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RHEOLOGICAL BEHAVIOUR OF CHOCOLATE AT DIFFERENT TEMPERATURES

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ABSTRACT
The rheological behaviour of the chocolate at different temperatures was studied using a concentric cylinder viscometer with precision small samples adapter, temperature sensor and standard spindle. BIO chocolate (100% organic cocoa) has been used for the whole types of experiments. At the first, the range of temperature has been chosen 36 °C, 38 °C, 40 °C, 42 °C, and 44 °C. The shear deformation rate was established from the 0.1 s^{-1} up to 68 s^{-1}. Rheological behaviour was non–Newtonian (plastic) with inconsiderable yield stress in all temperatures. The chocolate unambiguously demonstrated plastic behaviour and flow curves were fitted by the power law model (Herschel–Bulkley model), Bingham model, and Casson model with taking into account the coefficient of determination R^2. The obtained results of rheological behaviour of chocolate can be best described as Casson fluid. Exactly coefficients of models can be used for modelling of flow velocity, volume flow, friction factor, Reynolds number, two dimensional and three dimensional velocity profiles and much more for flow in the real technical elements e.g. pipes, trough, tubes. Finally, temperature dependence of apparent viscosity of chocolate was also continuously measured in the range from 35 °C up to 62 °C. The apparent viscosity decreased in the temperature range. This decrease was fitted using power law equation. The knowledge of the plastic flow behaviour of chocolate is very important, because it is not quite common flow behaviour of foodstuffs.

Keywords: plastic fluid; yield stress; flow model; chocolate; temperature

INTRODUCTION
In the paper **(Lapčík et al., 2017)** states that 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.

There are many methods for testing properties of chocolate e.g. colour and hardness measuring **(Machálková et al., 2015)**, in this paper we are focused on rheological measuring.

Precision knowledge of the rheological properties of foodstuffs is essential for the product development, sensory evaluation and design, quality control, and evaluation of the process equipment. The flow behaviour of a fluid and semisolid food can be varied from Newtonian to time dependent non-Newtonian depending on its origin, composition and structure behaviour **(Trávníček et al., 2016; Hlaváč et al., 2016; Kumbár et al., 2017)**. This behaviour is necessary to model. The rigorous knowledge of rheological behaviour is also very important for chocolate **(Bozkurt and Icier, 2009; Gonçalves and da Silva Lannes, 2010)**. Especially, the temperature dependence of flow properties is very important for processing liquid chocolate as a topping or filling **(Quiñones-Muñoz et al., 2011; Božiková and Hlaváč, 2013; Glicerina et al., 2013)**. Most of the researchers studied the rheological characteristics of chocolate reported as non-Newtonian plastic fluid with inconsiderable yield stress **(Ačkar et al., 2015; Cikrikci et al., 2017)**. Many papers deals with rheological behaviour blends of cocoa and supplements (hydrocolloids, milk, butter or other fat) and used many mathematical models e.g. Casson model, Windhab model, Carreau model, and Power Law model **(Fernandes et al., 2013; Barbosa et al., 2016; Glicerina et al., 2016)**.

Protective effect of cocoa flavonoids on the heart and blood vessels is declared for longer time, and is associated with their ability to change the course of many pathological processes at the development of cardiovascular diseases **(Adriefdjohan et al., 2005; Ding et al., 2006)**.

There is strong evidence that high cocoa intake lowers blood pressure, improves vascular endothelial function, and potentially increases insulin sensitivity **(Kozelová et al., 2014)**. With increased calories in chocolate consumption, further careful risk-benefit analysis is needed to assess whether consuming cocoa in the form of energy-dense chocolate products may yield a net benefit on cardiovascular risks **(Bauer et al., 2011).**

Scientific hypothesis

The main hypothesis of this work is to determine rheological behaviour of the pure chocolate for five different temperatures. The flow curves will be modeled using several mathematical models. Herschel-Bulkley model, Bingham model, and Casson model will be used for description of chocolate flow behaviour. With these mathematical models is possible to get value of yield stress.

