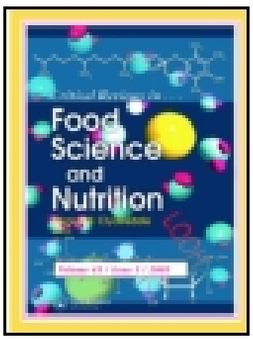

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Application of differential scanning calorimetry to estimate quality and nutritional properties of food products

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Abstract

Over the last years, both food researchers and food industry have shown an increased interest in finding techniques that can estimate the modifications in quality, nutritional and thermophysical properties of food products during processing and/or storage. For instance, differential scanning calorimetry (DSC) has attracted the interest of the scientific community because only a small amount of sample is needed for the analysis. Moreover, it does not require any specific sample preparation and it is a repeatable and reliable method. In addition, DSC methodology needs a short time of experiments compared to other techniques used for the same purpose. At this stage of investigation, there is a need to evaluate the commonly accepted and new emerging DSC applications in order to establish the optimum conditions of emerging processing. This paper reviews the current and new insights of DSC technique for the estimation of quality, nutritional and thermophysical properties of food products during conventional and emerging processing and/or subsequent storage. The estimation of the different properties in several food matrices after processing and/or storage is also discussed.

Keywords

Differential scanning calorimetry • Thermophysical properties • Nutritional modifications • Quality modifications • Emerging processing

Nomenclature

C	specific heat (J/g K)
E	electric field strength (V/cm)
ΔH	enthalpy (J/g)
ΔH_{gel}	enthalpy of gelatinization (J/g)
I	heat flow (mW/mg)
m	total mass of water in the sample (g)
m^u	mass of unfreezable (bound) water (g)
m^f	mass of freezable (free) water (g)
m_d	mass of dry matter in the sample (g)
m_r	mass of the reference (g)
m_s	mass of the sample (g)
R	fraction of unfreezable water, m^u/m
T	temperature (K)
T_e	temperature of endset (K)
T_g	glass transition temperature (K)

T_o temperature of onset (K)

T_p temperature of peak maximum (K)

W wet basis moisture content in the sample, m/m_s

W_d dry basis moisture content in the sample, m/m_d

W^u wet basis unfreezable moisture content in the sample, m^u/m_s

W_d^u dry basis unfreezable moisture content in the sample, m^u/m_d

Y_e deviation of DSC curves from the base lines for empty container

Y_r deviation of DSC curves from the base lines for container with the reference

Y_s deviation of DSC curves from the base lines for container with sample

Z electrical conductivity disintegration index

Greeks

σ electrical conductivity (S/cm)

Abbreviations

PEF pulsed electric field

WG water-glycerol sample

AWG PEF-treated and osmotically treated apple in water + glycerol mixture

INTRODUCTION

Thermophysical properties (specific heat, enthalpy, thermal conductivity, and thermal diffusivity, temperatures of phase transitions, etc.) of foods and beverages are very important to perform the various heat transfer calculations involved in the design of storage and refrigeration equipment as well as to estimate the processing time for refrigerating, freezing, heating, or drying foods and beverages.

Differential scanning calorimetry (DSC) has been traditionally used for measuring thermophysical properties of foods, biomaterials and pharmaceuticals (Gabbott, 2008; Kaletunç, 2009a). The numerical applications of this technique in food processing and/or storage were already demonstrated. The most important and comprehensive reviews on applications of DSC for investigation of food products were devoted to the examination of:

- Calorimetric methods as applied to food (Kaletunç, 2009b)
- Order-disorder transition processes of proteins, granular starch, gelling polysaccharides and state of the water in foodstuffs (Biliaderis, 1983);
- Glass transitions, enthalpy relaxation, their mathematical descriptions and models, and influence on food stability (Le Meste et al., 2002; Liu et al., 2006; Roos, 2010), state diagram of foods as a function of water or solids content and temperature (Rahman, 2006);

- Thermal properties of lipid polymorphs (Sato, 1987), oils and fats (Chiavaro et al., 2009), oxidation in vegetable oils (Tan and Man, 2002, 1999), phase transitions food emulsions (Coupland, 2002);

- Thermal denaturation of proteins and protein interactions in a real food systems (Grinberg et al., 2009), thermal denaturation of whey proteins (Mulvihill and Donovan, 1987), thermal behaviour of soybean proteins, effects of pH, ionic strength, calcium, and solvents on their thermal stability of soybean proteins, non-freezing water of soybean protein components (Huang et al. 2003), protein denaturation of meat biopolymers mixtures (Sarker et al., 2013);

- Gelatinization characteristics of starch and factors affecting gelatinization (time, temperature, effects of lipids, moisture content, nonionic constituents and electrolytes) (Lund and Lorenz, 1984), thermal properties and gelatinization of starches (Biliaderis, 1991; Singh et al., 2007), annealing of starches (Tester and Debon, 2000), thermal behaviours of starches (sago, potato, sweet potato, cassava, yam, and corn) (Elgadir et al., 2009), and hydrothermally-treated starches (Da Rosa Zavareze and Dias, 2011).

This review summarized the recent efforts to study thermal properties of food products by differential scanning calorimetry (DSC). The methodology of estimation of thermophysical properties (specific heat, enthalpy and temperatures of phase transitions, determination of states of the water) is briefly discussed. Applications of DSC to estimate the nutritional and quality modifications of foods, and the effects of different processing operations (high pressure, pulsed electric fields, ultrasound, microwaves) as well as benefits and limitations of DSC method are also analyzed.

METHODOLOGIES OF DSC

The different DSC methodologies can be used to measure the apparent specific heat, enthalpy of phase transitions (heat of fusion), phase transition temperatures and other characteristics of foods and biomaterials.

Specific heat

Specific heat measures the energy required to change the temperature of a sample by one degree. Therefore, the specific heat of foods and beverages can be used to calculate the heat load imposed on the refrigeration equipment by the cooling or freezing of foods and beverages. In unfrozen foods, specific heat becomes slightly lower as the temperature rises from 273 K to 293 K. For frozen foods, there is a large decrease in specific heat as the temperature decreases.

Different methods are proposed for the determination of the specific heat: 1) the method of mixtures (Suter et al., 1975), 2) the adiabatic calorimetry assay (Pham et al., 1994) and 3) the DSC technique (Schilling and Jeandupeux, 1995).

The method of mixtures is based on adding the heat exchange medium (usually water) at higher temperature than that used for the targeted material, whose specific heat will be determined (Suter et al., 1975). This procedure allows the direct contact between the food and the heat exchange medium, thus not being a reliable method for the determination of the specific heat of foodstuffs that contain soluble solids because it involves heating of solution for soluble chemical species in the materials.

Adiabatic calorimetry is a very precise technique and can be used to determine the latent heat at strong first order transitions (Pham et al., 1994). However, it usually lacks in achieving the resolution needed to characterize the temperature dependence of $C_p(T)$ close to the critical temperature for a second-order transition. In the adiabatic calorimeter, adequate resolution of sharp transitions is possible only at extremely slow scanning rates. The duration of the analysis is prohibitively long, large samples are required, and sample geometries must be carefully controlled. Adiabatic conditions become more and more difficult to be fulfilled when the temperature and dimensions of the sample decrease.

In the DSC method, the energy required to establish a zero temperature difference between a sample and a reference material is measured, and the specific heat of the sample is calculated from the energy requirement (Rodriguez et al., 1995).

The specific heat of different materials can be measured in the differential scanning calorimeter using step-by-step protocols for DSC (Hu et al., 2009; McHugh et al., 2010; Mykhailyk and Lebovka, 2014). Such protocol is schematically presented in Fig.1, which includes a comparison of the deviations of DSC-curves from the baseline during transition from the scanning regime to the isothermal regime, observed for different samples. The measurements were done using the empty container in the reference cell and the empty container (a), either the container filled with the reference substance of specific heat (b), either the container with the targeted investigated sample (c) in the operating cell. Samples were heated at 8 K/min in the temperature range of 283 to 363 K. The instrument was calibrated before measurement using Al_2O_3 as a specific heat standard reference material.

The specific heat *C* of the sample can be calculated from equation

$$C = C_r \left[\left(Y_s - Y_e \right) m_r \right] / \left[\left(Y_r - Y_e \right) m_s \right], \quad (1)$$

where C_r is the specific heat of the reference, m_s and m_r are the masses of the sample and reference, respectively, Y_e, Y_r and Y_s are the corresponding deviations of DSC curves from the base lines for the experiments a), b), and c).

Enthalpy of phase transitions

DSC is a useful tool to determine the enthalpy of phase transition. The change in a food's enthalpy can be used to estimate the energy that must be added or removed to observe a temperature change. Above the freezing point, enthalpy consists of sensible energy. Below the freezing point, enthalpy consists of both sensible and latent energy. The process of melting of free water registered on the DSC-curves like spread over time endothermic peak. Fusion or melting are the equilibrium processes so the peak area can be quantified (Gill et al., 2010).

During the phase transition, some changes of the specific heat of the sample are observed. In calorimetric measurements, the sum of all heat flows, *I*, resulting from the phase transition and changes in the specific heat are recorded. For the first order transition (melting) the changes of the specific heat in comparison with heat of the phase transition are rather low (Hohne et al., 2003). So, the area under the DSC peak can be used as a good approximation to estimate the enthalpy of phase transition ΔH (Hatakeyama et al., 2010). The absolute value of ΔH may be determined by using reference substances.

Figure 2 presents some examples of the DSC heating curves for the distilled water (W) and glycerol-water (G-W) mixtures (20% wt and 50% wt of G) (Parniakov et al., 2015). The DSC calibration curve for distilled water can be used for the determination of the reference value of ΔH. Figure 2 also demonstrated the presence of glass transition and low temperature crystallization at sub-zero temperatures for G-W mixture at noticeable concentration of glycerol, 50% wt.

Temperatures of phase transitions

Temperature, time and water content have an important influence on food quality. Therefore, the knowledge about phase transition is very important in order to control food processing and storage conditions. Changes in phase behavior of confectionary may occur during storage, usually with a negative effect on shelf-life (Hartel et al., 2011).

For the first order transition, the melting peak can be characterized by the onset, T_o, peak, T_p and endset T_e temperatures of transition (Fig. 2) (Parniakov et al., 2015). The values of T_o and T_e are determined by the points of intersection of the tangent of the heat curve to the baseline. Some authors recommend determining the melting point as the peak temperature, T_p. The value of T_p, is not highly dependent on the scanning speed as compared with the values of T_o and T_e.

For the glass transition, the noticeable changes in the heat capacity ΔC can be observed in the vicinity of glass transition temperature, T_g (Fig. 2).

States of the water: freezable and unfreezable water

The structure and properties of water (density, viscosity, specific heat, temperature of crystallization, solvent power, etc.) can be significantly changed due to the interactions between

a solid/water interface. The depth of these changes depends on the energy of the interactions of water with the surface. The freezable water is weakly bound to the food matrix, it has large mobility and it is able to freeze. On the other hand, in plant systems, due to the strong interactions of water with plant components, some parts of water become unfreezable (or bound). Water in porous systems can be bound in two ways: by lowering the energy state of the water in the system, and by reducing the rate of movement of water to interfaces.

Considerable research has been done on the water activity of foods and biological materials at above-freezing temperature, and important relationships have been established between this property and food stability (Barbosa-Cánovas et al., 2007). The concept of bound water is widely accepted and accounts for the possibility of structural changes in the regular structure of water in hydration shells (Galamba, 2013; Zheng Li and Lazaridis, 2007) and anomalous behaviour of the specific heat of water confined to pores (Nagoe et al., 2010). The concept of bound water (Wolfe et al., 2002) is of great significance with regard to texture, chemical deterioration and microbial stability of foods (Blanch et al., 2015). In unfrozen biological systems and foods, it is generally recognized that food stability is more closely related to water activity than total moisture content.

The melting DSC data can be easily used to estimate the mass of unfreezable, m^u, and freezable (free), m^f, water in samples. The melting peak in the water-containing sample (Fig. 2) reflects the presence of free water in it. The amount of free water m^f can be experimentally determined by the comparison of the melting enthalpies of a given sample ΔH_s and the reference sample ΔH_r (distilled water) (Fig. 2):

$$C = 8.37E-5\times T^2 - 1.60E-5\times T\times -1.54E-5\times -7.23E-3\times T - 1.68E-2\times +4.18 \quad (2)$$

where m_s is the total mass of the sample.

The amount of unfreezable (bound) water, m^u, can be calculated as

$$m^u = m - m^f \quad (3)$$

where m is the total mass of water in the sample ($m = m_s W_s$, m_s and W_s are the mass and the moisture content (wet basis moisture content) in the sample, respectively).

For example, the experimental data presented at the Fig. 2 evidence the values of ΔH_s decrease as the concentration of glycerol increase. It means that the water become more bound with a rising in the glycerol concentration (Parniakov et al., 2015). This fact can be explained by the ability of glycerol molecules to serve as "water blocker" (Weng et al., 2011b).

