

## THE RHEOLOGICAL BEHAVIOR OF MILK CHOCOLATE AT DIFFERENT TEMPERATURES

Morna Anamaria Aurelia\* Bura Giani Cătălin

\*University of Oradea, Faculty of Environmental Protection, 26 Gen. Magheru St., 410048 Oradea, Romania, e-mail: [amorna@uoradea.ro](mailto:amorna@uoradea.ro)

### **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 milk 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 milk chocolate samples have 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.*

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

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

### **INTRODUCTION**

The characteristics and level of the fat phase, the cocoa dry matter, the emulsifiers and the solid phases, together with the changes they undergo during processing, have a major impact on the flow characteristics of a chocolate.

The flow characteristics of chocolate are important, because product quality control is a necessity (Afoakwa, E. O. et al., 2008; Alberts, H.C. and Cidell, J.L., 2006; Božiková, M., Hlaváč, P., 2013; Kumbár, V., et al., 2017).

In his work "*Effect of cocoa fat content on wetting and surface energy of chocolate*" (Ačkar, Det all., 2015), states that chocolate is unique as a food, because it is solid at normal room temperatures, but melts easily as temperatures rise.

There are many methods for testing the properties of chocolate, but in this paper we focus on rheological measurements and sensory analysis (Quiñones-Muñoz, T., et al., 2011; Rao, M.A., 2014; Trávníček, P., et al., 2016).

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

Chocolate is a complex rheological system with solid particles such as cocoa, milk and sugar dispersed in cocoa butter.

Chocolate can be described as a suspension of non-fat particles (sugar and cocoa solids and possibly milk powder particles) dispersed in cocoa butter as a continuous phase (Beckett, S.T., 2000; Hlavač, P., et al., 2016; Sokmens ; Gonçalves, E. V., et al., 2010).

Melted chocolates are a dense mixture of sucrose coated with phospholipids and cocoa particles in the liquid fat.

The characteristic aroma of chocolate must be developed in several stages of processing.

During processing, the components are mixed, refined and assembled to achieve the desired rheological properties for a defined product texture and melting characteristics (Cikrikci, S., et al., 2017; Fernandes, V.A., et al., 2013; Glicerina, V., et al., 2013; Hílma Elena, 2016).

The chocolate fat will be released from the agglomerated chocolate mass and spread to cover these particles so that it can flow easily.

For processed foods, the composition and addition of ingredients to achieve a certain food quality and product performance, requires a deep rheological understanding of the individual ingredients related to food processing and final perception (Afoakwa, E. O. et al., 2009; Afoakwa, E., Paterson, A., et al., 2007; Abbasi, S.; Farzanmehr, H., 2009; Baker, B. Set all., 2006; Graef, V., et al., 2011; Hílma Elena, 2016).

The taste can be influenced by the texture of the product.

The consumer evaluates the quality of food (fresh, aged, tender and ripe) according to the physical sensations (hard, soft, crunchy, wet and dry) of the food produced inside the mouth.

## **MATERIAL AND METHOD**

This paper presents the analysis of the rheological and sensory properties of Africana, Laura, Primola and Milka milk chocolates.

Chocolate consumption is closely associated with rheological properties.

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 we started from to achieve the purpose of the paper were: analysis of the variation of the apparent viscosity of chocolate as a function of 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: Africana milk chocolate, manufactured by Mondelez Romania SA produced in Bucharest.
- ✚ Chocolate 2: Laura milk chocolate, manufactured by Kandia Dulce SA, produced in Bucharest.
- ✚ Chocolate 3: Primola milk chocolate, manufactured by Kandia Dulce SA, produced in Bucharest.
- ✚ Chocolate 4: Milka milk chocolate, manufactured by Mondelez Romania SA produced in Bucharest.

Viscosity measurements were performed on chocolate samples at two temperatures (45, 50°C), with the Brookfield viscometer (Brookfield Engineering Inc, Model DV-E) and 8 different Rpm speeds (0.3, 0.6, 1.5, 3, 6, 12, 20, 30) with axis LV-3C no. 67.

Before testing, I chopped 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.

I checked the temperature with a technical thermometer, but without exceeding the melting temperature of 50 °C of milk chocolate.