MATERIAL AND METHODOLOGY

The research was focused on evaluating rheological behaviour of pure BIO chocolate (100% cocoa) without lecithin and without traces of milk (Puratos Belcolade, Belgium). The original chocolate sample was in the form of chocolate chips. Samples of chocolate were slowly heating to required temperatures using water bath with a digital controllable thermostat TC-650 (Brookfield, USA).

Rheological measurements were carried out using the DV-3P rotary viscometer (Anton Paar, Austria) equipped with a coaxial cylinder sensor system with precision small samples adapter, temperature sensor pt100, and standard spindle TR9 according to Anton Paar (number 27 according to Brookfield). The geometry of the measuring device it can be seen in **Kumbár and Dostál (2014)**.

In the first step flow curves (shear strain rate versus shear stress) of chocolate were measured in shear strain rate between 0.1 s^{-1} and 68 s^{-1} for five different temperatures 36 °C, 38 °C, 40 °C, 42 °C, and 44 °C, see Table 1.

In the second step temperature dependence of apparent viscosity of chocolate was measured in the range from 35 °C up to 62 °C.

Statisic analysis

Statistical analysis were carried out using MATLAB® R2012a with Statistics toolbox (MathWorks, USA) - analysis of variance (ANOVA) with interaction, testing on the significance level of $p = 0.05$.

RESULTS AND DISCUSSION

In this section, it is provided a careful analysis of the rheological behaviour of pure chocolate in the different temperatures. Very important is selecting of a suitable mathematical flow model. As **Rao (2014)** written, flow model may be considered to be a mathematical equation that can describe rheological data, such as shear strain rate versus shear stress, in a basic shear diagram, and that provides a convenient and concise manner of describing the data.

Occasionally, such as for the (apparent) viscosity versus temperature data, more than one equation may be necessary to describe the rheological data. In addition to mathematical convenience, it is important to quantify how magnitudes of model parameters are affected by state variables, such as temperature, and the effect of structure or composition of foods and establish widely applicable relationships that may be called functional models **(Rao, 2014)**.

Obtained flow curves were modelled using three mathematical flow models which can possible to get value of yield stress, see Figure 1.

The first flow model was Herschel-Bulkley model **(Konar et al., 2015)**:

$$\tau = \tau_0 + K\dot{\gamma}^n, \qquad (1)$$

Where τ is shear stress, τ_0 is yield stress, K is consistency index, $\dot{\gamma}$ is shear strain rate, n is flow index. It is noted here that the concept of yield stress has been challenged **(Barnes and Walters, 1989)** because a fluid may deform minutely at stress values lower than the yield stress. Nevertheless, yield stress may be considered to be an engineering reality and plays an important role in many food products **(Rao, 2014)**. If $\tau < \tau_0$ the Herschel-Bulkley fluid behaves as a solid, otherwise it behaves as a fluid. For $n < 1$ the fluid is shear-thinning, whereas for $n > 1$ the fluid is shear-thickening. If $n = 1$ and $\tau_0 = 0$, this model reduces to the Newtonian fluid **(Kumbár et al., 2015)**.

The second flow model was Bingham plastic model **(Zzaman et al., 2014)**:

$$\tau = \tau_0 + \eta_B\dot{\gamma}, \qquad (2)$$

Where τ is shear stress, τ_0 is yield stress, η_B is the Bingham plastic viscosity, and $\dot{\gamma}$ is shear strain rate. Bingham plastic model can be described by straight lines in terms of shear rate and shear stress, and the former can be described by two parameters η_B and τ_0. However, the shear rate–shear stress data of shear-thinning and shear-thickening fluids are curves that require more than one parameter to describe their data. Given that the equation of a straight line is simple, it is easy to understand attempts to transform shear rate–shear stress data in to such lines (Rao, 2014).

The third flow model was Casson model (De Graef et al., 2011):

$$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta_c\dot{\gamma}}, \qquad (3)$$

Where τ is shear stress, τ_0 is yield stress, η_c is the Casson viscosity, and $\dot{\gamma}$ is shear strain rate. The Casson model is a structure-based model that, although was developed for characterizing printing inks originally, has been used to characterize a number of food dispersions **(Rao, 2014)**.