APPLICATION OF DSC IN STUDIES OF FOOD PRODUCTS

Specific heat

DSC method is widely used for the determination of the specific heat of food products. Many previous works were devoted to the study of different thermo-physical characteristics of apples and their dependences on the temperature and moisture content (Bozikova, 2009, 2007, 2006; Huang and Liu, 2009; Lisowa et al., 2003, 2002, 2000). Detailed investigations have shown that thermal conductivity *K*, thermal diffusivity *D*, temperature and moisture content have a significant influence on these parameters (Bozikova, 2009, 2007, 2006; Lisowa et al., 2003).

The rather important is the calculation of the specific heat of dry matter, C_d. For example, typically apples contain: water (85.56%), carbohydrates (11.42%), and unessential quantity of

fibres (2.4%), proteins (0.26%), fats (0.17%) and ashes (0.19%) (Srikiatden and Roberts, 2005). The temperature dependencies of specific heat C in different constituents of apples may be found (Chio and Okos, 2003; Lin et al., 2009).

DSC was used to determine the specific heat of apples in a wide interval of moisture contents (W = 0--0.9) and temperatures (T = 283--363 K) (Mykhailyk & Lebovka, 2014). The specific heat behavior can be related with the presence of the bound water. The excess of contribution of bound water to the specific heat (ΔC_b), was defined as:

$$\Delta C_b = C_h - C_d \quad (4)$$

where C_h is the specific heat of water plasticized apple and C_d is the specific heat of dry apple.

The examples of the temperature dependences of the specific heat components C_h, C_d and ΔC_b for apple are shown in Fig. 3. Note that contributions C_h, C_d grow and the excess contribution ΔC_b decreases as temperature increases. The observed decrease of ΔC_b with temperature evidences diminution of the excess contribution of bound water and may be explained by the damage of the specific structure of bound water. The excess values of ΔC_b were rather small (0.25-0.8 kJ kg^{-1} K^{-1}) in comparison to that of free H_2O ($C_w \approx 4.187$ kJ kg^{-1}K^{-1}).

The estimated amounts of bound water W_b were comparable with the monolayer moisture content in the apple (Mykhailyk & Lebovka, 2014).

DSC was used to determine the specific heat of different types of meat products and to correlate their modifications with changes in temperature (233--313 K) and moisture content (30--75%) (wet basis) (Hobani and Elansari, 2008). The developed multiple regression models with

high R^2 values used to correlate specific heat as a function of moisture content showed that the specific heat increased almost linearly more significantly with the increasing levels of moisture content than temperature. In another study, the apparent specific heat capacities of meat and meat products at temperatures ranging from 213 to 313 K, were evaluated using DSC technique (Tavman et al., 2007). Experimental data were compared with values calculated from different predictive models given in the literature. It was shown that developed models were found to be in good agreement with the experimental data.

The specific heat was measured for shucked oysters using DSC (Hu and Mallikarjunan, 2005). It was shown that *C* increased from 3.795 to 4.047 kJ/kg·K when temperature was increased from 283 to 323 K.

The thermo-physical properties of alginate-restructured sweet potato puree at freezing and refrigeration temperatures were determined using DSC (Fasina, 2005). In this study, it was postulated that during freezing (or melting), the specific heat increased from about 1.9 to 90 kJ/kg. After freezing, the specific heat of restructured and non-restructured sweet potato puree was 3.695 and 3.404 kJ/kg·K, respectively.

DSC technique was used to determine the heat capacity of fresh and osmotically dehydrated kiwifruit samples in the range from 233 K to 313 K (Tocci and Mascheroni, 2008). The specific heat of kiwifruit at equivalent temperatures was evaluated. The specific heats of kiwifruit were decreased when osmotic dehydration was increased at the fixed temperature.

The specific heat of corn under air drying and mechanical drying was measured in order to grasp heat and mass transfer during the process of conditioning, drying and cooling (Kang et al.,

2012). The apparent specific heat at different moisture content was determined in the temperature range from 323-353 K using DSC method. The results showed that the specific heat increased from 1.839 to 2.976 kJ/kg·K with an increase in temperature from 323 to 353 K and moisture content from 8% to 12%. The apparent specific heat of corn under air drying and mechanical drying increased while temperature rising, however, air drying corn had lower values. The specific heat of corn under high air drying tended to increase, with augmented drying temperature and moisture content. The specific heat displayed second order polynomial relationships with temperature and moisture content.

The heat capacity of several samples of hard cheese, semi-hard cheese and soft cheese was determined using conventional DSC and temperature modulated DSC. Additionally, the gross composition of the cheeses was analysed, and the equations from the literature were used to calculate the heat capacity. As the equation coefficients for particular constituents are responsible for the deviations in the calculated heat capacities, the differences between calculated and measured values increased when moisture content of the cheeses was decreased (Heidenreich et al., 2007).

DSC has been used to determine thermo-physical properties of liquid foods. For instance, (Roustapour and Gazor, 2013) analyzed the thermo-physical properties of pomegranate (*Punica granatum* L.) juice using DSC technique. The modifications of specific heat at different temperatures (from 298 to 243 K) and at three levels of soluble solid content (12, 40 and 65 °Brix) were measured. It was demonstrated that temperature and, especially, solid content had a significant influence in the thermo-physical properties of pomegranate juice. It was observed that

specific heat was reduced linearly when soluble solid content was increased (decreasing of water content) and temperature was decreased.

The apparent specific heats of different milks varying in fat mass contents from 0.1% to 35%, were determined in the temperature range 274--332 K by means of DSC (Hu et al., 2009). It was concluded that the apparent specific heat of milk was found to depend not only on the moisture level but also on the fat content, especially for milk having a high percentage of fat. It was proposed an empirical equation to correlate the results and predict the apparent specific heat of milk within the studied temperature and fat content ranges

$$C = 8.37E-5\times T^2 - 1.60E-5\times T\times -1.54E-5\times -7.23E-3\times T - 1.68E-2\times +4.18 \quad (5)$$

where X_f s mass fat content and T is temperature (°C).

DSC technique was applied to study the specific heat of coconut milk (Tansakul and Chaisawang, 2006). It was found that the specific heat of coconut milk samples with 20--35% of fat content at 333--353 K was in the range of 3.277--3.711 J/g·K. The empirical model for the dependence of the specific heat versus the fat content, X_f (g fat/g product) and temperature T in the temperature range of 333--353 K was obtained:

$$C = 4.018 - 2.553X_f + 0.003T \quad (6)$$

DSC was used to study the specific heat of chickpea flour, isolated starch, and isolated protein at different temperatures and bulk densities. Prediction models were obtained to determine the thermal properties of samples as a function of the experimental variables, and the authors

obtained that the specific heat had a linear relationship with the temperature and moisture content of the sample (Emami et al., 2007).

DSC was applied to evaluate the specific heat of cassava root, yam tuber and plantain fruit between 309 and 324 K in the moisture range 10--68%. It was found that heat capacity increased with moisture content and temperature, and varied from 1.64 to 3.26 kJ/kg·K (Njie et al., 1998).

DSC was used to obtain the specific heat of raw skipjack tuna (Zhang et al., 2001). The statistical analysis showed that there was no significant difference between the specific heat of loin meat (3.536 kJ/kg·K), red meat (3.505 kJ/kg·K), and viscera (2.263 kJ/kg·K). Likewise, there were significant differences between the backbone and loin meat, backbone and red meat, and backbone and viscera on specific heat values.

Thermal properties of tofu in the temperature range of 283--378 K and the moisture content range of 0.3--0.7 were estimated (Baik and Mittal, 2003). For this purpose, they developed simple empirical models as a function of the moisture content and temperature of the tofu. The main finding of this work is that they found a good agreement between perpendicular model and the thermal conductivity data when they used DSC, but not with parallel model.

State of the water

The state of the water in gelatine gel, the amount of freezing and non-freezing water in gelatine gels were evaluated by fusion enthalpy of DSC curves (Akiyama et al., 2007). Below water content of 40% (w/w), the whole amount of water was non-freezing water, whereas above water content of 40% (w/w) amount of water was presented by bound and free water. Moreover, the amount of freezing water was augmented according to an increase in water content. When the

water penetrates into the gelatin network, the water molecules form hydrogen bonds with hydrophilic groups inside the helical structure in gelatine gel. The water molecules inside the helical structure expand the structure outward, leading to an increase in the pore size. Three main stages of gelatin hydration were distinguished: (I) water bound by high-energy sorption centres; (II) structural water; (III) polymolecular layer water (Yakimets et al., 2005).

On the other hand, protein-water dynamics in mixtures of water and a globular protein, bovine serum albumin (BSA), was studied over wide ranges of composition, in the form of solutions or hydrated solid pellets (Panagopoulou et al., 2011). They reported about glass transition of the system for water contents higher than the critical water content corresponding to the formation of the first sorption layer of water molecules directly bound to primary hydration sites, namely 0.073 (grams of water per grams of dry protein). A strong plasticization of the glass transition, T_g, was observed using DSC technique for hydration levels lower than those necessary for crystallization of water during cooling, i.e. lower than about 0.3 (grams of water per grams of hydrated protein) followed by a stabilization of T_g at about 193 K for higher water contents. Moreover, DSC method was used for measuring the enthalpy of the product as a function of temperature during desorption of moist egg whites starting from various levels of the moisture content (Landfeld et al., 2006)

The polysaccharides are the most widely utilized food ingredients. The hydration of carbohydrates is a very important process in relation to their anti-freezing properties in food applications (Velickova et al., 2013) and their protecting effect for cryobiological applications (Chaytor et al., 2012). DSC was applied to examine the amounts of the different types of water

bound to pectin, a biomacromolecule that is used as gelling and stabilising agent in many food products (Einhorn-Stoll et al., 2012). They tested high-methoxylated citrus pectin and three modified samples, prepared by acidic and alkaline demethoxylation as well as amidation. The authors estimated that the water content of dried samples mainly depended on the molecular parameters, especially, the content of hydrophilic groups from galacturonic acid, which were increased by demethoxylation and amidation, as well as on monovalent cations of the pectin. They noted that small amorphous porous particles, whose polar groups were rapidly available without prior softening and swelling, accelerated water uptake. In another study, pectin hydration was examined (Iijima et al., 2000).

It was established that in pectin-water systems, the maximum temperature of endothermic peak (T_p) of pectin decreases with increasing of water content, W. When W_d was greater than 0.4 g/g, melting of free water and the glass transition of the pectin-water system were observed. The temperature of glass transition T_g of the pectin-water system decreased with increasing W in the bound water region. After reaching a minimum value, T_g slightly increased and approached a constant value. Other authors investigated the impact of freezing and thawing processes on gel structure, bound states, and mobility of water in wheat and potato starch gels (Freschi et al., 2014).

Thermal properties of Locust bean gum (LBG) hydrogels prepared by freezing and thawing method were investigated (Hatakeyama et al., 2005). Non-freezing water content calculated from the DSC melting peak of water in the gel indicates that the junction zone became dense with increasing freezing and thawing. It was shown that phase transition of water restraining by

curdlan suspension annealed at a temperature from 293 to 383 K. The melting temperature of water restrained by annealed curdlan discontinuously decreased at around 333 K, while the amount of bound water calculated from enthalpy of melting increased at 33 K, regardless of water content.

The corn starch-water system was characterized by DSC. Non-freezing water of starch augmented as moisture content increased and levelled off at 29.5% moisture content. The gelatinized cornstarch had less non-freezing water at low moisture compared to the native cornstarch. Water in the system was thought to exist in three forms: bound water, loosely bound water, and free water, all of which were moisture content dependent (Zhong and Sun, 2005). Common buckwheat (*Fagopyrum esculentum Moench*) flour is widely used in food products due to its desirable taste, textural structure and nutrients. The effect of water content varying from ≈20% to ≈80% on the thermal behavior of common buckwheat flour and its isolated starch was investigated using DSC at 313--378 K and at 213--433 K (Zhou et al., 2009). The authors established that the gelatinization temperature of buckwheat flour was between 333 K and 358 K and it decreased while the water content increased.

Hydration of cellulose, chitosan, schizophyllan, hyaluronan, and carboxymethyl cellulose was studied by DSC (Mlcoch & Kucerik, 2013). Comparison of determined hydration numbers showed that part of non-freezing water in hyaluronan is not bound to sorption sites but occurs presumably in small temporary pores. By contrast, water-soluble schizophyllan forms temporary pores as well but presumably with higher dimension and the non-freezing water is formed mostly by water molecules interacting with sorption sites.

Hydration of neutral galactomannans was experimentally evaluated (Naoi et al., 2002). In this study, water content ($W_d = m/m_d$) of these systems was varied from 0.2 to 3.6 g/g. The maximum amount of non-freezing water was observed at $W_d = 0.7$ g/g, where temperature of glass transition showed the lowest value. Phase transitions of sorbed water in Konjac mannan (KM)-water system with various water contents, W_c, were investigated using DSC. The equivalent value of non-freezing water per pyranose ring was 5.2 (mol/mol) (Prawitwong et al., 2007). In another study, Yudianti et al. (2009) evaluated the role of the water structure present in hydrogels from nutlets of three species of salvias, *S. miltiorrhiza* (SM), *S. sclarea* (SS) and *S. viridis* (SV) using DSC. The endothermic peaks related with melting of freezable free water at 278.9 K (SM), 275.8 K (SS) and 274.8 K (SV) in 1.0% hydrogels were observed. Absorbed water in the *Salvia* hydrogels was distributed as freezable (10.4-15.8%) and non-freezable (80.2-88.5%).

