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Abstract:	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 (Tg) modification of solid products. This study aims to evaluate the effect of PEF treatment on the Tg of different vegetable tissues. Obtained thermograms revealed the existence of two Tg (TIg , and TIIg), 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 TIIg . PEF treated samples of dried apple, carrot, and potato compared to the untreated ones showed a TIIg 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 TIIg shift confirmed the mobility raise of the system promoted by PEF treatment, creating a less stable matrix.
Response to Reviewers:	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)

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 Tg^{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 Tg^{II}. Another event visible for apple and carrot was an overshoot area around Tg, 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.

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Highlights

- 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 analised.

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

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Abstract

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_g^I, and T_g^{II}), 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_g^{II}. PEF treated samples of dried apple, carrot, and potato compared to the 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

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

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

1. Introduction

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

From a chemical point of view, the vegetable material subjected to PEF can be considered as a mixture of low and high molecular weight solids and water. Solids in foods can exist in a crystalline state or is an amorphous metastable one, the glassy state (Roos, 2010). Crystallization occurs in polymers that have a sufficiently ordered chain structure. The occurrence of complete crystallization of polymers is unlikely, while the crystallites are usually embedded in a residual amorphous matrix (Slade et al., 1993). A common feature of amorphous materials is that they contain excess of free energy and entropy in comparison to their crystalline counterparts at the same temperature and pressure conditions. The study of the relation between water content and structural modifications in terms of physical events in complex foods is usually approached in terms of water activity (a_w) and glass transition temperature (T_g) assessment (Moraga et al., 2011). Macroscopically, temperature, time and liquid plasticizers have an enormous effect on the physical state and the quality of the product, particularly above the T_g value. In this critical temperature range the coexistence of different structures is present during the phase transition of a glassy solid structure into a rubbery one (Roos, 2010).

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

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

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

Considering these findings, it is possible to hypothesize that the structural modification induced by PEF can promote a T_g modification. Theoretically fruit and vegetable tissue pre-treated by PEF and then dehydrated becomes glassy and not crystalline, with a consequent limited volume reduction (Figueiredo et al., 1999). Other novel technologies have been combined with drying giving the possibility to relate the effect of the treatment on the product structure (Aguilera et al., 2003). Chou and Chua (2001) presented methods to generate ultrasound inducing significant changes in food that reduce external and internal mass transfer during drying. Controlled ultrasound accelerates diffusion through membranes and changes in concentration and size of sugar crystals. Osmotic dehydration of foodstuff generally applied to fruits is worth to study in the understanding of the mass transport mechanisms. Fito (1994) reported the microstructural mechanism of vacuum pulsed osmotic dehydration in which mass transfer of water and solute are related to pressure gradients in open pores. A previous work of Castagnini et al. (2020) demonstrated that PEF and drying process enhance system mobility in terms of water holding capacity and mechanical properties of apple tissue.

Although the effects induced by PEF and related reactions have been studied as a function of many parameters and even related to several aspects, no studies have been performed in terms of induced T_g and system meta-stability modifications.

To our knowledge, this pioneering study is the first investigation on the effect on T_g induced by PEF on different vegetable tissues, along with other physical state modifications.

2.Material and Methods

2.1 Material and samples preparation

Potatoes (*Solanum tuberosum* var. Agata), apples (*Malus pumila* var. Granny Smith) and carrots (*Daucus carota* var. Amsterdam) were purchased from the local market in Cesena, Italy. The water content for fresh 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 (measured using vacuum oven at 70°C, according to AOAC official method n. 972.20). Cylindrical samples (9 ± 0.1 mm diameter) were obtained using a manual cork borer and then reduced with a manual cutter to a length of 10 ± 0.1 mm.

2.2 Pulsed Electric Field (PEF) treatment

Twenty cylindrical samples per treatment were placed in a 50 x 50 x 50 mm treatment chamber and filled up with tap water with the ratio of 1:2 (10g sample/20g water) having a conductivity of 515 ± 20 μs cm^{-1}, as measured by an electrical conductivity meter (mod. Basic 30, Crison Instrument, Spain). 100 near-rectangular shaped pulses, with a fixed pulse width (10 μs) and a pulse frequency of 100 Hz were applied in the present work. Three electric field strength (0.5, 1 and 1.5 kV.cm-1) were tested at 25º (chamber temperature was monitored before and after treatment). A control sample not subjected to PEF was also prepared. Preliminary experiment was performed to set the procedure according to previous research (Lebovka et al., 2007, 2002, 2001, 2000). The voltage and current were registered by using a digital oscilloscope (PicoScope 2204a, Pico Technology, UK) connected to a personal computer.

