

EFFECT OF DIFFERENT STORAGE CONDITIONS ON FAT BLOOM FORMATION IN DIFFERENT TYPES OF CHOCOLATE

Svjetlana Škrabal¹, Đurđica Ačkar^{2*}, Jurislav Babić², Borislav Miličević²,
Antun Jozinović², Drago Šubarić²

¹Polytechnic in Požega, Vukovarska ul. 17, 34000, Požega, Croatia

²Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača 20, 31000 Osijek, Croatia

original scientific paper

Summary

Chocolate is a product that is mostly composed of cocoa butter, cocoa mass and sugar. Cocoa butter is a sensitive component that is susceptible to changes when temperature fluctuations occur during storage. Moreover, chocolate is sensitive to changes in the humidity of the surrounding environment. At inappropriate temperatures, part of stable crystals of cocoa butter will melt, fat will come out on the surface of chocolate and fat bloom will appear. This phenomenon is one of the most common problems in the chocolate industry since it highly affects consumers' acceptability – grey layer on the surface will make consumers dislike the product and ones that are less familiar with the phenomenon will question the safety. In this research, chocolates with different contents of cocoa butter, milk fat and substitute fats were prepared. We examined the effects of different humidity (50, 65 and 75%) and temperatures (20 and 29 °C) during storage on the formation of fat bloom. Measurements of surface colour and thermophysical properties of the surface of chocolate were performed. Chocolates with higher content of milk fat proved to be the most stable. Chocolate containing only cocoa butter was also stable under different storage conditions. The substitute fat and high humidity additives have had a great impact on formation of fat bloom on surface of chocolate.

Keywords: fat bloom, chocolate, relative humidity, storage

Introduction

One of the major problems of the confectionery industry is the fat bloom of chocolate products. Fat bloom of the surface of chocolate is the result of complex processes that take place in chocolate over a period of time or as a consequence of a poorly managed production process, the use of inadequate raw materials or poor storage conditions (Kinta and Hatta, 2012; Silva et al., 2017).

Fat bloom results in changes in product properties, above all in appearance and texture, and thus in reducing the consumer's acceptance of the product. The grey look of the chocolate surface is caused by irregular shapes of cocoa butter crystals. Chocolate fat bloom does not appear only because of transition from the β (V) form of cacao butter to the β (VI) form but also because of transition of the unstable lower polymorphic forms to the β (V) form (Kinta and Hatta, 2007; Bahari and Akoh, 2018). Due to the partial mixing ability with the fat, the emulsifiers damage the crystalline structure of triglycerides and thereby increase the content of the liquid phase which leads to polymorphic transitions. However, they do not affect the transition of form V to form VI of cocoa butter, which slows down formation of fat bloom of the chocolate (Jovanović and Pajin, 2004). If temperature rises during storage of chocolate products, the lower melting triglycerides are transferred to the liquid state

after which they are crystallized again by cooling. However, recrystallized fat will not be associated with the solid phase that has fats with higher melting point (Zhao and James, 2018).

Fat bloom of the surface of chocolate may also result from eutectic incompatibility of two fats (e.g., solid butter and cocoa butter or milk fat) (Ghosh et al., 2002; Timms, 2003). Fat compatibility depends on the thermal properties of fat (melting point and solid fat content), the size and shape of molecules (affected by fatty acid chain lengths and *cis* and *trans* structures of unsaturated acids) and polymorphism. As these properties are more similar, fats are more compatible. The formation of eutectic is achieved by mixing two incompatible fats (fat of a different percentage of solid triglycerides), the mixture of which has a lower melting point than each component. The final product is sensitive to fluctuations in temperature and appearance of fat bloom (Graef et al., 2005). If the fats of a similar fatty acid composition are mixed but have a different form or size of molecules, a stable crystal network is not formed, so the final product is also sensitive to fat bloom (Timms, 2003). Separation of certain fatty fractions in chocolate is often associated with migration of liquid fats to the surface by capillary transition that is supported by the difference in the concentration of triacylglycerols (TAG) (Smith et al., 2007).