The International Office of Cocoa and Chocolate has adopted the Casson model as the official method for interpretation of flow data on chocolates. However, it was suggested that the vane yield stress would be a more reliable measure of the yield stress of chocolate and cocoa products **(Servais et al., 2004)**.

The Figure 2 shows flow curves created by Casson model in five different temperatures of samples. In the Table 2 there are all regression coefficients of three used flow curve models – Herschel-Bulkley, Bingham, and Casson model.

The temperature dependence of apparent viscosity of pure chocolate was measured at constant shear strain rate 50 s^{-1}. This dependence was fitted using power law model (Figure 3) according to **Alvarez et al. (2006)** and **Kumbár and Nedomová (2015)**:

Table 1 Values of shear stress of pure chocolate.

Shear strain rate, s^{-1}	Shear stress, Pa				
	36 °C	38 °C	40 °C	42 °C	44 °C
0.10	9.13	9.08	8.74	8.40	8.05
0.17	10.08	9.83	9.49	9.08	8.86
0.20	10.45	10.00	9.55	9.26	9.04
0.34	11.61	11.05	10.71	10.30	10.08
0.51	12.78	12.10	11.70	11.22	11.09
0.68	13.80	13.03	12.55	12.17	11.92
0.85	14.72	13.78	13.29	12.79	12.54
1.02	15.44	14.42	13.88	13.39	13.09
1.36	16.86	15.63	15.04	14.49	14.14
1.70	18.06	16.62	15.99	15.32	14.92
2.04	19.10	17.62	16.94	16.25	15.80
3.40	23.13	21.04	20.10	19.19	18.58
4.08	24.71	22.46	21.44	20.49	19.77
6.80	31.24	28.40	27.00	25.66	24.70
10.2	37.66	34.11	32.27	30.53	29.30
17.0	49.96	45.15	42.47	40.09	38.13
20.4	55.22	49.98	46.84	44.10	42.00
34.0	76.87	69.12	64.84	60.93	57.63
51.0	98.89	92.06	86.09	80.68	76.04
68.0	***	***	106.08	99.14	93.16

Note: *** denotes out of range.