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

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

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

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

2.3 Air-drying

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

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

2.4 Sample conditioning, moisture, and water activity determination

All the samples were conditioned for about 30 days into a desiccator containing phosphorus pentoxide (P_2O_5) in order to dehydrate and stabilize the samples to the minimum water activity. Next, moisture equilibration took place at 22 °C inside six sterilised desiccators (Mod. DES 2000), each containing saturated salt solution in the range of 11-75% relative humidity. Each hydration experiment comprised a reference sample and samples treated at a specific field strength (0.5, 1 and 1.5 kV.cm^{-1}).

Apple, carrot and potato samples inserted in open glass container were positioned in the hermetically closed desiccators containing, on the bottom, the different saturated salt solutions at the required a_w (0.11 LiCl; 0.22 CH_3CO_2K; 0.33 $MgCl_2$; 0.44 K_2CO_3; 0.57 NaBr and 0.75 NaCl). Samples were periodically weighed after closing until they reached a constant weight for three consecutive weightings ($\Delta w < 0.0005$ g).

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

2.5 Differential scanning calorimetry (DSC)

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

2.6 Glass transition model

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

$$Tg = \frac{Tg_s\, X_s + k\, Tg_w\, X_w}{X_s + k\, X_w} \quad \text{(eq.1)}$$

Where T_g, T_{gs} and T_{gw} are the glass transition temperatures respectively of the sample, solid and water, X_s and X_w are the percentage of solid and water content in the sample on wet basis, and k is an empirical parameter. The T_{gw} was taken as -135°C, as average value of the literature data (from -125 to -150°C) (Roos, 1995).

2.7 Statistical analysis

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

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

3. Results and discussion

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

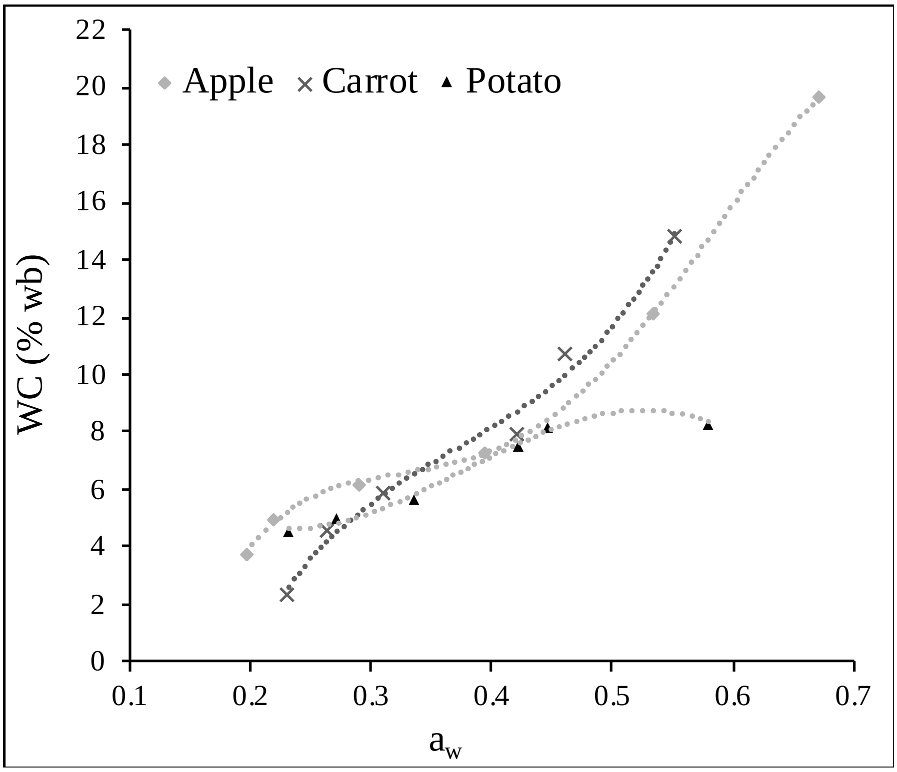

Figure 1. Water content (WC) expressed on wet basis and water activity (a_w) relations of control samples (apple; carrot; potato) at the different levels of hydration showing the sorption behaviour of the different vegetables.