When the chocolate reached the melting temperature, I added the remaining 20% chocolate in the solid state and mixed until I reached the working temperature of 45 °C and 50 °C, respectively.

## **RESULTS AND DISCUSSION**

The first part of the results includes the analysis of the rheological behavior of melted milk 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 (24.5%) 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 as the temperature rises at a constant shear rate.

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

Next, I 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 of description of the data.

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

The Casson yield value is important in determining the flow rate of chocolate (Beckett 2000).

Apparent viscosity and yield are affected by fat content, temperature and emulsifiers.

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 Casson yield value (Pa) decreased, with increasing temperature, in the case of Laura, Africana and Milka melted chocolate samples, and increases in Primola.

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 value of the yield has been exceeded, thinning of the shear appears, the elastic deformation ceases and the plastic deformation is installed.

As the shear rate increases, the three-dimensional structure of the material aligns in the flow lines, which were previously collapsed and turned into asymmetric particles.

This incident causes a decrease in viscosity and, at some point, is independent of the shear rate at high shear force (Afoakwa, 2009).

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

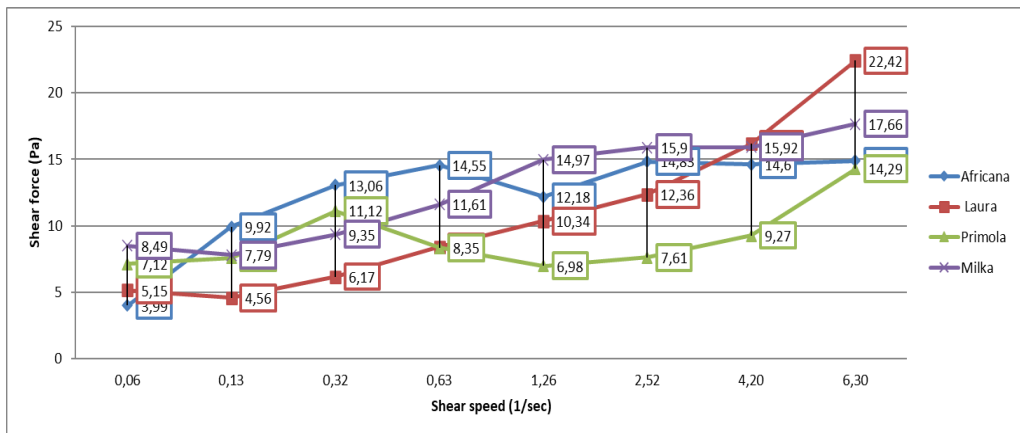


Fig. 1. Comparison of milk chocolate flow curve models at 45 °C

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 frame Milka and Africana chocolates as pseudoplastic liquids, and Laura and Primola as plastic liquids.

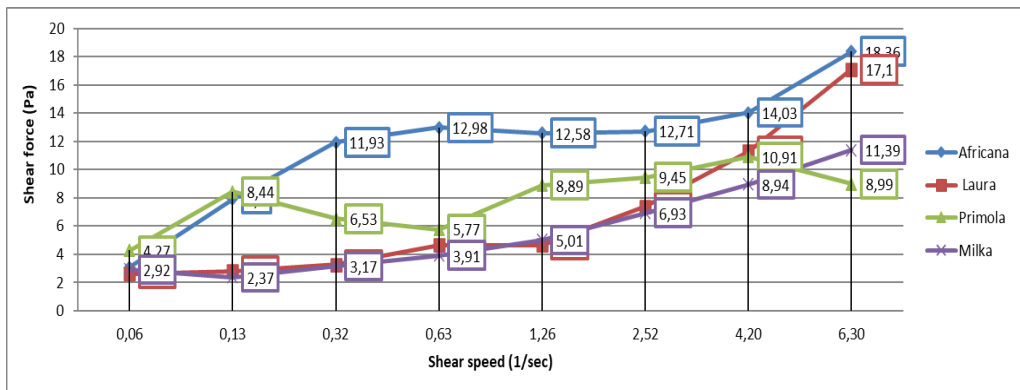


Fig. 2. Comparison of milk chocolate flow curve models at 50 °C

Raising the temperature to 50 °C leads to a decrease in shear stress in the case of milk melted chocolate samples.