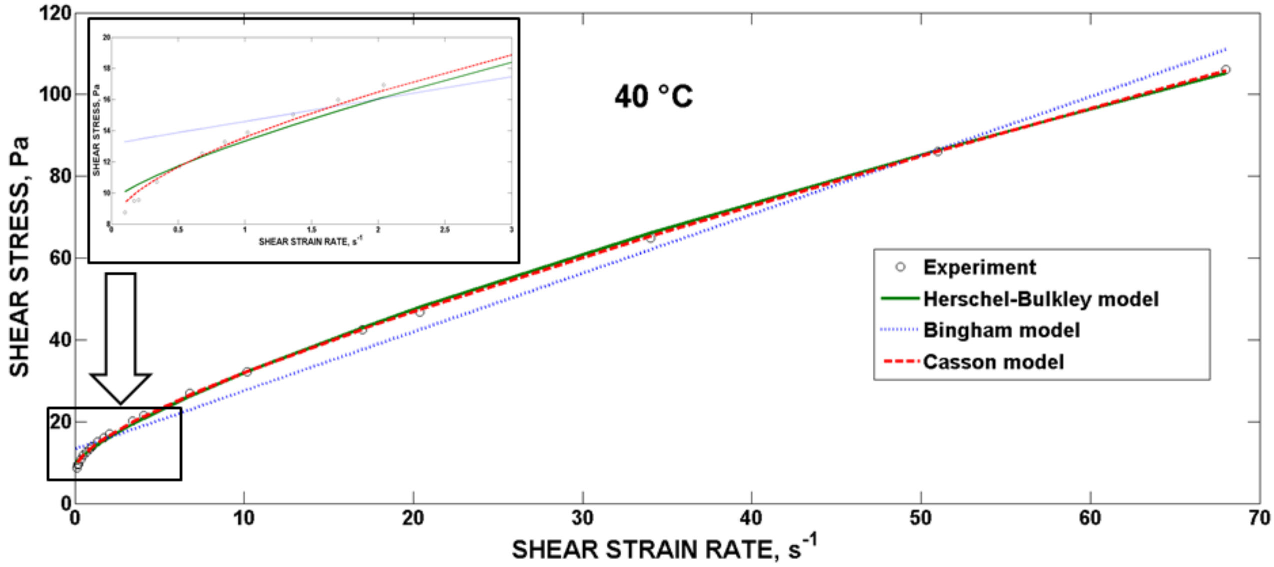

Figure 1 Comparison of the flow curve models of pure chocolate at the temperature 40 °C.

Table 2 Regresion coefficients of the flow models.

Temperature	Herschel-Bulkley model				Bingham model			Casson model		
	τ_0	K	n	R^2	τ_0	η_B	R^2	τ_0	η_c	R^2
°C	Pa	Pa·s^n	–	–	Pa	Pa·s	–	Pa	Pa·s	–
36	9.096	5.764	0.6973	0.9994	14.23	1.792	0.9774	8.549	0.987	0.9991
38	9.339	4.525	0.7359	0.9991	13.17	1.638	0.9831	7.906	0.899	0.9998
40	9.386	3.939	0.7560	0.9992	13.15	1.438	0.9866	7.679	0.830	0.9998
42	9.053	3.755	0.7506	0.9991	12.67	1.340	0.9851	7.489	0.764	0.9998
44	8.838	3.651	0.7414	0.9990	12.41	1.254	0.9847	7.450	0.703	0.9997

Note: R^2 denotes coefficients of determination.

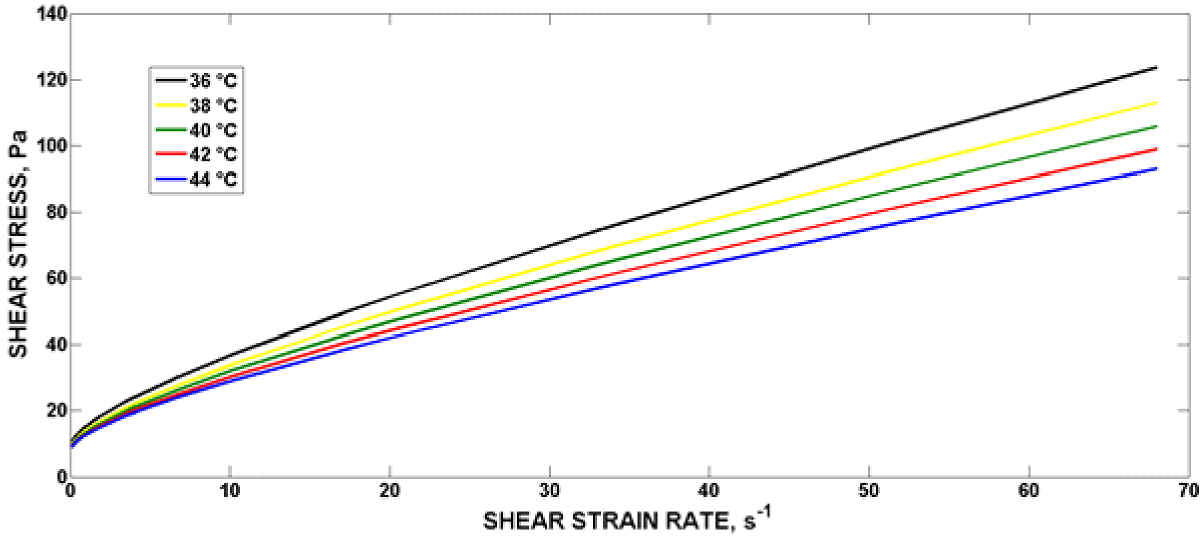

Figure 2 Flow curves (using Casson model) of pure chocolate at five different temperatures.

