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THERMAL CHARACTERIZATION OF CHOCOLATE. THE POLYMORPHISM OF COCOA BUTTER

BY

VICTORIA BEJENARI, LAURA MIHĂILĂ, ANDREEA-IOANA PRISACARIU, GEORGIANA TĂRĂBOANŢĂ and GABRIELA LISA[*]

"Gheorghe Asachi" Technical University of Iași, Romania,
"Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection

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Abstract. The thermal behavior of seven chocolate samples from various countries of origin, which cover all the three types of chocolate – dark, with milk and white – was analyzed. They revealed the influence of composition on thermal stability. Also, it was set out that the presence of coffee in the composition leads to a different decomposition mechanism, respectively, to an additional stage with the T_{peak} of approximately 462ºC. The differential calorimetry emphasized the butter cocoa polymorphism in the composition of mass chocolate. It was concluded that a proper storage of chocolate was urgently needed in order to avoid the emergence of the fat bloom phenomenon.

Keywords: chocolate; TG; DTG; DSC; polymorphism.

1. Introduction

Thermal analysis offers extremely useful information for the food industry regarding the raw material used, but it also contributes to the resolution of certain manufacturing and storage issues. As for the chocolate production, differential scanning calorimetry (DSC) is the most largely used technique for

[*]Corresponding author; *e-mail*: gapreot@ch.tuiasi.ro

its characterization. By applying this technique, certain information about chocolate crystallization, its polymorphism and melting behavior can be obtained. All this information can help the specialists to maintain the quality of the obtained products. According to the market research (Eurostat), a Romanian consumes an average of 2.2 kg of chocolate per year and the level of consumption has increased significantly in the last 2-3 years. We can identify the existence of three types of chocolate. Dark chocolate is a mix of cocoa and butter cocoa with sugar and, depending on the producer, it contains at least 35% cocoa. Milk chocolate contains at least 25% dry cocoa solids and 12% dry milk solids (usually, milk powder or condensed milk). White chocolate is made of cocoa butter, sugar, milk, vanilla and other flavors. A famous chemist named Justus von Liebig stated that "Chocolate is a perfect food, as wholesome as it is delicious, a beneficent restorer of exhausted power...". Researchers show a great interest in setting out the best chocolate storage conditions (van Malssen *et al.*, 1999; Walter and Cornillon, 2001; Fourbet *et al.*, 2004; Noordin and Chung, 2009; Ray *et al.*, 2012), but also in introducing new ingredients in order to improve its quality (Biswas *et al.*, 2018; Svanberg *et al.*, 2011; Sullo *et al.* 2014; Zaliha and Norizzah, 2012). This paper analyzes for the first time the influence of coffee on the thermal behavior of chocolate. In addition, it emphasizes the influence of storage conditions on the emergence of fat bloom phenomenon.

2. Material and Methods

Chocolate samples analyzed

There were used chocolate samples from various countries of origin and with different compositions (Table 1). The dry cocoa solids content (cocoa) varied between 30 and 53%. The sampled noted by BC is a homemade chocolate bar which contains milk, vegetal fat and coffee. Coffee also contains the sample noted by HC. We subjected to analysis a white chocolate noted by CA, three milk chocolates (noted by CS, CR and CM) and two types of dark chocolate noted by CO and HC.

Thermogravimetric analysis

The thermogravimetric analysis was carried out by using a Mettler Toledo TGA-SDTA851^e derivatograph, in an N_2 atmosphere, with a flow of 20ml/min, a rate of heat of 5°C /min (25 – 700°C) and sample mass comprised between 4 and 6 mg.

Thermogravimetry (TG) is a method of thermal analysis in which the mass of the sample is measured as a function of time or temperature, while sample temperature is under control in a controlled atmosphere. This method is applied in multiple industries, such as food, pharmaceutical and petrochemical industry. TG offers information about thermal stability of materials, oxidative stability of materials, composition of multicomponent systems, estimated lifetime of a product, decomposition kinetics of materials, moisture and volatiles content of material, etc.