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

Phase transitions in low-moisture fruits and vegetables are dominated by sugars present in the material, within the same moisture content (Figueiredo et al., 1999; Roos, 2010), and it is recognized that the presence of long chain polymers, like starch, produces a T_g increase (Caballero-Cerón et al., 2018). Thus, the higher Tg values are attributable to high weight molecules. Confirming that, potato had the highest starch content than that of carrot and apple and it presented the highest Tg values, maintaining constant a_w level. Accordingly, the effect of PEF on T_g^{II} is mainly attributable to macromolecules interaction in the food matrix.

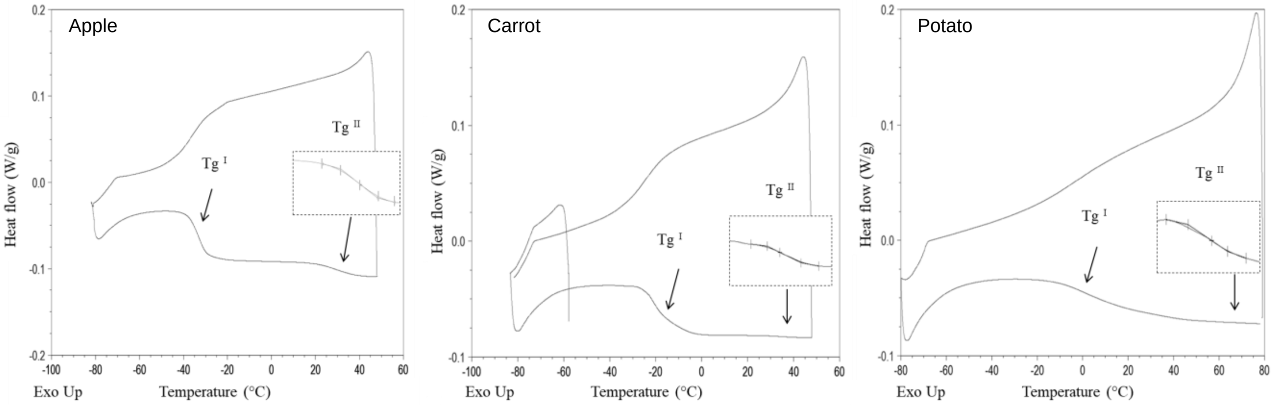

Figure 2. Thermograms of control samples at 0.57 a_w of apple, carrot and potato showing the two-glass transition T_g^I *and* T_g^{II}.

