APPLICATION **NOTE**

Food – Rotational Rheometry

Rheological Properties of Chocolate Wanted? Kinexus Makes it Easy!

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General

Melted chocolate can be described as a concentrated suspension of coarse fine solid particles, such as cocoa powder, sugar, and milk powder dispersed in a fat continuous phase, usually cocoa butter [1]. Its rheological behavior is determined by the physicochemical characteristics of its components, along with several other factors such as composition and temperature. Among others, the particle size distribution, type of emulsifier and sugar crystallization determine the viscosity of the product to be processed.

From the Viscosity of Chocolate to Satisfied Customers ... and Manufacturers!

In turn, the shear viscosity of melted chocolate influences its mouthfeel to consumers. This viscosity of chocolate is extremely important not only in terms of delighting the consumer, but also in the manufacturing process and in the quality control of the final product. Having the proper viscoelastic properties in melted chocolate, for example, guarantees the efficiency of the piping and casting processes, preventing the formation of air bubbles during molding and ensuring the production of homogeneous shells during enrobing.

The shear viscosity and the yield point are the main rheological properties of interest in the chocolate industrial processes. The shear viscosity is simply calculated by dividing the shear stress by the shear rate. The yield stress can be determined in different ways [2]. One of them applies different model functions, like the Casson model, on the flow curve.

To ensure high quality standards over the industrial processes to which the different cocoa formulations are subjected, the International Office of Cocoa, Chocolate and Sugar Confectionary (IOCCC) released a revision of the Analytical Method 46 in 2000, which defines a standard protocol for measuring the viscosity of chocolate and cocoa products [3].

Analytical Method 46 with the Kinexus Prime Rotational Rheometer

In following this method, the viscosity of the melted chocolate is measured with a rotational rheometer equipped with a cup-and-bob geometry made of polished steel. The end of the bob, or rotor, can be conical or recessed.

The method prescribes the sample preparation in detail, giving specific orientation for liquid and solid samples of white, milk, or dark chocolate, with or without sugar. In brief, the samples must initially be warmed up for a period of time, whereby temperature and duration depend on the type of cocoa product. The geometry must be pre-conditioned to 40°C to avoid crystallization of the melted chocolate during the loading process. A pre-shearing step is also needed to assure temperature equilibrium, homogeneous sample distribution inside the geometry, and the elimination of air bubbles.

Pre-shearing is carried out at 40°C (± 0.1°C) at a constant shear rate, typically 5 s^{-1} (or 2 s^{-1} for thicker products); it must be continued until the torque remains constant for at least 2 minutes with a maximum deviation of 2%. Stabilization must be achieved within 15 minutes, or the measurement cannot be carried out.

The measurement is conducted at 40°C in three steps:

1. The shear rate is increased from 2 s^{-1} to 50 s^{-1} over a period of 3 minutes. It can be done continuously or stepwise at shear rates of 2, 5, 10, 20, and 50 s^{-1}.
2. The shear rate is kept at 50 s^{-1} for 1 minute.
3. The shear rate is reduced from 50 s^{-1} to 2 s^{-1} in 3 minutes, again continuously or stepwise, following the same shear rate scheme defined in the first step.

