Determining casson yield value, casson viscosity and thixotropy of molten Chocolate using viscometer

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Abstract. Flow properties of chocolate highly determine mouthfeel and consumer acceptance. Aside from these, they are also important factors in determining the incorporation of chocolate in food products. This work investigated the possibility of using viscometer to determine the flow properties of molten chocolate. The data obtained from viscometer was fitted to Casson Model. Afterwards, Casson yield value and Casson viscosity were then derived. To observe the homogeneity of molten chocolate, thixotropy value was also determined. In this study, molten chocolate was produced using a stone melanger as an alternative processing method. Four grinding durations, namely 4, 8, 12, and 16 hours, were used to produce 4 types of dark chocolate. The results showed that viscometer was able to determine the value of Casson Model parameters, eventhough the shear rate reached was only approximately 45 s⁻¹. Using this approach, it can be observed that the Casson Yield Value and Casson Viscosity increased as the grinding durations were increased.

1. Introduction
Chocolate is one of food products made from cocoa beans (Theobroma cacao L). Its popularity in the world is due to its good taste. One of the important parameters that needs to be controlled during chocolate processing is rheological behaviour. Rheological behaviour can provide information related to the sensorial characteristics of chocolate [1]. In addition, rheological behaviour also determines the handling properties needed during chocolate making process [1, 2]. Therefore, controlling the rheological nature of chocolate is imperative.

The most common model used to depict the rheological behaviour of chocolate is Casson model [3]. From this model, Casson yield value describes the stress needed to start the flow and Casson viscosity assesses internal friction during the flow are derived [4]. Another flow behaviour parameter obtained from the measurement is thixotropy. This parameter can be used to improve the chocolate making process. Servais et al. (2004) and Afoakwa (2010) stated that well chonced chocolate does not exhibit thixotropic behaviour [1, 3]. Hence, method and processing equipments which can create chocolate with the lowest thixotropy are highly needed.
Standardised measurement of chocolate rheological behaviour is conducted using rheometer completed with concentric cylinder geometry [4, 5]. However, this instrument has a very expensive price. Thus, it doesn’t fit for the small-medium scale chocolate industry in a cocoa producing countries. Therefore, this research aimed to find an alternative methods of measuring the rheological properties of chocolate which are more applicable in developing countries. In this research, molten chocolate was measured using a viscometer. The measured data is then processed and plotted on the Casson Model.

2. Methodology
This research was conducted at the Postharvest and Food Engineering Laboratory, Faculty of Agricultural Technology, Universitas Gadjah Mada. Materials used in this research were consisted of cacao bean (52.57% fat content) and sucrose. Cacao bean were obtained from Indonesian Cocoa and Coffee Research Institute (ICCRI), Jember, East Java, Indonesia. Sucrose was purchased from the Supermarket in Yogyakarta.

2.1. Sample Preparation
Dark chocolate (750 grams) was made with total fat content of 31.45%. The composition used was 60% of cocoa beans and 40% of sucrose. Chocolate was produced using melanger with grinding time as variable, namely 4, 8, 12 and 16 hours. Prior to the grinding process, in order to reduce the size, cocoa beans were chopped using Electrolux EBR 2501 chopper. Afterwards, the chopped cocoa beans and sucrose were gradually put into the melanger so that there was no blockage on the grinding wheel. Grinding process was stopped according to the variations in refining duration (4, 8, 12, 16, hours).

2.2. Analytical Methods
2.2.1. Moisture content. Moisture content of chocolate was measured using thermogravimetric method. Three grams of chocolate was weighed (M0). Afterwards, the sample was heated at 105°C for 24 hours. Then, it was cooled in the desiccator for 1 hour and weighed again as the final mass of the sample (M1). The weight loss occurred was the mass of water in the sample. The final mass of the sample considered was only mass of solid particles. Chocolate water content can be calculated using equation 1.

\[ \text{Moisture content (wb)} = \frac{(M0 - M1)}{M0} \times 100\% \]  

(1)

2.2.2. Particle Size. Approximately 0.5 gram of molten chocolate was diluted in 10 ml of cooking oil. After that, the solution was heated in the oven at 55°C for 1 hour. Prior to the measurement, the diluted chocolate was then vigorously shaken. Subsequently, a drop of it was then put on the glass slide. A cover slip was then placed over the sample. Observation was done using an OptiLab Microscope. Particles size were measured using the Image Raster 3 application.

