EFFECT OF EMULSIFIERS OF THE STARCH GELATINIZATION IN SPONGE CAKE BATTER
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Abstract. The present research investigated the effect of three types of emulsifiers on the starch gelatinization in sponge cake batter. The method of differential scanning calorimetry (DSC) was applied to determine the changes in the gelatinization temperature and the endothermic transition enthalpy during the baking of sponge cake batters. The following 4 samples were examined – control sponge cake, prepared by traditional recipe, sponge cakes with added 1% of one of the following emulsifiers-polyglycerol monostearate ester (E475), sucrose stearate ester (E473) and modified inulin palmitate ester (HP-25). It was found that the presence of emulsifier affected both the gelatinization temperature and the phase transition enthalpy. The starch gelatinization in the control was carried out in the lowest temperature range and was characterized with the lowest transition energy (enthalpy of the endothermic transition) - 1.78 J/g. The addition of emulsifiers let to narrowing the temperature range where the gelatinization is observed and to increasing the gelatinization temperature and the transition energy. The most pronounced effect was observed for the samples, which were with the sucrose stearate ester. The transition energy in this case was 2.68 J/g. The results obtained confirmed the emulsifiers retard the starch gelatinization in sponge cake batter.

INTRODUCTION
The degree of water absorption in starch determines the change of the foamed mixture into a stable porous structure during baking in the production of sponge cake (Baeva, Terzieva, & Panchev, 2003; Guadarrama-Lezama, Carrillo-Navas, Pérez-Alonso, Vernon-Carter, & Alvarez-Ramirez, 2016; Handleman, Conn, & Lyons, 1961; Muzukoshi, 1985). The incorporation of emulsifiers in the batter composition affects the degree of starch gelatinization (Chevallier, Colonna, Della Valle, & Lourdin, 2000; Gomez et al., 2004; Kohajdová, Karovičová, & Schmidt, 2009). The emulsifiers control this process by shifting the starch gelatinization temperature to higher values (Buck & Walker, 1988; Derby, Miller, Miller, & Trimbo, 1975; Handlema et al., 1961; Kim & Walker, 1992; Richardson, Langton, Bark, & Hermansson, 2003). Some studies (Buck, & Walker, 1988; Eliasson, 1985;
Richardson et al., 2003) report the application of emulsifiers such as monoglycerides, diglycerides and polyglycerol esters, which affect the initial temperature of gelatinization.

The amount of added emulsifiers from in the concentration range of 1 to 3% from the weight of the flour increases the gelatinization temperature from 67 °C to 86 °C (Buck, & Walker, 1988; Eliasson, 1985). It has been shown (Eliasson, 1985; Kim & Walker, 1992; Marcotte, Sablani, Kasapis, Baik, & Fustier, 2004; Nunes, Moore, Ryan, & Arendt, 2009; Richardson, Kidman, Langton, & Hermansson, 2004; Sahi & Alava, 2003) that this effect is due to the emulsifier’s ability to absorb water and to bind to the starch macromolecular chains in a way, similar to the sucrose (Baeva, Terzieva, & Markov, 1997; Chevallier, Colonna, Della Valle, & Lourdin, 2000; Perry & Donald, 2002; Spies & Hoseney, 1990; Wootton & Bamunuarachchi, 1980).

The complex between the emulsifier and the amylose is described as an amylose helix formation around the hydrophobic part of the emulsifier (Richardson et al., 2004). The use of emulsifiers with a higher degree of polymerization significantly increased the retarding effect on the starch gelatinization (Sahi & Alava, 2003). The retarded starch gelatinization increases the extent of air bubbles expansion, which determines the formation of the porous structure in the baked product (Baeva et al., 2003; Guadarrama-Lezama et al., 2016; Handleman et al., 1961; Muzukoshi, 1985). Thus, the addition of emulsifiers to the bakery products leads to specific product features - extending the shelf life of bread and bakery products, reducing the stickiness of the batter and controlling the rheological properties of batter (Adheeb Usaid, Premkumar, & Ranganathan, 2014; Fessas & Schiraldi, 2000; Gomez, et al., 2004; Kohajdová et al., 2009; Münzing, 1991; Nunes et al., 2009).

The aim of the present research is to investigate the effect of different kinds of emulsifiers on the starch gelatinization in sponge cake system using the method of the differential scanning calorimetry.