*Corresponding author: dackar@ptfos.hr

Milk fat is present in milk chocolate. The triglyceride composition of milk fat is very complex because it contains more than 400 different triglycerides (Breitschuh-Apostolakis and Flöter, 2002). By studying the properties of chocolate after the addition of anhydrous milk fat and five dairy fractions obtained by dry fractionation of milk fat, Tietz and Hartel (2000) concluded that the lipids which are present in milk fat in much smaller proportions greatly affect the time of nucleation, rate of crystallization and the rate of fat bloom of chocolate surface. Milk fat affects the size of crystals, the way of crystallization and the transition of less stable polymorphic forms to more stable ones (Sonwai and Rousseau, 2010). The influence of milk fat depends on its type and on polar lipids in milk fat. It has been found that fat bloom of milk chocolates is directly related to the proportion of free fatty acids, diacylglycerol and monoacylglycerol (Ransom-Painter et al., 1997; Tietz and Hartel, 2000; Rousseau, 2006). Milk fat accelerates the appearance of fat bloom if lauric fat is present. Namely, milk fat fractions with higher melting point form a mixture with lauric acid which destabilizes β (V) crystals and accelerates the formation of fat bloom (Ransom-Painter et al., 1997). Fat bloom occurring during storage is characterized by the growth of small crystals on the surface and within the product after a certain period (Kinta and Hatta, 2012; Timms, 2003). Due to the oscillation of temperature during storage, there is a change in fat crystals, which creates new polymorphic forms (Sonwai and Rousseau, 2006). The chocolate surface is more sensitive to temperature changes than its interior. Increasing the temperature increases the proportion of liquid fat that is suppressed to the surface of the chocolate. Late temperature drop does not crystallize all liquid fat, but one part remains liquid inside of the chocolate. In addition, the surface of the chocolate becomes porous and the liquid can undisturbedly travel to the surface of the chocolate where it crystallizes under certain conditions. Properly packed chocolates are more resistant to fat bloom than those who are not packed properly (Torbica et al., 2013; Lonchamp and Hartel, 2004). Even when production meets all the requirements necessary to prevent fat bloom, the fat bloom may occur due to inadequate storage conditions. When the temperature is high enough (above 32 °C),

cocoa butter is partially melted. Cooling cocoa butter that was melted uncontrollably crystallizes into unstable polymorphic forms due to lack of stable centres. Even the slightest temperature oscillations accelerate the appearance of fat bloom (Torbica et al., 2013). Sahari et al. (2013) have found in their research that it is possible to use *Camellia sinensis* tea as Cocoa Butter Replacer in the production of dark chocolates and that there is a possibility of inhibiting fat bloom.

Materials and methods

Materials

The materials used in this study were:

- whole milk powder, roller dried (Zvečevo, d.d., Požega, Croatia);
- whole milk powder, spray dried (Zvečevo, d.d., Požega, Croatia);
- whole milk powder, spray dried ("Laktopol" Sp.z. o.o. Warszawa, Poland);
- caramelized whole milk powder, roller dried (Zvečevo, d.d., Požega, Croatia);
- caramelized whole milk powder, roller dried (Hochdorf Swiss Milk AG, Hochdorf, Switzerland);
- skim milk powder ("Laktopol" Sp.z. o.o. Warszawa, Poland);
- hazelnut paste (Zvečevo, d.d., Požega, Croatia);
- cocoa butter equivalent (Illexao™ CB 40, AarhusKarlshamn, Sweden).

Preparation of chocolate samples

The chocolates were produced by the standard process of production of chocolate masses in the "Zvečevo" confectionery factory. Technological parameters in the preparation of chocolate masses: mixing time 360 seconds, refining on a two-roll refiner, refining on a five-roll refiner, dry conching for 4 hours at a temperature of 52 to 56 °C and liquid conching for 20 hours at a temperature of 55 to 59 °C.

Percentages of different fats used in production of samples are given in Table 1.

Table 1. Fats used in formulations of chocolates

Sample	Cocoa butter (%)	Milk fat (%)	Hazelnut fat (%)	Vegetable fat (%)
MC-1	23.5	3.7 (roller dried and skim milk powder)	2.1	-
MC-2	23.5	3.7 (spray dried and skim milk powder)	2.1	-
MC-3	23.0	4.4 (spray dried and skim milk powder)	2.1	-
MC-4	19.48	3.9 (spray dried milk and powdered whey)	-	4.0
MC-5	23.8	6.0 (condensed milk)	-	-
MC-6	27.0	4.9 (spray dried and skim milk powder)	-	-
CO-1	23.8	-	-	4.0
CO-2	40.8	-	-	-

Moulding

Chocolate mass temperature (before pouring into moulds) was 30 - 30.5 °C, mould temperature was 29 °C, refrigerator temperature was 5 °C, the temperature of chocolate was 18 - 20 °C and the working room temperature for packing of chocolate was 21 - 24 °C.

Storage of samples

Produced chocolate was kept open for 55 days in a cooled incubator with humidity control (Climacell, Medical Intertrade) under controlled conditions:

- 12 hours at 20 °C and 12 hours at 29 °C with relative humidity below 50%,
- 12 hours at 20 °C and 12 hours at 29 °C with a relative humidity of 65% and
- 12 hours at 20 °C and 12 hours at 29 °C with 75% relative humidity.

