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EFFECT OF COCOA FAT CONTENT ON WETTING AND SURFACE ENERGY OF CHOCOLATE

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ABSTRACT

The aim of this study was the quantification of the effect of the cocoa fat content on the wetting characteristics and surface free energy of different chocolate compositions. On the market, there are many different types of chocolate products which differ both in the sensory and physico-chemical properties together with their raw material compositions and the contents of the individual components. This paper focuses on differences in the use of different types of fats – cocoa butter, milk fat, equivalents or cocoa butter substitutes in chocolate products. Studied samples (prepared at Carla, Ltd. Company) were followed by static contact angles of wetting measurements and by calculated surface free energies. There were investigated the effects of fat content and used fat types of the chocolate products on their final wettabilities and resulting surface free energies. There was found a linear dependence between total fat content and the surface free energy, which was gradually increasing with increasing fat content. Additionally, there were performed TG DTG and NIR spectrometry measurements of the tested materials with the aim to determine the melting point of studied fats used, as well as to determine and identify individual fat components of chocolate products which may affect the resulting value of surface free energy.

Keywords: chocolate; cocoa fat; surface energy; wetting

INTRODUCTION

Chocolate is unique as a food in that fact which is solid at normal room temperatures however it melts easily in the mouth. Since the properties of the main fat component, cocoa butter, is essentially solid at temperatures below 25 °C when it holds all the solid sugar and cocoa particles together. However, this fat is almost entirely liquid at body temperature, enabling the particles to flow past one another, thus the chocolate becomes a smooth liquid by heating in the mouth.

The first known cocoa plantations were established by the Maya in the lowlands of south Yucatan about 600 AD. Cocoa trees were being grown by the Aztecs of Mexico and the Incas of Peru when the Europeans discovered the Central America. The beans were highly prized and used as money as well as to produce a drink known as chocolatl.

In 1828 Van Houten developed the cocoa press which was quite remarkable, as his entire factory was manualy operated at the time **(Becket, 2008)**. The cocoa bean cotyledons (known as cocoa nibs) were pressed to produce a hard ''cake'' with about half the fat removed. This was milled into a powder, which could be used to produce a much less fatty drink. In order to make this powder disperse better in the hot water or milk, the Dutch treated the cocoa beans during the roasting process with an alkali liquid. This has subsequently become known as the Dutching process. By changing the type of alkalising agent, it also became possible to adjust the colour of the cocoa powder.

Almost twenty years after the invention of the press in 1847, the first British factory to produce a plain eating chocolate was established in Bristol in the UK by Joseph Fry. Unlike Van Houten, Fry used the recently developed steam engines to power his factory. In order for the chocolate to feel smooth on the tongue when it melts in the mouth, the solid non-fat particles must be smaller than 30 μm. The chocolates made by Fry and Peter were ground using granite rollers, but still had a gritty texture. This was because of the presence of some large particles and some groups of particles joined together to form agglomerates, also because the fat was not coating the particles very well. In addition, the chocolate tended to taste bitter because of the presence of some acidic chemicals.

In 1880 Rodolphe Lindt, in his factory in Berne in Switzerland, invented a machine which produced a smoother, better tasting chocolate **(Becket, 2008)**. This machine was known as a conche, because its shape was similar to the shell with that name. It consisted of a granite trough, with a roller, normally constructed of the same material, which pushed the warm liquid chocolate backwards and forwards for several days. This broke up the agglomerates and some of the larger particles and coated them all with fat. Meanwhile, moisture and some

acidic chemicals were evaporated into the air, producing a smoother, less astringent tasting chocolate.

When two or more fats are mixed together, it is important that the final chocolate sets at a suitable rate and more importantly, that it has the correct texture and melting properties in the mouth.

