The temperature influence on the rheological behaviour of chocolate

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Abstract: Three samples of commercially available dark chocolate with a minimum cocoa content of 50%, 78% and 99% were used to experimentally verify the temperature influence on the rheological behaviour of chocolate. The change in the shear stress with an increasing shear strain rate was measured using an RST rheometer with a cone-plate spindle arrangement at a shear strain rate from 0.01/s to 100/s at temperatures of 36 °C, 38 °C, 40 °C, 42 °C and 44 °C for a 1 minute load. To describe the flow curves at selected temperatures, a mathematical flow model according to Casson was used, which, according to the calculated coefficient of determination R^2, seemed to be the most suitable. The results show that with an increasing chocolate sample temperature, their viscosity decreased, with respect to the shear stress.

Key Words: dark chocolate, viscosity, flow curves, Casson model, cocoa butter

INTRODUCTION

The basic raw materials used to make chocolate include cocoa mass, cocoa butter, sugar and emulsifiers. Milk powder, vegetable fats (other than cocoa butter) and flavourings (Becket 2008) are some of the other raw materials that can be used. Cocoa butter is a natural fat obtained from the seeds of cacao trees and, thanks to its properties, is an essential component of chocolate. Cocoa butter makes up about 55% of the cocoa beans. It is known for its specific physical properties, such as its hardness at room temperature, but its complete melting at body temperature (Momeny et al. 2013, Afoakwa 2010).

The principles of rheology are commonly used to understand and improve the flow behaviour and textural properties of food and to reveal the relationships between the physical properties and the functionality of the material (Arana 2012). The rheological properties are important in the production of chocolate for quality control purposes and may be related to its composition, e.g., a higher content of cocoa butter in chocolate results in a decrease in the flow and viscosity (Servais et al. 2007). General rheology deals with the physical and mathematical description of the behaviour of the substances between three quantities – the stress to which the material is exposed, the final amount of deformation of the material and time, with respect to the combination of time and the deformation. Mathematically, the flow properties of liquids are expressed by the rheological equations of state, which usually express the relationship between the deformation shear stress τ and the deformation of the liquid. They are expressed graphically using flow curves (Kadlec et al. 2013). The flow limit is the point where the shear stress and shear strain rate curve begin to show the deviation of the shear rate from zero. This condition indicates the start of the flow and the corresponding shear stress is considered as the flow limit (Cruz et al. 2014).

Viscosity and yield strength are important rheological properties in chocolate production technologies and for its final quality. It is important when pumping chocolate, mixing it and pouring it into moulds. Viscosity is also important for the sensory perception of the final product when consumed by the consumer. Viscosity is defined as the resistance of a fluid to creep (the energy required to keep the fluid moving) and the flow limit as the minimum amount of energy required for the fluid to begin to flow. For liquids such as water or cocoa butter, the viscosity is the same throughout the flow regardless of the shear rate. These fluids are called Newtonian. However, the vast majority of all fluids are non-Newtonian, which means that the viscosity changes with the shear rate. This group also includes chocolate, which belongs to the subgroup of pseudoplastic liquids. This means that its viscosity decreases with an increasing shear rate (Afoakwa et al. 2008, Cikrikci et al. 2017, Glicerina et al. 2013, Pandey and Singh 2011, Talbot 2009).

MATERIAL AND METHODS

Table 1 shows the characteristics of the chocolate samples used to measure the change in the shear stress with increasing shear strain rate at 36 °C, 38 °C, 40 °C, 42 °C and 44 °C. All the chocolate samples were from the same commercial manufacturer LINDT & SPRÜNGLI GMBH (Germany). It was a dark chocolate with a minimum cocoa content of 50%, 78% and 99%.