Table 1
Code of the Analyzed Chocolate Samples and Information Concerning the Composition and Country of Origin

Sample code	Country of origin	Dry cocoa solids, [%]	Milk [%]	Other ingredients
CO	Netherlands	53	No	soya lecithin
CS	Spain	33	Yes	soya lecithin
CR	Romania	50	Yes	vegetal fat, soya lecithin
CM	Switzerland	30	Yes	soya lecithin
CA	Austria	30	21	soya lecithin
BC	Romania	–	Yes	coffee, vegetal fat
HC	Romania	45	No	coffee 1.5%, soya lecithin

Differential scanning calorimetry

The DSC curves were registered with an Mettler Toledo DSC1 equipment, in an inert atmosphere, with a speed of heat of 5°C /min. Scans in the temperature range of -30 – 50ºC were carried out, with two heating stages and a cooling. The mass of the samples introduced in the standard aluminum crucible (40 μL) was comprised between 9 and 12 mg.

Differential scanning calorimetry is a method of thermal analysis which measures the difference in the amount of heat required to increase the temperature of the sample and the reference material. The sample and the reference are subject to the same temperature program (Skoog *et al.*, 2011). Differential scanning calorimetry is a very useful thermal analysis method in the food industry. This method provides information about thermal properties and phase changes of food during processing and storage (Zhou and Labuza, 2011).

The cocoa butter contained by the chocolate mass composition has polymorphism, which means that it is able to form six different types of crystals with different melting points (Loisel *et al.*, 1998; Benjamin *et al.*, 2010): **I** unstable **ϒ(17.3°C), II** meta-stable **α (23.3°C), III** meta-stable $\boldsymbol{\beta_1}'$ **(25.5°C), IV** meta-stable $\boldsymbol{\beta_2}'$ **(27.5°C), V** stable $\boldsymbol{\beta_2}$ **(33.8°C), VI** most stable $\boldsymbol{\beta_1}$ **(36.3°C)**. Some of them are unstable and get converted into other types quickly enough after crystal formation. In order to obtain a high quality chocolate, it is necessary to obtain **V** type crystals, which are stable enough and have a good melting point. Chocolate with such crystals remains solid at room temperature, but it melts away fast in the mouth (Benjamin *et al.*, 2010). Differential scanning calorimetry (DSC) is frequently used in literature (Fessas *et al.*, 2005; Fourbet *et al.*, 2003; Smith, 2016; Afoakwa *et al.*, 2008; Hussain *et al.*, 2018) to emphasize the melting and crystallizing behavior of cocoa butter, which is a key ingredient for any type of chocolate. The DSC curves offer information about cocoa butter polymorphism.

Results and discussions

Thermogravimetric analysis

The DTG curves registered at a rate of 5°C/min for the 7 chocolate samples in an inert atmosphere, respectively nitrogen, are presented comparatively in Fig. 1.

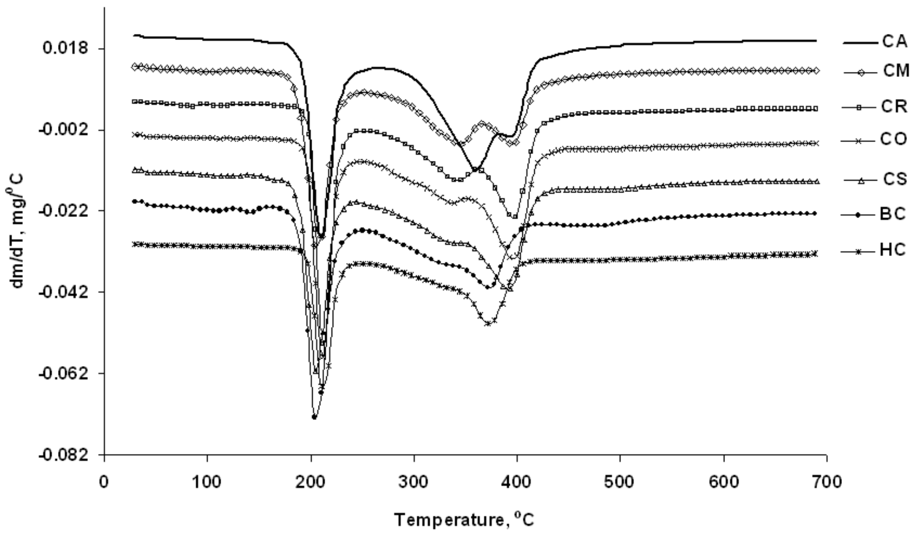

Fig. 1 – DTG curve.