Cocoa butter equivalents to be able to be added to cocoa butter without having a eutectic effect, the vegetable fat must crystallise in the same way as cocoa butter. Cocoa butter contains palmitic, stearic and oleic acids on a glycerol backbone. The fat manufacturer has therefore to obtain these different fractions from different sources and then blend them. The palmitic oleic acids are the easiest to find as they are a major component of palm oil, which is obtained from the palm (Eleaeis guineensis) widely grown in Malaysia.

Chocolate and cocoa products are a rich source of flavonoids, where 100 g of unsweeted cocoa powder can contain up to 250 mg of flavonols **(Godočíková et al., 2016)**.

Chocolate production technological procedures, the composition of the base chocolate matter and the storage conditions (generally thermal history) are affecting the final product quality e.g. by formation of blooming defects **(Machálková et al., 2015)**. A wide range of technological processes (e.g. cleaning, dyeing or gluing) depends on "how well" the liquid wets the surface of solid material. The term wetting and non-wetting as employed in various practical situations tend to be defined in terms of the effect desired. Usually, however, wetting means that the contact angle between a liquid and a solid is zero or so close to zero that the liquid spreads over the solid easily, and non-wetting means that the angle is greater than 90°, so that liquid tends to ball up and run off the surface easily. Contact angle of wetting is a result of the balance of three vectors acting on the three-phase line among solid, liquid and vapour, namely solid surface energy γ_{SV}, liquid surface energy γ_{LV}, and solid-liquid tension γ_{SL}. This exhibits an equilibrium contact angle that can be expressed by Young's equation **(Gajdošíková, Lapčíková & Lapčík, 2011)**:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}.\cos\theta \qquad (1)$$

where γ_{SG} and γ_{LG} are the surface tension of a solid and the surface tension of a liquid in the equilibrium with the liquid vapour, respectively, γ_{SL} interfacial tension between the liquid and solid, and θ is the equilibrium contact angle. It is to be pointed out that γ_{SG} is not the surface tension of the solid (γ_S in vacuum); the difference in between is referred as the spreading pressure π_e:

$$\pi_e = \gamma_S - \gamma_{SG} \qquad (2)$$

An assumption was made to neglect the vapour adsorption for low surface tension solids, e.g. polymers, $\gamma_S = \gamma_{SG}$.

According to the Fowkes, the surface energy is separated into its components:

$$\gamma = \gamma^C + \gamma^I + \gamma^D + \gamma^{AB} + \gamma^H + ... \qquad (3)$$

where $\gamma^D, \gamma^P, \gamma^H, \gamma^I$ and γ^{AB} are the contributions from London disperse forces, polar (Keesom forces, hydrogen-bonding forces, induction (Debye) forces, and acid-base interactions, respectively. Based on these assumptions, the following equation has been proposed, which is applicable to systems in which only dispersion forces are common to both phases:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^D.\gamma_2^D} \qquad (4)$$

where subscripts 1 and 2 represent phases 1 and 2, respectively. Applying Equation (4) to a solid-liquid interface in given:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^D.\gamma_L^D} \qquad (5)$$

If π_e is assumed to be small and $\gamma_{LV} \approx \gamma_L$, γ_S can be eliminated by combining Equation (5) and Equation (1):

$$\cos\theta = 1 - 2\sqrt{\frac{\gamma_{SV}^D \gamma_{LV}^D}{\gamma_{LV}}} \qquad (6)$$

Then the value of $\sqrt{\gamma_{SV}^D}$ can be calculated from the slop of $\cos\theta$ plotted as a function of $\sqrt{\gamma_{LV}^D / \gamma_{LV}}$. The most recent approach was given by van Oss, Chaudhury and Good (vOCG) **(Gajdošíková et al., 2011)**. According to this method, the surface tension of solid is equal to a sum of two components: γ_S^{LW}, connected with Lifthitz-van der Waals (LW) interactions, and γ_S^{AB}, connected with acid-base (AB) interactions. The dispersion (London), orientation (Keeson), and induction (Debye) forces, being dipolar forces, present the same type dependence on distance and are usually treated with the same combining rules. All these interactions are generally named by the van der Waals contribution (LW). However, the donor-acceptor contribution to the work of adhesion (currently termed acid-base contribution) is associated with the transfer of electrons between an electron donor and an electron acceptor.