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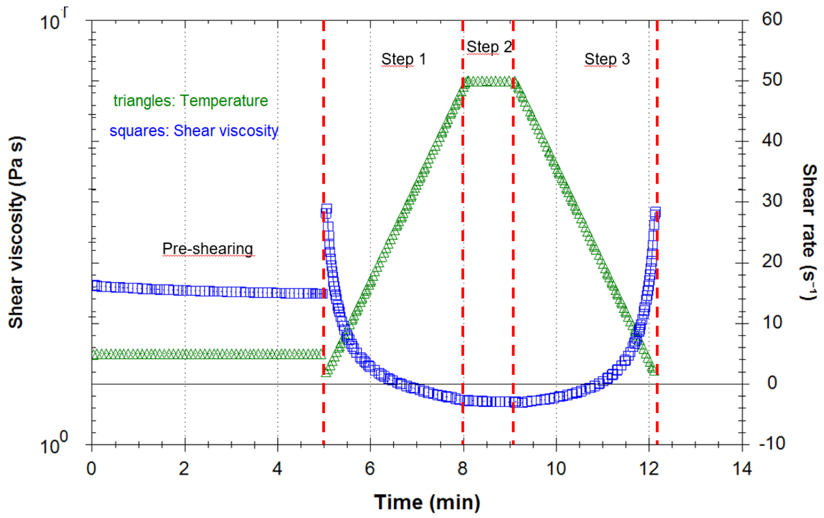
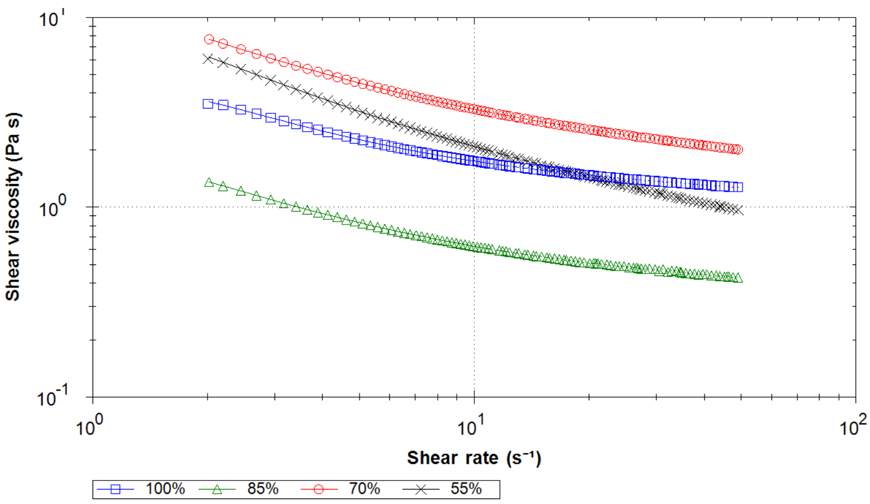
To illustrate the application of this sequence, the results obtained from the comparison of four different commercial chocolate bars of a single brand are discussed in the following. The first was a milk chocolate containing 55% cocoa, and remaining three were dark chocolate bars containing 70, 85, and 100% cocoa. The measurements were performed using the Kinexus Prime ultra+ rotational rheometer equipped with a cylinder cartridge and a 34-mm cup-and-bob geometry. Temperature and the analytical steps were applied exactly as defined in the Analytical Method 46. Figure 1 displays the shear rate (in green) applied during the pre-shearing and the three steps as well as the shear viscosity (in blue) reached for a 100-% cocoa chocolate.

The shear viscosity curves of the four chocolates tested show shear-thinning behavior: the higher the shear rate, the lower the shear viscosity; figure 2. The flow curves do not depict an intuitive result. The composition, concentration of each component, and size distribution of the suspended solid particles directly affect the viscosity of the melted chocolate.



1 Applied shear rate (green) and the corresponding shear viscosity (blue) of 100% cocoa chocolate



2 Shear viscosity of 55% (black), 70% (red), 85% (green), and 100% (blue) cocoa chocolate.

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These four different samples have different compositions, as can be seen in table 1, and therefore different viscosities. The 55% cocoa milk chocolate, for example, is the only one containing cream powder and emulsifier.

As mentioned before, the Casson model is applied on the resulting flow curve to determine the Casson yield stress, i.e., the minimum shear stress needed to induce flowing as well as the Casson viscosity, i.e., the terminal viscosity in the high shear region. Following equation describes the Casson model fit:

$$\sqrt{\sigma} = \sqrt{\sigma_0} + \sqrt{k\dot{\gamma}}$$

σ: Shear stress [Pa]

σ_0: Casson yield stress [Pa]

k: Terminal shear viscosity [Pa·s]