Table 1 The characteristics of the used chocolates

Chocolate with a minimum cocoa solids content of	Ingredients	Nutritional information per 100 g				
		Energy value	Fats Of which are saturated fatty acids	Carbohydrates Of which are sugars	Protein	Salt
50%	cocoa mass, sugar, concentrated butter, cocoa butter and vanilla	2302 kJ 533 kcal	36 g 22 g	48 g 45 g	5.6 g	0.04 g
78%	cocoa mass, cocoa butter, sugar, low-fat cocoa powder, anhydrous milk fat, may contain traces of hazelnuts and other nuts, milk, soybeans	2384 kJ 576 kcal	46 g 29 g	24 g 17 g	10 g	0.05 g
99%	cocoa mass, low-fat cocoa powder, cocoa butter, sugar	2433 kJ 590 kcal	51 g 31 g	8 g 1 g	15 g	0.01 g

The chocolate samples were measured using an RST rheometer (Brookfield, USA) with a cone-plate spindle arrangement (RCT-50-2) equipped with a duplicator to temper the sample. This rheometer is suitable for measuring the flow properties of chocolate. Specialised software Rheo 3000 (Brookfield, USA) was used to evaluate the measured data. Thanks to the software, it is possible to programme the measuring cycles, to obtain and process the obtained data, including the insertion of mathematical models and the statistical evaluation. In our case, the flow curves were modelled using the Casson mathematical flow model, which was adopted by The International Office of Cocoa and Chocolate as the official method for describing the flow properties of chocolates (Servais et al. 2007).

The individual chocolate samples were gradually dissolved at 36 °C on an RTS rheometer plate, which was pressed against a rotating cone followed by the overall tightening of the rheometer mechanism. The temperature of 36 °C was the starting temperature for measuring the shear stress at a shear strain rate ranging from 0.01/s to 100/s for 1 minute. Between the measurements, the temperature was continuously increased by 2 °C to a final measurement temperature of 44 °C.

RESULTS AND DISCUSSION

The measured values of the flow limit, Casson's viscosity and the coefficient of determination according to Casson's model are given in Table 2. To determine which mathematical model is most suitable for a given type of liquid (semi-solid), it is necessary to measure the stable shear stress during the interval of the assessed shear deformation velocity and substitute the resulting values into the mathematical relations of the individual models. The resulting value of the coefficient of determination will then show whether the given calculation model is satisfactory or not (Balmforth et al. 2014).

Casson's model is given by:

$$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta_c \dot{\gamma}},$$

where τ is the shear stress, τ_0 is the value of the stress at the flow limit, η_c is the value of Casson's viscosity and $\dot{\gamma}$ is the shear strain rate. Casson's model is a very close alternative to Bingham's model. Although this model is based on the Bingham model, all the variables are increased by a certain constant, which makes the transition between the flow limit and the Newtonian region more pronounced (Glicerina et al. 2016). Casson's model can describe the behaviour of plastics. It is also used to characterise dispersion systems in foods and also to characterise the flow properties of chocolates (Rao 2007).

Table 2 Coefficients of the Casson model

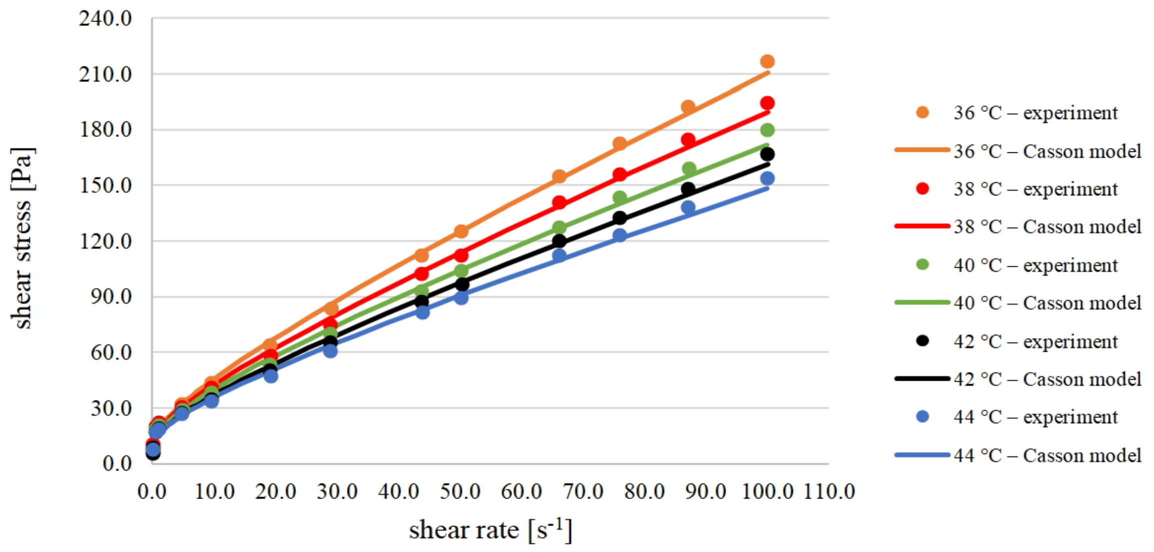
Temperature	Casson model								
	Cocoa content 50%			Cocoa content 78%			Cocoa content 99%		
[°C]	τ_0 [Pa]	η_c [Pa/s]	R^2	τ_0 [Pa]	η_c[Pa/s]	R^2	τ_0 [Pa]	η_c [Pa/s]	R^2
36	10.0495	1.2863	0.9935	5.0406	0.5978	0.9935	10.8338	4.0713	0.9980
38	10.0126	1.1244	0.9950	3.7063	0.5832	0.9965	7.5497	3.4816	0.9990
40	10.1931	0.9841	0.9951	3.6089	0.5168	0.9934	6.4432	3.1586	0.9988
42	9.2372	0.9321	0.9950	3.7789	0.4661	0.9940	5.6532	2.9056	0.9987
44	9.6185	0.8240	0.9940	3.0405	0.4670	0.9956	5.8116	2.5817	0.9979