$$\gamma_S = \gamma_S^{LW} + \gamma_S^{AB} \qquad (7)$$

$$\gamma^{AB} = 2.\sqrt{\gamma^+.\gamma^-} \qquad (8)$$

where γ_S^+ and γ_S^- are components corresponding to the interactions of the Lewis acid (donor) and base (acceptor), respectively. Hence, the calculation of γ_S consists in the

Table 1 Material compositions of dark chocolates under study.

Sample labelling	Cocoa dry matter content (w. %)	Cocoa butter content (w. %)
Dark basic	44.0 ±1.5	28
Dark 35%	49.0 ±1.5	35
Dark 40%	53.0 ±1.5	40
Dark 45%	57.0 ±1.5	45

Table 2 Material compositions of milk chocolates under study.

Sample labelling	Cocoa dry matter content (w. %)	Cocoa butter content (w. %)	Milk dry matter content (w. %)
Milk basic	32.0 ±1.5	27	3.99
Milk 30%	35.0 ±1.5	30	3.82
Milk 33%	37.0 ±1.5	33	3.66
Milk 36%	40.0 ±1.5	36	3.50

determination of three unknown components: γ_S^{LW}, γ_S^+ and γ_S^-, it is required performing contact angle measurements using different liquids, two of them being polar and one non-polar. Combining Equations 7 and 8 with Young´s equation is given (**Gajdošíková et al., 2011**):

$$(1+\cos\theta)\gamma_l = 2\left(\sqrt{\gamma_l^{LW}\gamma_s^{LW}} + \sqrt{\gamma_l^+\gamma_s^-}\sqrt{\gamma_l^-\gamma_s^+}\right) \quad (9)$$

The vOCG approach to the evaluation of acid-base properties of solid surfaces by contact measurements is undoubtedly the most important development of present-day interface science.

MATERIAL AND METHODOLOGY

Chocolate samples were prepared in CARLA Ltd. (Czech Republic). For dark chocolate preparation, the following raw material compositions were used: sugar, cocoa butter, cocoa mass, dried whey, milk fat, natural cocoa, emulgator (soya lecitine) and flavors. For milk chocolate preparation the following raw material compositions were used: sugar, cocoa butter, cocoa mass, dried whole milk, dried skimmed milk, dried whey, lactose, emulgator (soya lecitine) and flavors.

The magnitude of the contact angle θ, between the liquid and solid can be determined by various methods. The selection of the method to be used depends on the character of the studied sample system, as well as on the accuracy required. The two most common methods are: a static measurement of sessile drop by See System with CCD camera and a dynamic Wilhelmy plate method. The static contact angle of wetting was measured by a sessile drop resting on a flat solid surface using a video camera equipped and interfaced to a computer with image-analysis

software to determine the tangent value precisely on the captured image. De-ionised distilled water (conductivity of 0.07×10^{-4} S.m^{-1}) (Watek Demiwa 3ROS, Czech Republic), glycerol (98%, Sigma-Aldrich, USA), diiodomethane (Sigma Aldrich, USA) and ethylene glycol (98%, Sigma-Aldrich, USA) were used as testing liquids for the determination of dispersive and polar components of surface energy as well as for Lifshitz-van der Waals contributions.

Thermogravimetry (TG) and differential thermal analysis (DTA) experiments were performed on simultaneous DTA-TG apparatus (Shimadzu DTG 60, Japan). Throughout the experiment, the sample temperature and weight-heat flow changes were continuously monitored. The measurements were performed at heat flow rate of 10°C/min in the static air atmosphere at the temperature range from 30°C to 300°C.