In Table 2, there are presented the main thermogravimetric characteristics of the analyzed samples: T_{onset} – onset temperature of degradation in every stage; T_{peak} – temperature corresponding to the maximum degradation rate; T_{endset} – end temperature in every stage and W – mass loss percentage. The amount of residue obtained at a temperature of 700°C is also mentioned.

Table 2

The Main Thermogravimetric Characteristics

Sample	Stage	T_{onset} [°C]	T_{peak} [°C]	T_{endset} [°C]	W [%]	Residue [%]	$T_{melting}$ [°C]
CO	I	203	211	219	23.11	16.04	185
	II	279	336	362	24.62		
	III	362	397	411	36.23		
CS	I	192	206	220	22.46	17.19	176
	II	269	336	358	25.08		
	III	358	393	409	35.27		
CA	I	197	211	222	25.93	18.43	190
	II	315	360	370	26.49		
	III	370	394	408	29.15		
CM	I	190	207	218	28.81	22.73	183
	II	295	346	372	25.53		
	III	372	397	410	22.93		
CR	I	204	213	224	23.32	20.65	188
	II	293	342	373	28.67		
	III	373	398	413	27.36		
BC	I	193	206	222	29.09	14.18	180
	II	279	323	350	19.90		
	III	350	378	390	17.13		
	IV	390	460	517	19.70		
HC	I	203	212	220	24.90	7.55	187
	II	296	310	358	26.09		
	III	358	375	389	20.24		
	IV	389	464	–	21.22		

The obtained results reveal the fact that the degradation of different types of chocolate in an inert atmosphere takes place in three or four stages, with different loss mass percentages. There can be observed a degradation stage with a T_{peak} of approximately 462°C, only in the case of the two samples that contain coffee. At a temperature of 700°C for the chocolate samples analyzed, there results an amount of residue comprised between 7 and 23%. From the differential thermal analysis (DTA), it results that the melting temperature of sugar contained by the analyzed chocolates is approximately 185°C. A lower value, respectively, 176°C, was set out for CS, which originates in Spain. If we consider the temperature T_{onset} from the first decomposition stage (a criteria of thermal stability), we can set out the next series of stability decrease: CR = HC ≅ CO > CA > BC ≅ CS > CM. It is found out that the samples with a content of dry cocoa solid greater than 45% have a better thermal stability.

Differential scanning calorimetry

DSC curves registered during the first heating stage at a rate of 5°C/min, are presented comparatively in Fig. 2, while for the second heating stage, they are presented in Fig. 3. Fig. 4 shows the DSC curves obtained in the cooling stage.

The DSC curves resulting from the first heating stage show that in the case of all chocolate samples analyzed, there occur transitions specific to the V stable form with a melting point around the value of 34°C. Nevertheless, except the CO and HC samples, we notice the presence of a small amount of crystals with melting points of: I (17°C), II (23°C), III (25°C) and IV (27°C). This behavior is due to the presence of milk fat in these types of chocolate (Reddy *et al*., 1996; Metin and Hartel, 1998). The results presented in Fig. 2 shows a different behavior in the heating stage at a rate of 5°C/min for the homemade chocolate bar noted by BC, and besides milk fat, it probably contains a significant amount of vegetal fat. The crystallization drops obtained at negative values are characteristic to the unsaturated vegetal fat.

The DSC curves resulting from the second heating stage also indicates the presence of type I crystals (17°), II (23°) and III (25°). All these remarks prove that the cocoa butter contained by the chocolate mass composition has polymorphism, meaning it is able to form different types of crystals. The cocoa butter polymorphism from the chocolate was also identified by Fessas and his collaborators (Fessas *et al*., 2005) by applying the DSC techniques. Compared to the study carried out by us, they have identified only α and β (II, III, IV and V) type crystals, but not the first Υ (I) type. The presence of Υ type crystals along with α and β was also obtained by Smith in the DSC analysis of some different types of chocolate from the trade market (Smith, 2016).

In order to simulate the conditions under which chocolate can be inappropriately stored and thus determine the occurrence of fat bloom or fat sugar phenomenon, we subjected samples of chocolate at constant temperatures and at an uncontrolled slow-paced cooling. For three chocolate samples, CO (Fig. 5), CM (Fig. 6) and HC (Fig. 7), we set out the following protocol for DSC curves registration: we maintained the samples for 60 min at 30ºC and let them cool down slowly, then we subjected them to the heating cooling cycles within the range of -30 and 50ºC, as in the case of the initial registrations. Other transitions during the first heating stage can be noticed. This behavior is due to the fact that certain amounts of unstable forms which were left in the final product get melted and, in time, get converted into a stable form. Under these conditions, chocolate shall be covered in a thin crystal layer of cocoa butter, called fat bloom.

