EFFECT OF AERATION MODE AND STORAGE ON SELECTED PHYSICAL PROPERTIES OF AGAR BASED CONFECTIONERY FILLING WITH CHOCOLATE COATING

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Abstract. In this research the influence of aeration mode and time of the storage on selected features of aerated agar based confectionery filling with vanilla flavouring was determined. Samples obtained by introducing compressed air had significantly lower density and higher porosity, and the time of storage did not have a significant influence on the density and porosity of the filling. Both the aerated agar filling and the chocolate coating of the vanilla flavoured aerated agar based confectionery filling created heterogenic and multiphase structures, wherein during the time of the storage the water activity present, caused by diffusion and secretion of the water, were a result of the syneresis of the agar gel and the crystallization of its components. These processes caused significant changes in the rheological parameters of the filling, showing changes in its structure. The obtained rheological parameters (the work of the compression and relaxation moduli) confirmed higher elasticity of the samples obtained by mode A and showed that the aeration level caused faster damage to the structure of the samples.

Keywords: aerated confectionery filling, chocolate coating, density, porosity, water activity, work of compression, asymptotic residual stress.

INTRODUCTION

The shelf life of food products is determined by numerous and complex interactions between parameters related to the product itself and/or associated with the external environment. The interaction between moisture and food is the most important, and moisture migration in food products often leads to the deterioration of quality.

Moisture migration in foods is very important in multi-domains, as there is different water activity in each domain. Moisture migrates from the domain with higher water activity to the domain with lower water activity, or to the environment,
until there is thermodynamic equilibrium. Moisture migration can be prevented by changing the water activity of food ingredients, either by decreasing the effective diffusivity of the water or by adding lipid-based edible film that is the barrier to moisture migration due to its hydrophobic nature [5].

In confectionery products with "soft-centres," including aerated agar based confectionery fillings, chocolate and chocolate-flavoured coatings are used. However, the moisture barrier properties of chocolate coatings are limited. In chocolate coatings sucrose, coca powder, and milk solids in the case of milk chocolate, are embedded in a continuous lipid phase. The pores between fat crystals do not have spherical shape and are filled completely or partially with the liquid fraction [6]. Water diffuses through the oil present between the fat crystals or through free void spaces. Moisture transfer through chocolate coatings depends on the type and physical state of fats, amount and type of hydrophilic components, and storage conditions. Kamper and Fennema [4] noticed that an increase in solid fat content from 0% to 30% decreased the water vapour permeability of lipid-based films.

Ghosh et al. [3] noticed that there was no significant difference between coatings of 0.8 mm thickness to those of 2 mm thickness.

The aim of this research was to determine the effect of aeration mode and storage on moisture migration and on rheological properties of aerated agar based confectionery filling with chocolate coating.

MATERIALS AND METHODS

Samples of branded aerated agar based confectionery filling with chocolate coating were used in this research. They were obtained by two different methods of aeration: Method A, mechanical mixing, and Method B, introducing compressed air. The samples of the aerated agar based confectionery filling with chocolate coating were received from the same batch of production, were stored in the brand barrier boxes in a room with controlled temperature +18°C ± 1°C, with a relative humidity equal to 45 ±3% for a period of 14 weeks. The first examination was performed 24 hours after production, and the examination process was repeated every 2 weeks.

Water content and water activity were determined in three different places of the cube of aerated agar based confectionery filling with chocolate coating: in chocolate coating, 2 mm depth from all six walls of the filling, and in the centre of the filing. The average size of the cubes of aerated agar based confectionery filling were equal to: \( L = 0.036 \text{ m}, \ h = s = 0.018 \text{ m} \) and the thickness of the chocolate flavoured coating was 0.0006 m.

The moisture content was determined by drying the samples with sand according to the standard PN-84/A-88027.
Water activity of the confectionery filling and chocolate flavoured coating was measured using Aqua Lab CX-2 /Decagan Devices Inc., USA. All water activity determinations were performed in three replications.

The density of the confectionery aerated filling was determined by applying the displacement method using a hydrostatic balance.