Near infra red spectra (NIR) were recorded on ParticuLAB NIR spectrometer (Harrer & Kassen, Germany).

All measurements were done at least in four replicates, each measurement was repeated at least 5×. Data were analysed using one way analysis of variance (ANOVA) method (Microsoft Excel, USA). These analysis allowed to detect the significance of the effect of fat content addition as well as of type of the fat used on contact angles of wetting results. For all tested samples combinations the observed differences were of high statistical significance ($p \leq 0.05$).

RESULTS AND DISCUSSION

Process of the migration of the cocoa butter fat to the surface of chocolate known as "blooming" is strongly affecting overall perception of the final chocolate product by the customers e.g. by the color changes and the creation of the non-uniform color patterns at the chocolate bar

Table 3. Obtained values of the contact angles of wetting for dark chocolates under study as observed for different wetting liquids.

Sample	Mean contact angle of wetting θ_s (°)			
	Water	Glycerol	Ethylene glycol	Diiodomethane
Dark basic	87.3 ±1.5	95.5 ±0.6	75.2 ±1.3	51.2 ±1.5
Dark 35%	81.7 ±1.2	89.4 ±1.8	77.3 ±1.3	57.6 ±2.6
Dark 40%	88.5 ±1.8	93.3 ±2.1	80.0 ±2.5	56.0 ±1.9
Dark 45%	93.8 ±2.3	93.7 ±3.2	79.3 ±1.7	53.0 ±2.3

Table 4. Obtained values of the contact angles of wetting for milk chocolates under study as observed for different wetting liquids.

Sample	Mean contact angle of wetting θ_s (°)			
	Water	Glycerol	Ethylene glycol	Diiodomethane
Milk basic	94.6 ±2.4	89.3 ±2.2	76.6 ±1.2	50.7 ±2.3
Milk 30%	99.8 ±0.9	98.0 ±1.9	73.8 ±1.0	52.6 ±1.6
Milk 33%	91.2 ±1.9	102.4 ±2.5	81.0 ±1.6	47.6 ±2.0
Milk 36%	93.2 ±1.2	90.8 ±1.7	71.8 ±1.6	48.7 ±2.5

Table 5. Results of the calculated surface energies (γ_S) and their standard deviations according to the model Wu - equation of state as observed for tested dark chocolates.

Dark basic				Dark 35%			
Liquid	γ_S	γ_{S^-}	γ_{S^+}	Liquid	γ_S	γ_{S^-}	γ_{S^+}
Water	19.95	1.53	1.54	Water	23.85	0.90	1.51
Glycerol	13.09	0.41	0.38	Glycerol	16.35	0.81	2.05
Ethylene glycol	18.94	0.65	1.23	Ethylene glycol	17.85	0.76	0.97
Diiodomethane	33.63	1.62	0.81	Diiodomethane	29.96	1.85	2.02
Dark 40%				**Dark 45%**			
Liquid	γ_S	γ_{S^-}	γ_{S^+}	Liquid	γ_S	γ_{S^-}	γ_{S^+}
Water	19.16	0.94	2.32	Water	15.89	2.12	1.35
Glycerol	14.19	1.79	1.24	Glycerol	14.02	1.77	2.17
Ethylene glycol	16.56	1.30	1.68	Ethylene glycol	16.89	0.99	1.00
Diiodomethane	30.89	1.53	1.37	Diiodomethane	32.58	1.60	2.39

Table 6. Results of the calculated surface energies (γ_S) and their standard deviations according to the model Wu - equation of state as observed for tested milk chocolates.