Colour of the chocolate

Measurement of the colour of the upper surface of the samples was carried out immediately after the preparation of the samples and every 10 days. Last measurement was done on the 55th day. Chocolate colour measurement was performed using a Conica Minolta CR-600, and colour parameters L^* , a^* and b^* . L^* values range from 0 to 100 and give a rating of whether it is dark or light. If $L^*=0$, the object is black, and if $L^*=100$ then it is white. a^* value can be positive or negative. Positive values point to red and negative to green. The b^* value can also be positive or negative. If the value is positive, the result is yellow and, if negative, blue (Bricknell and Hartel, 1998).

Based on the measured values (10 for each sample), the whitening index (WI), whitening index change (ΔWI) and total colour change (ΔE) were calculated according to the following expressions:

$$WI = 100 - [(100 - L^*)^2 + a^{*2} + b^{*2}]^{0.5} \quad (1)$$

$$\Delta WI = WI_n - WI_1 \quad (2)$$

$$\Delta E = [(\Delta L^*)^2 - (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (3)$$

Determination of thermophysical properties

To measure of thermophysical properties of chocolate samples were taken after 55 days of storage. The measurement was conducted on samples previously used to measure colour change and samples stored at room temperature (control samples). Samples were retrieved with scratching the surface layer of chocolate that changed colour during storage. 10 to 20 mg of samples were used, and the samples were weighed in a standard aluminium container (40 μL). The weighing vessel was hermetically sealed, and the measurement of thermophysical properties was conducted. The samples were subjected to the following temperature program:

- isothermal at 50 °C, 1 min;
- cooling from 50 °C to 0 °C (cooling rate was 10 °C/min);
- isothermal at 0 °C, 1 min;
- heating from 0 °C to 200 °C (heating rate was 10 °C/min).

To determine the thermophysical properties of the samples, Mettler-Toledo DSC model 822e was used, and the measurements were carried out under a nitrogen purity 5.0 (Linde). Enthalpy change (ΔH) was obtained from the DSC exothermic curve using the software STAR^e (Fig. 1).

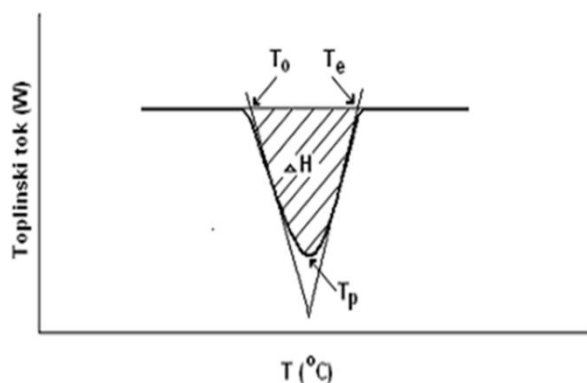


Fig. 1. Exothermic DSC curve and parameters determined by STAR^e software

Statistical analysis

Pearson correlation coefficient was performed using Statistica®, Version 13.4.0.14 (1984-2018 TIBCO Software Inc). Total colour change, whitening index, enthalpy of melting of sucrose and enthalpy of melting of cocoa butter were used as a variables. The data used for determination of correlation between variables were measured after 55 days at different relative humidities. Significant p-value was set at 0.05.

Results and discussion

Total colour change and whiteness index

Some of the ingredients and air humidity of the area in which samples were kept had a different effect on the fat bloom of the examined chocolates. Changes in some samples, especially those stored in the 75% air humidity, are so advanced that fat bloom appeared on the surface of the product along with changes in texture. Chocolates became brittle and “dry”. Liang and Hartel (2004) stated that milk fat positively affects the stability of chocolate colour. This claim was confirmed in this study if samples MC-1 and MC-2 (containing 3.7% milk fat) were taken into account, especially at air humidity of 65% (Table 2). From previous research by Jovanović and Pajin (2004) it can be concluded that milk fat acts as a fat bloom inhibitor. Timms (2003) stated that at temperatures above 18 °C and relative humidity greater than 60%, polymorphic transition of cocoa butter increases and fat blooming process is accelerated. In accordance with this study, all samples had the most significant colour change at 75% relative humidity. The sample MC-1 contained roller dried milk powder, which resulted in a higher proportion of free milk fat that inhibits fat bloom (Metin and Hartel, 2012). As a result, the value of ΔWI in sample MC-1, after 55 days and at 65% humidity, was 3.17 (Table 2), and in sample MC-2, containing spray dried milk powder, 5.99. Sonwai and Ruosseau (2010) concluded that free dairy fat interacts with other fats and that its content affects the stability of the product. At air humidity of 75% both samples behaved similarly (intense fat bloom