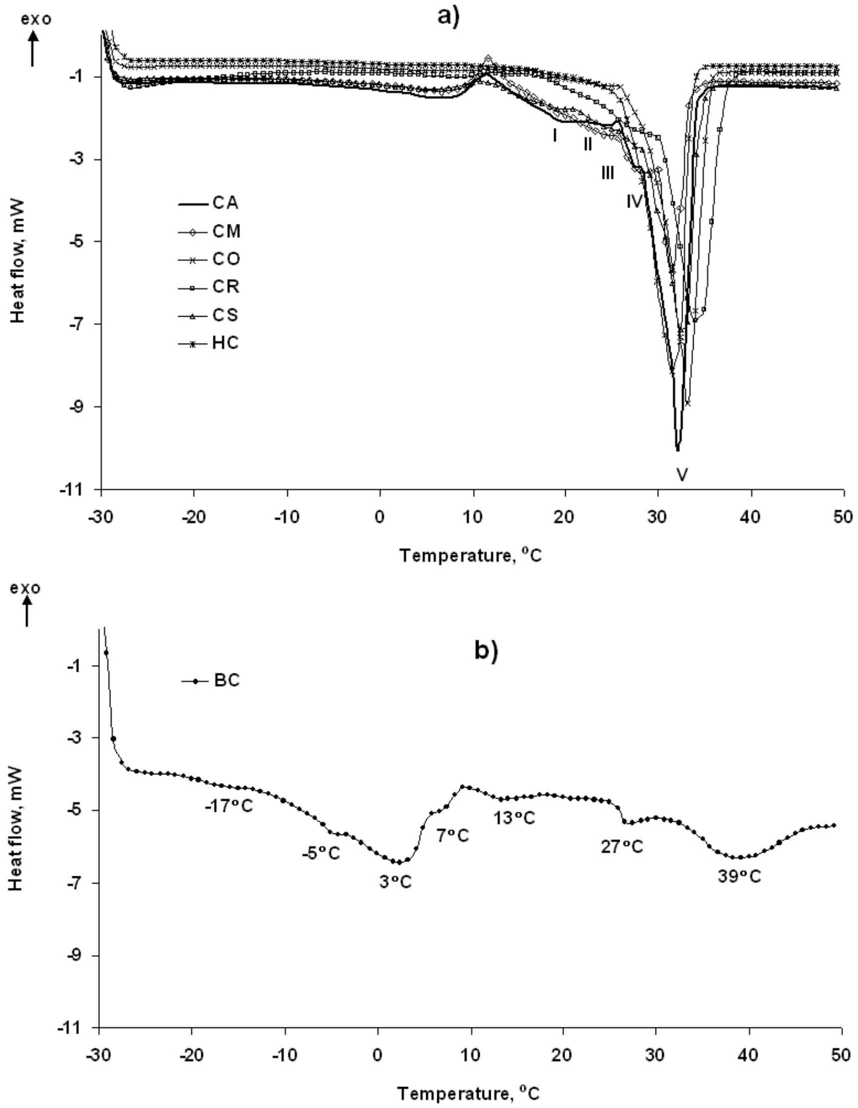

Fig. 2 – DSC curves obtained in the first scanning (first heating stage) *a*) for CO, CS, CR, CM, CA and HC; *b*) for BC.