| Milk basic				Milk 30%			
Liquid	γ_S	γ_{S^-}	γ_{S^+}	Liquid	γ_S	γ_{S^-}	γ_{S^+}
Water	15.38	1.70	1.66	Water	12.52	0.79	0.42
Glycerol	16.39	1.55	1.98	Glycerol	11.96	1.35	1.34
Ethylene glycol	18.20	0.88	0.74	Ethylene glycol	19.65	0.97	0.35
Diiodomethane	33.90	1.80	2.04	Diiodomethane	32.79	0.94	1.46
Milk 33%				**Milk 36 %**			
Liquid	γ_S	γ_{S^-}	γ_{S^+}	Liquid	γ_S	γ_{S^-}	γ_{S^+}
Water	17.47	1.45	1.96	Water	16.21	0.66	1.43
Glycerol	9.87	1.38	1.28	Glycerol	15.54	0.97	1.61
Ethylene glycol	16.04	1.29	0.91	Ethylene glycol	20.65	1.03	1.43
Diiodomethane	35.62	1.52	1.66	Diiodomethane	35.00	1.51	1.91
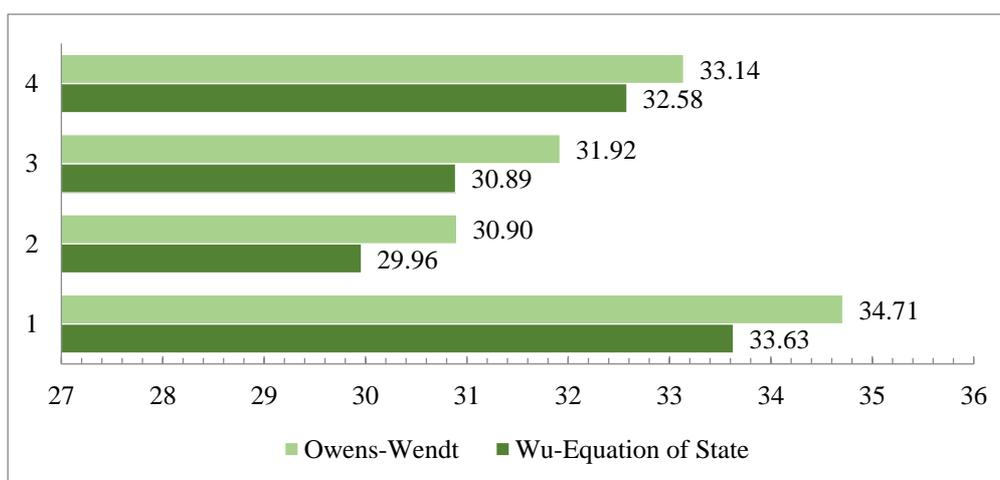
Figure 1. Results of the calculated total surface energies (mJ.m^{-2}) of studied dark chocolates: 1 – Dark basic. 2 – Dark 35%. 3 – Dark 40%. 4 – Dark 45%.

surface. This phenomenon is strongly dependend on fat composition and the storage conditions (**Briones and Aguilera 2005**). It was found, that the mechanism of

bloom development is a complex process involving both the phase separation associated with the growth of xenomorphic fat crystals (**Kinta and Hatta, 2005**). As a
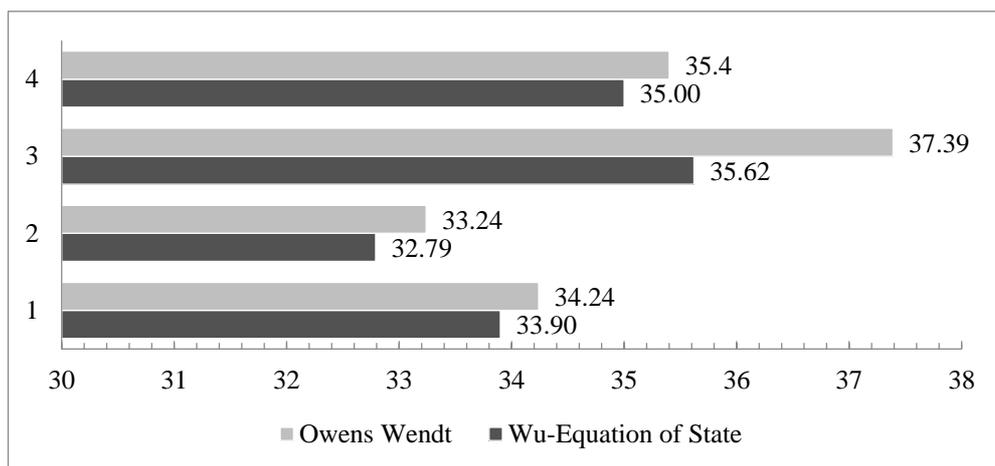
Figure 2. Results of the calculated total surface energies (mJ.m^{-2}) of studied milk chocolates: 1 – Milk basic. 2 – Milk 30%. 3 – Milk 33%. 4 – Milk 36%.

