch modification with such low intensities of PEF. I would suggest making a slight modification in line 274-278. --> In this direction, the effect of PEF on detected in our study was reasonably caused by changes in the interaction of starch with water and other surrounding molecules.

[According to reviewer suggestion, the sentence has been corrected \(line 276-278 of the revised version\)](#)

- PEF treated and dried apples, carrots and potatoes show two T_g (T_g^I and T_g^{II}).
- T_g^I is affected by water plasticization while T_g^{II} slide as a function of PEF voltage.
- T_g^{II} decrease with PEF enhance metastability of the food matrices analysed.

1 **New insights into the glass transition of dried fruits and vegetables and the effect of pulsed**
2 **electric field treatment**

3

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15 **Abstract**

16 Pulsed Electric Field (PEF) pre-treatment has been recently studied to be applied to fresh apple, carrot, and
17 potato tissue as novel food technology to improve the drying performances and the quality of final products.
18 Although the modification induced by PEF and the related reactions have been studied as a function of many
19 parameters and related to several quality aspects, no relationship has been investigated with glass transition
20 temperature (T_g) modification of solid products. This study aims to evaluate the effect of PEF treatment on the
21 T_g of different vegetable tissues. Obtained thermograms revealed the existence of two T_g (T_g^I , and T_g^{II}), the
22 first one mainly dependent from the presence of small molecules, such as sugars, organic acids and small
23 amount of amino acids, while high molecular weight starch, fibers and small amount of proteins are associated
24 to higher temperature values of T_g^{II} . PEF treated samples of dried apple, carrot, and potato compared to the
25 untreated ones showed a T_g^{II} shift at 0.22 a_w to a lower temperature, from 45.12 to 43.37, from 45.15 to 31.04

26 and from 90.23 to 85.81 °C for apple, carrot and potato respectively. The T_g^{II} shift confirmed the mobility
27 raise of the system promoted by PEF treatment, creating a less stable matrix.

28

29 **Keywords:** Pulsed electric fields; Glass transitions; Dried Fruits and vegetables; Air-drying; Water
30 sorption isotherm

31

32 **1. Introduction**

33 Nowadays, pulsed electric fields (PEF) treatment is of growing interest for application in food processing, for
34 microorganism inactivation in fluid products, as well as for the enhancement of mass transfer phenomena on
35 solid matrices subjected to further processing steps (e.g. dehydration) (Gongora-Nieto M. et al., 2010). When
36 PEF is applied to vegetable tissue, the cell membranes can be permeabilized or irreversibly damaged
37 (Weaver, 1994), with remarkable influence on mass transfer (Ade-Omowaye et al., 2002; Lebovka et al.,
38 2002). The increasing consumer demand for high-quality fruit and vegetable products has prompted to study
39 combined methods like PEF as a pre-treatment to dehydration, in order to obtain a stabilized product with high
40 nutritive and organoleptic quality, reducing energy consumption and minimizing thermal degradation (Ade-
41 Omowaye et al., 2002). The knowledge of the degree of the induced permeation on cellular food, through the
42 cell membrane electroporation of the tissue, and its impact on the further processing or storage steps is a key
43 factor for the final food quality, functionality, stability and safety (Ade-Omowaye et al., 2002). For plant tissue,
44 a considerable electroporation effect can be observed at moderate electric fields of 0.5-1 kV/cm, as previously
45 showed on carrots, potatoes and apples (Lebovka et al., 2007, 2002, 2001, 2000). PEF has been reported to
46 increase the permeability of plant cells, demonstrating its potentiality to reduce the drying time for potatoes
47 (Liu et al., 2018).

48 From a chemical point of view, the vegetable material subjected to PEF can be considered as a mixture of low
49 and high molecular weight solids and water. Solids in foods can exist in a crystalline state or is an amorphous
50 metastable one, the glassy state (Roos, 2010). Crystallization occurs in polymers that have a sufficiently
51 ordered chain structure. The occurrence of complete crystallization of polymers is unlikely, while the
52 crystallites are usually embedded in a residual amorphous matrix (Slade et al., 1993). A common feature of
53 amorphous materials is that they contain excess of free energy and entropy in comparison to their crystalline

54 counterparts at the same temperature and pressure conditions. The study of the relation between water content
55 and structural modifications in terms of physical events in complex foods is usually approached in terms of
56 water activity (a_w) and glass transition temperature (T_g) assessment (Moraga et al., 2011). Macroscopically,
57 temperature, time and liquid plasticizers have an enormous effect on the physical state and the quality of the
58 product, particularly above the T_g value. In this critical temperature range the coexistence of different structures
59 is present during the phase transition of a glassy solid structure into a rubbery one (Roos, 2010).

60 Gums, proteins, maltodextrins and all high molecular weight substances are characterized by a high T_g , while
61 sugar and acids and all low molecular weight substances are recognised for their high hygroscopicity and low
62 T_g (Djendoubi Mrad et al., 2013; Fan and Roos, 2017; Roos, 2010; Roos and Potes, 2015). Even if sugars are
63 in a crystalline form at room temperature, they are generally amorphous when in contact with water (Fan and
64 Roos, 2017; Roos and Karel, 1991). The amorphous sugars are in a high-energy state compared with the
65 corresponding crystalline form, being ‘metastable’ (Fan and Roos, 2017).