covered the entire surface of the product). This phenomenon is caused probably because of bounding of water to the protein and carbohydrates (sugar). This leads to the dissolution of sugar and the creation of pathways to release fat to the surface of chocolate (Rousseau, 2006). Changes observed at air humidity of 50% in both samples were of such intensity that the average consumer would not characterize it as negative, also those changes did not lead to changes in other product properties. For these two samples, the fact that they contain hazelnut paste should be also taken into account. Hazelnut paste contains oil fractions, which are relatively liquid at low temperatures and can easily migrate to the surface. Cocoa butter is easily dissolved in it, thereby tendency to migrate to the surface of chocolate is increased and because of that it creates a space for migration of other fats to the surface of the product. Hazelnut oil contains triolein as the main component and this TAG plays an important role in migration of fats (Smith et al., 2007). The MC-3 sample contained the same ingredients as the MC-2 sample, but the proportion of those ingredients was different. MC-3 sample contained about 0.7% more milk fat, which ultimately had a strong effect on product stability. At 75% moisture, colour change of the surface occurred on the 20th day. Changes in the MC-2 sample were significantly more pronounced at lower humidity. The MC-4 sample contained 19.48% cocoa butter, 3.9% milk fat, powdered whey and 4% vegetable fat. From the results shown in the Table 2 it is evident that the chocolate made from these raw materials was unstable even at lower humidity. At 65% humidity there was a significant change in the colour of the surface (the most intense of all tested samples), most likely due to the high hygroscopicity of whey and low milk fat content in the product (Keogh et al., 2006). The MC-5 sample contained 6% of milk fat (condensed milk) and was relatively stable during storage. Certain variations were recorded when measuring the surface colour of this sample, probably due to the raw material composition and the "non-homogeneous" colour of the surface. Stability of this sample can be attributed to a high proportion of milk fat. The same stability was observed in MC-6 sample which contained 4.90% of milk fat.

Table 2. Influence of relative humidity on whitening index (ΔWI) and total color change (ΔE) of chocolate samples

Sample	MC - 1		MC - 2		MC - 3		MC - 4		MC - 5		MC - 6		CO - 1		CO - 2	
	Relative humidity < 50%															
Days	ΔWI	ΔE	ΔWI	ΔE	ΔWI	ΔE	ΔWI	ΔE	ΔWI	ΔE	ΔWI	ΔE	ΔWI	ΔE	ΔWI	ΔE
10	1.8	1.31	1.2	1.35	-0.46	1.15	1.01	1.1	1.76	1.84	0.38	0.58	1.1	1.13	1.24	1.26
20	2.4	2.64	1.83	2.08	0.63	1.01	2.18	2.5	2.25	2.57	1.21	1.67	2.34	2.58	1.88	1.95
30	2.01	2.08	2.28	2.39	0.38	1.25	1.99	2.2	2.21	2.44	0.56	0.94	1.91	2.1	1.64	1.68

Table 2. Cont.

40	2.63	2.92	2.37	2.61	0.86	1.16	1.75	2	2.73	3.17	0.51	0.82	2.25	2.53	1.93	1.97
50	1.85	1.95	2.11	2.17	0.48	1.41	7.17	7.9	3.93	5.47	1.54	2.47	5.25	6.08	1.88	2.17
55	2.56	2.72	2.38	2.53	0.72	1.53	2.11	2.3	2.3	2.58	0.86	1.26	3.15	3.28	2.06	2.11
Relative humidity 65%																
10	2.05	2.14	6.74	6.9	0.72	1.72	4.22	4.4	2.81	3.15	2.71	2.92	3.52	3.72	2.19	2.23
20	2.3	2.55	4.73	5.01	1.29	1.38	3.1	3.4	4.86	5.76	1.68	2.37	2.69	3.3	2.48	2.77
30	2.25	2.55	5.33	5.67	1	1.4	2.83	3.4	5.87	6.84	1.25	1.94	2.08	2.64	1.36	1.72
40	2.22	3.33	6.7	7.22	1.05	1.2	6.15	6.8	4.31	5.36	1.94	3.22	4.45	5.23	1.42	1.66
50	3.26	4.01	6.57	6.98	1.06	1.86	1.88	2.1	2.11	2.45	0.62	0.82	2.69	2.83	2.11	2.16
55	3.17	4.08	5.99	6.42	2.81	3.16	7.19	8.1	3.85	5.21	0.69	1.42	5.8	6.65	1.5	1.85
Relative humidity 75%																
10	0.77	0.89	2.34	2.41	0.5	2.43	0.56	0.9	0.8	1.03	0.96	1.13	0.96	1.22	2.19	2.23
20	9.91	10.8	9.71	10.4	3.04	3.56	7.87	8.6	3.2	3.14	8.36	10.7	11.9	15.88	2.48	2.77
30	12.1	13.3	10.9	11.7	4.29	4.71	8.89	9.8	3.25	3.18	8.03	10.1	11.43	17.08	1.36	1.72
40	12.5	14	11.1	12.2	4.24	4.76	11.4	13	1.01	1	8.09	11	9.93	14.77	1.42	1.66
50	14.1	17	11.4	12.6	5.82	6.5	11.3	13	3.83	3.97	9.85	12.8	11.79	20.08	2.11	2.16
55	14.2	16.8	13.5	15.4	4.63	5.38	14.9	18	4.19	4.41	11.58	15.5	13.99	23.63	1.5	1.85