DSC was used to study complementary information on the mobility changes of water and solute in osmodehydrated pomegranate seeds (Bchir et al., 2009). The DSC analysis of water-hydrated *Nicotiana tabacum* leaves cell wall preparations distinguished two pools of water, freezable and non-freezable water. The amount of non-freezable water, which corresponded to strongly bound water, was higher in the transgenic line (64 versus 55%). DSC thermograms of the transgenic cell wall were displaced to lower temperatures, and this may be interpreted as the result of a stronger interaction between this freezable water and this wall. Water sorption and desorption isotherms, obtained at relative humidity ranging from 5 to 93%, demonstrated the presence of very strongly bound water in the transgenic cell walls that was absent in controls (Mercado et al., 2004).

Heats of phase transitions and hydration of sucrose solutions with different concentration have been investigated by DSC (Mykhailyk, 1998). It was shown that obtained DSC curves were a reflection of complex physical and chemical changes occurring in the sucrose-water solution at subzero temperatures. However, the melting of the ice crystals can be attributed to the equilibrium phase transition. The rest of the observed phenomena reflect the metastable state of the investigated solution.

Figure 4 shows the fraction of unfreezable water R versus concentration of water W in the glycerol (Parniakov et al., 2015) or sucrose solutions (Mykhailyk, 1998). For the water glycerol solutions, the water became totally unfreezable (i.e. $R \approx 1$), below the concentrations that approximately correspond to the eutectic concentration, $W \approx 33.3\%$ wt. However, for the water-sucrose solution $R = 1$ at $W = 24.87\%$ wt. It is interesting that for the water glycerol solution, the value of $R = 1$ corresponds to the following number of bound water molecules by one glycerol molecule (hydration number) $N_w/N_g = 3.07 \pm 0.25$. While for water-sucrose solutions hydration number is equal to $N_w/N_s = 5.5 \pm 0.5$, this behavior can be explained by formation of associate of sucrose molecules.

The state of water in the corn and potato starch suspensions with different water content was studied by means of DSC (Grabovska and Mykhailyk, 2008). The starch suspensions with different water content were prepared and maintained for 24 h at $T = 293$ K. Then swollen starch was hermetically sealed in aluminium container.

Figure 5 shows the DSC heating curves of cornstarch suspension with different water content. The changes in water content resulted in significant changes in the shape of the DSC curves and

in the content of bound water. Inset to Fig. 5 compares the fraction of unfreezable water R versus moisture content W in the corn and potato starch suspensions. The data evidence that at the same water content the cornstarch has a smaller quantity of bound water than the potato starch.

The impact of starch thermal treatment at different temperatures (T_T = 293-343 K) on the content of bound water in different starch-water systems was studied by DSC (Grabovska et al., 2011). The starch suspensions with W = 90% were prepared and maintained at room temperature T = 293K. The obtained suspensions were thermally treated at different temperatures (T = 293--343K) for 15 min. The obtained DSC heating curves for potato starch are presented in Fig. 6.

The melting started at $T \approx 262$ K. However, the most dramatic changes in heating flow were observed at $T \approx 273$ K. The thermal treatment in the vicinity temperature of starch gelatinization resulted in noticeable changes in the melting peak. The melting behaviour in the temperature range 262-273 K could reflect the melting of water in the pores of starch granules. Inset to Fig. 6 presents unfreezable moisture contents (dry basis), W^u_d ($= m^u/m_d$), versus the temperature of thermal treatment, T_T, for potato and cornstarches. At room temperatures, the bound water content in potato starch was ≈ by 1.3 times higher than in cornstarch. Below the temperature of starch gelatinization the values of W^u_d near linearly increased with the temperature increase. However, the gelatinization processes at T>330 K resulted in a noticeable increase in the unfreezable (bound) water contents.

The unfreezable water content was estimated for fresh sugar beet and those after storage at different moisture content (Mykhailyk and Davydova, 2000). In this study two type of sugar beet were used. First one was fresh but second was after long lasting storage. The storage of sugar

beet was done for 8 months in a chamber at T = 279 K, W_{air} = 85%. The sugar beet after storage had significantly lower unfreezable moisture contents, W^u_d, compare to fresh tissue (Fig. 7). The overall decrease in the quantity of unfreezable water in the sugar beet after storage could reflect the destruction of the sugar beet tissue. However, the decomposition of sucrose during storage can also explain the small quantity of bound water in old sugar beet. It was concluded that dry basis unfreezable moisture contents, W^u_d, decreased during all drying process.

The state of water in dehydrated apple and potato tissues was investigated using DSC technique (Snejkin et al., 2011). Figure 8 compares the DSC heating flow curves for these products at different moisture contents (dry basis), W_d (= m/m_d). The moisture contents influenced noticeably the melting temperature for apple. However, for potato, the positions of the melting peaks were approximately the same at different moisture contents. These differences were explained by the differences in carbohydrate composition of these plant tissues. Inset to Fig. 8 shows unfreezable (bound) water content W_d^u versus the total water W_d (= m/m_d) (both on dry basis) for apple and potato. The dependences $W_d^u(W_d)$ were nearly linear and the bound water contents for apple was higher than those for potato.

The thermal analysis was used for the determination of the state of water in the polysaccharide that was produced by red microalgae *Porphyridium* sp.(Ginzberg et al., 2008). DSC analysis of the water adsorbed on the charged groups of the polysaccharide showed that drying at higher temperatures increased the bound water content due to dissociation of the polymer chains.

The changes of tightly and loosely bound water relative content in bread were studied (Kerch et al., 2012a). It was shown that the combination of chitosan with ascorbic acid changes water redistribution between starch and gluten and in such a way could be related to bread quality and sensory properties. The decrease of the water vaporization temperatures, melting temperatures and enthalpies in fresh bread containing chitosan were detected when ascorbic acid was added in combination with chitosan. The decrease of melting peak temperature has been attributed to the increase of interaction of loosely bound water while the decrease of vaporization peak temperature is mainly due to the decrease in the interaction of tightly bound water with bread components as a result of ascorbic acid addition. Freezable water amount and total water amount in crumb decrease more rapidly during first stage of staling and more slowly at the second stage of staling in the bread nutritionally fortified with chitosan (Kerch et al., 2012b).

The interesting example of the application of DSC method is to investigate the influence of the mixing mode on the properties of ethanol-water solutions (Mykhailyk, 2010). The solutions were prepared by adding water to ethanol (W→E) or ethanol to water (E→W). The DSC heating curves for different concentrations of water (vol. %) are presented in Fig. 9.

The peak of melting temperature T_p and the amount of free water decreased as the concentration of ethanol increased. The melting peaks of different hydrates with composition of E·4.75W, E·3W and E·2W were observed at T≈202 K, T≈204 K and T≈212 K, respectively. The single melting peaks of hydrates E·4.75W and E·2W were observed for small (<40% vol., Fig. 9a) or large (>50% vol., Fig. 9b) ethanol concentrations, respectively. However, in the intermediate region of concentration, between 60% and 50% vol., the two separate peaks can be

observed simultaneously. For example, at ethanol concentration of 40.8 vol.% the two melting peaks were registered in W→E solution and one melting peak was registered in E→W solution (Fig. 9a).

DSC measurement was applied to characterize the effects of osmotic dehydration of apple in concentrated sucrose solutions (Cornillon, 2000). The freezing point of the dehydrated fruits and the unfrozen water fractions were estimated from the melting endotherms. The nuclear magnetic resonance (NMR) measurements were also used and they showed a reduction of mobility of water molecules in the cells due to greater sucrose concentration and interaction.

The status of water in green and roasted coffee beans was studied using sorption isotherms, DSC, and NMR techniques (Rocculi et al., 2011). The joint use of these techniques permitted the identification of different types of water causing hardening/stiffness, plasticization, and softening effects. DSC measurements were used to elucidate the effect of osmotic dehydration on two kiwifruit species, *A. deliciosa and A. chinensis* (Tylewicz et al., 2011). During the osmotic treatment of sucrose solutions, the initial freezing temperature and the freezable water content decreased with increasing of the treatment time and the temperature of osmotic treatment. The similar tendencies were observed for both kiwifruit species. NMR measurements were used to obtain a complementary view concerning the effects of osmotic dehydration. Compared to the DSC, analysis via NMR gives additional details about embedded water in contained and other different food compartments. It was concluded that DSC method could give better analysis of macroscopic water changes of vegetable tissue, whereas NMR method is better suitable for analysis of the microscopic modifications of cell compartment.

Freezing-melting thermal hysteresis

The thermal hysteresis assay measures the difference in temperature between freezing and melting points of a solution in the presence of ice structuring proteins (Zachariassen and Kristiansen, 2000). Thermal hysteresis *in vitro* is measured by using a nanoliter osmometer. In this assay, a very low amount (submicroliter volumes) of ice structuring proteins solution is injected in a cylindrical well drilled in a metal plate which has been filled already with an oil droplet (to hold the surface tension) in a cold stage. The chamber temperature is controlled by a Peltier device and the sample is viewed under a microscope. The growth and shrinking of the ice crystals during the measurement can be recorded by video photography and studied (Fletcher et al., 2001).

DSC method to measure the thermal hysteresis activity of fish antifreezing proteins (AFP) was proposed (Hansen and Baust, 1988). In this method, AFP containing samples were suspended in oil in the DSC pan. This assay brought a high level of accuracy into thermal hysteresis measurements since DSC is able to record melting and freezing temperature of samples, meticulously. One of the limitations of the proposed method was using an oil environment, which is not only very different than the natural condition but interferes with AFP, thus affecting the results. Thermal hysteresis of AFPs was assayed using DSC in aqueous solution directly obtained from plants (Lu et al., 2002), on the basis of Hansen and Baust's method. This assay provided a more repeatable and reliable tool for studying thermal hysteresis of plant AFPs. Data obtained from other authors showed consistency and accuracy of this technique (Hassas-Roudsari and Goff, 2012).

Glass transitions

Many food materials exist in a disordered amorphous solid state due to processing. Therefore, understanding the concept of amorphous state, phase transition such as glass transition, and the related phenomena, including enthalpy relaxation, is of paramount importance to both food scientists and food researchers (Liu et al., 2006).

Over the last years, DSC has been used to evaluate phase/state transitions in model systems of amorphous lactose and lactose co-lyophilized with trehalose (Mazzobre et al., 2001). For instance, DSC technique allows to glass transition temperatures and enthalpies of crystallization for these systems, thus facilitating the development of models to predict their behaviors. DSC can be used to determine the compatibility between sugars (Mazzobre et al., 2001). The thermograms of low moisture lactose-trehalose mixtures showed only one glass transition temperature, which indicates the compatibility between lactose and trehalose. A delay of lactose crystallization in isothermal runs was observed when trehalose concentration was augmented in the mixture. Moreover, a delay of crystallization temperature in dynamic experiments was observed. In addition, the presence of trehalose delayed lactose crystallization, without affecting the glass transition temperatures. This fact could be attributed to several factors such as thermodynamic, geometric and kinetics, which can modify the molecular environment in the combined systems, affecting nucleation and/or crystal growth.

Glass transition temperatures, T_g, of amorphous sugar samples, prepared from 0% to 14% moisture content were determined during both cooling and heating using DSC (Ruiz-Cabrera and Schmidt, 2015). For this purpose, the DSC technique was used involving heating, cooling, and

reheating the sugar samples, where T_g was obtained during both cooling and reheating steps. It was used the Gordon-Taylor equation in order to study the water plasticization impact, where the T_g of anhydrous solids and constant (*k*) values were determined simultaneously. It was found that sugar composition had a significant influence in the cooling and heating glass transition temperature values, while non-significant effect was observed for k values, thus observing discrepancies regarding Gordon-Taylor model for solid mass fractions below 0.84. This fact justifies the need to estimate *k* values from measured T_g data at low solid mass fractions rather than extrapolated from high solid mass fractions, when T_g curve at high moisture contents is used.

Freezing a high moisture food may involve the crystallization of pure water and therefore concentrate the solute, which sometimes forms a concentrated amorphous solution (CAS). The CAS may be formed via hot air drying as well, although most hot air dried foods available on the market are porous and/or in powder form and are inconvenient for use in fracture tests.

Glass transition temperature, T_g, and enthalpy relaxation of amorphous lactose glass at different temperatures (298-363 K) below T_g were studied (Haque et al., 2006). This study is of a paramount importance to improve the processing and storage stability of amorphous lactose and lactose containing food and pharmaceutical products. For instance, it was observed that both T_g and relaxation enthalpy were augmented with increasing aging time and temperature. The relaxation enthalpy increased approximately exponentially with aging time at a temperature close to glass transition temperature while non-significant modifications were observed in the relaxation enthalpy around room temperature over the aging period. The experimental relaxation

data on enthalpy were well fitted using the Kohlrausch--Williams--Watts functions. The relaxation enthalpy time constant, τ, was augmented with increasing the aging temperature. The relaxation distribution parameter (β) was found to be in the range 0.81--0.89. The molecular mobility in amorphous lactose glass was higher at temperatures closer to T_g.