66 The molecular motion does not occur generally below the T_g , but it changes dramatically within the T_g range.
67 Despite this, also in the glassy state, substances retain some degree of molecular mobility that is detectable in
68 terms of mechanical relaxation. Changes that occur in the solid state are extremely slow, and they are often
69 referred to rotational movement of glassy structures characterized by Maxwell-Wagner polarization effect
70 (Perez-De Eulate and Cangialosi, 2018). Intact membrane interfaces can be determined based on impedance
71 measurements in a frequency range of the so-called β dispersion (Ade-Omowaye et al., 2002).

72 In amorphous material, plasticizers may be considered as compounds that increase the free volume and
73 therefore depress the T_g . The free volume of polymers has been discussed by (Sherrington, 2003 and Slade et
74 al., 1993). These authors hypothesized that the modification of T_g is caused by the change in availability of
75 ‘holes or places’ for molecular rearrangement (Sherrington, 2003). The material expansion occurs differently
76 in the glassy or rubbery states, whereas the free volume is constant at the glass transition (Sherrington, 2003).
77 Moreover, every phase transition is accompanied by volume modification and it can be observed also as
78 relaxation process (Roos, 2010).

79 Considering these findings, it is possible to hypothesize that the structural modification induced by PEF can
80 promote a T_g modification. Theoretically fruit and vegetable tissue pre-treated by PEF and then dehydrated
81 becomes glassy and not crystalline, with a consequent limited volume reduction (Figueiredo et al., 1999). Other

82 novel technologies have been combined with drying giving the possibility to relate the effect of the treatment
83 on the product structure (Aguilera et al., 2003). Chou and Chua (2001) presented methods to generate
84 ultrasound inducing significant changes in food that reduce external and internal mass transfer during drying.
85 Controlled ultrasound accelerates diffusion through membranes and changes in concentration and size of sugar
86 crystals. Osmotic dehydration of foodstuff generally applied to fruits is worth to study in the understanding
87 of the mass transport mechanisms. Fito (1994) reported the microstructural mechanism of vacuum pulsed
88 osmotic dehydration in which mass transfer of water and solute are related to pressure gradients in open pores.
89 A previous work of Castagnini et al. (2020) demonstrated that PEF and drying process enhance system mobility
90 in terms of water holding capacity and mechanical properties of apple tissue.
91 Although the effects induced by PEF and related reactions have been studied as a function of many parameters
92 and even related to several aspects, no studies have been performed in terms of induced T_g and system meta-
93 stability modifications.
94 To our knowledge, this pioneering study is the first investigation on the effect on T_g induced by PEF on
95 different vegetable tissues, along with other physical state modifications.

96

97 **2. Material and Methods**

98 **2.1 Material and samples preparation**

99 Potatoes (*Solanum tuberosum* var. Agata), apples (*Malus pumila* var. Granny Smith) and carrots (*Daucus*
100 *carota* var. Amsterdam) were purchased from the local market in Cesena, Italy. The water content for fresh
101 potato, apple and carrot was of 5.73 ± 0.64 , 9.66 ± 0.32 and 9.85 ± 0.44 kg water/kg dry weight respectively
102 (measured using vacuum oven at 70°C, according to AOAC official method n. 972.20). Cylindrical samples
103 (9 ± 0.1 mm diameter) were obtained using a manual cork borer and then reduced with a manual cutter to a
104 length of 10 ± 0.1 mm.

105

106 **2.2 Pulsed Electric Field (PEF) treatment**

107 Twenty cylindrical samples per treatment were placed in a 50 x 50 x 50 mm treatment chamber and filled up
108 with tap water with the ratio of 1:2 (10g sample/20g water) having a conductivity of $515 \pm 20 \mu\text{s cm}^{-1}$, as
109 measured by an electrical conductivity meter (mod. Basic 30, Crison Instrument, Spain). 100 near-rectangular

110 shaped pulses, with a fixed pulse width (10 μ s) and a pulse frequency of 100 Hz were applied in the present
111 work. Three electric field strength (0.5, 1 and 1.5 kV.cm⁻¹) were tested at 25° (chamber temperature was
112 monitored before and after treatment). A control sample not subjected to PEF was also prepared. Preliminary
113 experiment was performed to set the procedure according to previous research (Lebovka et al., 2007, 2002,
114 2001, 2000). The voltage and current were registered by using a digital oscilloscope (PicoScope 2204a, Pico
115 Technology, UK) connected to a personal computer.

116 The total treatment time was set to 1s, and the energy specific intake (W_T) was calculated 0.121, 0.483 and
117 1.086 kJ/kg for the samples treated at 0.5, 1 and 1.5 kV/cm respectively (Castagnini et al., 2020).

118 The W_T was calculated using the equation proposed by Raso et al. (2016) for rectangular pulse:

119

$$120 \quad W_T = \frac{n}{m} \int_0^{\infty} U(t) \cdot I(t) dt \quad \text{eq. 1}$$

121

122 n is the number of pulses applied, m is the mass of treated sample, U(t) is the voltage across the treatment
123 chamber, and I(t) is the current through the treatment chamber.

124

125 **2.3 Air-drying**

126 All the samples were air-dried at 60 °C in a tray drier with transverse airflow, air velocity 2 m/s and an air
127 renewal fee of 50%, until they reached a water activity typical of a vegetable dried product, of about 0.2 (mod.
128 CLW 750 TOP + Pol-Eko- Aparatura SP.J., Poland). After drying, the moisture content of samples treated and
129 untreated with PEF ranged for carrot between 0.26 to 0.13 kg water/kg dry weight, for apple between 0.48 to
130 0.13 kg water/kg dry weight and potato between 0.31-0.21 kg water/kg dry weight.