**MATERIALS AND METHODS**

**Sponge cake preparation**

Standard raw materials such as wheat flour of “Type 500” – ash 0.5% (GoodMills, Bulgaria EAD), granulated sugar (Zaharni zavodi AD), eggs (local market), glycerol, water and emulsifiers used in the current study are authorized by the Ministry of Health as manufactured in Bulgaria. Three different emulsifiers (food surfactants or surface active agents) are considered as optional additives and are used as batter and cake improvers: polyglycerol monostearate E475 (Radiamuls Poly 2248K) (Oleion Group, Belgium), sucrose stearate E473 (Sisterna SP70-C) (SISTerna, Netherlands) and modified inulin palmitate (HP-25), produced by University of Food Technologies, Department of Organic Chemistry and Microbiology, Bulgaria. Emulsifiers are added to the formulation at 1% (amount based on the batter).

The batter formulations of the studied sponge cakes are given in Table 1. The mixture for the control sponge cake (batter-control) was prepared following a traditional technology and formulation (Angelov, Bekirov, Genadieva, & Atanasov, 1974), according a double-bowl mixing procedure. The recipe for making batter included preliminary separation of egg whites and yolks. The batter with the
addition of surfactant as an emulsifier gel is prepared by a single-bowl mixing process of the components.

The sponge cakes were baked in a metallic pan containing 75 g of batter and placed in an electric oven (Rahovetz -02, Bulgaria) for 30 min at 180 °C.

Physical characteristics of the batters and cakes

The thermal properties of the sponge batter were characterised by means of a differential scanning calorimeter DSC 204F1 Phoenix (Netzsch Geräebau GmbH, Germany). The calorimeter was calibrated by indium standard. Sponge cake batter samples (10 - 15 mg) were closed hermetically in aluminium pans and heated in the calorimeter from 20 to 150 °C at a rate of 5°C/min. These conditions are similar to those of the center of the batter during the baking. The temperatures and the enthalpy of the thermal transitions were determined with the use of instrument’s software Proteus Analysis (Netzsch, Germany). The enthalpy values were expressed as J/g.

The moisture content in the batter and the crumb cake (2 h after baking) was determined using the AACC method 44–11 (AACC, 2000) after drying out in an oven at 105 °C to constant weight. The measurements were done in triplicate and the mean values were presented.

The water activity of the batter and the crumb samples was determined using a Novasina AG CH-8853 water activity meter (Zurich, Switzerland) at 20 °C. The samples were put in sample cups and hermetically covered before analysis to avoid moisture loss or gain. The a_w-metre was calibrated with a saturated sodium chloride (NaCl) salt solution. The water activity was measured in triplicate on cake batters and crumb cakes.

For the determination of the sponge cake crumb structure, optical photographs were taken of the cross sections of the half-cut cake.

Data analysis

All analyses were conducted in triplicate and the average values are reported. For the assessment of the measured results accuracy a statistical method with level of significance p ≤ 0.05 was used. The data were analyzed and presented as mean values ± standard deviation.

RESULTS AND DISCUSSION

The progress of the starch gelatinization process is related to the absorption of energy required for destroying the native structure of the starch grains, accompanied by water adsorption (swelling). The observed changes in the endothermic peaks in the DSC curves are due to the different degree of the starch swelling in the sponge batters during the heating. Therefore the change in the energy value of the sponge system is caused to some extent by the change in the forms of the bound water. As a result the water activity of the sponge system correlates to the forms of the bound water. The water activity characterizes the reaction ability (chemical potential) of the water in the system. If the water activity decreases, the chemical potential and decreases too, and then the reactions involving the water in the colloidal system will require more energy in comparison with the free water. The factors affecting the water activity: type and concentration of the ingredients and the temperature of the environment, determine the forms of the bound water, which is involved in the process of the starch gelatinization.
Table 1: Sponge cake batters formulations

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Amount based on wheat flour, [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>control sample</td>
</tr>
<tr>
<td>Yolk of egg</td>
<td>43.22</td>
</tr>
<tr>
<td>White of egg</td>
<td>96.77</td>
</tr>
<tr>
<td>Refined granulated sugar</td>
<td>83.87</td>
</tr>
<tr>
<td>Wheat flour type 500</td>
<td>100.00</td>
</tr>
<tr>
<td>Emulsifier (Surfactants)</td>
<td>-</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
</tr>
<tr>
<td>Glycerol</td>
<td>-</td>
</tr>
</tbody>
</table>

This fact enables to recognize the relationship between the sponge batter ingredients and to analyse their impact on the quality of the final crust. The amount of the total water in the system depends on the type of the components in the batter formulation (Table 1), moisture content and water activity of the batter and the crumb of the baked cake (Table 3).