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

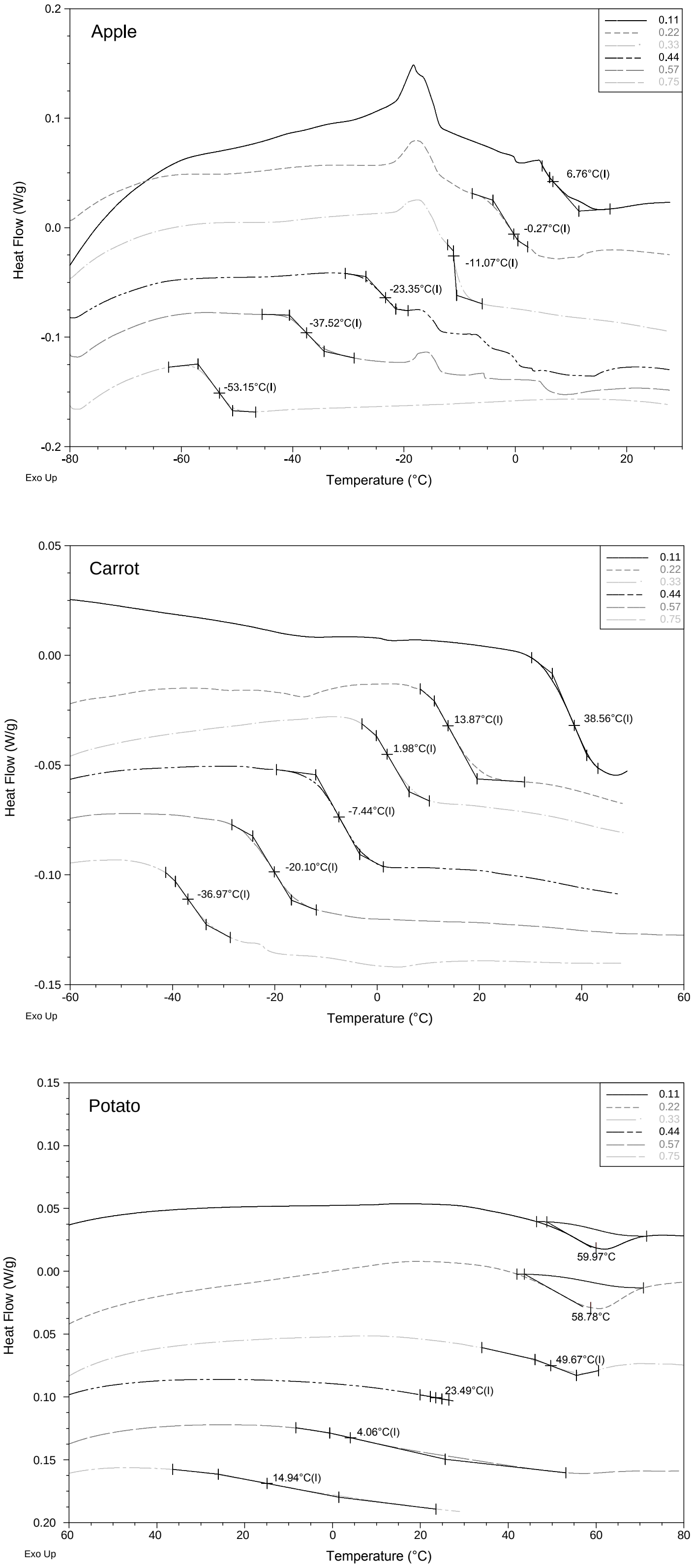

Figure 3. Thermograms of control apple, carrot, and potato samples at different hydration levels (a_w values) where Tg^I values for each thermogram are reported.

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

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

a_w	Voltage	Apple		Carrot		Potato	
	(kV)	Tg ^{I}	Tg ^{II}	Tg ^{I}	Tg ^{II}	Tg ^{I}	Tg ^{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}

