

## THE RHEOLOGICAL BEHAVIOR OF BITTER CHOCOLATE AT DIFFERENT TEMPERATURES

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### **Abstract**

*The objectives we started from to achieve the purpose of the paper were: analysis of the variation of the apparent viscosity of chocolate depending on temperature and shear rate, quantification of the size of Casson mathematical model parameters affected by state variables: temperature and bitter chocolate ingredients.*

*The rheological properties of chocolate are important in determining the quality of the final product. Melted chocolate is known to exhibit non-Newtonian behavior and the same behavior was observed in this paper.*

*The four samples of bitter chocolate have ideal pseudo-plastic and thixotropic properties, because after removing the shear stress the initial viscosity is not restored, an irreversible structural change taking place.*

*These results indicate that these four melted chocolate samples have the same sensitivity to viscosity as the temperature increases.*

**Key words:** bitter chocolate, viscosity, Casson mathematical model.

### **INTRODUCTION**

Accurate knowledge of the rheological properties of food is essential for product development, sensory evaluation and design, quality control and evaluation of process equipment.

The flow behavior of a fluid and semi-solid food can vary from Newtonian to non-Newtonian depending on time, depending on the origin, composition and behavior of its structure (Trávníček et al., 2016; Hlaváč et al., 2016; Kumbár et al., 2017). This behavior is necessary for modeling.

Rigorous knowledge of rheological behavior is also very important for chocolate (Bozkurt and Icier, 2009; Gonçalves and da Silva Lannes, 2010).

In particular, the temperature dependence of the flow properties is very important for the processing of liquid chocolate as a topping or filling (Quiñones Muñoz et al., 2011; Božiková and Hlaváč, 2013; Glicerina et al., 2013).

Most researchers have studied the rheological characteristics of chocolate reported as a non-Newtonian plastic liquid with incredible yield stress (Ačkar et al., 2015; Cikrikci et al., 2017).

Many papers treat mixtures of rheological behavior of cocoa and supplements (hydrocolloids, milk, butter, or other fats) and have used many mathematical models: the Casson model, the Windhab model, the Carreau model, and the power law model (Fernandes et al., 2013; Baker et al. ., 2006; Glicerina et al., 2013).

The protective effect of cocoa flavonoids on the heart and blood vessels has been reported for a long time and is associated with their ability to change the course of many pathological processes in the development of cardiovascular disease (Alberts, et al., 2006; Briggs, et al., 2004).

There is strong evidence that a high intake of cocoa lowers blood pressure, improves vascular endothelial function and potentially increases insulin sensitivity (Graef et al., 2011).

With the increase in calories in chocolate consumption, a careful risk-benefit analysis is needed to assess whether consumption of cocoa in the form of energy-dense chocolate products can produce a net benefit on the risks (Fernandes, et al., 2013).

## **MATERIAL AND METHOD**

The aim of this paper is to evaluate the rheological behavior of Poiana, Kandia, Roshen and Milka bitter chocolate.

The control of the rheological properties of chocolate is important, because the viscosity of chocolate is given by its liquid consistency, respectively how thick/dense/fluid the liquid chocolate is.

The rheological properties of chocolate are important in the manufacturing process to obtain high quality products with a well-defined texture.

The objectives I started from to achieve the purpose of the paper were: analysis of the variation of the apparent viscosity of chocolate depending on temperature and shear rate, quantification of the size of Casson mathematical model parameters affected by state variables: temperature and chocolate ingredients.

Four brands of bitter chocolate were purchased from the Auchan supermarket in Oradea. Commercial chocolates were used to ensure repeatability and standardization. The four brands of dark chocolate used are the following:

- ✚ Chocolate 1: Poiana bitter chocolate, manufactured by Mondelez România SA produced in Bucharest.
- ✚ Chocolate 2: Kandia bitter chocolate, manufactured by Kandia Dulce SA, produced in Bucharest.
- ✚ Chocolate 3: Roshen bitter chocolate, manufactured by Roshen SA, produced in Ukraine.

