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THERMAL ANALYSIS OF FOOD PRODUCTS USING DIFFERENTIAL SCANNING CALORIMETRY (DSC)

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Summary: Intensity of changes during the freezing storage of frozen foods, depends on several factors. Changes of foods during freezing and thawing can be rapidly determined by scanning calorimetry (DSC). The aim of this study was to test the influence of scanning rate on the thermal properties of previously heat-treated food products (boiled apple), using the differential scanning calorimetry method. By increasing the scanning rate, significant changes ($p<0.05$) $T_c$on from -14,20 °C (rate 5 °C/min) to -15.57 °C (rate 15 °C/min) and $T_c$end (from -17.53 °C to -22.90 °C) were determined, and ΔT_c increased from 3.33 °C to 7.33 °C. At the same time, the width of the melting temperature interval (ΔT_m) increased from 7.80 °C to 12.87 °C. The glass transition temperature ($T_g$mid) ranged from -7.15 °C (rate 5 °C/min) to -6.60 °C (rate 15 °C/min). Based on the obtained results, it was found that the scanning rate during the DSC determination statistically significantly ($p<0.05$) influenced the measured values of the thermal properties of the tested heat-treated apple samples.

Keywords: DSC, food products, apple, frezing, thermal properties.

1. INTRODUCTION

The applications of low temperature are very common during canning of fresh or processed foods [1-3]. Many authors [4] consider that changes in products are smallest if they are stored at low temperatures, which is also a kind of canning process. Frozen fruit can retain desirable nutritional properties for many months. Studies conducted on the effect of freezing on the composition and properties of meat have shown that the freezing process (temperature, freezing rate), storage and thawing conditions of previously frozen different food products affect their thermal properties [5 –7].

Water plays a crucial role in changing food properties during freezing. Water in food products can be in a different state, that is, for other ingredients in food, it can be bound in different ways and by different forces. During freezing, water changes from a liquid to a solid state, changing its relation to other ingredients, especially to proteins and carbohydrates. The change in the aggregate state of water takes place in very complex conditions. Changing the status of the water molecule in a product surely affects the state of proteins, simple sugars, polysaccharides and other ingredients, which can lead to changes in the structure and other properties of freezing products, and directs the flow of the technological process that will be applied during processing [8,9].

The water content in the fruit is high. Water affects the biochemical properties and microbial sustainability of fresh fruits [10]. During the ripening of the fruit, the starch splits into simple sugars, which manifests as an increase in sweetness. At the same time, there is a change in the consistency of the fruits, during which the softness increases. Starch and other polysaccharides are poorly soluble or insoluble in water, while the created simple sugars have good solubility in water. Due to the increase in concentration of water, sugars, some proteins and other molecules act to reduce the freezing point (cryoscopy). Part of the liquid water in the fruit, at the initial freezing temperature, is transferred to ice, while the dissolved substances migrate to the remaining liquid part and thus further reduce the temperature required for freezing of the new amount of water [11]. On the other hand, the change in the aggregate state of water during freezing of whole fruits or pieces of fruits, depends on the ability of carbohydrate molecules and proteins to retain water molecules, that is, the ability of these molecules to

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release water molecules more easily or harder, which will subsequently transition to a solid aggregate state.

Very often, before freezing, in the food industry, fresh fruits are blanched. Blanching is a process of short-term heat treatment for the purpose of denaturing enzymes that affect color or in order to increase the softness of a product.

The demand of the manufacturing industry and markets goes towards high and consistent quality of finished fruit products. To meet these requirements, manufacturers apply different processes during the processing or production of semi-finished products in order to keep under control the influence of the composition (content of water, protein, carbohydrates) and the condition of other ingredients (starch/simple sugars ratio, starch state, degree of denaturation protein). Manufacturers apply different freezing procedures, which differ from each other in the rate of heat removal, that is, the rate of cooling of the product.