2.2.3. Rheological Properties. Casson yield value, casson viscosity, and thixotropy were measured using Viscometer (Brook Field type of RV 9, United States) with spindle number 7. The stages are as follow; a. Measurement of shear stress and shear rate
Approximately 150 gram of molten chocolate was placed in 100 ml beaker glass. The temperature of the chocolate was conditioned at 40°C using a waterbath positioned at the bottom of the viscometer. The viscometer spindle was dipped in the chocolate sample until the spindle limit was immersed. Measurements were carried out with a rotating speed of 0.5; 1; 2.5; 5; 10; 20; 50; and 100 rpm. The determination of the shear stress and shear rate was done by converting the value which was read on the viscometer to the factor values in the Mitschka Table [6]. Shear stress values were obtained using equation 2:

\[ \tau = \text{dial reading} \times 8.4 \]  

(2)
\[ \tau \text{ is shear stress, dial reading is numbers read on the viscometer with a scale of 0-100. Whereas 8,4 is the value of shear stress consistency index of molten chocolate which is measured based on spindle number 7. The determination of the shear rate value can be done by converting the RPM value used with the value of the factors in the Mitschka Table (1982) according to the spindle number used and the flow index value of the fluid. Shear rate value on molten chocolate paste can be calculated using equation 3:} \]

\[ \gamma = \text{RPM} \times \text{Kny} \]  

(3)

\[ \gamma = \text{shear rate}, \text{Kny is shear rate consistency index obtained from Mitschka Table (1982) by matching the flow index value and the spindle number used. The flow index (n) can be obtained by plotting } \ln \tau \text{ vs } \ln \text{ RPM in a graph. The slope obtained from equation formed } (y = bx + a) \text{ shows the value of fluid flow index.} \]

b. Casson model

Molten chocolate has a nature of non-ideal pseudo plastic [3]. By adjusting this behaviour, the International Confectionery Association (ICA, 2000) states that determining the rheological properties of chocolate can be calculated using Casson model equation [7]. The Casson model is the most widely used model in the chocolate industry. The value of Casson yield and Casson plastic of molten chocolate can be determined using equation 4:

\[ \sqrt{\tau} = \sqrt{\tau_{CA}} + \sqrt{\mu_{CA}} \cdot \sqrt{\gamma} \]  

(4)

\[ T \text{ is shear stress, } \tau_{CA} \text{ is Casson yield value (Pa), } \mu_{CA} \text{ is Casson viscosity (Pa.s) and } \gamma \text{ is shear rate. Thixotropy is obtained by determining the difference between the ramp up and ramp down shear stress at 5 s}^{-1}. \]

2.2.4. Data Analysis. The results were analysed using IBM statistic SPSS 25. The rheological behaviour parameters were subjected to variance analysis (ANOVA) with 95% significance level. Testing for homogeneity of variances was performed with Levene Test. Tukey test was used to determine differences among samples.

3. Results and Discussion

3.1. Moisture Content

Rheological behaviour of molten chocolate are affected by moisture level, fat content, lecithin, particle size distribution [3, 8]. In general, high water level increases the chocolate viscosity. Therefore, the ability of a chocolate processing machine to vaporize water is very necessary [4]. In addition, high water levels trigger agglomeration. From Table 1, it can be seen that the longer the grinding time, the lower the moisture content was observed. This showed that the processing of chocolate using melanger, which was equipped with a heat gun was effective enough to evaporate water at an increasingly long processing duration.

| Chocolate sample | Moisture content (%) |
|------------------|----------------------|
| 4H               | 1,30 ± 0,01<sup>c</sup> |
| 8H               | 1,31 ± 0,08<sup>c</sup> |
| 12H              | 1,03 ± 0,10<sup>b</sup> |
| 16H              | 0,62 ± 0,07<sup>a</sup> |

Different superscripts indicate significant differences (p < 0.05) among samples

Table 1. Moisture content of chocolate processed using melanger
3.2. Particle Size
Particle size is an important parameter which directly and indirectly affects the chocolate quality, such as roughness and color [9]. In addition, particle size also shows the level of smoothness or grittiness that can be felt during chocolate consumption. Particle size also affects the sensory reception of chocolate. Chocolate which has a particle size of $\geq 30$ µm is considered as gritty chocolate [3]. As according to Bolenz and Manske (2013), the grittiness of chocolate is not felt when chocolate has a particle size of $\leq 30$ µm [10]. Indirectly, particle size has an effect on rheological properties [11].