The porosity of the filling was determined based on measured density obtained from the chemical component of the filling [7].

The rheological parameters of the confectionary aerated filling (after the removal of the chocolate coating) were determined based on the compression and relaxation tests, using the Texture Analyzer type TA-XT2. The samples were compressed with a speed of 0.1 mm s\(^{-1}\), until reaching the force of 15N. Then relaxation was applied for 3 minutes.

**CALCULATION METHODS**

The work of the compression was determined by calculating area under a curve axis force vs. deformation.

The relaxation curve was linearized according to Peleg and Pollak [8]:

\[
\frac{F_o \cdot \tau}{F_o - F_\tau} = k_1 + k_2 \cdot \tau
\]

where: \(F_o\) – force (N) at which compression was terminated, \(F_\tau\) – force (N) at time \(\tau\), \(\tau\) – time (s), \(k_1\) and \(k_2\) – constants.

Differentiating eqn (1) with respect to force \(F_\tau\) and time and solving for differential equal 0 an asymptotic residual stress is obtained,

\[
S_\tau = 1 - \frac{1}{k_2}
\]

that is the stress which is not relaxed even after an infinite relaxation time.

**RESULTS AND DISCUSSION**

**Characteristic of the Product**

The results of the chemical composition of the aerated agar based confectionery filling vanilla flavour with chocolate coating are shown in Table 1. The average chemical composition of the chocolate coating is as follows: 0.5-1.5% water, 50-51.5% carbohydrates, 29.5-32% cocoa butter and 18-18.5% cocoa solids (data from the manufacturer).
Table 1. Chemical composition of the aerated confectionery filling

<table>
<thead>
<tr>
<th>Component</th>
<th>Content as a mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.206</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>0.497</td>
</tr>
<tr>
<td>Fat</td>
<td>0.175</td>
</tr>
<tr>
<td>Protein</td>
<td>0.122</td>
</tr>
</tbody>
</table>

Effect of storage time on density and porosity of the aerated agar based confectionery filling

Changes of the density of the aerated agar based confectionery filling during the 14 week period of storage are shown in Figure 1. The method of aeration of confectionery filling had an essential influence on its density. The filling obtained by method B (by introducing compressed air) has about 14% lower density than the filling aerated by method A (mechanical mixing). Furthermore, the storage time did not have any substantial influence on the density. Average density was constant during the storage, between 0.861 ± 0.006 g cm$^{-3}$ for the filling obtained by method A, and 0.741 ± 0.004 g cm$^{-3}$ for the filling obtained by method B.

![Fig. 1. Effect of storage time on density of confectionery filling obtained by two methods of aeration](image_url)
The porosity of the aerated agar based confectionery fillings during the 14 week period of storage is shown in Figure 2. Neither the calculated porosity nor the density of the confectionery filling obtained by methods A and B changed during the storage. The porosity of the filing obtained by method B was 41.6 ± 0.3% and was 10 percentage points higher than the porosity obtained by method A. The obtained values of the density and porosity of the aerated confectionery filling corresponded to the values shown by Campbell and Mugeot [2] and by Pałacha and Sitkiewicz [7].

![Porosity of aerated confectionery filling](image)

**Fig. 2.** Effect of storage time on porosity of confectionery filling obtained by two methods of aeration

**Effect of storage time on water content and water activity of the aerated agar based confectionery filling**

Changes of the water content and water activity in specific places in the tested cubes of the aerated agar based confectionery filling during storage are shown in Figures 3a, 3b and Figures 4a, 4b.

Regardless of the mode of aeration, the duration of storage affects the process of changes in the water content and water activity in the specific places tested in the cubes of aerated filling. Only in the centre of the aerated agar based confectionery filling there were no significant changes in water content during the 14-week period of storage. Thus, in the centre of the aerated agar based confectionery filling ob-
tained by aeration method A, the water content amounted to 21.37± 0.21%, and in the filling obtained by aeration method B the water content was slightly lower and amounted to 20.18 ± 0.33%. Regardless of the aeration mode, a linear decrease of water content on the surface of the filling was noticed.