These factors influence the onset of phase changes (the transition of water from liquid to solid state and inversely) and the rate of phase change. Savanović et al. [12] observed phase changes during DSC analysis of fresh fruits and vegetables. The aim of this paper was to investigate the effect of the scanning rate on the thermal-physical properties of heat-treated apple fruits during phase changes (freezing, thawing, glassy state).

2. MATERIAL AND METHODS

2.1. Material

Samples of heat-treated apples were used during testing in this work. Fresh apple fruits were purchased from the sales network in 5 separate shops (parallel samples for analysis). The criteria for sample selection were freshness (product picked the same day or the day before the test) and product temperature (below 15 °C). In addition, the products were visually evaluated (fruits without damage and whole fruits, fruits of uniform size and color).

2.2. Methods

Differential scanning calorimetry was used to record thermograms (*DSC calorimeter, Model 204 F1, Phoenix, Netszch*). Samples (14±2 mg) were weighed into 25 µl capacity aluminum pans. After that, pans were hermetically sealed. An identical empty pan was used as a reference sample during the experiments. The calibration of the cell was made following the DSC manufacturer's recommendation. All scanning was made in nitrogen atmosphere (purity 99.999%), and flow rate was 20 ml/min. The samples were exposed to the following temperature program:

1. isothermal phase at 20 °C, 5 min;
2. heating at a specified rate from 20 °C to 100 °C
3. isothermal phase at 100 °C, 5 min
4. cooling at a specified rate from 100 °C to -40 °C;
5. isothermal phase at -40 °C, 5 min;
6. heating at the same rate from -40 °C to 20 °C.

The tested samples were scanned at different rates (a pre-set program for cooling and heating of the samples): 5, 10, 15 °C / min [12]. Three measurements were taken for each sample. As a result of measurements, freezing and thawing curves were obtained as a function of time (Figure 1) and temperature (Figure 2), which were processed using appropriate software (*Proteus software, version 6.1.0, NETZSCH – Gerätebau GmbH, Germany*). From the DSC freezing curve the temperature of onset crystallization ($T_c$on), peak crystallization (T_c), end crystallization ($T_c$end) and crystallization temperature interval (ΔT_c = $T_c$on-$T_c$end) were determined, while from the thawing curve the temperature of onset melting ($T_m$on), the peak melting (T_m), the end melting ($T_m$end), and the melting temperature interval (ΔT_m = $T_m$end-$T_m$on) were determined (Figure 3). From the heating curve, a temperature interval was determined that defines the glassy state parameters ($T_g$on, $T_g$mid, and $T_g$end) (Figure 4).

Statistical analysis. The results were presented as the mean values accompanied by their standard deviations of three measurements. One factor analysis of variance (ANOVA) was performed using *IBM SPSS Statistics for Windows, version 22.0 (Armonk, NY, USA*). Where significant differences ($p < 0.05$) were detected, Dancan multiple comparison was used to compare treatment means and create statistically homogeneous groups.

3. RESULTS AND DISCUSSION

Differential scanning calorimetry belongs to a group of thermal analysis based on measuring the heat flux difference between the sample and the reference substance, that is, the energy required to equalize the temperature between the sample and the reference substance, during heating or cooling of the sample, under controlled conditions. In food products, due to the heterogeneous nature of the

products, it is difficult to perform a mathematical description of phase transitions [2, 13,14], therefore the DSC technique can be successfully used to determine phase transitions in different food systems [6,7,15,16]. The DSC thermogram or heat flow curve represents the relationship between heat flow and temperature (°C) obtained during the scanning of food samples. During the realization of this experiment, DSC analysis of thermally treated apples (at 100 °C) were performed (Figures 1 and 2). The DSC thermogram (Figure 2) shows the cooling curve of samples from 100 °C to -40 °C (exothermic process) and the heating of samples from -40 °C to 20 °C (endothermic process). The heating curve includes the glass transition phase (second order equation) and the peak of ice melting. The thermograms obtained in this paper are similar to thermograms in previously published papers for other food products with high water content [10, 12, 17].