Chocolate production is increasingly using various CBE's to improve some of the quality parameters such as gloss, stability, solubility, etc. Also, CBE's can significantly affect the cost of the product. In chocolate production, CBE's replaces no more than 5% of cocoa butter. Although the triglyceride composition of CBE's fat is similar to the triglyceride composition of cocoa butter, it is not identical, and hence the formation of fat bloom may result from differences in composition (Yates, 2003). The presence of stable crystals of cocoa butter will allow proper nucleation and thus slow down the fat bloom (Kinta and Hartel, 2010). If the results for similar chocolates are compared, it is apparent that the changes at all storage conditions are very similar. The CO-1 sample contained 4% of CBE's, same as MC-4 sample. However, the MC-4 sample contained 3.9% milk fat, which resulted in a significantly lower colour change in the surface (inhibiting effect of milk fat) (Tietz and Hartel, 2000). The CO-1 had a change in colour at humidity below 50% and at 75% it was of a high intensity (ΔE was 23.63). The reason for this is probably the incompatibility of mixing CBE's with cocoa butter (Ghosh et al., 2002; Timms, 2003). In addition to this statement, the results obtained for the CO-2 sample, which was the only sample containing only cocoa butter, showed it was very resistant to the fat bloom under all conditions under which the research was carried out. Sample CO-2 which had a low sugar content and a high content of cocoa butter (from cocoa butter and cocoa

mass), proved to be extremely stable during the 55 day storage at all conditions under which the research was conducted. The stability of such chocolate can be explained by the fact that there is one type of fat in the chocolate (cocoa butter) so there is no risk of fat bloom of the chocolate due to the incompatibility of mixing of fats (Kinta and Hatta, 2007).

On the other hand, low sugar content as well as other non-fat particles that have tendency to adsorb water did not affect the increase of the whitening index at higher relative humidity (the value of ΔWI at the beginning of storage was 1.24, while at the end of storage at 65% humidity was 1.50, and at 75% 2.59). Adsorption of moisture to hydrophilic particles that are the ingredients of chocolate can cause melting of sugar on the surface of chocolate (Kinta and Hatta, 2012). The results given in Table 2 confirm this conclusion. CO-1 sample contained 58% of sugar and it is apparent from the results that the value of whitening index significantly increased at 75% humidity after only 20 days of storage (ΔWI 11.9), which manifested itself through total colour change (ΔE 23.63 at the end of storage).

From the data obtained by the statistical analysis (Table 3), it is evident that there is a significant correlation between the whitening index and total colour change. This proves that in fact the color change that occurs on chocolates is patterned by mostly fat bloom, that is, an increase in the whitening index.

Table 3. Coefficient of correlation between analysed parameters

Variable	Total colour change	Whitening index	Enthalpy of melting of sucrose	Enthalpy of melting of cocoa butter
Total colour change	1.000000			
Whitening index	0.957685	1.000000		
Enthalpy of melting of sucrose	-0.219245	-0.226829	1.000000	
Enthalpy of melting of cocoa butter	0.440923	0.412273	-0.637463	1.000000

Bold values were considered significant at $p < 0.05$

Thermophysical properties

Differential scanning calorimetry (DSC) was conducted prior to storage (control sample) and after storing chocolates under the following conditions: 50, 65 and 75% relative humidity, at 20 °C for 12 hours followed by 12 hours at 29 °C for 55 days. DSC analysis gave the results of relative content and proportion of fat (cocoa butter and other fat) and sucrose on the surface of the chocolate. The relative content and fat to sucrose ratio on the surface of the examined samples of chocolate is proportional to the enthalpy of melting of the above mentioned ingredients. From the results, it is apparent that in almost all samples (except MC-1 at 65% relative humidity) during storage at a higher relative humidity (65 and 75%), a change in the composition of the surface layer manifested by decreasing the sucrose content and increasing the proportion of fat. Svanberg et al. (2013) also concluded that during storage of incorrectly processed chocolate comes to increase of fat content on surface of chocolate. On the other hand, the temperature fluctuations during storage did not cause significant changes in composition of the chocolate surface at relative humidity of 50%. Figs. 2 and 3 show enthalpy of melting of sucrose and fat of chocolate samples. As mentioned, in most samples the temperature fluctuation during storage with higher relative humidity has reduced the sucrose content and increased the fat content on the surface. In the sample MC-6 (27.0% cocoa butter, 4.9% milk fat, spray dried and skimmed milk), the smallest changes in sucrose content on the surface of chocolate were observed, while in other samples there was a significant decrease in sucrose content during storage