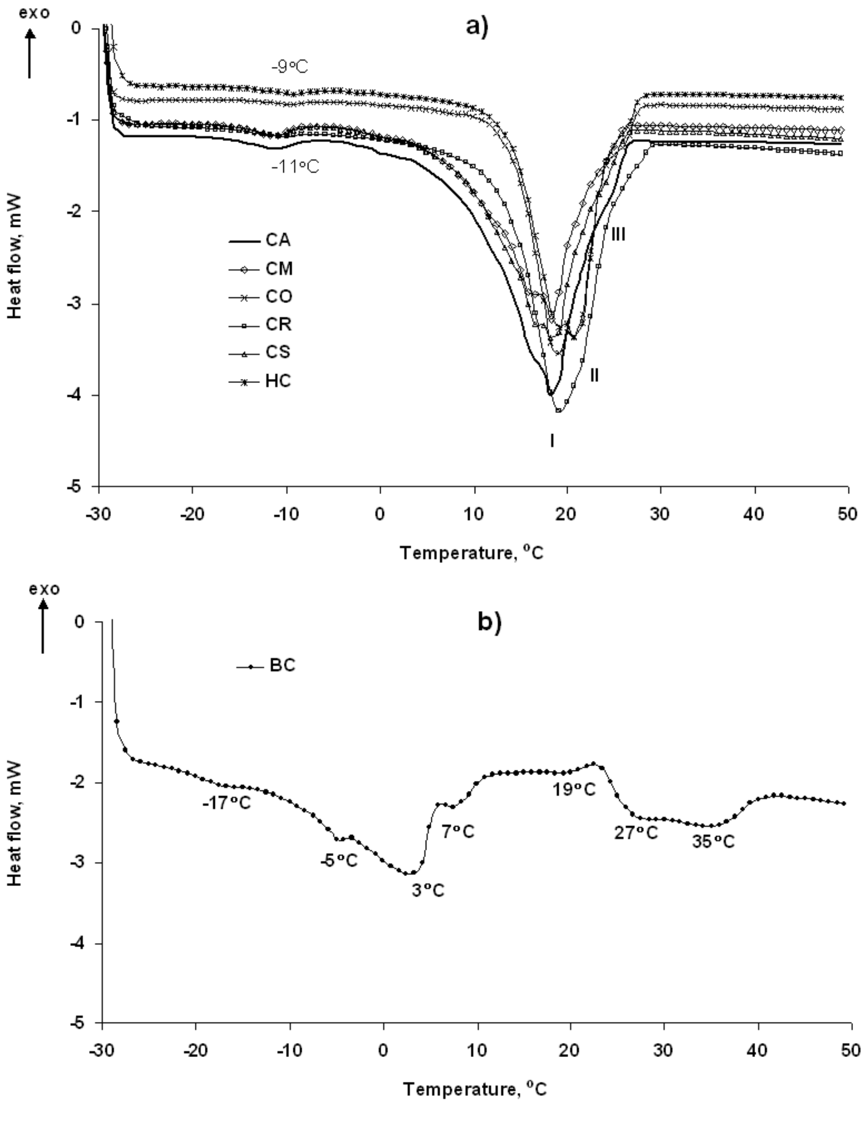

Fig. 3 – DSC curves obtained in the third scanning
(second heating stage) *a*) for CO, CS, CR, CM, CA and HC; *b*) for BC.