The surfactants (emulsifiers) used in the present research play an important role in the retarding of the starch gelatinization during the baking process and in this way the immobilized in the batter air bubbles can sufficiently increase their volume before the solidification of the sponge system. The sponge batter, which is in the state of liquid aerated mixture (foam) transforms to porous stable structure. As a result of these processes a crumb with specific porous structure and high volume is formed. The energy, transmitted during the heating to the sponge system with added surfactants, is involved in the destruction of the bonds between the emulsifier and the amylose in the starch, destruction of the bonds between the sucrose and the starch molecules (Baeva, Terzieva, & Markov, 1997; Chevallier, Colonna, Della Valle, & Lourdin, 2000; Perry & Donald, 2002; Spies & Hoseney, 1982; White & Lauer, 1990; Wootton & Bamunuarachchi, 1980).

Therefore the change in the energy value of the sponge system is caused to some extent by the change in the water state. Depending on the balance between the three processes an endothermic phase transition of the starch gelatinization in the sponge mass with added surfactants forms. An increase in the initial starch gelatinization temperature in sponge batters with added emulsifiers in comparison to the control batter is clearly detected. The lowest value of the initial starch gelatinization temperature (70 °C) is detected for the control batter. The starch gelatinization for all the samples containing emulsifier gels starts at 72 °C. Therefore the binding of water in the starch gelatinization in its initial degree of swelling starts for the control batter at lower temperatures and with lower energy.
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consumption compared to other samples – Fig. 1-4 and Table 2. This fact is due to the relatively high water activity of the control batter in comparison to the other batters – Table 3.

Table 2: Values of the thermal transitions

<table>
<thead>
<tr>
<th>Type of sponge cake batter</th>
<th>Gelatinization temperature ranges (ΔT), °C</th>
<th>Peak gelatinization temperature, (T_p), °C</th>
<th>Gelatinization enthalpies (ΔH), [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sponge cake batter control</td>
<td>(70 - 92) Peak 1 – 80.5 Peak 2 – 88.1</td>
<td></td>
<td>1.78±0.08</td>
</tr>
<tr>
<td>Batter with 1% polyglycerol monostearate ester (E475) /PGE/</td>
<td>(72 – 100) Peak 1 – 87.3 Peak 2 – 90.0</td>
<td></td>
<td>2.66±0.51</td>
</tr>
<tr>
<td>Batter with 1% sucrose stearate ester (E473) /SE/</td>
<td>(72 – 100) Peak 1 – 85.5 Peak 2 – 89.3</td>
<td></td>
<td>2.68±0.33</td>
</tr>
<tr>
<td>Batter with 1 % modified inulin palmitate ester (HP 25)</td>
<td>(72 – 100) Peak 1 – 86.5</td>
<td></td>
<td>2.46±0.48</td>
</tr>
</tbody>
</table>

Figure 1
Thermograms for the starch gelatinization in batter sponge cake control


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Figure 2
Thermograms for the starch gelatinization in batter sponge cake the addition of polyglycerol monostearate ester (E475)

Figure 3
Thermograms for the starch gelatinization in batter sponge cake the addition of sucrose stearate ester (E473)


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Figure 4

Thermograms for the starch gelatinization in batter sponge cake the addition of modified inulin palmitate ester (HP-25)

Table 3: Mean values¹ of the moisture content and the water activity of the batter and crumb cake

<table>
<thead>
<tr>
<th>Sample</th>
<th>Physical characteristics² of the batters and cakes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a_w ) cake batter</td>
</tr>
<tr>
<td>Control</td>
<td>0.977 ± 0.001</td>
</tr>
<tr>
<td>With addition of polyglycerol monostearate ester (E475)</td>
<td>0.916 ± 0.001</td>
</tr>
<tr>
<td>With addition of sucrose stearate ester (E473)</td>
<td>0.904 ± 0.001</td>
</tr>
<tr>
<td>With the addition of inulin palmitate ester (HP-25)</td>
<td>0.898 ± 0.001</td>
</tr>
</tbody>
</table>

¹ The values are mean ± SD (p ≤ 0.05).
² The temperature of the batter and crumb is on the average 20.0 ± 0.5 °C.