✚ Chocolate 4: Milka bitter chocolate, manufactured by Mondelez Romania SA produced in Bucharest.

Viscosity measurements were performed on melted chocolate samples at two temperatures (50, 55° C), with Brookfield viscometer (Brookfield Engineering Inc, Model DV E) and 6 different Rpm speeds (6, 12, 30, 50, 60, 100) with LV 3C axis no. 67.

Before testing, I crushed and divided the chocolate tablets as follows: 20% I left them in a solid state, 80% I melted them on a steam bath, stirring constantly.

We checked the temperature with a technical thermometer, but without exceeding the melting temperature of 55° C of the bitter chocolate.

When the chocolate reached the melting temperature, I added the remaining 20% chocolate in a solid state and mixed until I reached the working temperature of 50° C and 55° C, respectively.

## **RESULTS AND DISCUSSION**

The first part of the results includes the analysis of the rheological behavior of melted bitter chocolate at different temperatures.

All samples show the same shear force, regardless of temperature, under conditions of a constant shear rate.

The viscosity of liquid chocolate samples decreases with increasing temperature.

The results obtained at a constant torsion (73.98%) frame chocolate as a thixotropic non-Newtonian liquid.

Thus, all melted chocolate samples, regardless of the manufacturer, are non-Newtonian, thixotropic time-dependent liquids, which suffer from decreases in viscosity, with increasing temperature at a constant shear rate.

Melted chocolate exhibits non-Newtonian behavior and the same behavior was observed in this paper.

Next, we presented the analysis of the rheological behavior of the melted chocolate samples at different temperatures.

As Rao (2014) wrote, the Casson model is considered a mathematical equation that describes rheological data, such as shear rate versus shear force, in a basic shear diagram, and provides a convenient and concise way to describe its data.

In addition, it is important to quantify how model parameter sizes are affected by state variables: temperature and chocolate ingredients (Rao, 2014).

The value of the Casson yield is important to determine the flow rate of chocolate (Beckett, 2000).

Analyzing the results, the apparent viscosity of the melted chocolate samples decreased in all brands as the speed and shear strength increased.

The apparent viscosity is inversely proportional to the shear rate and shear stress.

The viscosity of the melted chocolate samples, regardless of brand, was affected by temperature. The increase in temperature has led to a decrease in viscosity.

The yield value of Casson (Pa) decreased, with increasing temperature, in all samples of melted bitter chocolate.

Figures 1 and 2 show the typical graphs of shear force and shear rate of melted chocolate samples.

The flow curves of melted chocolates show us that they are non-Newtonian liquids that exhibit non-ideal plastic behavior; when the yield value has been exceeded, thinning of the shear occurs, the elastic deformation ceases and the plastic deformation is installed.

The flow curve of the melted chocolate sample shows the measurement of the shear force as a function of increasing the shear rate.

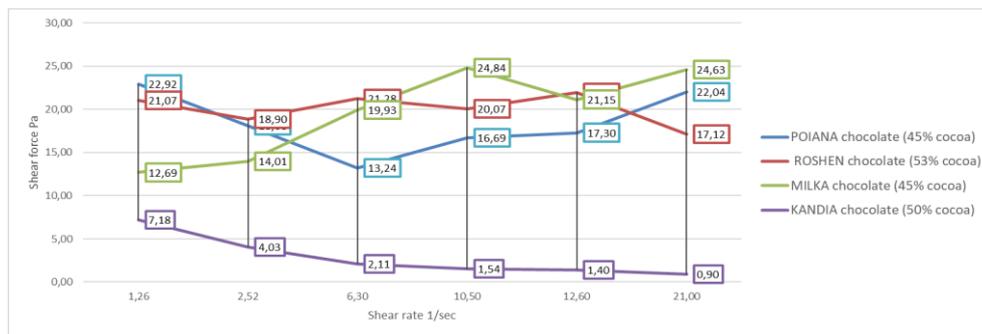


Fig. 1. Comparison of flow curves of melted chocolate samples at 50°C

The four samples show stress yield.