Fig. 3. Effect of storage time on water content (a) and water activity (b) of confectionery filling aerated by mechanical mixing (method A)
Fig. 4. Effect of storage time on water content (a) and water activity (b) of confectionery filling aerated by introducing compressed air (method B)
After the 14 week period of storage, the water content on the surface of the filling obtained by aeration method A decreased by 3 percentage points from 20.18% to 17.11%, and on the surface of the filling obtained by aeration method B by more than 2 percentage points from 19.50% to 17.21%. Different processes of change in the water content were noticed in the chocolate coating. The water content in the chocolate coating covering the filling obtained by aeration method A increased after the storage period by 1.72 %, from 0.86% to 2.5%, compared to the chocolate coating covering the filling obtained by aeration method B in which the water content increased by 0.79% percent, from 1.44% to 2.23%.

During the preparation of samples for measuring the water content and water activity, the authors noticed that after four weeks of storage a small water film was formed between the surface of the filing and the inner surface of the chocolate coating.

The results of the water balance of the cube of aerated agar based confectionery filing confirmed the formation of the water film (Tab. 2).

<table>
<thead>
<tr>
<th>Method of aeration of the confectionery filing</th>
<th>Storage time (weeks)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.025</td>
</tr>
<tr>
<td>6</td>
<td>0.054</td>
</tr>
<tr>
<td>8</td>
<td>0.137</td>
</tr>
<tr>
<td>10</td>
<td>0.066</td>
</tr>
<tr>
<td>12</td>
<td>0.046</td>
</tr>
<tr>
<td>14</td>
<td>0.095</td>
</tr>
</tbody>
</table>

The formation of the water film between the filling and the chocolate coating is most probably due to syneresis, as well as to changes in sucrose crystals, occurring in the surface of the filling. Agar gels are characterized by syneresis [1]. As a result of syneresis, the filling most probably reaches a state of equilibrium which is achieved by the alteration of any changes in the water activity during the 14 weeks of storage (Fig. 3b and 4b). Generally, the water activity in both the centre of the filling and/or the surface, did not change significantly during the 14 weeks of storage, regardless of the mode of aeration, and the differences between the methods of aeration A and B were statistically insignificant.
A different process of changes in water activity was noticed in the chocolate coating. In the chocolate coating covering the filling obtained by method A (Fig. 3b) up to the fourth week of storage the water activity slightly increased, and from the sixth until the twelfth week of the storage water activity decreased. For the chocolate coating covering the filling obtained by method B (Fig. 4b) the water activity decreased until the twelfth week of storage.

The chocolate coating was exposed to stress conditions. There was a water film on the filling and on the outside surface there was air with a certain relative humidity. Though the chocolate coating was the significant barrier for water activity due to the presence of much higher hydrophobic component in its content, the water activity was present but was much less than in the filling. During the storage period, the matrix of the chocolate coating most probably changed. The proceeding crystallization of carbohydrates and fats had a certain dynamics and, due to this process of crystallization, equilibrium was not achieved during the 14 weeks of storage. The noticed water activity of the chocolate coating (Fig. 3b and 4b) was most probably caused by changes in water vapour pressure above the liquid phase present in the void spaces of the chocolate matrix caused by crystallization.

**Influence of the time of storage on the rheological parameters of the confectionery filling**

In Figures 5 and 6 the changes of the rheological parameters of the filling obtained by compression and relaxation tests are shown. The strength of the force up to which the samples of the filling were compressed and the time of storage had a significant influence on the behaviour of the tested samples. Only for samples of the filling obtained by method A, curves of compression up to 15 N were observed during the whole period of storage. Samples of the filling obtained by method B, after ten weeks of storage were destroyed already during compression with forces lower than 15 N.