Table 7 Results of the thermal analysis of the tested chocolates.

Sample	Heat of fusion (J.g^{-1})	T_m (°C)
Dark basic	-16.19	34.63
Milk basic	-22.32	33.60
Dark 35%	-29.61	34.62
Milk 36%	-33.51	33.78
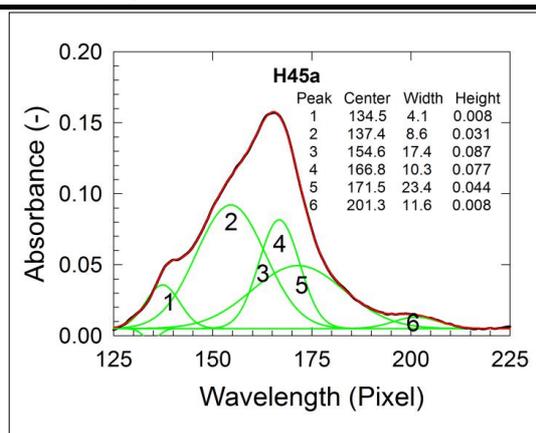
Figure 3. NIR spectrum of Dark 45 % chocolate and its components.
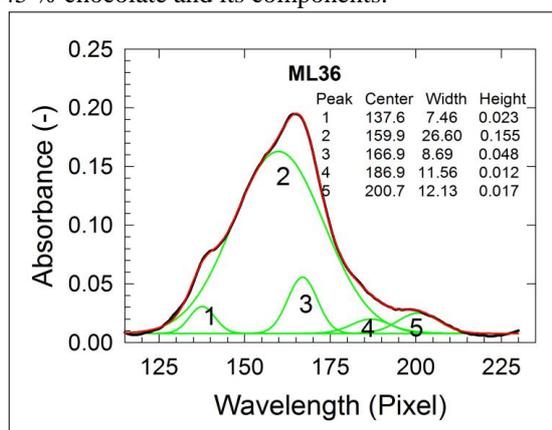
Figure 4. NIR spectrum of Milk 36 % chocolate and its components.

result of the above mentioned phenomena, the resulting surface heterogeneity will be strongly affected and of diverse fassion **(Lapčík et al., 2016)**.