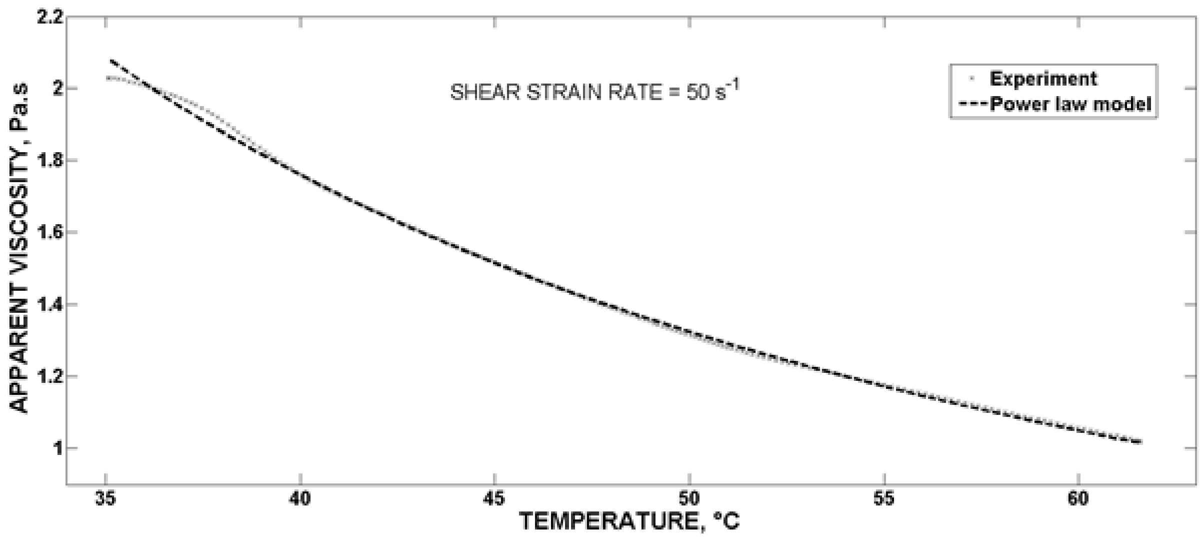

Figure 3 Temperature dependence of apparent viscosity of pure chocolate.

$$\eta_{app} = at^b, \quad (4)$$

Where η_{app} is apparent viscosity, t is temperature, a and b are coefficients. The values of coefficients for Eq. (4) are a = 195.6 Pa·s·°C^{-b}, b = -1.277, and R^2 = 0.9983.

It was found out that all of the calculated regression coefficients of all used models are statisticaly significantly different (p <0.05).

It is evident that apparent viscosity of pure chocolate decreased with increasing temperature (p <0.05). This decrease **Aguilera et al. (2004)** described that chocolate microstructurally regarded as a particulate medium formed by an assembly of fat-coated particles. Within this matrix the liquid fraction of cocoa fat (which increases with temperature) is likely to move under capillary forces through interparticle passages and connected pores.

CONCLUSION

Obtained results demonstrated effect of temperature on the rheological behaviour of pure chocolate. The significant yield stress τ_0 (p <0.05) and plastic behaviour of pure chocolate were observed and described in the five different temperatures between 36 °C and 44 °C.

Experimental data was successfully fitted using Herschel-Bulkley model (R^2 ranged from 0.9990 up to 0.9994), Bingham model (R^2 ranged from 0.9774 up to 0.9866), and Casson model (R^2 ranged from 0.9991 up to 0.9998). The best model for fitted flow curves of chocolate was chosen Casson model, which also had the best values of coefficient of determination R^2 (average R^2 of five models is 0.99964). At the other hand, Herschel-Bulkley model gives also very accurate results of pure chocolate flow curve modelling (average R^2 of five models is 0.99916).

Finally, the liquid pure chocolate shows behaviour of Casson fluid. We can also conclude that apparent viscosity of pure chocolate decreased with increasing temperature (p <0.05).

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