131 After dehydration, all the samples were put in hygrometers and conditioned, as reported in the following section.

132

133 **2.4 Sample conditioning, moisture, and water activity determination**

134 All the samples were conditioned for about 30 days into a desiccator containing phosphorus pentoxide (P₂O₅)
135 in order to dehydrate and stabilize the samples to the minimum water activity. Next, moisture equilibration
136 took place at 22 °C inside six sterilised desiccators (Mod. DES 2000), each containing saturated salt solution
137 in the range of 11-75% relative humidity. Each hydration experiment comprised a reference sample and
138 samples treated at a specific field strength (0.5, 1 and 1.5 kV.cm⁻¹).

139 Apple, carrot and potato samples inserted in open glass container were positioned in the hermetically closed
140 desiccators containing, on the bottom, the different saturated salt solutions at the required a_w (0.11 LiCl; 0.22
141 $\text{CH}_3\text{CO}_2\text{K}$; 0.33 MgCl_2 ; 0.44 K_2CO_3 ; 0.57 NaBr and 0.75 NaCl). Samples were periodically weighed after
142 closing until they reached a constant weight for three consecutive weightings ($\Delta w < 0.0005$ g).

143 The water activity of equilibrated sample was measured by a dewpoint hygrometer, mod. Aqualab (Decagon
144 Devices Inc., Pullman, WA) and the water content percentages are expressed on a dry matter basis.

145

146 **2.5 Differential scanning calorimetry (DSC)**

147 The glass transition temperature (T_g) was evaluated by a DSC mod. Q20 (TA Instrument, Germany). The DSC
148 was equipped with a low-temperature cooling unit mod. System90 (TA Instrument, Germany). Heat flow was
149 calibrated using the heat of fusion of indium (ΔH 28.71 J/g). For the calibration, the experimental heating rate
150 was applied under a dry nitrogen gas flux of 50 mL/min. Each sample (about 15 mg) was weighed in 50 μl
151 hermetic aluminium pans and then loaded onto the DSC instrument at room temperature, using an empty pan
152 of the same type for reference. Samples were equilibrated at -40°C for 10 min, and then two heat-cool cycles
153 were applied from -60°C to 80°C at $5^\circ\text{C}/\text{min}$. The T_g was evaluated by using the automatic tool of the Software
154 TA-Universal analyser (TA Instrument, Germany).

155

156 **2.6 Glass transition model**

157 The Gordon and Taylor model (eq. 1) was applied to T_g vs X_s and X_w experimental data according to the
158 following equation:

159

$$160 \quad T_g = \frac{T_{gs} X_s + k T_{gw} X_w}{X_s + k X_w} \quad (\text{eq.1})$$

161

162 Where T_g , T_{gs} and T_{gw} are the glass transition temperatures respectively of the sample, solid and water, X_s and
163 X_w are the percentage of solid and water content in the sample on wet basis, and k is an empirical parameter.

164 The T_{gw} was taken as -135°C , as average value of the literature data (from -125 to -150°C) (Roos, 1995).

165

166 **2.7 Statistical analysis**

167 The experimental data were fitted with eq.1 by nonlinear regression using the Marquardt algorithm (Marquardt,
168 1963) with MATLAB (MathWorks, Natick, USA). The algorithm calculates the set of parameters and their
169 95% confidence interval. The goodness of the fit was checked by the estimation of the determination
170 coefficient R^2 and the associated average RMSE values.

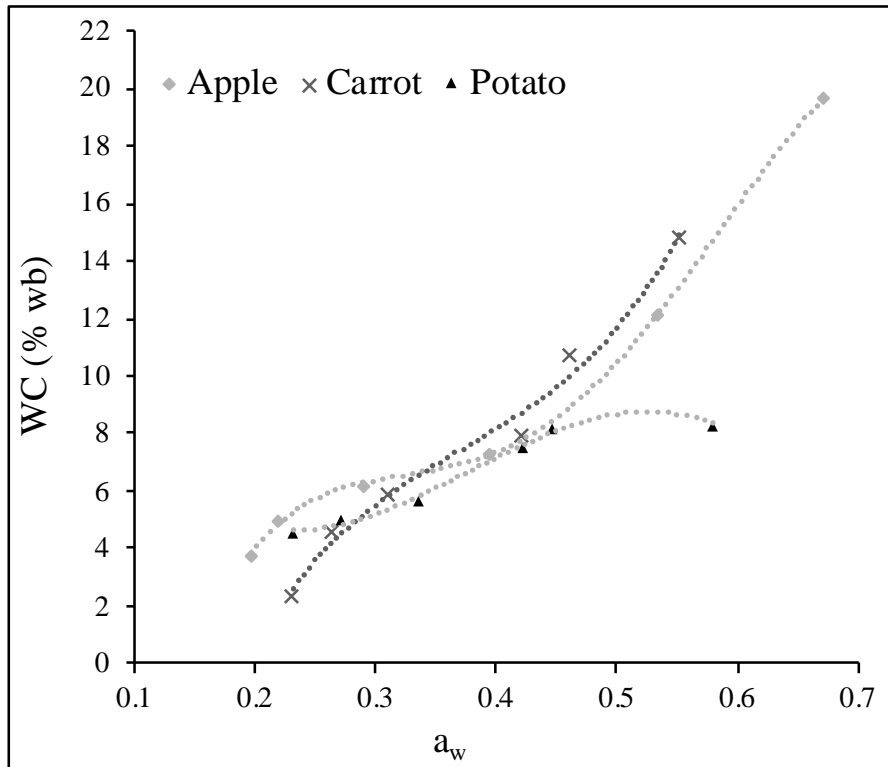
171 Within the same water activity level, significant differences between means of T_g^I and T_g^{II} affected by PEF
172 treatments were analysed by means of ANOVA (analysis of variance, p-level < 0.05, post-hoc Tukey, Stat
173 graphics Centurion XVI software).