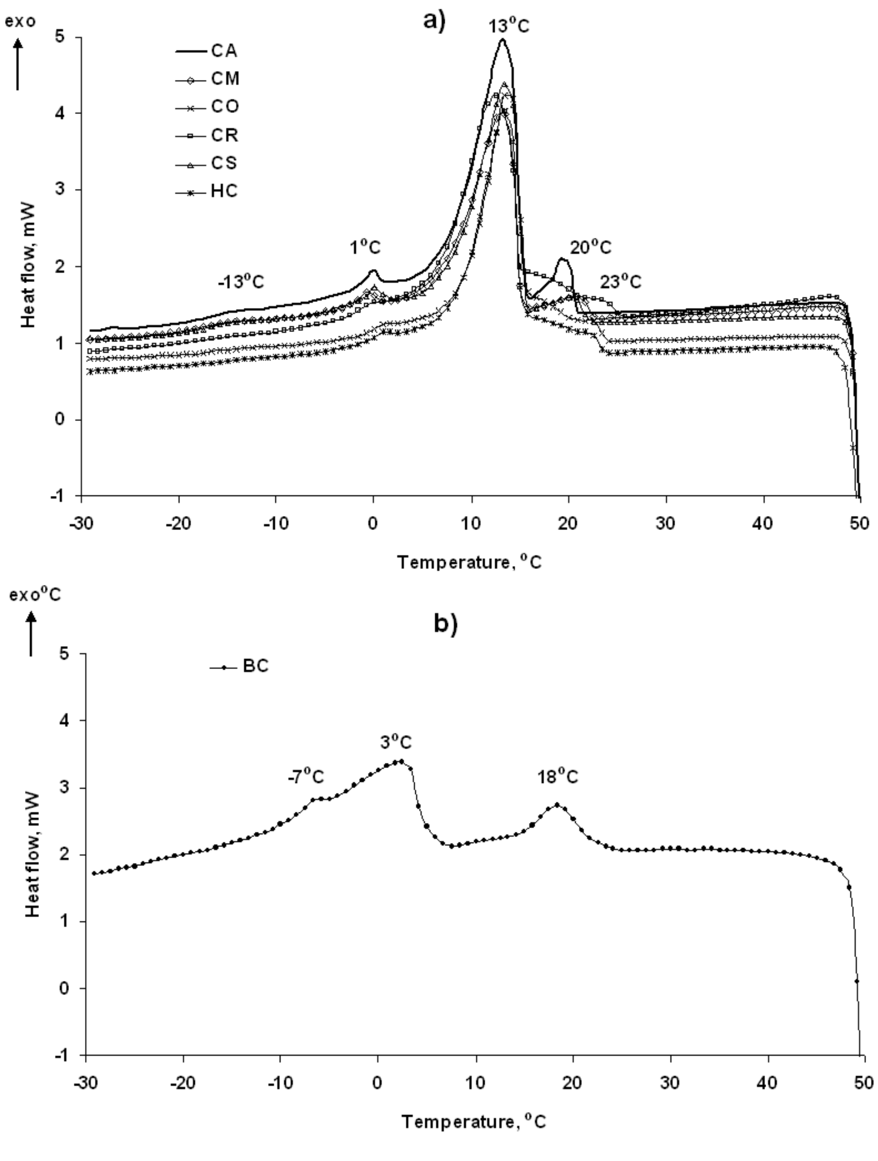

Fig. 4 – DSC curves obtained in the second scanning (cooling stage).

Chocolate noted by CO was stored in the laboratory for a year, during which temperature varied between 12 and 30ºC. The chocolate sample reveals the fat bloom phenomenon. The DSC curve registered for this sample during the first heating stage reveals the presence of the most stable form of crystallization VI. This behavior suggests that even if the chocolate was properly tempered and it initially had the V crystalline form, following the inappropriate storage, it turned into the VI form of crystallization. A kinetic study of the isothermal crystallization process of cocoa butter was carried out by Foubert and his collaborators (Foubert *et al.*, 2003). They set out that there is no significant difference between the applied melting protocols: 65ºC for 15 min, 65ºC for 30 min and 80°C for 15 min. Thus, they concluded that the 65ºC for 15 min protocol is enough to melt all the homogenous nuclei of cocoa butter (Foubert *et al.*, 2003).

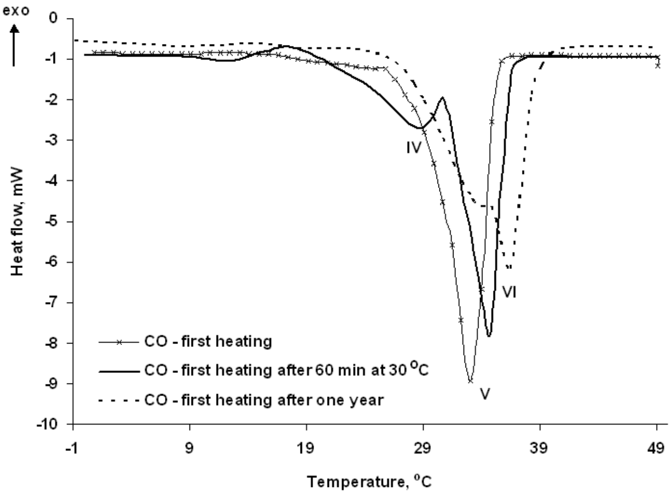

Fig. 5 – Comparative DSC for the first heating stage (with and without thermal treatment) for CO.

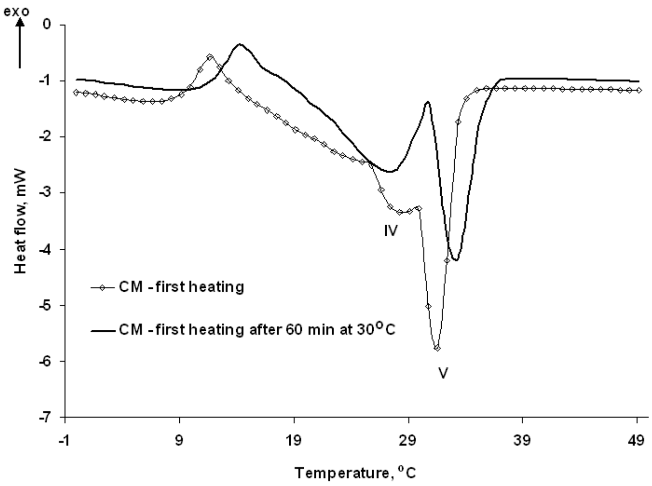

Fig. 6 – Comparative DSC for the first heating stage (with and without thermal treatment) for CM.