ESTIMATIONS OF NUTRITIONAL PROPERTIES AND QUALITY MODIFICATIONS

Carbohydrates

Starch gelatinization

Starch can exhibit two different types of thermal properties known as gelatinization and retrogradation (Liu et al., 2010). Frequently, DSC thermograms for starch samples with excess water (above 65%) give a single narrow gelatinization endothermic peak and this process is known as gelatinization. Gelatinization is commonly considered as a combination of glass transition of amorphous regions and the melting of crystalline regions (Tester and Debon, 2000)(Bertolini, 2009). This phenomenon has been ascribed to the water-mediated transformations of starch crystallites initiated by the stripping of starch chains in the hydrated amorphous regions of the granule. The water is able to penetrate into the starch granules and to cause their disruption. Several investigators have established the principle that cross-linked and substituted starch granules exhibit lower gelatinization temperatures (Bertolini, 2009). On the other hand, retrogradation process reflects the changes that occur during processing and storage of gelatinized starch related with the reassociation of starch chains into an ordered structure (Bertolini, 2009).

The starch gelatinization process is one of the most important in food industry mainly due to its impact on the structure of starch-based products (Lelievre & Liu, 1994). The gelatinization temperature depends on the type of starch (e.g. corn, potato, smooth pea, etc.) and on its modification (chemical, mechanical, biological).

The thermal behavior of dry native starch, amylose and amylopectin extracted from wheat and maize was investigated (Zhiqiang et al., 1999). DSC analyses confirmed that the amorphous phase in the samples was swollen by bound water within a temperature range of 323-428 K. The change in swelling enthalpy divided by the peak temperature or swelling depended linearly on the volume fraction of bound water, regardless of the origin and the composition or purity of the specimens. Furthermore, bound water depressed the melting points of crystallites in the specimens, which agreed well with the prediction of Flory's lattice theory (Zhiqiang et al., 1999).

The gelatinization temperatures could be related to the degree of perfection of crystallites in the starch granules, whereas gelatinization enthalpies could be related to the degree of crystallinity. Moreover, during heating process in DSC, few double helices would unravel and melt during gelatinization; water molecules could react with molecules in crystalline region more easily, causing the decrease of ΔH_{gel} of gelatinization (Gunaratne and Hoover, 2002).

The influence of drying conditions (air velocity and temperature) on thermal properties of starch from green banana flour (*Musa cavendishii* L.) was evaluated (Tribess et al., 2009). A single endothermic transition and a flow of maximum heating at peak temperatures from 340.95 to 351.63 K were observed. Statistical analysis showed that only drying temperature influenced significantly ($p<0.05$) the gelatinization peak temperature (T_p). Moreover, it was found that

gelatinization enthalpy (ΔH_{gel}) varied from 9.04 J/g to 11.63 J/g and non-significant differences were observed for either temperature or air velocity.

Polysaccharide´s thermal behavior

The thermal behavior of polysaccharides from *Musa sapientum* L. was evaluated (Suvakanta et al., 2014). The glass transition was observed at 313.8 K without finding a melting peak. The lower value was thought to be due to plasticization caused by residual water molecules remaining unmoved during fast scanning. The continuous endothermic transition is indicative of moisture loss in the sample. The weight loss onset (representing the onset of oxidation or decomposition) at 513 K suggested that the polysaccharide had a good thermal stability. The onset peak and conclusion temperature of phase transition were observed to be 384.84 K. Structural and functional group differences in polysaccharides influenced the thermal behaviour and affected the transition temperature. Physical and chemical changes that occur in the polysaccharides during thermal processing and these methods yielded curves that are unique for a given polysaccharide (Vinod et al., 2008) The result implies that MSP may structurally be stable and can have a good thermal stability.

The thermal behavior of gum arabic and cashew gum, the exudate polysaccharides from *Acacia* and *Anacardium occidentale L,* was investigated (Mothe and Rao, 2000). DSC thermal profiles for gum arabic with low water content (0-40%) showed an endothermic event at about 363 K (T_o) and with increasing water content (50-80%) multiple melting endotherms and associated enthalpies were observed. The cashew gum showed a similar behavior compared to arabic gum but with $T_o \approx 370$ K. The thermal behavior of xanthan gums was studied by means of DSC (Salah et al., 2010) The enthalpy value was 1924±2.01 J/g for the commercial xanthan. The

onset (T_o) and peak (T_p) determined from the DSC heating curves were 379±1 K and 427±1 K, respectively. The thermal properties of natural gums obtained from the seeds of *Diospyros melonoxylon* Roxb, *Buchanania lanzan* spreng and *Manilkara zapota* were evaluated (Bothara and Singh, 2012). These authors obtained DSC curves which indicated a major intense exothermic transition (around 473 K) followed by weaker exotherm(s).

Proteins

Proteins are perhaps the most studied food components (Hammond, 2007) (Phillips and Williams, 2011)(Hettiarachchy, 2012) and the use of DSC to measure protein thermal stability is of particular technological value. Proteins consist of 20 different L-α-amino acids and may be in fibrous (water insoluble) or globular (water soluble) forms. Their studies include the confirmation of changes as affected by various factors, thermal denaturation of tissue proteins, food enzymes and enzyme preparations for the food industry as well as the effects of various additives on their thermal properties. In many food technology areas, thermodynamic treatment of data may be quite irrelevant.

Denaturation and interaction of proteins

DSC is widely used as sensitive technique to study thermal denaturation, conformational transitions and the thermodynamics involved with proteins (Hendrix et al., 2000). Thermal denaturation of several proteins (bovine serum albumin, lysozyme and whey protein isolate) in the presence of hydrocolloids was investigated using DSC (Ibanoglu, 2005). The highest thermal stability was observed in the presence of pectin, whereas the lowest transition temperature was observed in the presence of guar gum.

The mechanism of gelation of globular proteins on heating was discussed (Fitzsimons et al., 2007). It was demonstrated that gelation includes two separate stages: partial unfolding of the native globular structure (endothermic process) and formation of new bonds between protein molecules or intermolecular aggregation (exothermic process).

More recent studies demonstrated that the endothermic transition (denaturation temperature) of bovine plasma proteins could be shifted to higher temperatures, with application of polysaccharide which provokes the stabilizing effect: inulin > glucose > sucrose (Rodriguez Furlan et al., 2012). The conformational changes in whey protein (WP) were studied using DSC (Dissanayake et al., 2013). The data evidenced that WPs were denatured mainly by the disruption of hydrophobic interactions. The formation of protein aggregates during heating was affected by the pH. The influence of pH and protein concentration on WP denaturation during heating at 413 K was studied (Dissanayake et al., 2013). DSC data revealed the concentration-dependence of WP denaturation. DSC studies of mixtures of soybean protein isolates (SPI) and corn starch (CS) in water were done (Li et al., 2014). The data showed that the presence of SPI in the mixture restricted the CS gelatinization, while the presence of CS protected SPI from denaturation.

The different mixtures of whey protein concentrate, starch, gelatin, and sucrose with different water contents were studied by DSC method (Cassiani et al., 2013). The temperature for starch gelatinization is lower than the temperature for whey protein denaturation. However, in presence of sucrose, whey proteins are denatured, before the gelatinization of starch.

Thermal properties of high protein systems on the base of whey protein isolate (WPI) during storage for 14 weeks were investigated (Potes et al., 2014). The studied systems include rehumidified-WPI, WPI-oil, WPI-sugar, and WPI-oil-sugar mixtures. DSC data showed a presence of protein hydration transition for the studied systems. The nature of changes of protein conformation, denaturation (irreversible) and glass transitions is discussed. It was demonstrated that the stability of the studied high protein systems is dependent on hydration and reactions in both hydrophilic and hydrophobic phases.

The effects of different drying methods (freeze-drying and convective drying) on denaturation of chickpea protein concentrates (CPCs) were studied by DSC (Ghribi et al., 2015). The significant differences in peak denaturation temperature and enthalpy of transition were observed for different drying methods used for the preparation of CPCs powders. The effects of protein denaturation under the electrohydrodynamically (EHD) assisted hot air drying of mushroom (*Agaricus bisporus*) slices were investigated by DSC (Dinani et al., 2015). The measured parameters included enthalpy ΔH and transition temperatures of endothermic peaks. The correlations between values of ΔH and parameters of EHD-treatment (electrode gap and voltage) were discussed. EHD-treatment had a significant effect on thermodynamic responses related to protein denaturation. The water state changes in DSC cooling thermograms of dried mushroom slices were also investigated. The data evidenced no existence of freezable water in the mushroom slices dried by all the combined hot air--EHD drying treatments. DSC did not reveal any denaturation of proteins in jumbo squid muscle for freezing storage at 253 K up to 30 days (García-Sánchez et al., 2015).

DSC studies evaluating the impact of biopolymers (starch, non-meat protein and hydrocolloids (carrageenan, flaxseed gum, curdlan and barley β-glucan)) on thermal behavior and denaturation of meat proteins were reviewed (Sarker et al., 2013). The three denaturation steps were identified in transition temperatures ranging from 216 to 340 K for myosin subunits, 340 to 342 K for sarcoplasmic proteins and collagen, and 344 to 356 K for actin.

Lipids

Thermal properties of lipids

DSC is a powerful technique that had been widely used to study thermal properties of food lipids with different composition including phase transition temperatures and the associated enthalpies. The detailed reviews on DSC studies of phospholipid membranes (Smith and Dea, 2013) and phospolipids in vegetable oils and fats in relation to lipid modification processes (Chiavaro, 2014) were recently reported.

Oxidative deterioration of oils

Thermal oxidative decomposition of edible oils examined by DSC can be used for predicting oil stability. The DSC is one of the evaluation methods of oxidative stability. The oxidation induction time (OIT) measurement was well described by (Tan et al., 2002) and consists on the following steps: a) Firstly, sample must be preheated in a N_2 atmosphere until the specified temperature is obtained; b) the atmosphere must be changed from N_2 to O_2; c) the time (OIT) of the changed gas to the observed exothermal peak should be measured. Oxidation onset temperature (OOT) can be measured in DSC.

For this purpose sample should be placed in non-covered aluminium pan and, subsequently included in the DSC measurement cell. The heating rate should be programmed at 10 K/min from ambient temperature to the onset of the exothermic heat flow. The oxygen flow rate should be maintained at 50 mL/min. The scanning DSC operation continues until the peak of the exothermic oxidation is observed or until an inflection point is observed, and the total displacement from the initial baseline exceeds 3 mW or 1 W/g. When the experiment is completed, it is necessary to cool the instrument until room temperature, 298 K. The OOT is measured in oxygen from the baseline to the extrapolated onset temperature of the exothermic process.

The influence of the oxidation level on the phase transition behavior of sunflower oil was evaluated (Calligaris et al., 2008). These authors determined that the crystalline structure changes upon oxidation as well as its crystallization and melting enthalpy, significantly decrease as the oxidation level increase. The effect of riboflavin on the photo-oxidation of vegetable oil in salad dressing was evaluated (Lee, Lee, Min, & Pascall, 2014). Crystallisation peaks in the DSC thermograms of the oil samples shifted to lower temperatures and the enthalpies decreased as the storage time increased. The DSC analysis showed that the addition of palm olein to canola oil altered the shapes of endo- or exotherm peaks of canola oil and became sharp. The authors attributed this change to the modifications in fatty acid composition. In another study, it was concluded that frying process caused the formation of comparatively lower amounts of oxidation products in the blends of palm and canola oils compared to canola oil (Abbas Ali et al., 2013).

Aguerrebere et al. (2011) extracted oils from *Prunus serotina* raw and toasted seeds with hexane and supercritical CO_2 and evaluated their physicochemical characteristics. Authors observed two exothermic effects and supposed that these peaks could be considered as an indication of the level of cross-linking. From the analysis of the obtained DSC curves, they supposed that thermoxidation could be characterised by at least two steps. DSC data revealed a three-step oxidation of *P. serotina* seed oil with the mean onset and oxidation temperatures at 394 and 403-546 K, respectively, depending on the processing. The supercritical CO_2 extracted oil had the lowest oxidation temperatures, with the characteristic absence of the third exothermic peak. However, the hexane extracted seed oil showed the highest oxidation temperature.

At the same time, DSC was applied for evaluating the oxidative stability of *Bauhinia purpurea*, rice bran and cotton seed oil. It was confirmed that *B. purpurea* oil was a very stable oil when compared to rice bran and cotton seed oils (Arain et al., 2009). DSC analysis showed a higher oxidative stability for heat-bodied soybean oil with even higher stability for microwave-irradiated soybean oil (Biswas et al., 2007). The onset temperature (T_o) of the exothermic thermal transition for heat-bodied soybean oil (T_o = 428.7 K) is considerably elevated compared with the untreated soybean oil (T_o = 405.7 K), thus indicating improved oxidative stability. Soybean oil microwave-irradiated at 473 K for 20 min had elevated T_o = 433 K than the untreated soybean oil, and even higher than the heat-bodied soybean oil. Enhanced oxidative stability is most likely due to the decrease in double bonds and the formation of cyclic triacylglyceride ring structures.