174

175 **3. Results and discussion**

176 Average data of water content (WC) and water activity (a_w) for control samples are shown in figure 1. As
177 expected, the sorption behaviour for apple, carrot and potato was different. The shape of the moisture sorption
178 isotherms is characterised by the state of the system constituents. Comparing the three curves, a higher water
179 holding capacity for apple, than that of carrot and potato, is shown. The differences in crystal (e.g. starch,
180 sugars and proteins) orientation and hydration affect the shape of sorption isotherms, producing different
181 properties of the solid-state (Barbosa-Canovas et al., 2007).

182



183

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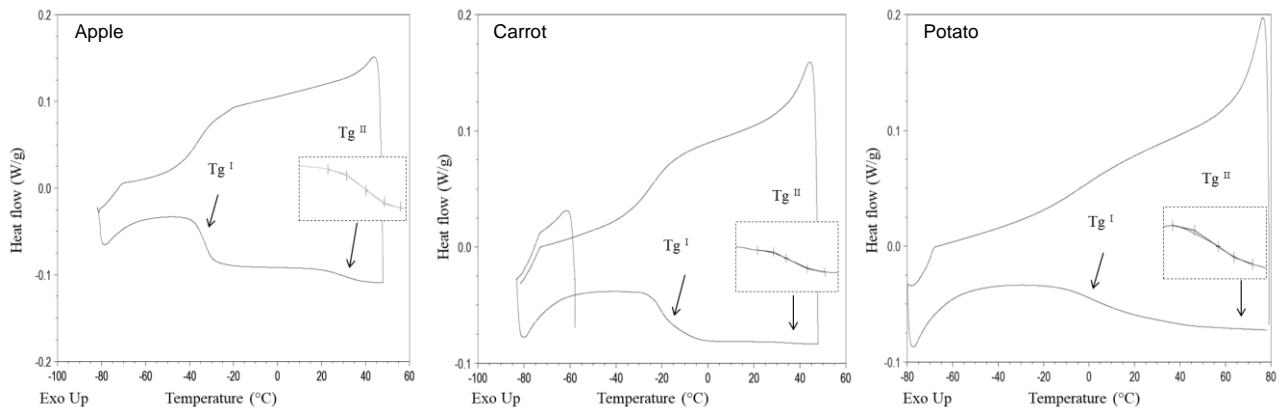
185 Figure 1. Water content (WC) expressed on wet basis and water activity (a_w) relations of control samples
 186 (apple; carrot; potato) at the different levels of hydration showing the sorption behaviour of the different
 187 vegetables.

188

189 In figure 2, as an example, the obtained thermograms for apple, carrot and potato samples at 0.57 a_w are
 190 reported, evidencing the presence of two glass transition temperature, T_g^I and T_g^{II} . In these food matrixes, the
 191 T_g^I is probably mainly dependent from the presence of sugars, organic acids and a small amount of amino acids
 192 while high molecular weight starch, fibres and small amount of proteins are associated to the T_g^{II} (Fan & Roos,
 193 2017). The presence of two T_g has been previously reported in literature also for different fruit and vegetable,
 194 such as dried papaya (Kurozawa et al., 2012), banana (Katekawa and Silva, 2008), plum skin (Telis et al.,
 195 2006) and tomato (Telis and Sobral, 2002). The resolution of T_g^{II} was lower than T_g^I in the thermograms since
 196 the accuracy of DSC to measure the T_g decrease as a less defined enthalpic change takes place in the
 197 macromolecules (Shrestha et al., 2007). It is worth noting that the T_g^{II} is a phenomenon of less intensity and
 198 slighter influenced by the hydration level than the T_g^I .

199 Phase transitions in low-moisture fruits and vegetables are dominated by sugars present in the material, within
 200 the same moisture content (Figueiredo et al., 1999; Roos, 2010), and it is recognized that the presence of long

201 chain polymers, like starch, produces a T_g increase (Caballero-Cerón et al., 2018). Thus, the higher T_g values
202 are attributable to high weight molecules. Confirming that, potato had the highest starch content than that of
203 carrot and apple and it presented the highest T_g values, maintaining constant a_w level. Accordingly, the effect
204 of PEF on T_g^{II} is mainly attributable to macromolecules interaction in the food matrix.
205