In thermally treated apple samples (water content in fresh samples was 85.79%), a statistically significant influence ($p>0.05$) of cooling rate on observed parameters of water crystallization in the tested samples was found (Table 1). With increasing cooling rate, a decrease in crystallization temperatures was observed, namely: $T_c$on from -14.20 °C to -15.57 °C; T_c from -14.70 °C to -17.30 °C; $T_c$end from -17.53 °C to -22.90 °C and an increase of the crystallization temperature interval from 3.33 °C (rate 5 °C/min) to 7.33 °C (rate 15 °C/min). Higher heating rates resulted in an increase in ΔT and surface area below the DSC crystallization curve and the peak area below the DSC melting curve. With an increasing heating rate, an increase in melting temperatures was observed: $T_m$on from -3.90 °C to -2.87 °C; T_m from 2.73 °C to 7.13 °C; $T_m$end from 3.90 °C to 10.00 °C, and increase in the melting temperature interval from 7.80 °C (rate 5 °C/min) to 12.87 °C (rate 15 °C/min) (Table 2). Drissi et al. [18], examining the influence of the melting rate of paraffin-based materials, found that ΔT_c increased from 0.5 °C/min to 20 °C/min with an increase in the DSC scanning rate, that is, melting of crystal.

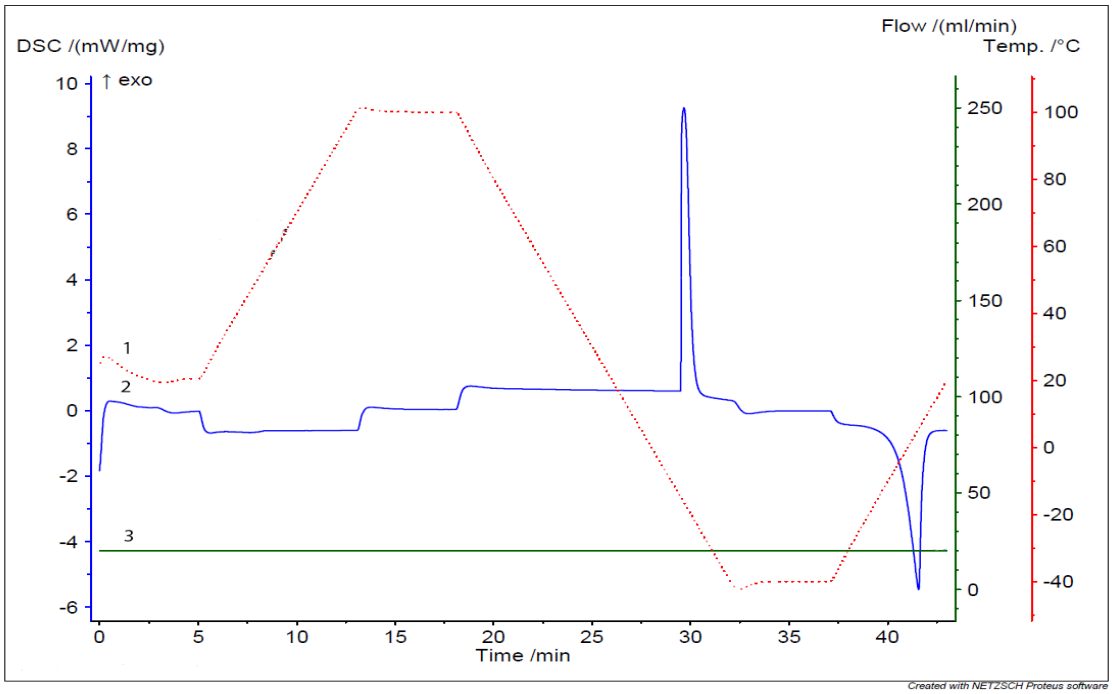

Figure 1. Typical DSC/Time curves heat-treated apples (water content 85.79%), scanning rate 10 °C/min.