It can be seen in Figure 1 that chocolate produced for 4 hours had particle size in the range of 42-50 µm. The longer the grinding duration, it can be seen that the smaller the particle was observed, with a small size was in the range of 18-26 µm. The size reduction occurred due to friction between the grinding wheels with the granite stone slab. The raw chocolate material crushed between the wheels and the granite slab were split into smaller particles. Therefore, repeated grinding process of cocoa particles resulted in the decrease of the particle size. Similar to Lucisano (2006)’s research on making chocolate with ball mill, which stated that during refining, solid particles were destroyed into smaller parts due to the force of force derived from stainless balls colliding with each other [14]. This indicates that the particle size will be smaller during the chocolate making process because it is eroded by the force of the tool movement.

![Particle size images](image1)

**Figure 1.** Particle size of chocolate processed with grinding time of 4 hours (a), 8 hours (b), 12 hours (c), 16 hours (d)

3.3 Rheological Properties
Rheological properties are characteristics showing chocolate flow in various condition. Rheological properties are important to evaluate the quality of chocolate [12, 13]. According to Aeschlimann and
Beckett (2000), the range of casson yield value for the type of dark chocolate is 4 - 32 Pa [15]. It can be seen in Figure 2 that the Cason yield value of chocolates made using melanger was within this range of values. Therefore chocolate produced in this study was classified as having good quality.

Figure 2. Casson yield value of chocolates produced using melanger as function of grinding duration

Figure 3. Casson viscosity of chocolates produced using melanger as function of grinding duration

Grinding time had a significant effect (p <0.05) on the value of Casson Yield and Casson viscosity. Based on Figure 2, it can be seen that the longer the grinding time, the higher the Casson yield value was observed. This phenomenon occurred because chocolate with a small particle size had a wider surface area which resulted in a stronger interaction between particles in chocolate [16-18]. According to Prasad et al. (2003), the longer the grinding time of chocolate, the smaller the particle size, so that strong interactions between particles are formed [19]. This is supported by Saputro (2017) who states that the Casson yield value increases as the duration of the chocolate milling increases [4].

Theoretically, the increase in the grinding duration causing a decrease in particle size increases the Casson viscosity. However, based on Figure 3, it can be seen that the Casson viscosity values did not differ significantly (p <0.05) at grinding duration of 4, 8, and 12 hours. Nevertheless, Casson viscosity increased in the chocolate ground for 16 hours. This phenomena may occur due to the effect of particle volume friction [20]. The increase in the Casson viscosity value could be clearly observed after 12 hours grinding time. At this stage, the effect of particle size was pronounced. According to Chevalley (1994), the reduction in particle size in the chocolate suspension increases the value of the Casson yield and Casson viscosity [21]. The value of Casson viscosity produced using melanger with variations in grinding time was in the range of 3.8 - 6.7 Pa. This range fell in the range of Casson viscosity of dark, which is 2.1 - 3.9 Pa.s [15]. Chocolate with high value of Casson viscosity cannot be applied for coatings, since the chocolate layer will be thick [3], which is not cost effective.

It can be seen in Table 2 that the value of thixotropy in melanger-produced chocolate with a variation of grinding time was in the range of 4.9 - 6.6 Pa. Fluctuating thixotropy values and high standard deviations indicated that the chocolates were not homogenous enough. This phenomena might occur due to the insufficient mixing process.

Table 2. Thixotropy of chocolate processed using melanger

| Chocolate sample | Thixotropy (Pa) |
|------------------|-----------------|
| 4H               | 4,90 ± 1,47\textsuperscript{ab} |
| 8H               | 5,04 ± 1,45\textsuperscript{ab} |
| 12H              | 6,58 ± 3,76\textsuperscript{ab} |
The typical graph of shear stress vs shear rate can be seen in Figure 4. A graph that has large gap between upward and downward curves is marked as a graph of chocolate with high thixotropy value. It can be seen that at grinding time of 12 and 16 hours, the graph exhibit high thixotropy values. The high value of thixotropy is due to structural damage in the chocolate suspension, as a result of a high level of matrix aggregation [22, 16].

\[ \frac{5.32 \pm 2.70^{ab}}{16H} \]

Different superscripts indicate significant differences (p < 0.05) among samples.

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**Figure 4.** Relationship between shear rate and shear stress of chocolate processed with grinding time of 8, 10, 12 and 16 hours.
4. Conclusion

The result showed that viscometer to some extent can be used to measure the rheological properties of molten chocolate. As expected, the longer the grinding time used, the lower the particle size and the higher the Casson Yield Value and Casson Viscosity were observed. Aside from this, moisture content of chocolate determined by the grinding duration influenced the rheological properties of molten chocolate.

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