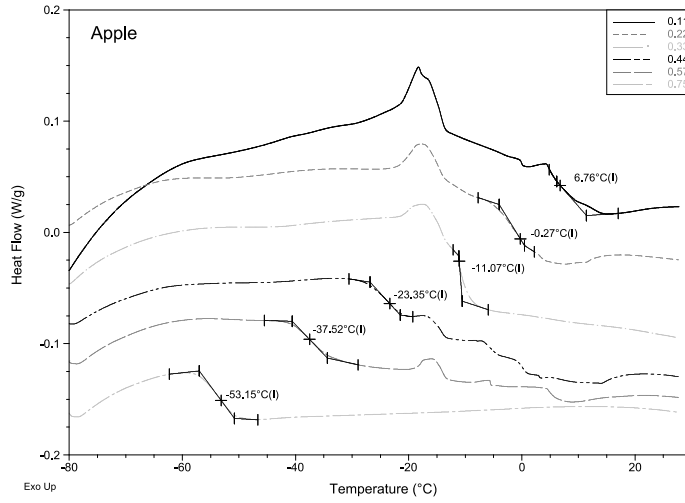


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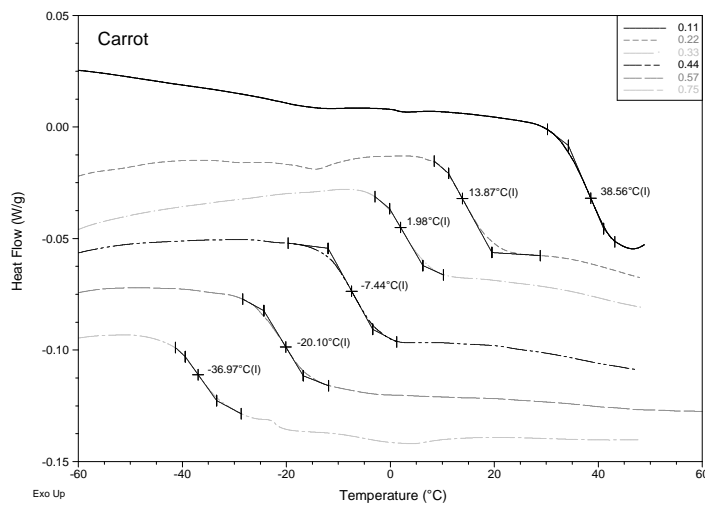
208 Figure 2. Thermograms of control samples at 0.57 a_w of apple, carrot and potato showing the two-glass
209 transition T_g^I and T_g^{II} .

211 In the thermograms of the differently hydrated samples of control apple (A), carrot (C) and potato (P) reported
212 in figure 3, the water content effect on T_g^I reduction is evident.

213



214



215

216

217 Figure 3. Thermograms of control apple, carrot, and potato samples at different hydration levels (a_w values)

218 where T_g^l values for each thermogram are reported.

219

220

221 As expected, conditioned samples show a hydration level decrease correspondent to a T_g^I raise, direct
 222 consequence of water unavailability. Water results mainly involved and compartmentalised among different
 223 structure (Roos, 2010). In table 1, the results of the obtained T_g^I and T_g^{II} values for control and PEF treated
 224 samples are reported.

225

226 Table 1. Glass transition temperature (T_g^I and T_g^{II}) values for control and PEF treated apple, carrot and potato
 227 samples at different water activity (a_w).

228

a_w	Voltage (kV)	Apple		Carrot		Potato	
		T_g^I	T_g^{II}	T_g^I	T_g^{II}	T_g^I	T_g^{II}
0.75	0	-53.79 ± 0.88 ^a	24.35 ± 0.12 ^c	-41.84 ± 0.22 ^a	28.65 ± 0.11 ^c	-8.52 ± 0.22 ^c	41.44 ± 0.19 ^c
	0.5	-52.98 ± 0.74 ^a	24.11 ± 0.37 ^{bc}	-41.85 ± 0.76 ^a	18.2 ± 0.82 ^b	-10.72 ± 0.34 ^b	42.69 ± 0.84 ^c
	1	-54.77 ± 0.45 ^a	22.73 ± 0.34 ^b	-37.37 ± 0.52 ^b	15.03 ± 0.43 ^a	-11.91 ± 0.56 ^b	38.37 ± 0.12 ^b
	1.5	-54.75 ± 0.43 ^a	21.11 ± 0.54 ^a	-39.14 ± 0.36 ^b	13.96 ± 0.51 ^a	-21.3 ± 0.11 ^a	34 ± 0.38 ^a
0.57	0	-35.37 ± 0.67 ^b	32.06 ± 0.64 ^c	-20.02 ± 0.67 ^b	38.49 ± 0.56 ^c	9.71 ± 0.23 ^a	60.95 ± 0.91 ^b
	0.5	-38.88 ± 0.5 ^a	30.03 ± 0.43 ^b	-14.17 ± 0.81 ^c	21.71 ± 0.09 ^b	12.03 ± 0.67 ^b	56.36 ± 0.95 ^{ab}
	1	-35.82 ± 0.67 ^b	28.1 ± 0.33 ^b	-22.43 ± 0.39 ^b	21.29 ± 0.32 ^b	11.75 ± 0.73 ^b	53.98 ± 0.66 ^{ab}
	1.5	-32.18 ± 0.68 ^c	11.32 ± 0.54 ^a	-30.2 ± 0.69 ^a	18.31 ± 0.21 ^a	9.12 ± 1.02 ^b	53.62 ± 0.99 ^a
0.44	0	-24.29 ± 0.14 ^a	38.7 ± 0.53 ^a	-11.33 ± 0.11 ^b	44.68 ± 0.35 ^d	16.56 ± 0.44 ^a	54.21 ± 0.17 ^c
	0.5	-24.34 ± 0.43 ^a	38.52 ± 0.62 ^a	-13.4 ± 0.65 ^a	41.29 ± 0.24 ^c	21.24 ± 0.23 ^b	47.67 ± 0.33 ^b
	1	-24.11 ± 0.25 ^a	37.78 ± 0.56 ^a	-12.38 ± 0.35 ^{ab}	38.36 ± 0.34 ^b	16.89 ± 0.34 ^a	42.07 ± 0.26 ^a
	1.5	-23.61 ± 0.91 ^a	37.09 ± 0.32 ^a	-12.4 ± 0.57 ^{ab}	37.23 ± 0.11 ^a	16.44 ± 0.47 ^a	42.43 ± 0.75 ^a
0.33	0	-12.07 ± 0.56 ^a	43.88 ± 0.26 ^c	-11.36 ± 0.41 ^a	44.39 ± 0.26 ^d	20.48 ± 0.55 ^a	55.3 ± 0.47 ^c
	0.5	-11.07 ± 0.68 ^{ab}	41.07 ± 0.25 ^b	1.24 ± 0.04 ^b	38.01 ± 0.51 ^c	21.13 ± 0.63 ^a	53.35 ± 0.5 ^c
	1	-10.22 ± 0.54 ^{ab}	40.91 ± 0.65 ^b	8.1 ± 0.91 ^c	35.73 ± 0.11 ^b	21.29 ± 0.45 ^a	47.25 ± 0.56 ^b
	1.5	-9.39 ± 0.45 ^b	36.93 ± 0.27 ^a	6.53 ± 0.34 ^c	33.53 ± 0.52 ^a	20.96 ± 0.41 ^a	43.29 ± 0.66 ^a
0.22	0	-0.8 ± 0.44 ^a	45.12 ± 0.52 ^a	13.36 ± 0.09 ^b	45.15 ± 0.56 ^c	43.36 ± 0.26 ^a	90.23 ± 0.71 ^b
	0.5	-0.87 ± 0.52 ^a	44.18 ± 0.76 ^a	6.75 ± 0.56 ^a	40.13 ± 0.77 ^b	50.01 ± 0.81 ^c	85.83 ± 0.28 ^a
	1	0.72 ± 0.16 ^a	43.45 ± 0.13 ^a	7.75 ± 0.44 ^a	37.64 ± 0.69 ^b	47.62 ± 0.33 ^b	86.12 ± 0.34 ^a
	1.5	-0.9 ± 0.46 ^a	43.37 ± 0.45 ^a	14.53 ± 0.51 ^b	31.04 ± 0.57 ^a	41.59 ± 0.56 ^a	85.81 ± 0.45 ^a
0.11	0	5.5 ± 0.56 ^a	51.1 ± 0.32 ^c	40.27 ± 0.63 ^d	64.89 ± 0.43 ^d	53.34 ± 0.58 ^b	86.69 ± 0.78 ^b
	0.5	11.2 ± 0.67 ^b	48.58 ± 0.37 ^b	32.87 ± 0.54 ^b	56.37 ± 0.22 ^c	49.17 ± 0.76 ^a	83.12 ± 0.63 ^a
	1	11.44 ± 0.77 ^b	47.18 ± 0.47 ^b	35.96 ± 0.22 ^c	51.59 ± 0.29 ^b	58.14 ± 0.21 ^c	83.06 ± 0.25 ^a
	1.5	9.35 ± 0.34 ^b	45.61 ± 0.41 ^a	15.03 ± 0.18 ^a	41.08 ± 0.37 ^a	51.14 ± 0.53 ^a	83.64 ± 0.01 ^a