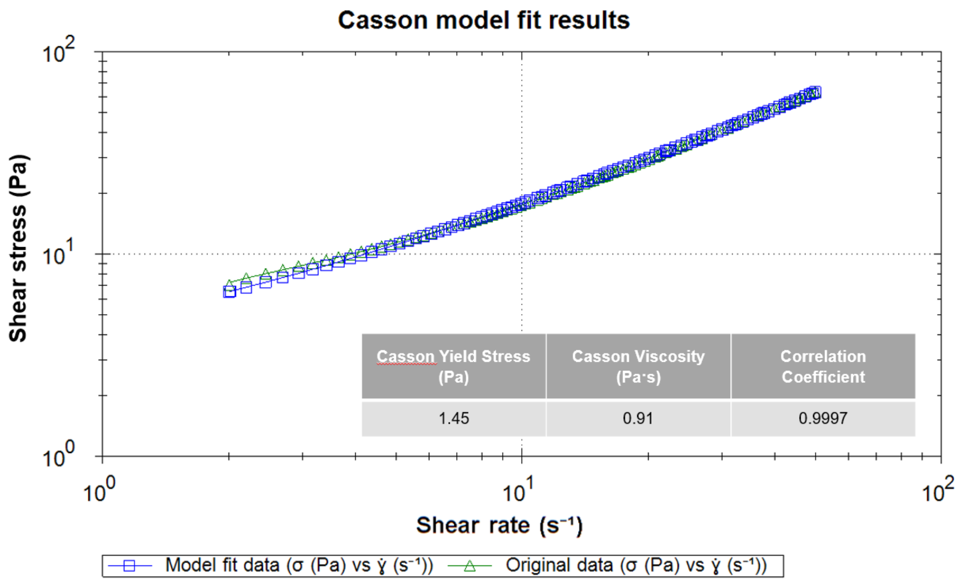
$\dot{\gamma}$: Shear rate [s^{-1}]

A typical flow curve with automatic Casson analysis is shown below in figure 3, while table 2 summarizes the results of the Casson analysis for all four chocolate types.

Table 1 Composition and order of weight of milk and dark chocolates, with different cocoa concentrations.

Ingredients	Order of Weight*			
	100%	85%	70%	55%
Cocoa mass	1	1	1	1
Cocoa butter	2	2	3	3
Light cocoa powder	3	3	-	-
Sugar	-	4	2	2
Emulsifier	-	-	-	5
Cream powder	-	-	-	4
Vanilla	-	5	4	-

*Order of weight: 1 = the highest concentration and 5 = the lowest concentration



3 Flow curve of 100% chocolate with model fit data of Casson analysis. The analysis is performed automatically in the measurement and evaluation rSpace software as soon as the measurement is finished.

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Table 2 Results of the Casson analysis for all four chocolates.

Sample	Casson Yield Stress (Pa)	Casson Shear Viscosity (Pa·s)
55%	7.07	0.37
70%	5.30	1.19
85%	0.68	0.29
100%	1.45	0.91

rSpace Software – Simple SOP Application (Standard Operating Procedures)

The yield stress is defined as the shear stress above which the viscoelastic material starts to flow. The lower the yield stress, the lower the resistance of the chocolate to flow. It is therefore an important characteristic that will define the processability of the cocoa formulation; for example, the force needed for pumping the melted chocolate [4].

Although Analytical Method 46 has been the subject of several suggestions for improvement in various publications proposing, for example, changes in the shear rate interval or the application of different mathematical models to correction of the parameters, its application associated with the Casson model is still the standard protocol for determination of the viscosity and yield point of chocolate [4]. The Casson model and the analysis sequence are available in the rSpace library.

The Kinexus rotational rheometer features the possibility of creating methods of analysis based on individual rheological actions in the rSpace software. These measurement sequences can be created and customized to fulfill the needs of any laboratory routine. Here, a measurement sequence containing all details of Analytical Method 46 was created and applied. With one click, the measurement is started; the subsequent analysis is carried out without any user intervention, and the final results, including the yield point, are automatically given.

References

[1] Schantz, B., & Rohm, H. (2005). Influence of lecithin-PGPR blends on the rheological properties of chocolate. LWT, 38(1). https://doi.org/10.1016/j.lwt.2004.03.014
[2] NETZSCH White Paper, Understanding yield stress measurements, Dr. Shona Marsh, LINK
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[4] Kumbár, V., Kouřilová, V., Dufková, R., Votava, J., & Hřivna, L. (2021). Rheological and pipe flow properties of chocolate masses at different temperatures. Foods, 10(11). https://doi.org/10.3390/foods10112519

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