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

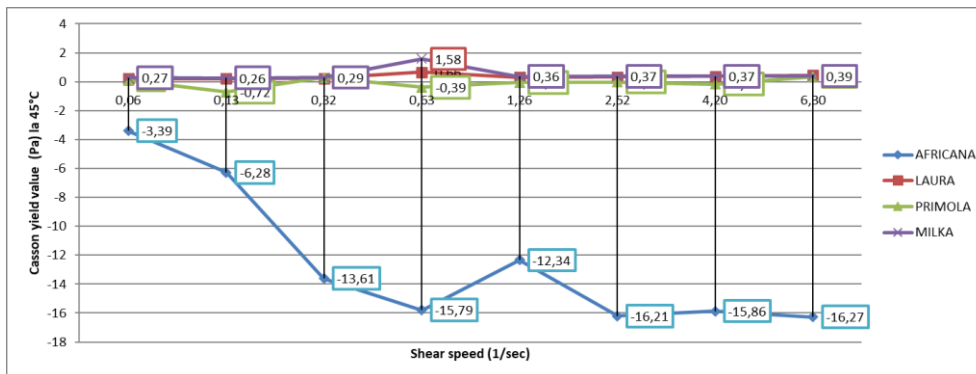


Fig.3. Casson yield value for melted chocolate samples at 45°C

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

It expresses the low properties of chocolate shear force and is influenced by specific surface area, particle fraction, emulsifiers and moisture, particle-particle interactions (Afoakwa et Al. 2009).

The highest value of the Casson yield was for Milka chocolate (1.58 Pa), followed by Laura chocolate (0.66 Pa) at the shear rate of  $0.63 \text{ s}^{-1}$  and the temperature  $45 \text{ }^\circ\text{C}$ , showing us the direct connection between the flow and the flow rate of liquid.

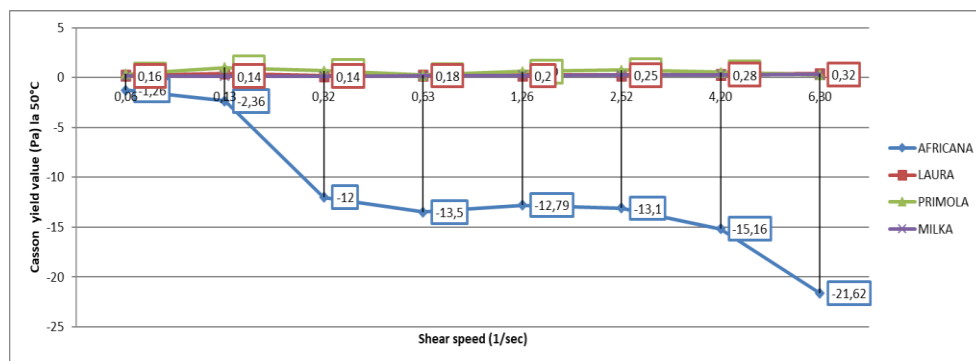


Fig.4. Casson yield value for melted chocolate samples at 50°C

Increasing the temperature to  $50 \text{ }^\circ\text{C}$  led to a decrease in the yield value of Milka (0.16 Pa) and Laura (0.19 Pa) chocolate, both at the minimum shear rate of  $0.06 \text{ s}^{-1}$  and at the maximum shear rate of  $6.30 \text{ s}^{-1}$ : Milka 0.32 Pa and Laura 0.39 Pa, because the elastic deformation stops and the plastic deformation is installed, the viscosity of the liquid chocolate samples decreases, with the increase of the temperature.

Primola chocolate (0.77 Pa), on the other hand, recorded the highest value of Casson yield at the minimum shear rate of  $0.06 \text{ s}^{-1}$ .

African chocolate recorded negative Casson yield values as the shear rate increased, from  $0.06 \text{ s}^{-1}$  ( $-0.5 \text{ Pa}$ ) to  $6.30 \text{ s}^{-1}$  ( $-1.62 \text{ Pa}$ ).

The flow behavior of chocolate and the value of yield 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 Figure 5 and 6.