The stress increases linearly as the speed of shear or deformation increases. The flow of melted chocolate belongs to the Casson model.

The characteristics of the flow include Kandia chocolate as a pseudoplastic liquid, and Milka, Roshen and Poiana as plastic liquids.

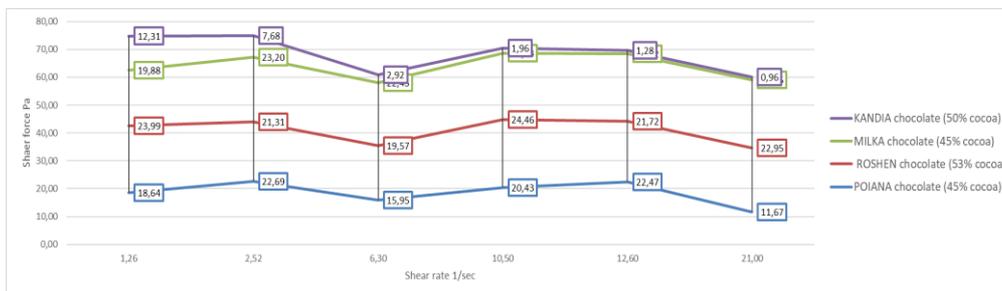


Fig. 2. Comparison of flow curves of melted chocolate samples at 55°C

Increasing the temperature to 50° leads to a decrease in shear stress in the case of samples of bitter melted chocolate.

The Casson rheological parameters of the melted chocolate samples calculated as a function of temperature are shown in Figures 3 and 4.

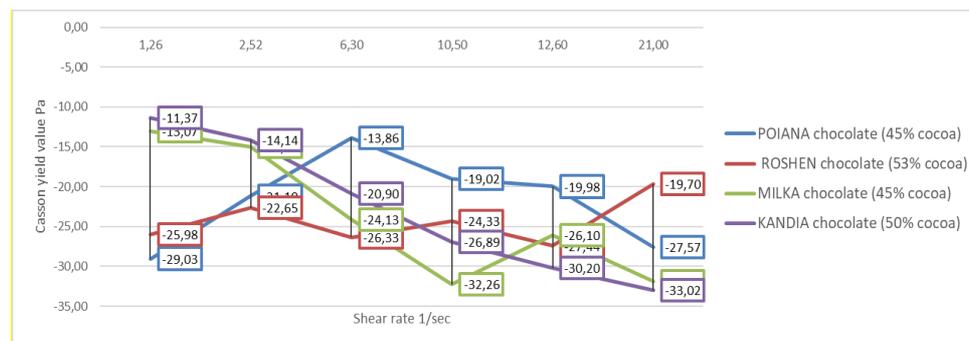


Fig.3. Casson yield value in samples of melted chocolate at 50°C

Casson efficiency is a material property that characterizes the minimum shear force required to induce flow.

It expresses the low properties of the chocolate's shear force and is influenced by the specific surface, particle fraction, emulsifiers and moisture, particle-particle interactions (Afoakwa et al. 2007, 2008, 2009; Abbasi et al. 2009).

The highest value of the Casson yield was for Kandia chocolate (-11.37 Pa), followed by Milka chocolate (-13.07 Pa) at the shear rate of 1.26 s<sup>-1</sup> and the temperature 50°C, showing us the direct connection between the flow and the flow rate of the liquid.