Bouanga-Kalou et al. (2011a) investigated the kinetics of degradation of roselle seed oil during heating using DSC. They showed that the thermal oxidation of the double bonds of the oil showed a first-order thermal oxidation kinetic and the Arrhenius plot yielded a straight line with a slope equivalent to activation energy, E_a = 9.041 kJ/mol. The same authors determined the degradation and activation energies, E_a, of gumbo seed oil (E_a = 8.646 kJ/mol) (Bouanga-Kalou et al., 2011c), *Moringa oleifera* seed oil (E_a = 1.593) kJ/mol (Bouanga-Kalou et al., 2014) and *Carica papaya* seed oil (E_a = 7.752 kJ/mol) (Bouanga-Kalou et al., 2011b).

On the other hand, Budryn et al. (2012) determined the optimal roasted conditions of Robusta coffee bean for the best nutritional properties (T = 483K and 1% humidity content in roasting air at 1 m/s flow velocity). In such conditions, roasted beans obtained a very high quality aroma and oil obtained from roasted coffee beans. The extracted *Sesamun indicum* L. oil by supercritical carbon dioxide and compressed propane and *n*- hexane as solvents was then checked for oxidative stability (Corso et al., 2010). The sesame oil is considered as an oil with high oxidative stability depending on the presence of natural antioxidants as tocopherols, sesamol and others lignans. The obtained results indicated that the temperature and pressure levels did not have a significant effect on the oxidative stability of the oils extracted with SC-CO_2. However, due to the higher temperature and time of extraction the oil extracted with *n*-hexane had lower oxidative stability, compared to the oils extracted SC-CO_2. They concluded that the oxidative stability characteristics of extracted oils, determined by DSC, were similar to those found after conventional solvent extraction with hexane and n-propane.

Nzikou et al. (2010) studied the oxidation properties of sesame oil. It was shown that the thermal oxidation of the double bonds of the oil showed a first-order thermal oxidation kinetic and E_a = 12.428 kJ/mol. The DSC analysis of sterculia seed kernel oil showed the existence of two exothermic events of energy transition, one of which is related to the oxidation reactions at a temperature (T_o = 561 K, T_f = 620K, ΔH = -11.69 J/g) and other to the decomposition of the oil (T_o = 657 K, T_f = 722 K, ΔH = -200.83 J/g). It was established that the bigger the size of the hydrocarbon chain, the higher the enthalpy of activation was (Diniz et al., 2008). In another study, Epaminondas et al. (2011) evaluated the thermo-oxidative behavior of flaxseed oils obtained from different variety of seeds. They concluded that there were not significant differences in the thermal and oxidative stabilities of oils obtained from the brown and the golden flaxseeds. (Gardette and Baba, 2013) characterized the oil extracted from the bean of *Balanites aegyptiaca*. The obtained results from DSC indicated that the triglycerides contained in this oil are well protected against aging due to the presence of natural antioxidants in the bean. DSC experiments showed that δ-tocopherol was the most effective antioxidant for sunflower oil and propyl gallate for the less unsaturated oils (Giuffrida et al., 2006)(Gortzi et al., 2008). The DSC was used as a rapid and effective method to characterize the olive oil at different levels of oxidation (Kanavouras and Selke, 2004) (Gouveia et al., 2006). For the grape seed oils obtained from the Cabernet Sauvignon variety was shown that, for both oxidative stability and antioxidant capacity, total polyphenols had a more important role than α-tocopherol (Malićanin et al., 2014). It was concluded that phenolics can act as antioxidants through their bonding with lipid free radicals, as reducing agents or as ''quenchers'' of free oxygen species. For their structural features, these compounds express higher antioxidant capacities than either tocopherols or

tocotrienols. DSC method was applied to evaluate the oxidative stability of buriti pulp oil (*Mauritia flexuosa Mart*), rubber seed oil (*Hevea brasiliensis*), and passion fruit oil (*Passiflora edulis).* The authors observed during the oxidation reaction an increase in heat as a sharp exothermic curve (Pardauil et al., 2011). The thermal stability of rambutan seed (*Nephelium lappaceum* L.) fat analyzed in an inert atmosphere of N_2 and in a normal oxidizing atmosphere, showed that in the latter, fat decomposition begins at 500 K and concludes at 802 K, with three stages of decomposition (Solís-Fuentes et al., 2010).

APPLICATION OF DSC TO EVALUATE THE EFFECTS OF DIFFERENT PROCESSING OPERATIONS

Different processing operations can have impact on the modification of food products. Nowadays the different physical treatments without application of chemical reagents are rather popular in food industry. Among these treatments the thermal (heat-moisture, ohmic heating, microwave heating, ultrasound) and non-thermal (high pressure processing, high pressure homogenization, pulsed electric fields, gamma and ultraviolet irradiation and cold plasma) methods can be marked out. The comprehensive reviews on the effects of different mode of physical treatments on the nutritional and quality properties of fruit and vegetable tissues, meat, milk and starch (BeMiller and Huber, 2015) and other food products were recently issued.

The DSC method has been used to evaluate modifications in the quality and nutritional characteristics of food products after non-conventional processing. Some of the most relevant findings are described below.

High pressure (HP) processing

It is of great interest in application of high-pressure calorimetry to characterize the changes in thermal properties of foods under the conditions relevant to high-pressure processing. The general aspects of high-pressure DSC were previously comprehensively reviewed (Höhne and Kaletunç, 2009)(Randzio and Bail, 2009). Some studies have evaluated the potential of DSC to evaluated protein changes after the high pressure (HP) processing. For instance, DSC data indicated that the application of HP processing (up to 200 MPa for 20 min) to black tiger shrimp muscle induced the denaturation of myosin and actin with subsequent formation of a network stabilized by hydrogen bonds (Jantakoson et al., 2012).

Moreover, the effects of HP on the protein structure and thermal stability of Sauvignon blanc wine and sweet potato protein were evaluated using DSC (Tabilo-Munizaga et al., 2014)(Sun et al., 2014). In these studies, it was found that the application of HP processing (200-600 MPa) resulted in a decrease of thermodynamic stability of proteins, with a significant modification the α-helical and β-sheet structures of wine (Tabilo-Munizaga et al., 2014) and sweet potato (Sun et al., 2014) proteins. Additionally, the analysis of the changes in melting temperature and melting enthalpy suggested that HP processing (450 MPa, 3-5 min) produces a partial wine protein unfolding, improves their thermal stability and delay haze formation.

The impact of HP processing on ovotransferrin physicochemical changes was investigated (Acero-Lopez et al., 2012). No clear denaturation peaks was found in DSC-curves at any level of pressure treatment at pH 3.

The effects of HP processing (50-200 MPa, 5 min) on the functional properties of peanut protein isolates (PPI) were also studied using DSC (He et al., 2014). The DSC results showed that HP processing had different effects on peanut protein denaturation (haperons of arachin and conarrachin). The untreated PPI showed two peaks of heat absorption at T_{d1} = 370.53 K (chaperon of conarrachin) and T_{d2} = 380.25 K (arachin). For chaperon of conarrachin the value of T_{d1} gradually decreased with the increasing pressure (50--100 MPa), and the peak became invisible at 150 and 200 MPa. On the contrary, the arachin was more stable and the peak was visible after HP processing.

A review of starch characterization studies by DSC relevant to heat and high pressure processing, and retrogradation of processed starch during storage was presented (Lowe and Kaletunç, 2009). It was concluded that application DSC allows prediction the effectiveness of high pressures to produce gelatinized starch. More recently, the impact of HP processing (400 MPa, 278-308 K, 15 min) on the degree of gelatinization of maize and rice starches was evaluated using DSC. The authors found a significant increase of gelatinization temperature with pressure for both maize and rice starches (Santos et al., 2015).

In another study, the retrogradation kinetics of cross-linked and acetylated corn starches after applying HP treatment (400 MPa, 298 K, 15 min) and subsequent storage was evaluated and compared with conventional treatments (Kim et al., 2015). It was found a similar trend in cornstarches retrogradation after HP and conventional treatments. The authors observed a significant increase in glass transition temperatures (T_g) values and relative crystallinities after both treatments during the first 7--10 days of storage, followed by stabilization. On the other

hand, in the same study, a significant decrease in the ice melting enthalpy was found after applying the treatments and subsequent storage during 10 days. A different behaviour was also reported in retrogradation kinetics of starch modified by HP compared to conventionally modified starch, although, in any case, the extent of retrogradation of both samples was lower than for native cornstarch.

The DSC was used to study ice content of the sugar rich dairy based frozen food foam and emulsions at different temperatures after high pressure--low temperature treatment (Volkert et al., 2012). DSC data showed that approximately 24.5% of the total water is frozen right after pressure release at 269.7 K. During subsequent atmospheric freezing, energy is emitted and the sample temperature progressively decreases.

DSC method was used as an effective tool to study protein denaturation after high pressure assisted thawing on the quality of fillets from fish (Schubring et al., 2003). The patterns of DSC curves of high-pressure thawed muscles confirm a denaturation of the muscle proteins as a result of applying high pressure.

High pressure homogenization (HPH)

DSC technique was used to establish the protein denaturation of almond and hazelnut milks after applying HPH (62-172 MPa) (Bernat et al., 2015). The authors did not observe any significant changes in the area and temperature peak of denaturation endotherms of HPH-treated compared to untreated samples, thus concluding that HPH treatment did not promote any significant protein denaturation in almond milk after HPH

The effect of HPH on gelatinization properties of maize and wheat starch was also evaluated using the DSC method (Wang et al. 2008)(Qiu et al., 2014). In the case of maize starch, it was found a significant decrease in the gelatinization temperatures, T_p, and gelatinization enthalpy, ΔH_{gel}, when the homogenizing pressure was increased. The authors indicated that the shear stress could enhance swelling and therefore promote the gelatinization of starch granules during high-pressure homogenization treatment (Wang et al. 2008). Similarly to the results reported for maize starch, other authors found a partial gelatinization of wheat starch when HPH treatment (100 MPa) was applied (Qiu et al., 2014).

Pulsed electric fields

The effect of pulsed electric fields (PEF) on the gelatinization properties of corn (Han et al., 2009) potato (Han, Zeng, Yu, Zhang, & Chen, 2009) and tapioca (Han et al., 2012) starches was investigated. In all these works starch--water suspensions (8.0%) were processed by PEF with different electric field strengths (up to 50 kV/cm). The gelatinization temperature, T_o, noticeably depended on the strength of the electrical treatment, E. With increasing of electric field strength, E, from 0 to 50 kV/cm, the value of T_o decreased. The enthalpy of gelatinization, ΔH_{gel}, of PEF-treated starch samples decreased with the increase of electric field strength. The noticeable granule distortion was observed at E = 50 kV/cm. The crystallinity was lost at high electric field strength and some of the double helices present in crystalline and non-crystalline regions of the starch granule were disrupted.

PEF-assisted acetylations (3 to 5 kV/cm) of cassava and potato starches were studied using different methods, including DSC (Hong et al., 2016) (Hong et al., 2016). The enthalpy of

gelatinization, ΔH_{gel}, and the onset, T_o, the endothermic peak, T_p, and the final, T_c, temperatures of the acetylated starches were lower than that of the native starch. The obtained results demonstrated that PEF treatment can be a beneficial method for the acetylation and can achieve higher degree of substitution DS with shorter reaction time than conventional methods.

Moreover, DSC method was used to study the impact of PEF (0 to 50 kV/cm) on the secondary structure and thermal properties of soy protein isolate (Liu et al., 2011). PEF treatment significantly affected the enthalpy changes of β-conglycinin and glycinin fractions and induced the denaturation of proteins. In another study, the impact of PEF treatment (30-50 kV/cm) on the morphology, thermal properties, and digestibility of waxy rice starch was investigated (Zeng et al., 2016). DSC experiments were done in heating regime from 303 to 403 K at the rate of 10 K/min. The enthalpy of gelatinization, ΔH_{gel}, and the onset, T_o, the endothermic peak, T_p, and the final, T_c, temperatures of PEF-treated starches were lower than that of native starch. The data suggested that the PEF-induced changes in waxy rice starch significantly affect its digestibility.

The effects of PEF and thermal treatments on the properties of whey protein isolate (WPI) were studied using the DSC assay (Sui et al., 2011). These authors did not find any significant changes in thermal parameters (onset, peak, and offset denaturation temperatures and denaturation enthalpy) of WPI after applying PEF treatments (30-35 kV/cm, 19.2-211 μs, 303-348 K). However, PEF treatment reduced the strength and increased the gelatinization time of the heat-induced gel.

Additionally, DSC was used for testing the changes in proteins of milk treated by PEF (Lee et al., 2013). The denaturation temperature of milk protein increased and alkaline phosphatase

activity decreased after the PEF treatment, whereas pH, protease, lactoperoxidase, and titratable acidity activities of milk were not affected by PEF treatment.

The effects of PEF (a near-rectangular monopolar pulses with duration of 100 μs and electric field strength of 800 V/cm) and osmotic impregnation in glycerol solution on the amount of unfreezable water in apple were determined by means of DSC (Parniakov et al., 2015). The osmotic impregnation of PEF-treated apple discs was done using aqueous glycerol (G) mixtures.