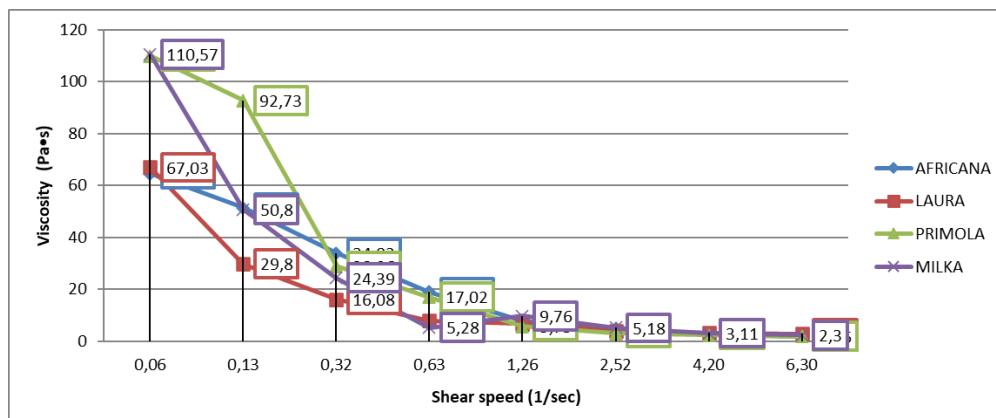


Fig. 5. Effect of temperature ( $45^{\circ}\text{C}$ ) on the viscosity of chocolate samples

The viscosities of Africana ( $51.5 \text{ Pa}$ ) and Laura ( $67.03 \text{ Pa}$ ) melted chocolates are lower than in Milka ( $110.57 \text{ Pa}$ ) and Primola ( $92.73$ ) chocolates at  $45^{\circ}\text{C}$ , at a minimum shear rate of  $0.06 \text{ s}^{-1}$ . The reason may be that Africana and Laura chocolates have a higher fat content and lower amounts of cocoa dry matter (African  $8\%$  minimum, Laura  $8.3\%$  minimum), compared to Milka and Primola which contain at least  $30\%$  cocoa dry matter, respectively minimum  $28\%$ .

Of all the samples of melted chocolate, the highest plastic viscosity was obtained in the Milka chocolate sample ( $110.57 \text{ Pa}$ ) at  $45^{\circ}\text{C}$  and shear rate  $0.06 \text{ s}^{-1}$ , as it contains the highest amount of cocoa dry matter. (minimum  $30\%$ ).

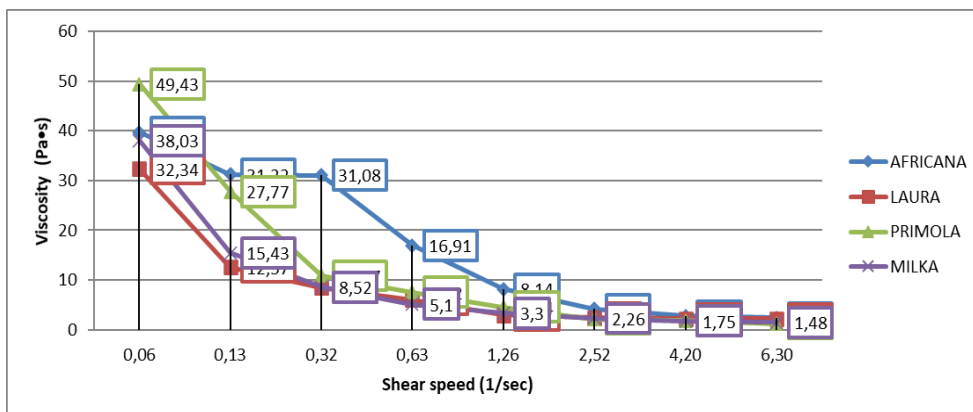


Fig.6. Effect of temperature (50°C) on the viscosity of chocolate samples

Figures 5-6 show that it has a shear and thixotropic behavior.

The hysteresis loop in the case of the Primola and Africana chocolate samples, both at 45 °C and at 50 °C shows us that the structure of the chocolate deteriorated after the shear occurred.

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.

Milka has a low viscosity because it contains the highest amount of cocoa butter.

High temperature from 45 °C to 50 °C increases the kinetic energy of chocolate molecules, decreasing the viscosity.

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 increases.

## CONCLUSIONS

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

The four chocolate samples have 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.

Analyzing the viscosity curves in the four chocolate samples, Milka and Laura can be classified as plastic liquids, and Primola and Africana as pseudoplastic liquids.



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