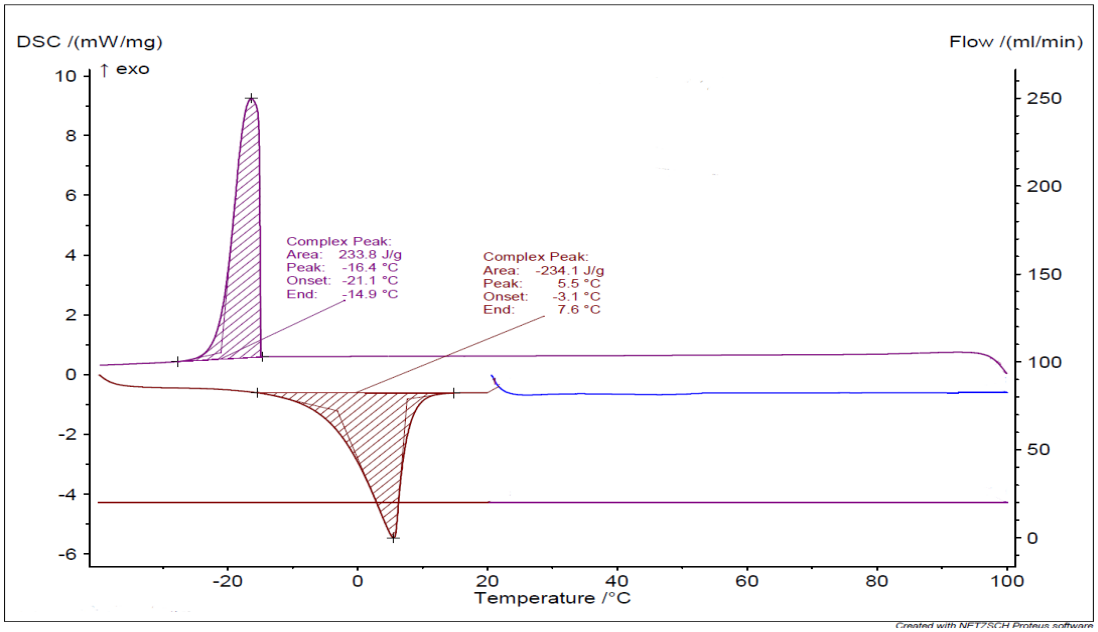

Figure 2. Typical DSC/Temperature curves heat-treated apples (water content 85.79%), scanning rate 10 °C/min.

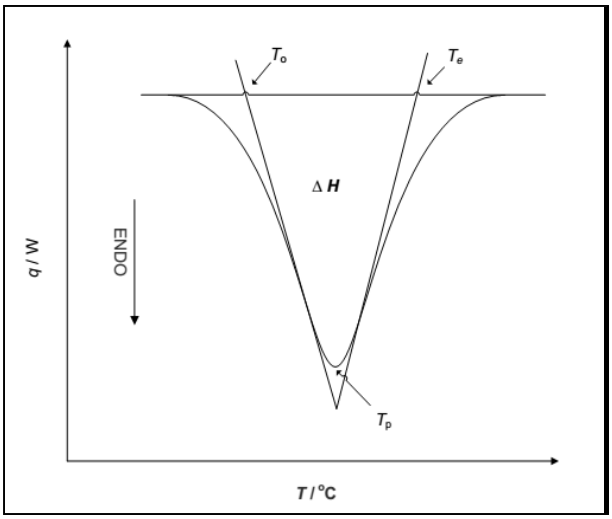

Figure 3. Typical thermogram of a frozen apple: onset (T_o), end (T_e) and peak temperature (T_p)