The work of compression defined from the curves up to 15 N (Fig. 5) was specifically changed during the time of storage. Generally, during the first six weeks of storage, the work of compression, regardless of the applied method of aeration, decreased, then increased to achieve the maximum value after fourteen weeks for samples of the filling for method A and after eight weeks for the filling for method B, respectively. Moreover, the samples of filling obtained by method A had a lower work of compression than those obtained by method B. It indicates that the samples of the filling obtained by the method A of aeration were more elastic, which is confirmed by the values of the modules of relaxation (Fig. 6). In the samples obtained by method A stored for almost eight weeks, the stable resilience module of elasticity equalled 0.64, while in the samples of filling obtained by method B soon
Fig. 5. Effect of storage time on work of compression of confectionery filling obtained by two methods of aeration

Fig. 6. Effect of storage time on asymptotic residual stress of confectionery filling obtained by two methods of aeration
after the eighth week of storage a significant decrease of the asymptotic residual stress, from 0.55 to 0.38, was noticed. Thus, the physical, chemical and physico-chemical changes which occurred in the samples during storage time had a greater influence on the decrease in elasticity of the filling obtained by method B.

The obtained values of compression work and relaxation modules of the agar confectionery filling indicate that the structure of the filling was firmer at the beginning of storage. Syneresis and crystallization, causing the loss of water immobilized as liospheres in the structure of a gel, led to a drop or even a loss of elasticity of the filling. The filing aerated by method B on the tenth week of storage lost more elasticity and became a crisp substance. The high porosity (41.6%) was most probably the reason for this process. Additionally, in the filling aerated by this mode, Pałacha and Sitkiewicz [7] noticed the presence of a higher quantity of pores with smaller diameters, evenly distributed in the bulk of the filling. Therefore the share of the solid phase in the bulk of the filling was too weak and its structure, already weakened by syneresis and crystallization of the saccharides, was broken by the applied force of 15 N. Larger by a ten percent share of the solid phase of the agar filling aerated by mode A, with the loss of its elasticity caused that the permanence of the structure of the filling was preserved.

CONCLUSIONS

1. The applied methods of aeration led to the obtaining of filling of aerated agar based confectionery with different levels of density and porosity. The samples of filling obtained by the aeration method of compressed air showed a lower density and higher porosity, and the time of storage had no significant influence on the density and porosity of the filling.

2. The aerated agar filling and the chocolate coating create complex heterogeneous and multiphase structures. During the time of storage there was a presence of water migration caused by diffusion, and secretion of water as a result of syneresis of the agar gel and crystallization of its components were observed. These processes took place simultaneously during the storage time and caused significant changes of the rheological parameters of the filling, showing change in its structure. The method of aeration had a significant influence on the elasticity of the confectionery filling. The samples of the filling aerated by mode A had a higher elasticity. Higher aeration with mode B caused faster damage to the structure soon after ten weeks of storage.
Wpływ metody napowietrzania i czasu przechowywania na wybrane cechy fizykochemiczne agarowego nadzienia cukierkowego w czekoladzie

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Streszczenie. W pracy określono wpływ metody napowietrzania oraz czasu przechowywania na wybrane cechy fizykochemiczne agarowego nadzienia cukierkowego w czekoladzie. Próbki nadzienia otrzymane metodą polegającą na napowietrzaniu przez wtłaczanie sprężonego powietrza posiadały mniejszą gęstość i większą porowatość; przy czym czas przechowywania nie miał istotnego wpływu na gęstość i porowatość nadzienia. Napowietrzzone nadzienie agarowe oraz pokrywająca go czekolada są złożonymi układami heterogenicznymi i wielofazowymi, w których w czasie przechowywania występuje ruch wody wywołany dyfuzją oraz wydzielanie wody w wyniku synerезy żelu agarowego i krystalizacji jego składników. Zjawiska te powodują istotne zmiany właściwości reologicznych nadzienia, będących odzwierciedleniem zmian jego struktury. Wyznaczone parametry reologiczne (praca ściskania i moduł relaksacji) potwierdziły wyższą sprężystość próbek nadzienia otrzymanego metodą A, jak również wykazały, że stopień napowietrzenia spowodował szybsze załamanie struktury materiału.

Słowa kluczowe: nadzienie cukierkowe piankowe, czekolada, gęstość, porowatość, aktywność wody, praca ściskania, moduł relaksacji