under the specified conditions. MC-1, MC-2, MC-4 had a reduction of sucrose content on the surface by about 40% during storage at a relative humidity of 65 and 75%. Also, in these samples and in MC-6 sample, the surface fat content raised at about 85% under the same conditions (except MC-1 at 65% relative humidity). Thereby, after storage at 75% moisture, the MC-6 sample had the highest enthalpy (38.22 J/g), probably due to the higher content of fat in the formulation (about 5% higher). CO-1 sample, which contained 4% of CBE's, stands out with a significant increase in fat content on the surface after storage at higher relative humidity. Therefore, when stored at 75% relative humidity the CO-1 sample showed an increase of fat slightly more than 100% (ΔH was 17.8 J/g for the control sample and after storage at 75% ΔH was 39.7 J/g). The increase of fat on the chocolate surface is also evident from the results for the whitening index. This correlation between whiteness index and enthalpy of melting of cocoa butter is confirmed by statistical analysis. Correlation coefficient also shows that there is statistically significant negative correlation between enthalpy of melting of sucrose and cocoa butter. The MC-4 sample also contained 4% of CBE's and there was also a significant increase in the fat content on the surface during storage (ΔH was 17.4 J/g for the control sample and after storage at 65% ΔH was 33.2 J/g). Relatively lower fat migration is likely the result of presence of milk fat (3.9%), which, as mentioned before, slows the appearance of fat bloom. MC-5 sample has higher content of cocoa butter and higher content of milk fat than MC-6. When these samples are compared it can be seen that sample MC-5 has higher enthalpy of melting of cocoa butter.

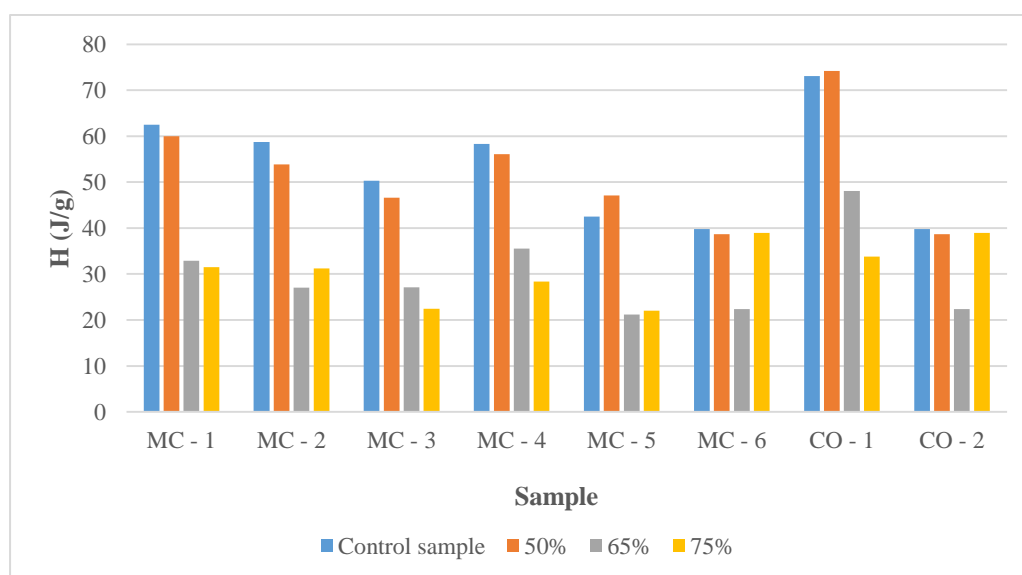


Fig. 2. Enthalpy of melting (H) of the sucrose obtained by DSC by analysing the surface layer of chocolates at different relative humidity