The flow limit τ_0 for all three chocolate samples decreased with an increasing temperature. The higher the temperature, the more thermal energy is contained in the material, and, therefore, less stress is sufficient to initiate the flow of material. Therefore, the flow limit tends to decrease with an increasing temperature, although there may not be any changes in the structure caused by the increased temperature (Balmforth et al. 2014).

The coefficients of determination R^2 ranged from 0.9934 to 0.9990, which indicate a correctly chosen mathematical model for the description of the flow properties of the chocolate.

Figures 1–3 show the flow curves for the individual chocolate samples at five different temperature regimes.

Figure 1 The flow curves (according to Casson's model) for the chocolate with a min. cocoa content of 50%



The highest shear stress values were measured in all three chocolate samples at a shear strain rate of 100/s at a temperature of 36 °C. The chocolate with a min. cocoa content of 50% had a shear stress of 216.94 Pa, the 78% chocolate had a shear stress of 106.56 Pa and the 99% chocolate had a value of 529.29 Pa. While the lowest values were measured at 44 °C for all the chocolates at the same shear strain rate. The measured values were as follows: 153.81 Pa for the 50% chocolate, 77.89 Pa for the 78% chocolate and 355.07 Pa for the 99% chocolate. As the temperature rises, the Casson plastic viscosity value decreases. This phenomenon can be eliminated, especially with dark chocolates, by adding lecithin (Čopíková 1999). If the temperature was low when the chocolate melted, not all the modifications of the cocoa butter would have to dissolve and the viscosity and flow rate could increase (Bourne 2002).

Figure 2 The flow curves (according to Casson's model) for the chocolate with a min. cocoa content of 78%