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

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

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

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

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

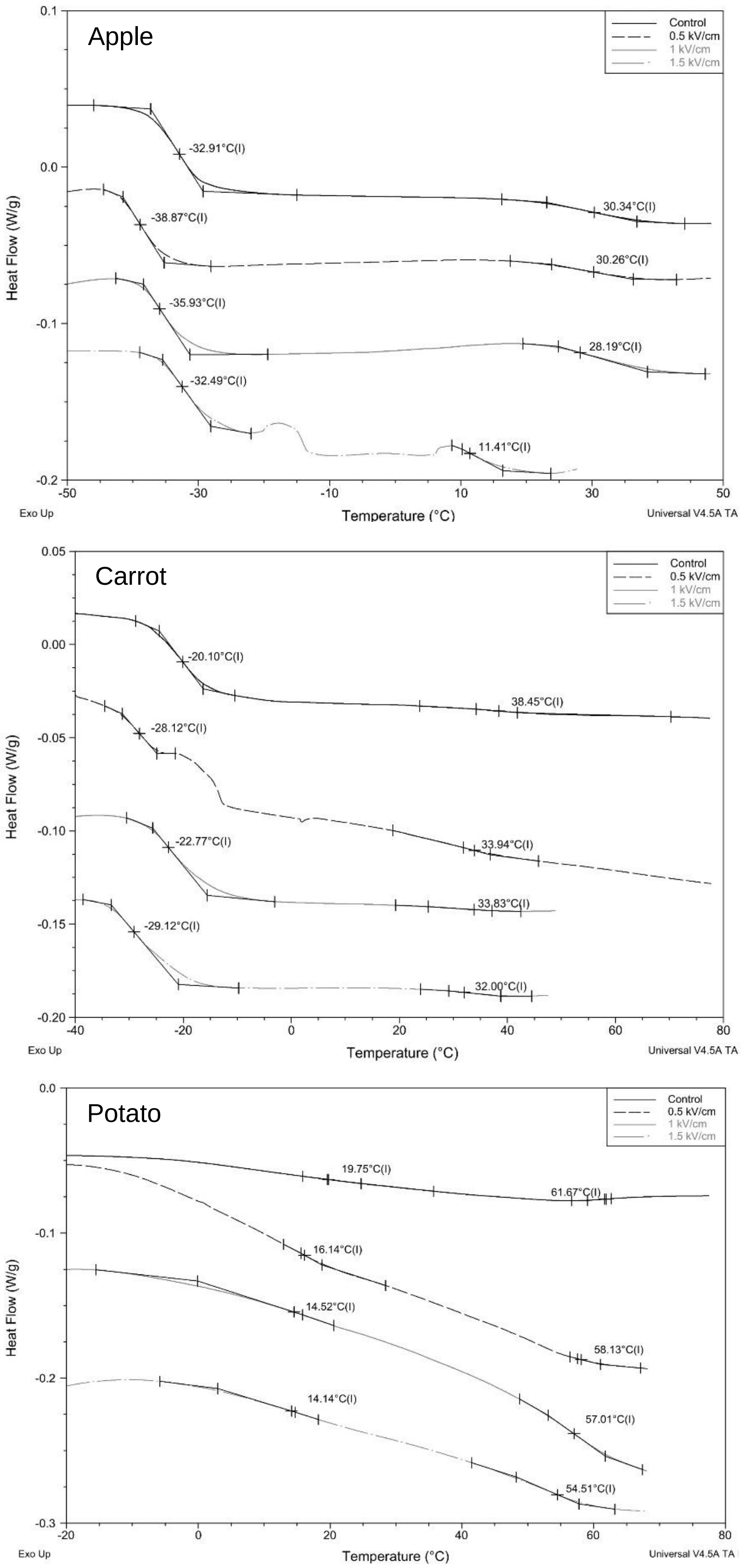

Figure 4. Tg [I] and Tg [II] of apple, carrot and potato at equilibrated 0.57 a_w. Control and PEF treated samples showing a Tg shift.

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

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

Table 2. Results of fitting of Tg^{I} experimental data with Gordon Taylor models: model parameters (p level< 0.05), coefficient of determination (R^2) and root mean square error (RMSE).

Samples	Gordon Taylor parameters	Control	0.5 kV	1 kV	1.5 kV
Apple	**Tg_s**	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
	R^2	0.953	0.951	0.985	0.946
	RMSE	4.40	4.75	2.46	4.71
Carrot	**Tg_s**	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
	R^2	0.997	0.963	0.866	0.988
	RMSE	1.18	4.34	5.89	2.13
Potato	**Tg_s**	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
	R^2	0.932	0.955	0.943	0.917
	RMSE	8.10	6.84	8.27	9.78

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

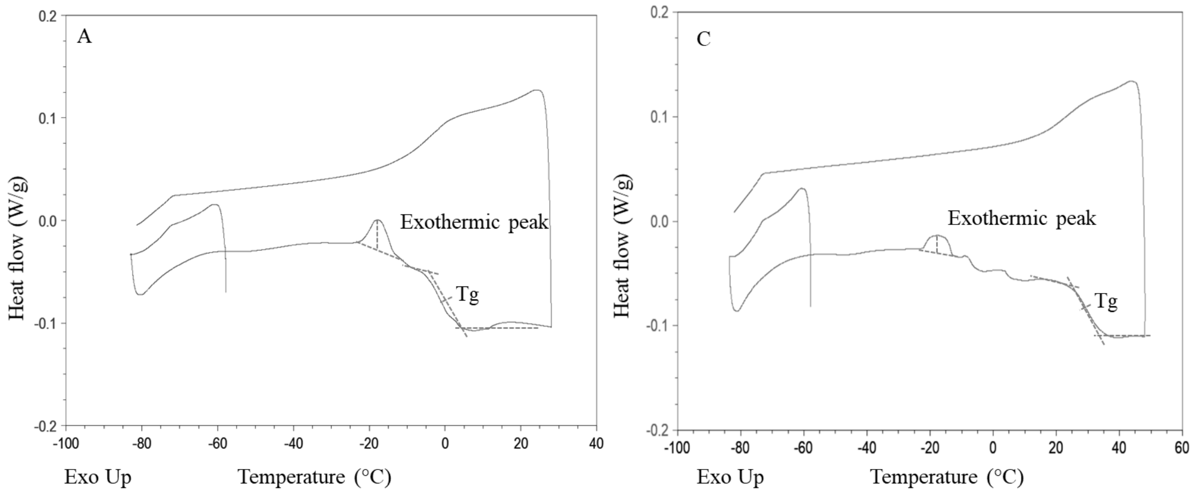

Figure 5. Apple and carrot control samples thermograms at the lowest a_w 0.11 shown an evident exothermic peak just before Tg region imputable to structural rearrangement before phase transition.

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

Conclusions

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

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

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

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

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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.