Figure 10 presents examples of concentration dependencies of melting point, T_p, water-glycerol mixtures (sample water-glycerol) in PEF-treated sample (with high disintegration index, $Z = 0.95$) subjected to osmotic impregnation in apple juice-glycerol mixtures (samples apple-glycerol). The obtained $T_m(W)$ for water-glycerol mixture was in good correspondence with previously reported data (Bohon and Conway, 1972; Weng et al., 2011b). At $W \approx 33.3\%$ wt and $T = 226.7$ K water-glycerol mixtures shown eutectic point. The difference between water-glycerol and apple-glycerol samples may reflect the supplementary effect of the apple tissue on the depression of melting temperature, T_m, of water-glycerol mixture trapped inside the tissue. However, the state diagrams for water-glycerol and apple-glycerol samples were rather similar (Fig. 10). The data evidenced that for the PEF-treated samples the glycerol was able to penetrate successfully inside the apple tissue.

Figure 11 presents the unfreezable moisture contents W_d^u (on dry basis, $W_d^u = m^u/m_d$) versus the total moisture contents W_d (on dry basis, $W_d = m/m_d$) in the samples WG and AJG ($Z = 0.95$). The value W_d^u decreased with decreasing of the total water content W_d to the limiting minimum value $(W_d^u)_{\min}$. Below this minimum value, the free water was absent in the samples. The

molecules of bound water in water-glycerol mixtures are probably associated with the glycerol OH groups (Dashnau et al., 2006) and the value of W_d^u with the rising water content in full correspondence with previously reported data (Weng et al., 2011a). Higher value of W_d^u in apple-glycerol samples in comparison with water-glycerol samples can reflect the supplementary binding of water by apple tissue. In fact, the values W_d^u for un-impregnated PEF-treated (W_d^u = 0.53±0.02) and intact (W_d^u = 0.42±0.02) apple tissues were noticeable, that reflects the impact of apple tissue on the binding of water.

Ultrasound

The impact of high intensity ultrasound (USN) on the heat-induced gelling (denaturation) of proteins in whey protein isolates was studied. For instance, the effects of ultrasound on thermal behavior, secondary structure and nature of intra- and intermolecular bonds were investigated by (Frydenberg et al., 2016). These authors found that ultrasonication caused a significant reduction in denaturation enthalpies. However, no significant changes in the secondary structure were detected by circular dichroism. The effect of power US on water--protein interactions during the salting of pork was also studied using DSC assay (McDonnell et al., 2014). USN-assisted salting can accelerate mass transfer and extraction of protein. However, at higher power inputs the DSC data indicated possibility of myosin denaturation at the surface of the sample.

The analyses of the technological properties of pork thawed by low intensity ultrasound thawed meat were studied by DSC (Gambuteanu and Alexe, 2015). The DSC thermograms had three characteristic peaks for myosin, lagen and actin at 330 K, 339 K and at 353 K, respectively. However, no significant differences were identified among the five thawing methods. Similarly,

the total enthalpy of protein denaturation did not change significantly. It was concluded and ultrasound thawing did not evidence any significant modification in protein structure.

The DSC analysis of polysaccharides from *I. obliquus* with or without ultrasonic treatment was done (Fu et al., 2010). The polysaccharide obtained by hot water extraction showed the ΔH_{gel} = 229.9 J/g. After the ultrasonic treatment, the ΔH_{gel} value in 1.13 times higher. It was found that ultrasonic treatment might result in changes of crystalline regions in the polysaccharide structure.

The USN effects on physical properties of corn starch were evaluated by means of DSC (Jambrak et al., 2010). It was shown that the gelatinization temperature of sonicated corn starch has not been statistically higher as compared to the gelatinization temperatures of native corn starch. However, $\Delta H_{gel,}$ was lower for treated samples (7.466 J/g) compared to the untreated corn starch (12.966 J/g). The obtained variation of gelatinization energy could be explained by differences amongst the bonding forces of the double helix forming the amylopectin crystallography, which resulted in different alignments of the hydrogen bonds within the starch molecules (Sandhu & Singh, 2007).

The state of water in ultrasound-assisted frozen wet gluten was investigated (Song et al., 2009). It was found that approximately 70% of the water in the wet gluten samples froze during the freezing process. The freezable water content was higher in the samples frozen with ultrasound than in the samples frozen without ultrasound. It was explained by the phenomenon that the ultrasonic effects loosened the weak interactions between the molecules, more loosely bound water was able to ice up when the wet gluten was frozen with ultrasound irradiation. It

was also shown that when the wet gluten was frozen with ultrasound, many small and uniform crystals were formed.

Microwawes heating

Microwave heating is widely used in the field of starchy food processing and heating. At this stage of development, there is a need to find predictive analytical tools to determine the impact of this technology on the different starchy products. For instance, the potential of DSC to evaluate these modifications has been studied by different authors.

In this line, the impact of microwave heating for different treatment times (5-15 min) on gelatinization of casava and potato starch as well as maize flours using DSC was determined (Colman et al., 2014)(Ma et al., 2015)(Roman et al., 2015) and it was observed that this technique was able to predict the gelatinisation of these samples. It was found that depending thermal- and microwave-specific effects differed according to the stage of gelatinization, observing a predominant effect of microwave at the beginning of the process and a subsequent predominant impact of thermal effects after gelatinization. In addition, DSC predicted a significant increase in the gelatinization when treatment time was augmented.

In another study, the potential of DSC to determine the extent of denaturation of protein during microwave cooking of fish was also demonstrated, observing that DSC allowed to establish the time-dependent degrees of protein denaturation during microwave cooking of fish (Liu et al., 2014).

Moreover, DSC has been used to evaluate the fat stability of a blend of hydrogenated palm kernel oil and butter (3:2) after microwave heating (5-15 min) (Sengar et al., 2015). DSC was

used to establish the relationship between thermal properties and the modification of physicochemical (peroxide value (PV), color values, and iodine value) and nutritional (free fatty acid content). It was found that DSC peak areas and heights had a significant relationship at all the settings of microwave time and power with FFA, whereas significant and negative with IV. The data showed non-significant and positive correlation with PV at all the heating times and power settings of microwave. C18:2/C16:0 ratios reflected their negative and significant correlation with peak areas at high power setting whereas color value revealed a positive and significant correlation with peak B area at both power settings.

BENEFITS AND LIMITATIONS OF DSC

DSC as predictor of the thermophysical, nutritional and quality changes of food products during processing and/or storage

DSC is a useful investigative tool for studying various heat-related phenomena in foods and their components by monitoring the associated changes in enthalpy, heat capacity and phase transition temperature. As a thermoanalytical method, DSC can predict stability of biomolecules in various environmental conditions such as pH, ionic strength, and osmolites (Gill et al., 2010)(Calmettes et al., 1991). Its ability to study these processes under the dynamic temperature conditions occurring during processing, as well as to provide both thermodynamic and kinetic data, constitute the main advantages of this technique. Using DSC in the freezing range has a great potential for measuring and modelling frozen food thermal properties, as well as to estimate the state of water in foods and food ingredients (Farkas and Mohacsi-Farkas, 1996). DSC method can be easily used as an alternative technique for the measurement of oxidative stability in edible

oil processing industries where mostly oxidative stability index technique is used. DSC can be very promise tool for determination of heat capacity of cooked food and initial food material because this method prevents contact between sample and heat transfer medium. This feature allow to eliminating the need for determination of heat of solution. The method could be used to determine the specific heat of foods at high, as well as low, temperatures, which are of interest in freezing preservation and in high temperature short time processing of foods. DSC has the advantage of using plant extract solutions without any specific preparation. Moreover, the samples can be recovered and reused for other purposes. DSC method requires a small amount of sample and can be performed in a relatively short time, it is a reliable, and can be easily computerized for evaluation of different thermodynamical parameters. Although, it is possible to calculate the ice fraction in the sample, this assay does not provide any data for ice crystal sizes.

Finally, some words about disadvantages of DSC method. The most important inconvenient of this technique are related with i) the high cost of the apparatus, ii) the need of careful sample preparation and iii) the difficulty of interpretation of thermal response curves of foods or biomasses. The measurement procedures and the experimental protocols (heat and gas flow rates) require an important adaptation for the specific products by well trained technical personnel (Rodriguez et al., 1995). In addition, one important factor of particular significance in studying heat treatments by DSC is the effect of heating rate on the apparent transition temperature values, whether it is related to thermal lag associated with the instrumentation, to the effect of heating rate on the resolution or to the kinetics of the transition (Farkas and Mohacsi-Farkas, 1996). It is important to use exact processing conditions for thermal analysis both in quality control and examining heat processing effects. But, in any case, taking into account of all

disadvantages of this method, DSC is a popular and sensible tool for investigating the thermodynamic properties of food components.

CONCLUSIONS

DSC has the potential to be used for both food researchers and food industry to predict modifications in the nutritional and physicochemical properties of food products after food processing when different thermal and non-thermal processing are used. The numerous studies have demonstrated the advantages of DSC techniques to predict the modifications that can occur in carbohydrates (eg. starch gelatinization), proteins (eg. denaturation), and lipids (eg. oxidation). However, at this stage of development, there is a need for further prediction models that can estimate the usefulness of this technique. Moreover, each food matrix should be studied separately. The use of DSC in food industry is very promising and can help to optimize processing conditions, thus reducing processing time and temperature and leading to a decrease in energy and economical cost.

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seedlings of Brussels sprouts for effective solution to preserve healthy compounds in vegetables).

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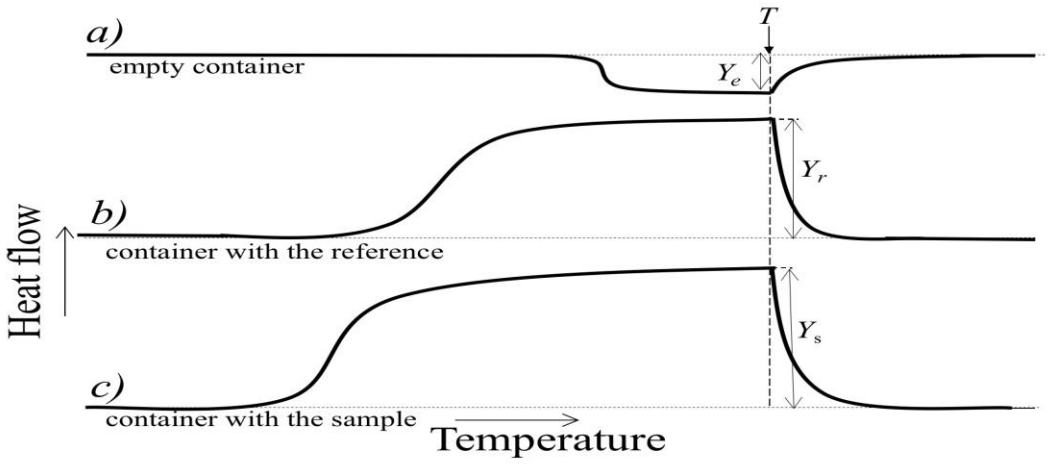

Fig.1. The schematic presentation of a step- by-step protocol, used for specific heat measurements by the DSC method. The deviations of DSC-curves from the basic line during the transition from the scanning regime to the isothermal regime were registered. The measurements were done using the empty container in the reference cell and the empty container (a), either the container filled with the reference substance of specific heat (b), either the container with the targeted investigated sample (c) in the operating cell. Here, T is the temperature, and Y_e, Y_r and Y_s are the deviations of the DSC curves from extrapolated start baselines in experiments a), b) and c), respectively.

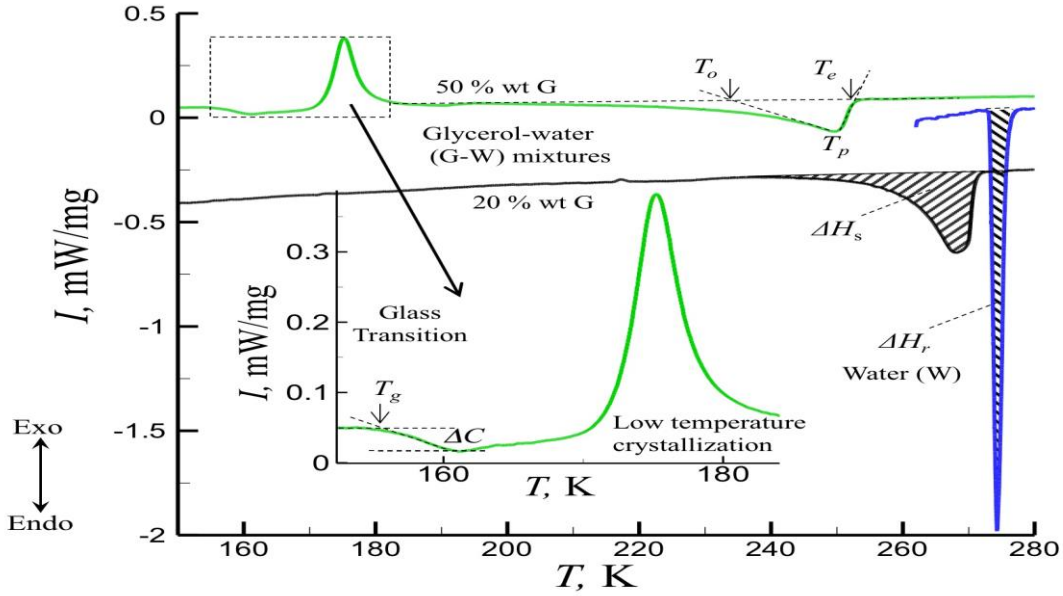

Fig. 2. The examples of DSC heating curves (heat flow *I* versus temperature *T*) obtained at the scanning 4 K/min for the distilled water and glycerol water solutions (20% wt and 50% wt of G). The values T_o, T_p, T_e and T_g are onset, peak, endset and glass transition temperatures, respectively. Compiled from the data (Parniakov et al., 2015).