The results of the contact angle of wetting measurements are given in Tables 3 and Table 4. As mentioned in the introduction, surface of the chocolate bar is predominantly hydrophobic due to the presence of the cocoa butter in the matter. That is why the best wetting was observed for diiodomethane as reflected in the obtained contact angles of wetting ranged approximately from 48 to 51° for milk chocolate, and from 51 to 53° for dark chocolate. The highest magnitudes of the contact angles were obtained for glycerole. Calculated surface energies and their componenets are shown in Table 5 and Table 6. Milk
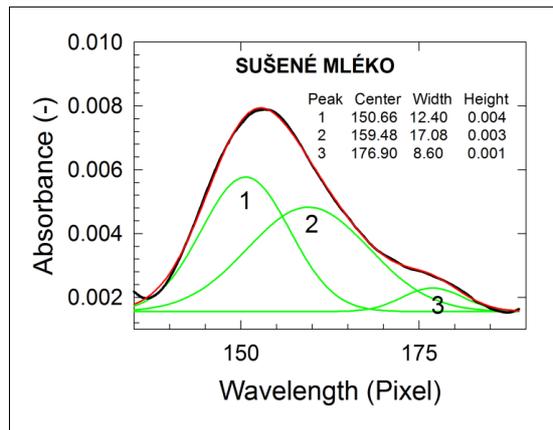
**Figure 5**. NIR spectrum of powdered skimmed milk and its components.
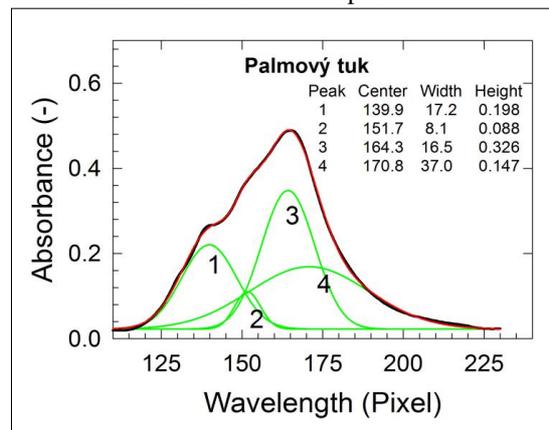
Figure 6. NIR spectrum of pure palm fat and its components.

chocolates contain milk components (milk fat) in comparison with dark chocolates. As studied earlier **(Lapčík et al. 2015)**, milk components are more of hydrophilic nature in comparison with the cocoa ones, that is why their inclusion into the chocolate material composition is increasing their surface energy. This fact is clearly visible from data given in Table 5 and Table 6 and Figure 1 and Figure 2. Exact knowledge of the surface energy and its components for individual chocolate products is a key parameter affecting proper selection of the mould material used for the chocolate bars production. This is due to the fact, that the surface energy of the mould material is a key determining factor of chocolate-mould interaction and has a significant influence on the adhesion of cocoa butter and dark chocolate to the mould **(Keijbets et al., 2009)**. It was found, that the clean demould materal should have a surface energy below 30 $mJ.m^{-2}$ and an electron donor component of the surface energy of approximately 15 $mJ.m^{-2}$. Interestingly, the plotting of the thermodynamic work of adhesion vs. total surface energy is linear function implying the fact, that these two thermodynamic parameters are strongly correlated.

For determination of the melting points of the tested chocolates composition, the thermal analysis was performed by means of thermal gravimetry and difrential thermal analysis (TG DTA). Obtained results are summarized in Table 7. Observed melting enthalpies were lower for dark chocolates about -29.61 $J.g^{-1}$ at melting temperature of 34.62 °C in comparison to milk chocolates, where the heat of fusion was found to be -33.51 $J.g^{-1}$ as observed at 33.78 °C.

For evaluation of the composition of tested chocolates, a NIR spectra were recoreded and their absorbtion bands were deconvluted to the individual components. As shown in Figures 3 and 4 for an illustration, this teqnique allows in detail analysis and quantification of individual absorption spectral bands. For interpretation of the observed absorption bands, the palm fat and powder skimmed milk were measured as well as shown in Figure 5 and Figure 6.

CONCLUSION

It was found in this study, that the surface energy of the chocolates is sensitive on basic components composition ratio as well as by the thermal history of the tested chocolate bars. It was confirmed, that the addition of the cocoa fat as well is increasing the dispersive components of the surface energy. In contrary to the latter, the addition of the powdered skimmed milk is increasing the polar components of the surface energy. There was used NIR spectrometry for evaluation of the composition by means of the deconvolution of the individual absorption bands. Thermal analysis show effect of the composition on heats of fusion of the melting point transition, where polar milk components were increasing heat of fusion.

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