229 Averaged values and ± standard deviation of three replicates. Statistics were carried out for each PEF treatment
 230 and matrix at the same water activity. Different letters in the same column indicates statistical differences.

231

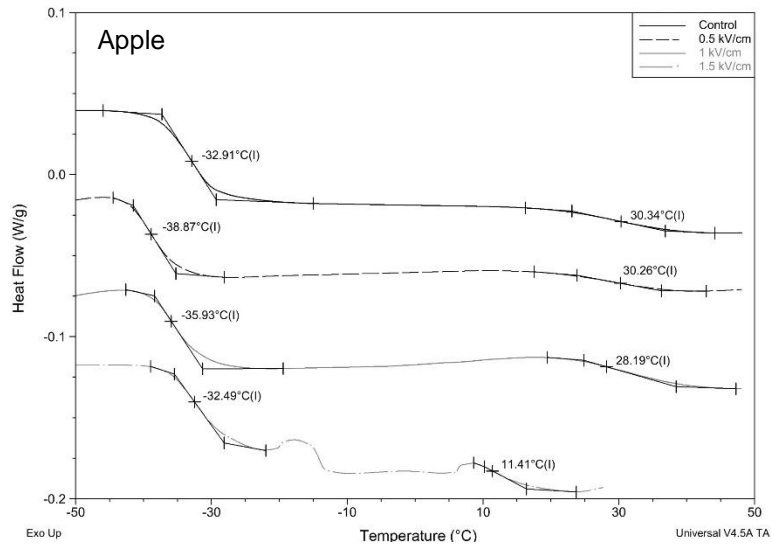
232 The plasticising effect of water on T_g^I was clearly observed for apple, carrot, and potato while less clear
233 dependence was related to PEF treatment. T_g^{II} shifted to lower temperatures showing system mobility
234 enhancement as a consequence of PEF treatment voltage increase, as also reported by Castagnini (et al. 2020).
235 T_g^{II} is mainly influenced by PEF treatment because related to big molecules, the main affected by PEF field
236 strength.

237 Free-volume is one of the most recognized theory to fundamental explain glass transition (Roos, 2010).
238 Accounting for free volume increase, also PEF treatment induces different long-lasting transition processes
239 inside the tissue, such as mass transfer, moisture and air redistribution (Labuza & Hyman, 1998), or also
240 resealing of cells (Knorr, 1999). The volume growth of the material occurs differently in the glassy and rubbery
241 states, whereas the free volume is constant at the glass transition (Sherrington, 2003). In this way, it can be
242 possible to hypothesise that PEF electroporation combined with thermal treatment improve glass transition
243 mechanisms allowed to attain additional volume for the investigated vegetables. The resulting change of
244 volume corresponds to structure modifications promotion, generating a high mobility degree and a consequent
245 T_g decrease.