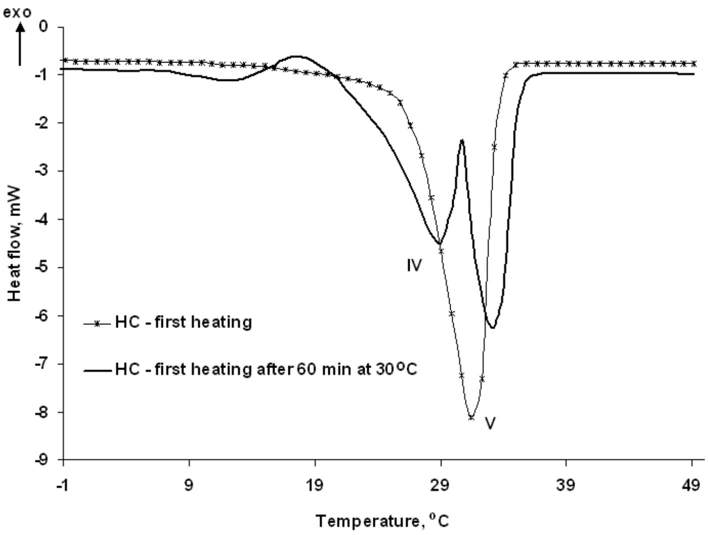

Fig. 7 – Comparative DSC for the first heating stage (with and without thermal treatment) for HC.

3. Conclusions

The thermogravimetric analysis emphasized the following aspects:

- Degradation of different types of chocolate takes place in three or four stages, with different loss mass percentages, according to the composition.
- In the case of the two samples containing coffee, there was found an additional degradation stage, compared to the other chocolate samples, with a T_{peak} of approximately 462ºC.
- At a temperature of 700°C, there results an amount of residue comprised between 7 and 21%. According to the DTA analysis, the temperature point of sugar present in the analyzed chocolates is of approximately 185°C. A smaller value, respectively, 176°C, was obtained for CS, which originated in Spain.
- If the T_{onset} in the first decomposition stage is considered the thermal stability criteria, the series of stability decrease is the following: CR = HC $\cong$ CO $>$ CA $>$ BC $\cong$ CS $>$ CM.

The differential scanning calorimetry (DSC) technique showed that:

- The cocoa butter from the mass chocolate composition has polymorphism and is able to form different types of crystals, due to the presence of various types of triglycerides which act in a way specific to fractional crystallization.
- It is necessary to properly store the chocolate in order to maintain a fine crystalline structure and to avoid the emergence of fat bloom phenomenon.

REFERENCES

Afoakwa E.O., Alistair P., Fowler M., Vieira J., *Characterization of Melting Properties in Dark Chocolates from Varying Particle Size Distribution and Composition Using Differential Scanning Calorimetry*, Food Res. Int., **41**, 751-757 (2008).

Benjamin J.D.L.R., Peter J.F., Simon Coles, Serafim Bakalis, *A Method to Qualify and Quantify the Crystalline State of Cocoa Butter in Industrial Chocolate*, J. Am. Oil Chem. Soc., **87**, 239-246 (2010).

Biswas N., Cheow Y.L., Tan C.P., Siow L.F., *Physicochemical Properties of Enzymatically Produced Palm-Oil-Based Cocoa Butter Substitute (CBS) with Cocoa Butter Mixture*, Eur. J. Lipid Sci. Technol., 1700205, 1-9 (2018).

Fessas D., Signorelli M., Schiraldi A., *Polymorphous Transitions in Cocoa Butter. A Quantitative DSC Study*, J. Therm. Anal. Calorim., **82**, 691-702 (2005).

Foubert I., Vanrolleghem P.A., Dewettinck K., *A Differential Scanning Calorimetry Method to Determine the Isothermal Crystallization Kinetics of Cocoa Butter*, Thermochim. Acta, **400**, 131-142 (2003).