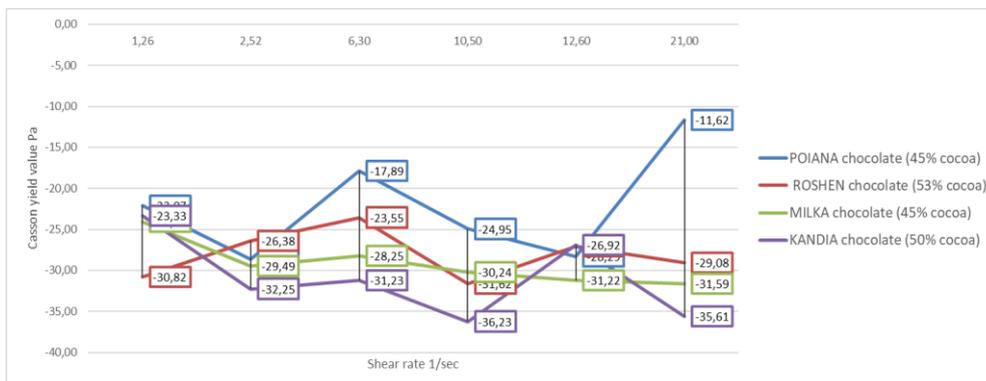


Fig.4. Casson yield value in samples of melted chocolate at 55°C

Increasing the temperature to 55°C led to a decrease in the yield value of Kandia chocolate (- 23.33 Pa) and Milka (- 24.05 Pa), both at the minimum shear speed of 1.26 s<sup>-1</sup> and at the maximum shear speed 21.00 s<sup>-1</sup>: Milka - 31.59 Pa and Kandia - 35.61 Pa, as the elastic deformation ceases and plastic deformation sets in, the viscosity of the liquid chocolate samples decreasing with increasing temperature.

The flow behavior of chocolate and the yield value are influenced by the ingredients.

Yield values increased due to the presence of lecithin, while plastic viscosity decreased.

The relationship between temperature, shear rate and viscosity of chocolate samples is shown in Figures 5 and 6.



Fig. 5. Efectul temperaturii (50°C) asupra vâscozității probelor de ciocolată

The viscosity of melted chocolate samples decreases at a similar rate as the temperature increases.

Of all the samples of melted chocolate, the highest plastic viscosity was obtained in the Poiana chocolate sample (14.92 Pa) at a temperature of 50° C and a shear rate of 1.26 s<sup>-1</sup>.

In general, the viscosity of chocolate will obviously increase if the content fat is reduced to a certain limit (Newtonian flux).

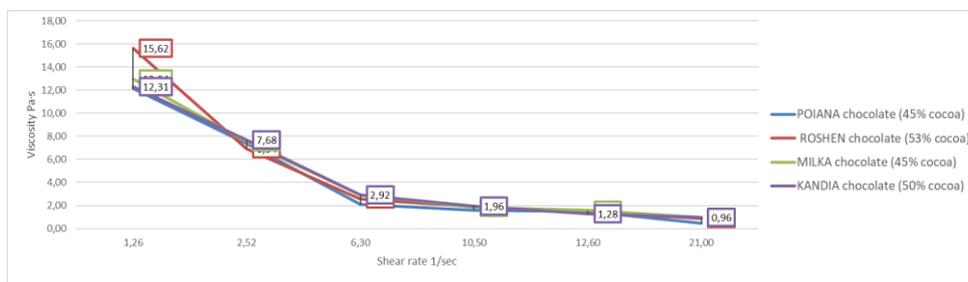


Fig.6. Efectul temperaturii (55°C) asupra vâscozității probelor de ciocolată

Figures 5 and 6 show that the melted chocolate samples exhibit a shear and thixotropic behavior. By analyzing the viscosity curves in the four chocolate samples, they can be classified as pseudoplastic liquids. The viscosity of chocolate depends on the content of cocoa butter at a certain temperature range. Increasing cocoa butter can cause a decrease in viscosity.

High temperature from 50° C to 55° C increases the kinetic energy of chocolate molecules, decreasing the viscosity (Rao, 2014). The viscosity of chocolate depends on the fat content at a certain temperature range.

Increasing the content of cocoa butter prevents the formation of crystals and reduces viscosity as the temperature rises.

## CONCLUSIONS

Melted chocolate is known to exhibit non-Newtonian behavior and the same behavior was observed in this study.

The four chocolate samples have non-ideal pseudo-plastic and thixotropic properties, because after the removal of the shear stress the initial viscosity is not restored, an irreversible structural change taking place.

By analyzing the viscosity curves in the four chocolate samples, all samples can be classified as pseudoplastic liquids.

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