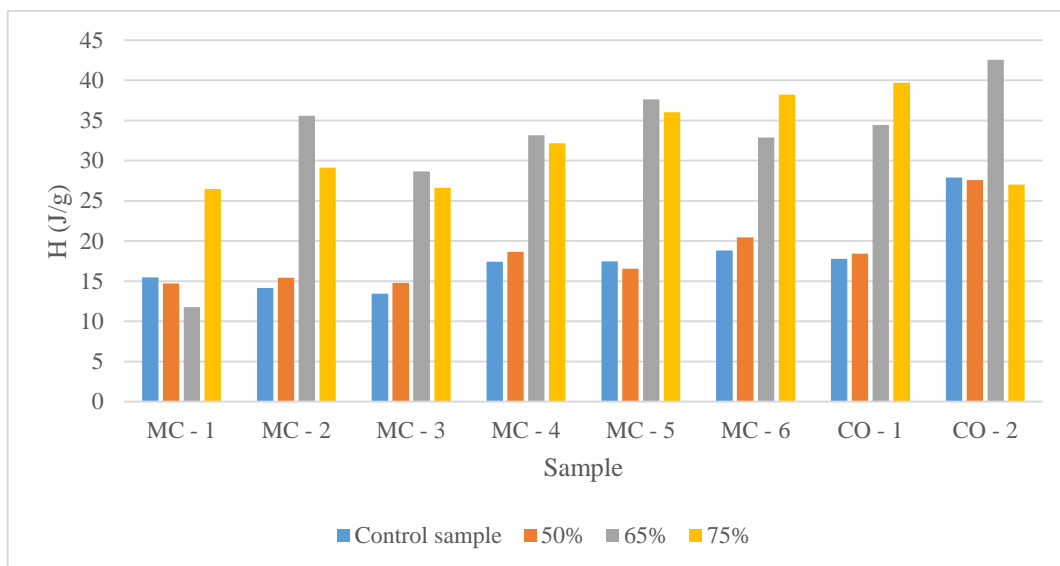


Fig. 3. Enthalpy of melting (H) of the cacao butter obtained by DSC by analysing the surface layer of chocolates at different relative humidity

Conclusions

Based on the research carried out it can be concluded that certain fat-containing ingredients and relative humidity during storage of samples had a significant effect on fat bloom formation on the surface of the examined chocolates. Changes in some samples, especially those kept at 75% relative humidity, were so advanced that along with appearance of fat bloom on the surface of the product, the change in the texture of chocolate also occurred. Chocolates containing milk fat, which originated from powdered roller dried milk, were more resistant to fat bloom due to the fact that the roller dried milk contains a higher content of free milk fat which is a fat bloom inhibitor. Similar behaviour was also observed in samples that contained more milk fat. Chocolates containing fat with lower melting point (hazelnut paste) were more prone to fat bloom at lower humidity. The addition of powdered whey in the manufacture of chocolate has led to the most intense formation of fat bloom due to the higher hygroscopicity of this ingredient. Similarly happened in samples containing spray-dried milk powder, which were more hygroscopic than the roller dried milk powder or condensed milk. Samples containing CBE's had more pronounced fat bloom than those with the same content of total fat but other types of fat. The reason for this occurrence is probably incompatibility of cocoa butter and added CBE's. A chocolate sample that did not contain any other fat except cocoa butter showed extremely good stability

at all storage conditions and temperature fluctuations. Based on the results obtained by DSC, important conclusions were made, which explained the mechanism of fat migration. Based on analysis of the surface of bloomed chocolate it was found that over time (55 days), depending on the humidity of the air in the area where the samples were kept, changes of chocolate surface occurred. The slightest changes occurred when samples were stored at 50% humidity. At higher air humidity (65 and 75%) there was a significant change in surface composition. There was an increase in the fat content and decrease of the sugar content. From the obtained results it can be concluded that due to the increase in moisture content of the air, sugar decomposition occurs in the surface layers of chocolate, creating "pore" that allow fat to enter the surface (increased by temperature fluctuations). An increasing amount of fat bloom on the surface of chocolate was dependent on the composition of chocolate. Milk fat influenced the slowing of fat migration. Samples with a higher milk fat content, as well as samples containing rolled dried milk powder had a lower fat content on the surface of the product. Samples containing fat with lower melting point (hazelnut fat) and samples with CBE's had a high fat content on the surface of chocolate.

Acknowledgement

This work has been supported in part by Croatian Science Foundation under the project 2017-05-8709.