Foubert I., Vanrolleghem P.A., Thas O., Dewettinck K., *Influence of Chemical Composition on the Isothermal Cocoa Butter Crystallization*, J. Food Sci., **69**, *9*, 478-487 (2004).

Hussain N., Agus B.A.P., Rahim S.N.F.A., Halim H.S.A., *Comparison of Quality Characteristics Between Compound and Pure Milk Chocolate*, MOJ Food Process. Technol., **6**, *3*, 292-296 (2018).

Loisel C., Keller G., Lec G., Bourgaux C., Ollivon M., *Phase Transitions and Polymorphism of Cocoa Butter*, J. Am. Oil Chem. Soc., **75**, *4*, 425-439 (1998).

Metin S., Hartel R.W, *Thermal Analysis of Isothermal Crystallisation Kinetics in Blends of Cocoa Butter with Milk Fat or Milk Fat Fractions*, J. Am. Oil Chem. Soc., **75**, *11*, 1617-1624 (1998).

Noordin M.I., Chung L.Y., *Thermostability and Polymorphism of Theobroma Oil and Palm Kernel Oil as Suppository Bases*, J. Therm. Anal. Calorim., **95**, *3*, 891-894 (2009).

Ray J., MacNaughtan W., Chong P.S., Vieira J., Wolf B., *The Effect of Limonene on the Crystallization of Cocoa Butter*, J. Am. Oil Chem. Soc., **89**, *3*, 437-445 (2012).

Reddy S.Y., Full N., Dimick P.S., Ziegler G.R, *Tempering Method for Chocolate Containing Milk-Fat Fractions*, J. Am. Oil Chem. Soc., **73**, *6*, 723-727 (1996).

Skoog D.A., Holler F.J., Crouch S.R., *Instrumental Analysis*, India Edition: Cengage Learning, 982-984, 2011.

Smith M.J., *Using Differential Scanning Calorimetry to Explore the Phase Behavior of Chocolate*, J. Chem. Educ., **93**, 898-902 (2016).

Sullo A., Arellano M., Norton I.T., *Formulation Engineering of Water in Cocoa - Butter Emulsion*, J. Food Eng., **142**, 100-110 (2014).

Svanberg L., Ahrné L., Lorén N., Windhab E., *Effect of Sugar, Cocoa Particles and Lecithin on Cocoa Butter Crystallisation in Seeded and Non-Seeded Chocolate Model Systems*, J. Food Eng., **104**, 70-80 (2011).

van Malssen K., van Langevelde A., Peschar R., Schenk H., *Phase Behavior and Extended Phase Scheme of Static Cocoa Butter Investigated with Real-Time X-Ray Powder Diffraction*, J. Am. Oil Chem. Soc., **76**, *6*, 669-676 (1999).

Walter P., Cornillon P., *Influence of Thermal Conditions and Presence of Additives on Fat Bloom in Chocolate*, J. Am. Oil Chem. Soc., **78**, *9*, 927-932 (2001).
Zaliha O., Norizzah A.R., *Physico-Chemical Properties and Compatibility on Palm Oil Products with Cocoa Butter*, J. Oil Palm Res., **24**, 1349-1352 (2012).
Zhou P., Labuza T.P., *Analytical Methods. Differential Scanning Calorimetry*, in Book: Encyclopedia of Dairy Sciences, Elsevier, 256-263, 2011.

CARACTERIZAREA TERMICĂ A CIOCOLATEI. POLIMORFISMUL UNTULUI DE CACAO

(Rezumat)

S-a analizat comportarea termică a şapte monstre de ciocolată cu diferite ţări de provenienţă şi care acoperă toate cele trei tipuri de ciocolată: neagră, cu lapte şi albă. S-a evidenţiat influenţa compoziţiei asupra stabilităţii termice. S-a stabilit că prezenţa în compoziţie a cafelei conduce la un mecanism de descompunere diferit, respectiv o etapă suplimentară cu T_{peak} la aproximativ 462°C. Prin calorimetrie diferenţială s-a evidenţiat polimorfismul untului de cacao prezent în compoziţia masei de ciocolată. S-a constatat că este imperios necesară o depozitare corespunzătoare a ciocolatei pentru a evita apariţia fenomenului de albire grasă.