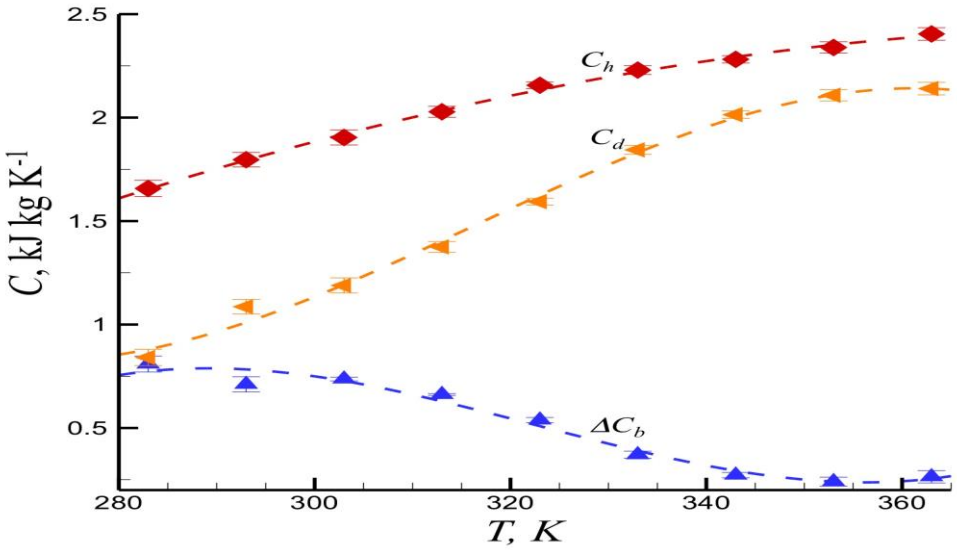

Fig. 3. The temperature dependences of different specific heat components C_h, C_d and ΔC_b, related to contributions of hypothetic hydrated tissue, completely dried tissue and bound water, respectively. Adapted from Mykhailyk & Lebovka (2014), with permission.

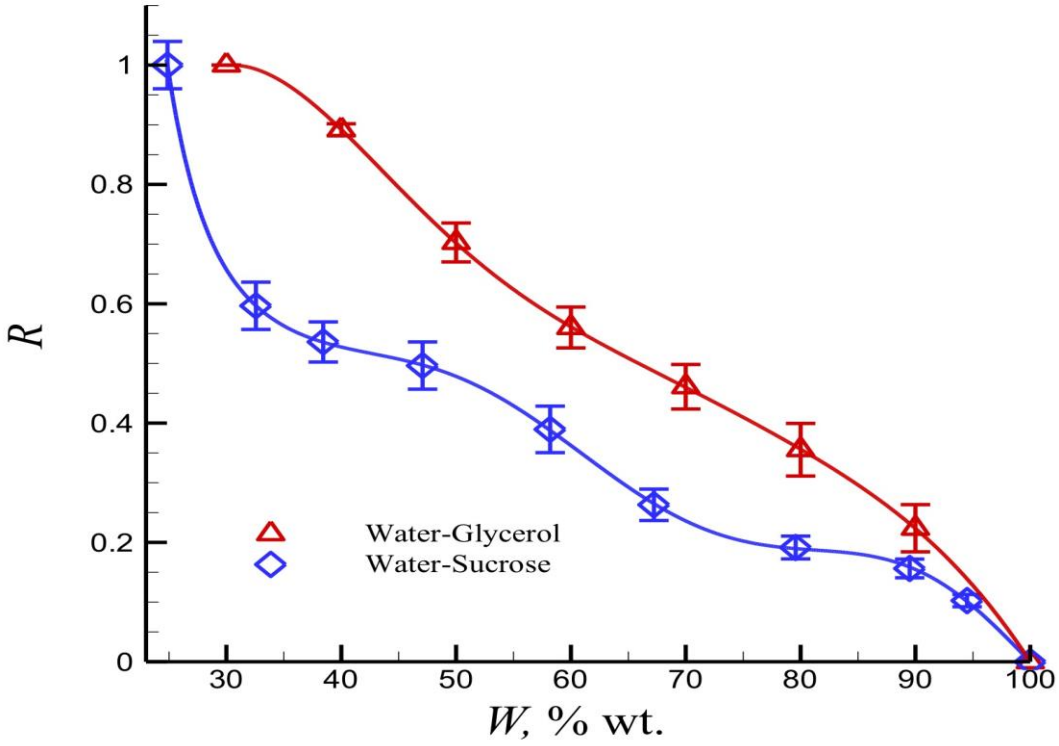

Fig. 4. Fraction of unfreezable water *R* versus concentration of water *W* in the glycerol and sucrose solutions. Adopted from (Parniakov et al., 2015) and (Mykhailyk, 1998).

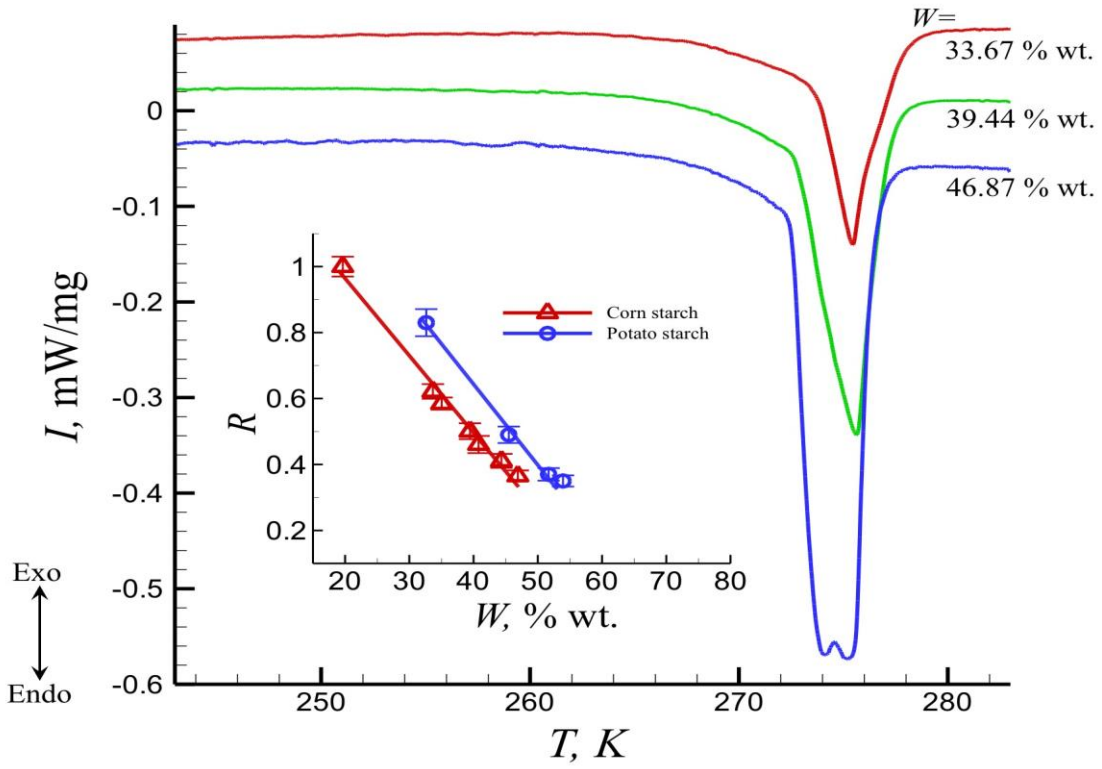

Fig. 5. Examples of DSC heating curves (heat flow *I* versus temperature *T*) of corn starch suspension with different water content. Insert shows the fraction of unfreezable water *R* versus moisture content *W* in the corn and potato starch suspensions. Adopted from (Grabovska and Mykhailyk, 2008).

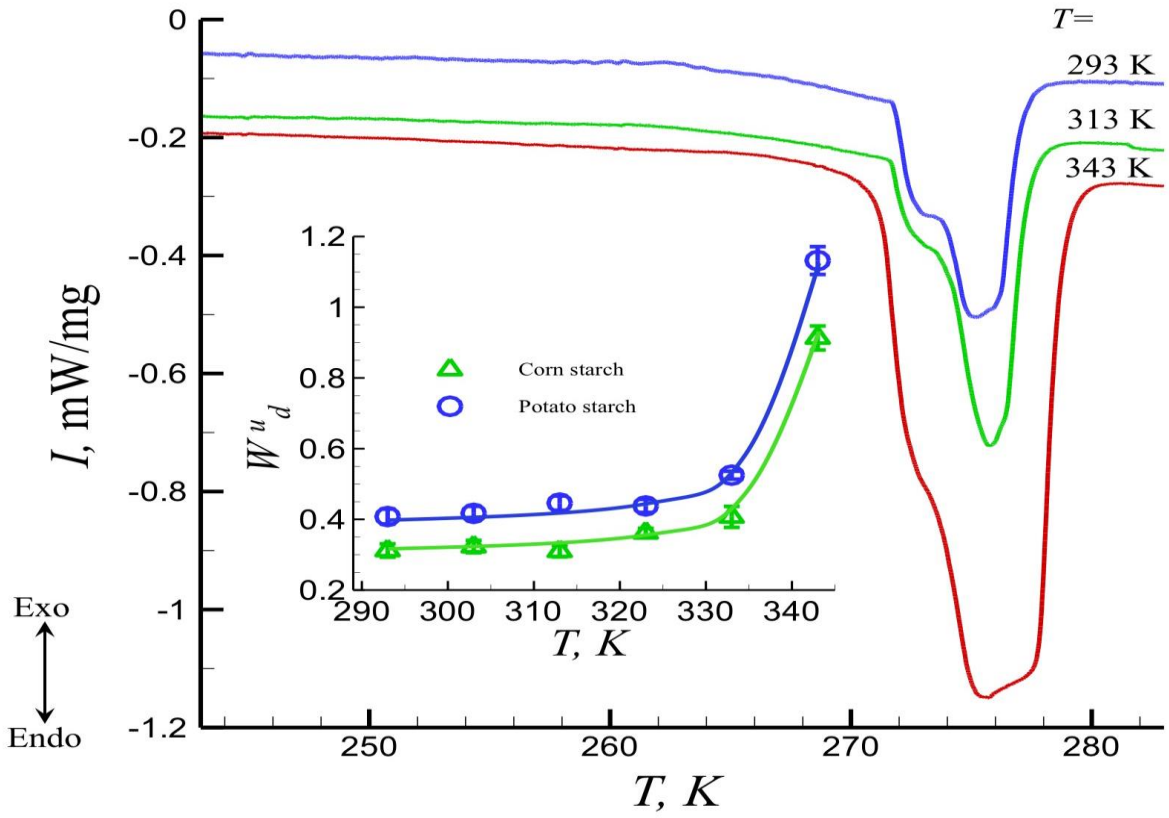

Fig. 6. Examples of DSC curves of melting of the "free" water (heat flow I versus temperature T) in potato starch suspensions treated thermally for 15 min at different temperatures, T_T = 293-343 K. Insert shows the unfreezable moisture contents (dry basis), W^u_d, versus the temperature of thermal treatment T_T for potato and corn starches. Adopted from (Grabovska et al., 2011).