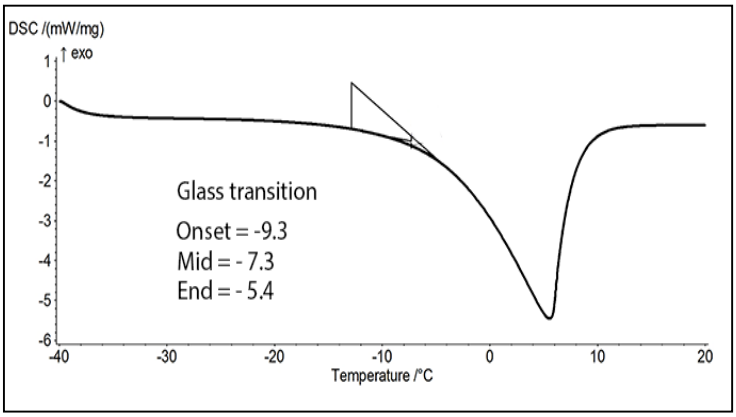

Figure 4. Glass transition stage on DSC heating curve, scanning rate of 10 °C/min, initial ($T_g$onset), medium ($T_g$mid) and end ($T_g$end) temperature

Table 1. The average values of the onset crystallization temperature ($T_c$on), peak crystallization temperature (T_c), end crystallization temperature ($T_c$end) (°C) of the heat treated apples samples determined by the DSC thermograms, obtained during scanning at different rates (5, 10, 15 °C /min)

Rate (°C/min)	*Crystalization (from +20°C to -40°C)*			
	$T_c$on (°C)	T_c (°C)	$T_c$end (°C)	ΔT_c (°C)
5	-14,20[b] ± 0,14	-14,70[a] ± 0,14	-17,53[a] ± 0,07	3,33[a] ± 0,07
10	-15,37[a] ± 0,64	-16,63[b] ± 0,49	-21,37[b] ± 0,25	6,00[b] ± 0,44
15	-15,57[a] ± 0,12	-17,30[c] ± 0,17	-22,90[c] ± 0,26	7,33[c] ± 0,38

[a-c] Mean values with a different letter in the same column are statistically significantly different from 95% probability ($p<0.05$)

Table 2. Average values of the onset melting temperature ($T_m$on), peak melting temperature (Tm), end melting temperature ($T_m$end) (°C) of heat treated apple samples determined with DSC thermograms, obtained during scanning at different rates (5, 10 and 15 °C /min)

Rate (°C/min)	*Melting (from +20°C to -40°C)*			
	$T_m$on (°C)	T_m (°C)	$T_m$end (°C)	ΔT_m (°C)
5	-3,90[a] ± 0,14	2,73[a] ± 0,07	3,90[a] ± 0,07	7,80[a] ± 0,21
10	-3,13[b] ± 0,06	5,63[b] ± 0,15	7,77[b] ± 0,29	10,90[b] ± 0,35
15	-2,87[c] ± 0,15	7,13[c] ± 0,57	10,00[c] ± 0,40	12,87[c] ± 0,38

[a-c] Mean values with a different letter in the same column are statistically significantly different from 95% probability ($p<0.05$)

The glassy state temperature (Tg) is the temperature above which solid amorphous substances transfer to soft, rubbery materials, with an increase in the mobility of molecules and a decrease in viscosity [19]. The simple sugars and organic acids present in the fruit become amorphous. Table 3 shows the average values of temperatures defining the glassy state. In all cases, the temperatures at the beginning, middle and end of the phase change were determined. With increasing the scanning rate, the glassy state begins and ends at lower temperatures (shown as $T_g$on and $T_g$end, respectively). Roos [20] considers that the temperature at which the glass transition ($T_g$onset) begins is more significant than the temperature of the end glass transition ($T_g$end), while a dramatic change in the properties of food products occurs at $T_g$onset. Sugars and organic acids, which are present in fruits, have a low glass transition temperature (T_g), are very hygroscopic in the amorphous state, so they act in the direction of increasing the stickiness of fruit products [21]. Water acts as a plasticizer and reduces the transition state temperature of the product. This problem can be overcome by the addition of ingredients that have high T_g: maltodextrins and substances against clotting [22].