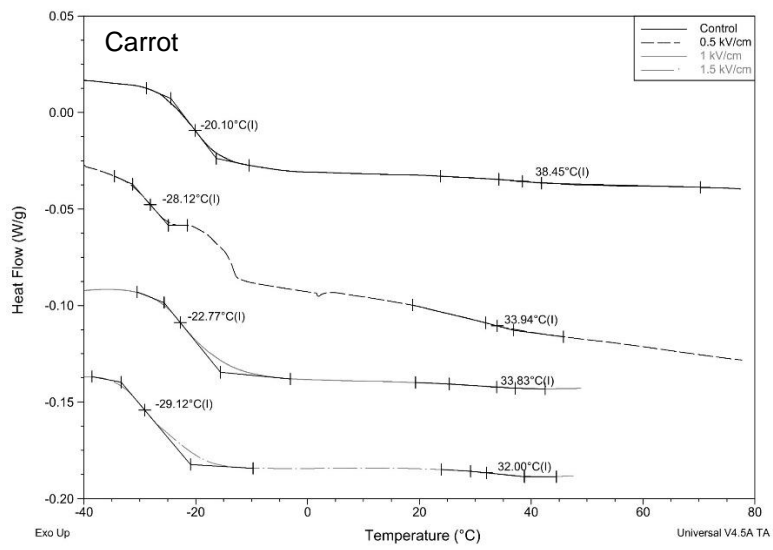
246 In Figure 4, the thermograms of control and PEF treated at the different strength field level (0.5, 1 and 1.5
247 kV/cm) apple, carrot and potato samples are reported.

248 The most appreciable change for apple is related to the second event, with about 21°C of glass transition
249 temperature shift. This shift can be attributable to high weight molecules, while T_g^I has a slighter temperature
250 shift compared to T_g^{II} , considering PEF treatment. Therefore, it can be assumed that on apple samples, the
251 increase of PEF level has a huge effect on macromolecules fraction, allowing a mobility raise due to their
252 structural rearrangement and modification of water interactions. Differently, carrot and potato samples
253 evidenced a glass transition shift of about 5-9°C and about 6-7°C for both T_g^I and T_g^{II} , respectively. As observed
254 from sorption isotherm, also T_g data evidence structural differences among the product analysed, and
255 consequently a different physical behaviour.

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259

260 Figure 4. T_g^I and T_g^{II} of apple, carrot and potato at equilibrated 0.57 a_w. Control and PEF treated samples
261 showing a T_g shift.

262

263

264 The T_g^I experimental data have been fitted with the Gordon Taylor model, and the estimated parameters are
265 reported in Table 2. The Gordon and Taylor model show a good fitting for apple and carrot samples,
266 considering the high coefficient of determination values (ranging from 0.866 to 0.997). The T_{gs} parameter
267 represents the glass transition temperature of the solids, confirming a higher value compared to the moisturised
268 samples. The k value is related to the thermal expansion coefficient and heat capacity of the components while
269 changing from the glassy to the liquid state during the glass transition (Couchman and Karasz, 1978). At the
270 applied energy levels, PEF treatment is non-destructive for the cell wall of considered plant materials
271 (Dellarosa et al., 2018). In these conditions, it enables effective and selective diffusion of low molecular weight
272 intracellular components even at low temperatures (Shrestha et al., 2007). Different authors (Han et al., 2009;
273 Wang et al., 2015) demonstrated that PEF treatment could destroy the crystalline region of corn and potatoes
274 starch resulting in the decrease of relative crystallinity. In these previous researches, higher field strengths
275 have been applied compared with our PEF conditions. However, according to Caballero-Cerón et al. (2018),
276 the T_g^{II} value in potato is mainly influenced by starch amount and conformation. **In this direction, the effect of**
277 **PEF on T_g^{II} detected in our study was reasonably caused by changes in the interaction of starch with water and**
278 **other surrounding molecules.**

279 After PEF treatment, during the heating process in DSC, water molecules could react more easily with the
280 molecules in the crystalline region (Liu et al., 2018). As a consequence, PEF treatment can lead to a molecular
281 rearrangement, decreasing the order of the structure (Liu et al., 2018). Pores induced by PEF produce a free
282 volume gain, this additional space given by treatment affects structure and allows reorganisation, as previously
283 reported also by Castagnini (et al. 2020).

284

285

286 Table 2. Results of fitting of T_g^1 experimental data with Gordon Taylor models: model parameters (p level <
 287 0.05), coefficient of determination (R^2) and root mean square error (RMSE).
 288