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The higher water activity of the control batter determines the higher degree of starch gelatinization, which affects the formation of porous structure in the final product (Figure 5).

The thermal transitions of starch gelatinization in the samples with added emulsifiers are characterized with higher enthalpies than the control batter. This fact could be explained with the relatively lower water activity for the batters with added emulsifiers in comparison with the control batter (0.977 ± 0.001) (Table 3). As shown in Table 2 the starch gelatinization process in the control batter finishes at lower temperature of 92°C. Higher energy values are required for starch gelatinization when emulsifiers are added to the batters and therefore the temperatures of the endothermic phase transitions are shifted to higher values (Table 2 and Fig. 1-4). Similarly the enthalpy of starch gelatinization for the control sample is the lowest (1.78 J/g) (Table 2), and it is higher for the batters with added sucrose stearate ester and polyglycerol monostearate ester (2.68 – 2.66 J/g).

The temperatures of the endothermic phase transitions in the sponge batters with added emulsifiers are shifted to higher values corresponding to higher energy levels (enthalpies). Therefore, the energy for starch gelatinization in the sponge batter with emulsifier gels is about 1.5 times bigger than the energy in the control batter (Table 2).

The most pronounced retarding effect on the process of starch gelatinization has the addition of 1% inulin-palmitate ester. The water activity of the sponge batter in this case is the lowest (0.898 ± 0.001). The DSC curve of heating the batter with inulin palmitate ester is characterized by sharp single endothermic peak (Fig. 4).

The role of the surfactants in the retarding of the starch gelatinization is confirmed by the measured values for the moisture content of the cake batters and the crumb cake. A relatively low water content (36.44 ± 1.71) but the highest water activity in comparison to the samples with added emulsifiers is observed for the control batter. This may be due to the different degree of dilution of the surfactant emulsifiers in the preparation of the gel in the composition of the sponge batter, and to the binding effect of the emulsifier to water in the system. This tendency of binding of the
emulsifiers to the water is retained in the process of baking, and it is most pronounced for sponge system with inulin palmitate ester whose water activity is statistically indistinguishable in the batter and in the cake crumb. The cake with addition of polyglycerol monostearate ester is characterized by the highest water activity (0.908 ± 0.001), and the water activity of the cake with inulin palmitate ester is comparable to that of the cake with addition of sucrose stearate ester (0.898 - 0.899). The change in the water activity during the thermal treatment is the greatest for the sponge system without addition of emulsifier. It is the highest at the initial state (control batter) and the lowest in the baked cake (0.808 ± 0.001). The water activity of the control cake was significantly lower than those with added surfactants, confirming a high degree of starch gelatinization in the control sample (Figure 1).

Therefore, effected by the addition of emulsifiers in the sponge batter, the starch gelatinization proceeds in a wider temperature range at higher temperatures and with higher energy consumption. Based on these facts, one could consider that the emulsifiers exhibit retarding effect on the starch gelatinization in sponge batter. The retarding effect of the emulsifiers on the starch gelatinization delays the solidification of the dough and extends the period of gas expansion in it, and hence affects the structure of the sponge cake (Figure 5).

**CONCLUSIONS**

1. Partial crystallization is observed for all investigated sponge cake batters. The process proceeds to varying degrees and finishes at different temperatures intervals covering the range of 70-100 °C. The incomplete starch gelatinization contributes to solidification of the batter and turns it into colloidal-porous structure.

2. The starch gelatinization in the presence of the emulsifier polyglycerol monostearate ester (E475), sucrose stearate ester (E473) and modified inulin palmitate ester proceeds in wider temperature range and at higher energy consumption. The highest enthalpy of gelatinization is calculated for batters with addition of sucrose stearate ester and polyglycerol monostearate ester (2.68 – 2.66 J/g).

3. It has been shown that the emulsifiers exhibit retarding effect on the starch gelatinization in sponge cake batters. The most pronounced retarding effect possess the inulin palmitate ester. The changes in the thermal transitions during the starch gelatinization are related to the emulsifier binding capability to both water and starch, which determines the lower degree of gelatinization. The shifting of the endothermic transitions to higher temperatures determines the strongest binding role of emulsifiers on the ability of starch to bind the water in the system. It is assumed that the concurrent binding of the emulsifier with the water and the amylose determines a low degree of starch gelatinization in the sponge system.

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