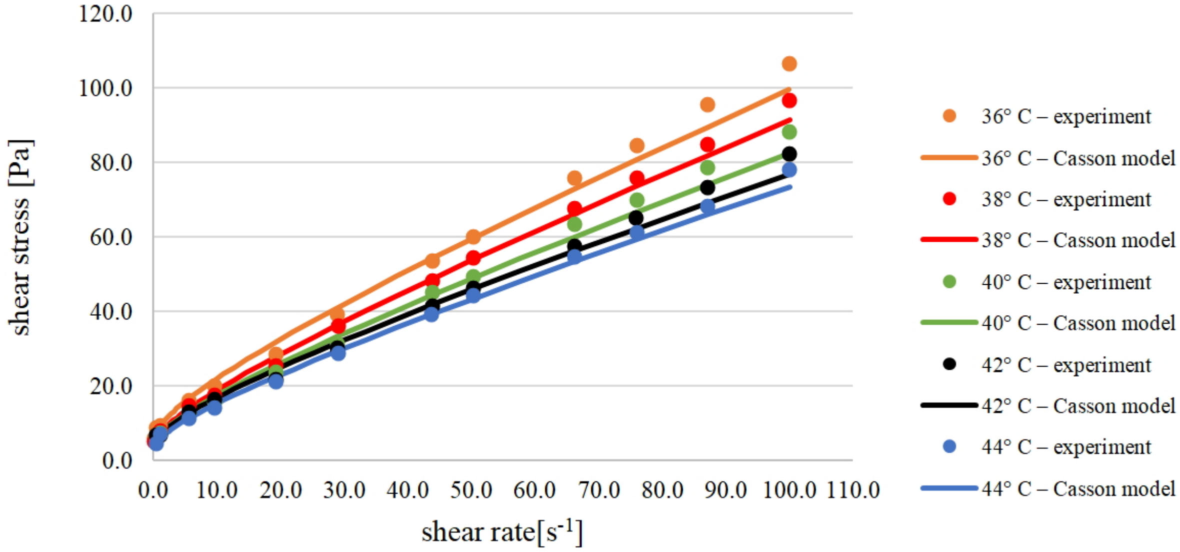
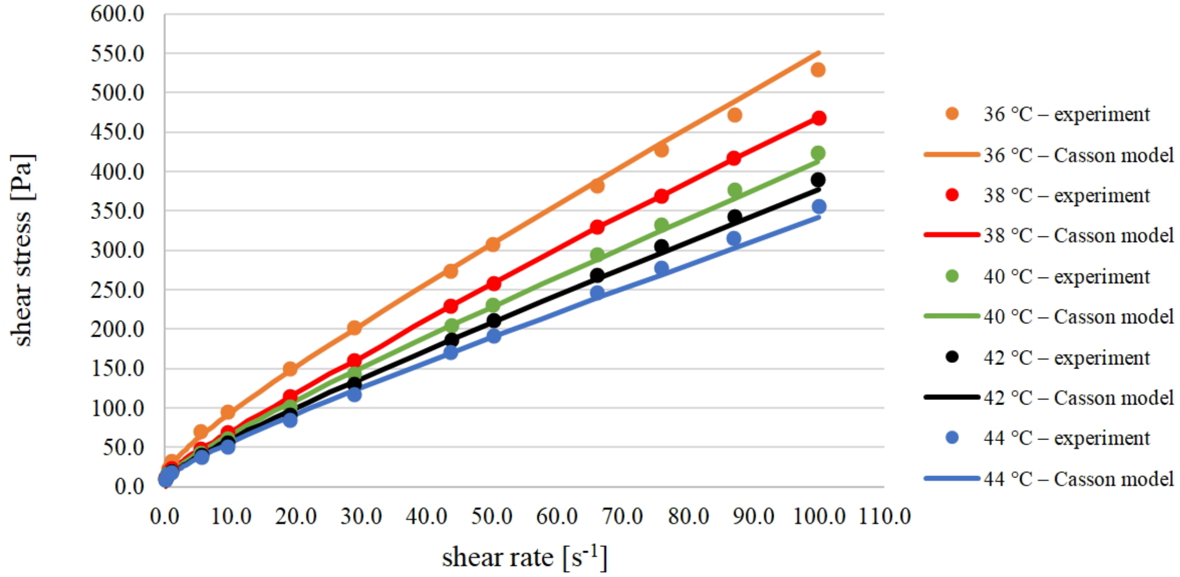


Figure 3 The flow curves (according to Casson's model) for the chocolate with a min. cocoa content of 99%



Up to a shear strain rate of 0.1/s, the shear stress values at all temperatures were very similar, then they began to diverge with an increasing shear strain rate depending on the temperature actually used.

CONCLUSION

Knowledge of the rheological properties in food production is important especially for the mathematical calculations of the equipment or processes, e.g., during mixing, kneading, pumping, centrifugation, etc. It is necessary to determine the exact range of shear rates and temperatures in the equipment. At five selected temperatures (36 °C, 38 °C, 40 °C, 42 °C and 44 °C), the change in the shear stress as a function of the shear strain rate was monitored in three dark chocolate samples with a min. cocoa content of 50%, 78% and 99%. The higher the exposure temperature of the sample, the lower the shear stress value. As a result of the rising temperature, the viscosity decreased, which is closely related to the content of the cocoa butter in the individual chocolate samples.

The high values of the determination coefficient R^2 (0.9934–0.9990) confirmed that the mathematical model according to Casson is suitable for the description of the flow properties of chocolate.

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