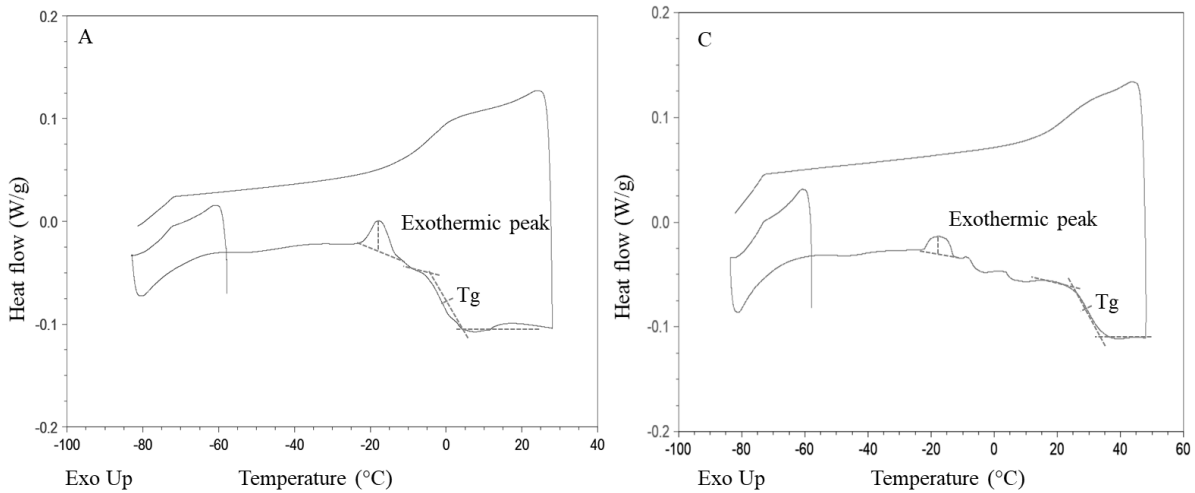
Samples	Gordon Taylor parameters	Control	0.5 kV	1 kV	1.5 kV
Apple	T_g	25.81 ± 7.88	37.80 ± 10.08	43.67 ± 6.45	37.58 ± 10.01
	K	4.46 ± 0.81	5.68 ± 1.12	7.11 ± 0.78	5.66 ± 1.07
	R²	0.953	0.951	0.985	0.946
	RMSE	4.40	4.75	2.46	4.71
Carrot	T_g	59.00 ± 2.09	65.78 ± 11.73	33.47 ± 10.47	58.08 ± 5.53
	K	5.87 ± 0.22	6.87 ± 1.17	3.66 ± 1.02	6.56 ± 0.58
	R²	0.997	0.963	0.866	0.988
	RMSE	1.18	4.34	5.89	2.13
Potato	T_g	169.56 ± 52.59	161.45 ± 38.69	179.50 ± 51.62	207.35 ± 85.44
	K	13.72 ± 5.02	12.83 ± 3.70	14.17 ± 4.84	17.11 ± 7.98
	R²	0.932	0.955	0.943	0.917
	RMSE	8.10	6.84	8.27	9.78

289

290

291 Finally, it is important to underline that DSC analyses of apple and carrot samples evidenced the presence of
 292 another thermal event, characterised by an exothermic peak at low hydration level (0.11_{a_w}), as shown in figure
 293 5.

294



295
 296 Figure 5. Apple and carrot control samples thermograms at the lowest a_w 0.11 shown an evident exothermic
 297 peak just before T_g region imputable to structural rearrangement before phase transition.
 298
 299

300 Often, an overshoot area around T_g is measured and linked to molecular rearrangement, referred to as β
 301 relaxation (Ade-Omowaye et al., 2002). According to Johari (1976), β relaxation is driven by diffusion of free
 302 volume at particles interfaces. Only low moisture hydration levels are characterized by relaxation enthalpy
 303 peak confirming to be a peculiar process of glassy structures. In this research, this phenomenon was nor
 304 quantified neither considered for PEF treated samples, but for the first time its presence is evidenced on apple
 305 and carrot tissues at low hydration levels. β relaxation phenomenon has to be confirmed by dielectric
 306 techniques, modulated DSC and mechanical measurements, to effort results in order to achieve additional
 307 information on product metastability.
 308
 309

310 Conclusions

311 Apple, carrot and potato samples were treated with Pulsed Electric Field at increasing filed strength and then
 312 dried. The Differential Scanning Calorimetric revealed the existence of two stepwise changes in the heat
 313 capacity at the phase transition, attributable to two T_g (T_g^I and T_g^{II}). Apple, carrot and potato PEF treated
 314 samples compared to the untreated ones showed a T_g shift to lower temperatures, confirming the mobility raise
 315 of the system after PEF treatment. The most appreciable change for apple was related to the second event, with

316 about 21°C of T_g^{II} shift, while carrot and potato were characterised by a on T_g^I shift of about 7-9°C and 2-7°C,
317 respectively.

318 Another event visible for apple and carrot was an overshoot area around T_g , linked to molecular rearrangement,
319 reasonably ascribable to β relaxation phenomenon.

320 Data shows some interesting aspects of structural modifications promoted by PEF pre-treatment to drying, also
321 opening a lot of question to be deeply understand in future researches. Some structural modification
322 phenomena promoted by the synergistic interactions of PEF and drying are here showed for the first time.

323 PEF treatment is often used to reduce drying time, but no information's are available on the structural changes
324 of the product as a consequence of the combination of these treatments. It is worth noting that the quality
325 characteristics of the dried product, particularly crispness, are strictly related to the relation between T_g and
326 storage temperature. Particularly, at critical water activity, when the product T_g corresponds to the product
327 temperature, a crispy dried vegetable product can become soft and plastic, losing its peculiar quality
328 parameters. The T_g^{II} can be used to define the final drying water activity, because PEF treatment, influencing
329 this value, can enhance mobility and compromise the stability of the system. In this way, T_g^{II} shift induced by
330 PEF has to be carefully considered in storage and packaging conditions management.

331

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335

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New insights into the glass transition of dried fruits and vegetables and effect of pulsed electric field treatment

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit Author Statement

All the authors contributed in the same way to the development of the research presented in this article.