References

- Bahari, A., Akoh, C.C. (2018): Texture, rheology and fat bloom study of “chocolates” made from cocoa butter equivalent synthesized from illipe butter and palm mid-fraction, *LWT* 97, 349–354.
- Breitschuh-Apostolakis, B., Flöter E. (2002): Solid immiscibility in milk fat fractions and methods to determine their occurrence, *Eur. J. Lipid Sci. Technol.* 104, 713-719.
- Bricknell, J., Hartel, R.W. (1998): Relation of fat bloom in chocolate to polymorphic transition of cocoa butter, *J. Am. Oil Chem. Soc.* 75, 1609-1615.
- Ghosh, V., Ziegler, G.R., Anantheswaran, R.C. (2002): Fat, Moisture and Ethanol Migration through Chocolates and Confectionary Coatings, *Crit. Rev. Food. Sci. Nutr.* 42, 583-626.
- Graef, V.D., Foubert, I., Agache, E., Bernaert, H., Landuyt, A., Vanrolleghem, P.A., Dewettinck, K. (2005): Prediction of migration fat bloom on chocolate, *Eur. J. Lipid Sci. Technol.* 107 (5), 295–306.
- Jovanović, O., Pajin, B. (2004): Influence of lactic acid ester on chocolate quality, *Trends in Food Sci. & Tech.* 15, 128–136.
- Keogh, M.K., Twomey, M., O’Kennedy, B.T., Kenedy, R., O’Keeffe, J., Kelleher, C. (2006): Dairy Ingredients for Chocolate and Confectionery, *Irish Ag. and Food Development*, End- of-Project (Armis No. 4519). Teagasc, Dublin.
- Kinta, Y., Hartel, R.W. (2010): Bloom Formation on Poorly – Tempered Chocolate and Effects of Seed Addition, *J. Amer Oil Chem. Soc.* 87, 19-27.
- Kinta Y., Hatta T. (2007): Composition, structure, and color of fat bloom due to the partial liquefaction of fat in dark chocolate, *J. Amer Oil Chem. Soc.* 84, 107-115.
- Kinta, Y., Hatta, T. (2012): Morphology of Chocolate Fat Bloom, *Cocoa Butter and Related Compounds* 195–212.
- Liang, B., Hartel, R.W. (2004): Effects of Milk Powders in Milk Chocolate, *J. Dairy Sci.* 87, 20-31.
- Lonchamp, P., Hartel, R.W. (2004): Fat bloom in chocolate and compound Coatings, *Eur. J. Lipid Sci. Technol.* 106, 241-274.
- Metin, S., Hartel, R.W. (2012): Milk Fat and Cocoa Butter, *Cocoa Butter and Related Compounds* 365–392.
- Rousseau, D. (2006): On the porous mesostructure of milk chocolate viewed with atomic force microscopy, *Lebensm. Wiss. u. Technolo.* 39, 852–860.
- Ransom – Painter, K.L, Willims, S.D., Hartel, R.W. (1997): Incorporation of Milk Fat and Milk Fat Fractions into Compound Coatings Made from Palm Kernel Oil, *J. Dairy Sci.* 80, 2237–2248.
- Sahari, M., Zarringhlami, S., Barzegar, M., Hamidi-Esfehani, Z. (2013): Fat Bloom and Polymorphism in Chocolate Prepared with Modified Tea Seed Oil., *J. Tea Sci. Res.* 1, 1-6.
- Silva, T.L.T. da, Grimaldi, R., Gonçalves, L.A.G. (2017): Temperature, time and fat composition effect on fat bloom formation in dark chocolate, *Food Structure* 14, 68–75.
- Smith, W.K., Cain, W.F., Talbot, G. (2007): Effect of nut oil migration on polymorphic transformation in a model system, *Food Chem.*, 102, 656–663.
- Sonwai, S., Rousseau, D. (2006): Structure evolution and bloom formation in tempered cocoa butter during long – term storage, *Eur. J. Lipid Sci. Technol.* 108, 735–745.
- Sonwai, S., Rousseau, D. (2010): Controlling fat bloom formation in chocolate – Impact of milk fat on microstructure and fat phase crystallisation, *Food Chem.* 119 (1), 286–297.
- Svanberg, L., Ahrné, L., Lorén, N., Windhab, E. (2013): Impact of pre-crystallization process on structure and product properties in dark chocolate, *J. Food Eng.* 114 (1), 90–98.
- Tietz, R.A., Hartel, R.W. (2000): Effects of minor lipids on crystallization of milk fat-cacao butter blends and bloom formation in chocolate, *J. Am. Oil Chem. Soc.* 77, 763-771.
- Timms, R.E. (2003): Confectionery fats handbook, *Oily lipid library & Lipid Technology* 223–227.
- Torbica, A.M., Pajin, B.S., Omorjan, R.P., Lončarević, I.S., Tomić, J.M. (2013): Physical Properties of Chocolate with Addition of Cocoa Butter Equivalent of Moderate Hardness, *J. Am. Oil Chem. Soc.* 91 (1), 39–48.
- Yates, P. (2003): Chocolate, Chocolate Fats and the new EU Chocolate Directive: Implications for Chocolate manufacturers in Europe, *Soc. Chem. Industry* 125, 1353-1361.
- Zhao, H., James, B.J. (2018): Fat bloom formation on model chocolate stored under steady and cycling temperatures, *J. Food Eng.* (in press).