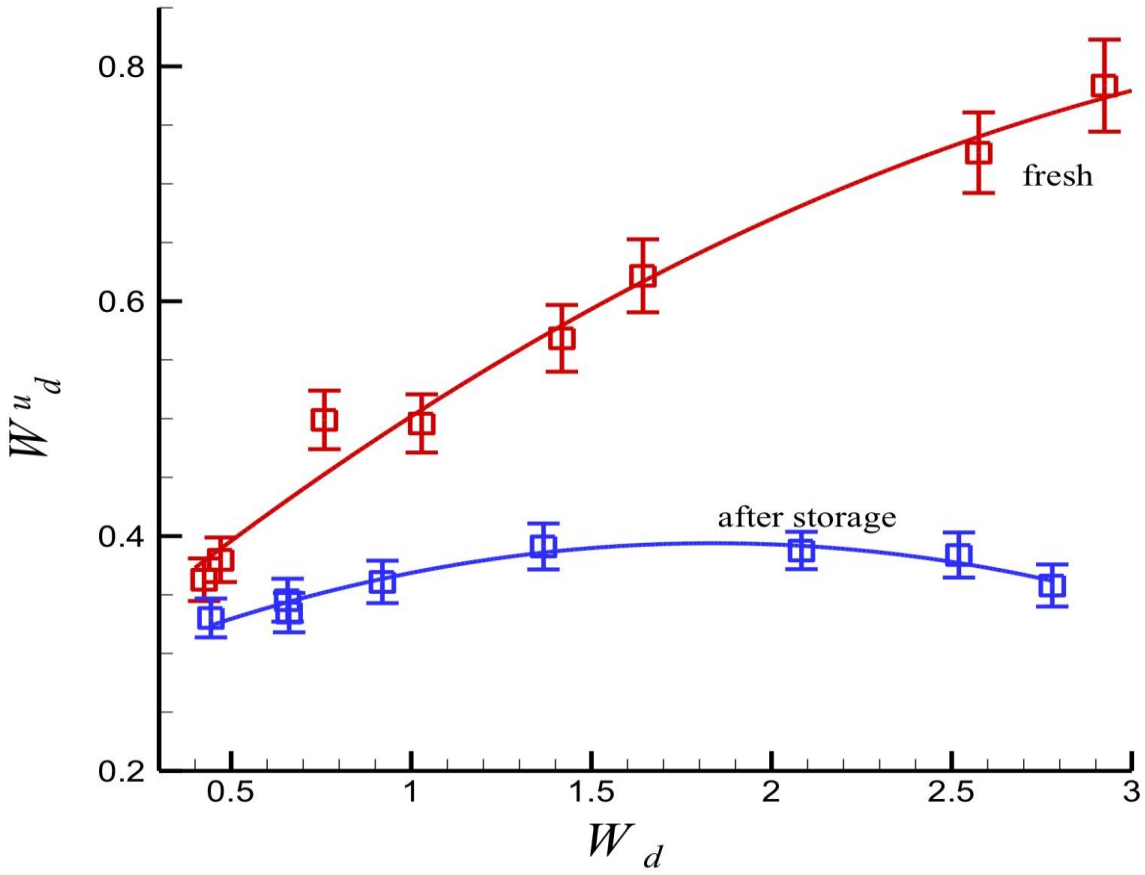

Fig. 7. Unfreezable moisture contents W_d^u (= m^u/m_d) versus the total moisture contents W_d (= m/m_d) for fresh sugar beet and after storage. Adopted from (Mykhailyk and Davydova, 2000).

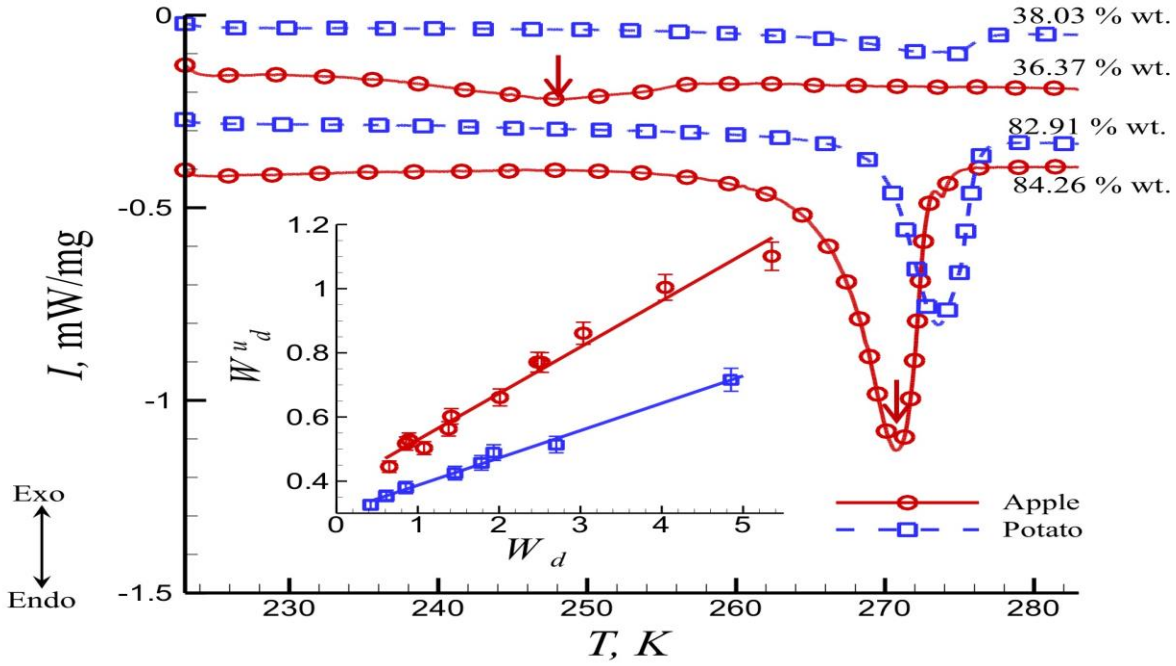

Fig. 8. Examples of DSC curves of melting of the "free" water (heat flow *I* versus temperature *T*) in apple, potato at different moisture content adopted. Insert shows dry basis unfreezable water contents W_d^u (= m^u/m_d) versus the total moisture contents W_d (= m/m_d) (both on dry basis) for apple and potato, adopted from (Snejkin et al. 2011).

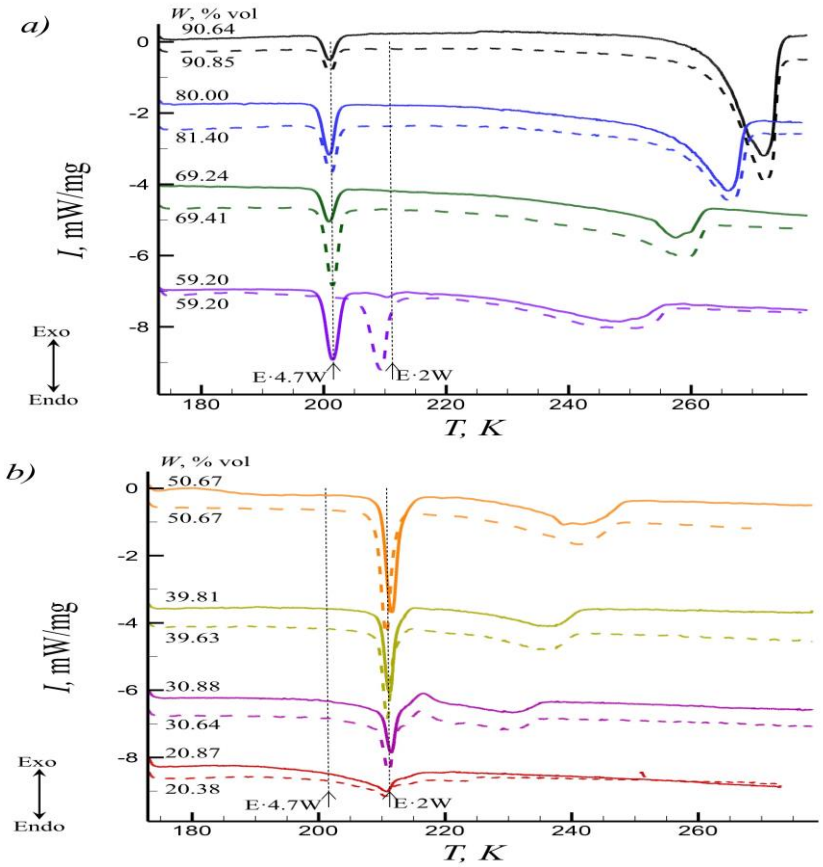

Fig. 9. DSC heating curves (heat flow *I* versus temperature *T*) of aqueous solutions of ethanol obtained by adding of water to ethanol (solid) and adding of ethanol to water (dashed) at different concentrations of water $W>59.2\%$ vol (a) and $W<50.67\%$ vol (b). Adopted from (Mykhailyk, 2010).

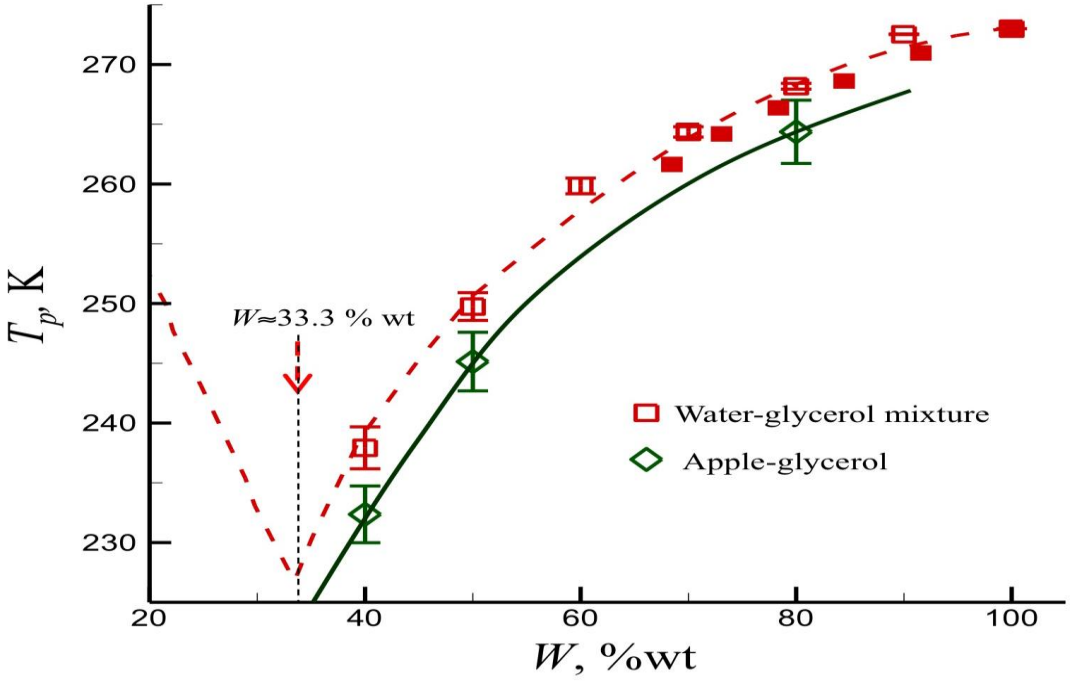

Fig 10. Melting point T_p versus concentration of water (samples water-glycerol) or juice (sample apple-glycerol) in glycerol, W. The samples of apples-glycerol were PEF-treated (Z = 0.95) and then subjected to osmotic impregnation. Dashed line and filled squares shows previously reported data on $T_p(W)$ dependence (Bohon and Conway, 1972; Weng et al., 2011b), arrow at W≈33.3% wt shows eutectic concentration with a melting point of 226.7 K. (Compiled from the data presented in (Parniakov et al., 2015)).

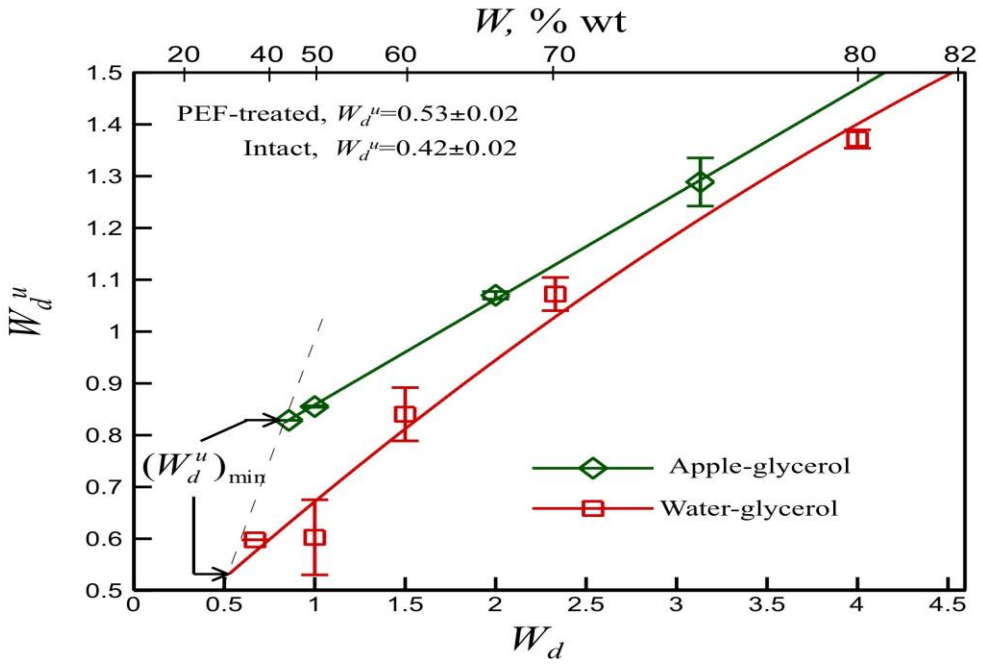

Fig. 11. Unfreezable dry basis moisture contents W_d^u (= m^u/m_d) versus the total moisture contents W_d (= m/m_d) for the samples water-glycerol mixture and apple+glycerol. (Compiled from the data presented in (Parniakov et al., 2015)).