Table 3. Average values of the onset temperature of the glass state ($T_g$on), the peak midpoint temperature ($T_g$mid), the end temperature of the glass state ($T_g$end) (°C) of the heat-treated apple samples determined from the DSC thermograms, obtained during scanning at different speeds (5, 10, and 15°C/min)

Rate (°C/min)	Glass state		
	Tg onset	Tg mid	Tg end
5	-8,80 ± 0,42[a]	-7,15 ± 0,49[a]	-5,45 ± 0,49[a]
10	-9,45 ± 0,21[a]	-7,45 ± 0,21[a]	-5,45 ± 0,07[a]
15	-9,55 ± 0,35[a]	-7,60 ± 0,42[a]	-5,70 ± 0,42[a]

[a-c] Mean values with a different letter in the same column are statistically significantly different from 95% probability ($p<0.05$)

Water, as the most abundant ingredient in most easily digestible foods, is in the free state, while only one part of the water is bound to proteins, carbohydrates and soluble salts [23,24]. Food products that have a low water content (fresh, dried) belong to amorphous materials, and they are in a glass or rubber state [25]. Guizani et al. [10] found that such state of the product decreases the activity of the ingredients that may affect the product's spoilage. In order to preserve the composition and high quality of the product, Roos [26] recommends that food should be kept below the glass transition temperature.

There is no sudden transition to the ice-water region, that is, the food gradually moves over the glassy state to the frozen, solid state. Therefore, only an initial freezing temperature can be defined for some product [27]. At which temperature will complete freezing occur, mostly depends on the concentration of the soluble part of the dry matter. The freezing point will be lower if the dry matter concentration is higher. In fact, with increasing concentration of soluble substances in water, intermolecular forces between water molecules are disturbed, their polarization occurs on the surface of dissolved substances, thus changing the property and behavior of water in the product.

4. CONCLUSION

Using the differential scanning calorimetry (DSC) it is possible to determine the thermal properties that describe the change in the state of food during freezing and thawing. The cooling and heating rate (5, 10, 15 °C/min) statistically significantly affects ($p < 0.05$) the onset temperatures of crystallization and melting, the maximum/minimum temperatures of the crystallization and melting curves, the end temperatures of crystallization and melting, as well as the temperature intervals of the phase changes of freezing and thawing of heat treated apple samples.

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ТОПЛОТНА АНАЛИЗА ПРЕХРАМБЕНИХ ПРОИЗВОДА ПОМОЋУ ДИФЕРЕНЦИЈАЛНЕ СКЕНИРАЈУЋЕ КАЛОРИМЕТРИЈЕ (DSC)

Сажетак: Интензитет промјена током смрзавања и складиштења хране у смрзнутом стању зависе од више фактора. Промјену стања хране током смрзавања и одмрзавања може се брзо одредити помоћу диференцијалне скенирајуће калориметрија (DSC). Циљ овог рада је био да се утврди утицај брзине скенирања на својства претходно топлотно обрађених прехрамбених производа (барена јабука), коришћењем диференцијалне скенирајуће калориметрије. Повећањем брзине скенирања установљена је значајна промјена ($p<0,05$) $T_c$on од -14,20 °C (брзина 5 °C/мин) до -15,57 °C (брзина 15 °C/мин) $T_c$end (од -17,53°C до -22,90 °C), односно ΔT_c је порастао са 3,33 °C на 7,33 °C. Истовремено је ширина температурног распона током топљења узорака (ΔT_m) порасла са 7,80 °C на 12,87 °C. Температура стакластог прелаза ($T_g$mid) се кретала од -7,15 °C (брзина 5 °C/мин) до -6,60 °C (брзина 15 °C/мин). На основу добијених резултата, установљено је да брзина скенирања током DSC одређивања статистички значајно ($p < 0,05$) утиче на измјерене вриједности топлотних својстава испитиваних узорака топлотно обрађене јабуке.

Кључне ријечи: DSC, прехрамбени производи, јабука, смрзавање, топлотна својства.

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