



# Effects of shear and cooling rates on the crystallization behavior of cocoa butter

## Kakao yağının kristalleşme davranışı üzerinde kayma hızı ve soğutma hızının etkileri

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### ABSTRACT

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The purpose of this study was to determine the effects of shear and cooling-heating rates on the rheological behavior of cocoa butter. Three different shear rates (25, 50 and 100 s<sup>-1</sup>) and two different cooling rates (1 and 10 °C.min<sup>-1</sup>) were applied for crystallization of cocoa butter at 20, 22 and 24°C. Also, effects of shear and heating-cooling rates were monitored during the cooling and heating cycle between 70-20°C. When the cooling rate was 1 °C.min<sup>-1</sup>, viscosity reached the highest value of 0.6 Pa.s with a shear rate of 25 s<sup>-1</sup>. A rapid rate of cooling generally led to nucleation at a lower temperature compared to slow cooling. It was observed that crystallization of Form V was improved by shear and induction time of crystallization decreased as the rate of shear increased. The longest induction period was obtained at 24°C. Effect of cooling rate was more significant at low temperatures (P < 0.05). It was also concluded that the crystallization behavior of cocoa butter was dependent on both shear and cooling rates under isothermal conditions.

**Key Words:** Chocolate, Cocoa butter, Crystallization, Rheological behavior, Viscosity

### Öz

Bu çalışmanın amacı kakao yağının akışkanlık özellikleri üzerinde soğutma-ısıtma hızının ve kayma hızının etkisini belirlemektir. Kakao yağının 20, 22 ve 24°C de kristallendirilmesinde üç farklı kayma hızı (25, 50 ve 100 s<sup>-1</sup>) ve iki farklı soğutma hızı (1 ve 10 °C.dak<sup>-1</sup>) uygulanmıştır. Ayrıca, 70-20°C aralığında uygulanan soğutma ve ısıtma evrelerinde, kayma hızı ve ısıtma-soğutma hızının etkisi takip edilmiştir. Ulaşılan en yüksek viskozite değeri 0.6 Pa.s olup, 1 °C.dak<sup>-1</sup> soğutma hızı ve 25 s<sup>-1</sup> kayma hızı uygulandığında ölçülmüştür. Hızlı soğutma, yavaş soğutmaya göre genellikle daha düşük sıcaklıklarda çekirdeklenme oluşuma yol açmıştır. Kayma hızındaki artışla beraber, Form V tipindeki kristalleşme artarken, kristalleşme indüksiyon süresinin de azaldığı gözlenmiştir. En uzun indüklenme süresi 24°C de elde edilmiştir. Soğutma hızının etkisinin, düşük sıcaklıklarda daha önemli olduğu tespit edilmiştir (P < 0.05). Ayrıca, kakao yağının izotermal koşullardaki kristalleşme davranışında hem kayma hızının hem de soğutma hızının etkili olduğu sonucuna varılmıştır.

**Anahtar Kelimeler:** Çikolata, Kakao yağı, Kristalleşme, Reolojik davranış, Viskozite

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## Introduction

Chocolate is a complex rheological system in which sugar and non-fat cocoa particles coated with cocoa butter. Crystallization is often critical

step in chocolate production and poor crystallization results fat bloom in chocolate products (Afoakwa et al., 2007; Schenk and Peschar, 2004; Beckett, 1999). Cocoa butter is a pale yellow natural fat, obtained from cocoa nib

by hydraulic or expeller pressing (Yıldırım et al., 2016). Cocoa butter makes up about one-third of the chocolate composition, and its crystalline state governs the physical and thermal properties of the chocolate (Padar et al., 2009).

The solidification properties of cocoa butter are important phenomena that influence its functional properties in chocolate (Campos and Marangoni, 2014). The expected mouth feel of chocolate depends mainly on the composition of cocoa butter which means melting point of fractions in cocoa butter (Beckett, 2006; Toro-Vazquez et al., 2004). Cocoa butter is a mixture of triacylglycerol (TAG) and other compounds (Foubert et al., 2006). Although more than 25 different TAG have been identified in cocoa butter, approximately 85% of composition consists of mainly three TAG; POP, POS and SOS where stearic (S), palmitic (P) and oleic (O) acids are attached to the glycerol bone (Le Révérend, et al., 2009; Perez-Martinez et al., 2007; Lipp and Anklam, 1998a; Loisel et al., 1998; Koyano et al., 1990). The studies show that they were the most important ones and the crystallization property of cocoa butter was directly related to these three TAG (MacMillan et al., 2002; Sato and Koyano, 2001).

In cocoa butter, the polymorphic variabilities are quite diverse. The confectionery industry uses Roman numerals as described by Willie and Lutton (1966) in which the six forms are given the names from Form I to Form VI. The forms have different melting points reported in the literature and the conversion from Form I to Form VI increases the stability and melting point of polymorphs (Rogers et al, 2008). The convention defined by Vaeck (1960) is more generally used in the oils and fat industry. This uses the Greek letters ( $\gamma$ ,  $\alpha$ ,  $\beta'$  and  $\beta$ ) to describe the main polymorphic forms.

Since cocoa butter can crystallize into six different polymorphic forms, type and amount of different forms have a considerable effect on the quality of confectioneries and chocolates (MacMillan et al., 2002). Form V is the most desirable form in chocolate products and

formation of Form VI crystals is unwanted because it is often accompanied by the formation of fat bloom (Şekeroğlu, 2014; Sonwai and Rousseau, 2010; Afoakwa et al., 2009a; Afoakwa et al., 2009b). First of all, a bloomed chocolate is characterized by the loss of the surface's initial gloss. A bloomed chocolate can have different appearances, from a marble aspect to uniform dull gray, as well as from having small or large white spots on the chocolate surface (Şekeroğlu, 2014). Fat bloom is caused by many factors including compositions, improper processes and storage conditions (Altimiras et al., 2007; Lonchamp and Hartel, 2006; Sonwai and Rousseau, 2006). Tempering and cooling are the most important steps during chocolate production because controlling of polymorphism of cocoa butter is important for making chocolate with desired textural properties (Campos and Marangoni, 2014; Le Révérend, et al., 2009; Hartel, 2008; Koyano et al., 1990).

Many techniques such as pulsed Nuclear Magnetic Resonance (p-NMR), X-ray diffractometer (XRD), Polarized Light Microscopy (PLM) and Differential Scanning Calorimetry (DSC) can be used to study the crystallization behavior of fats (Şekeroğlu, 2014; Fessas et al., 2005; Marangoni, 2005; MacMillan et al., 2002; Spigno et al., 2001; Van Malssen, et al., 1999; Lipp and Anklam, 1998b; Metin and Hartel, 1998; Ziegleder, 1990). Also, effect of shear on the crystallization and polymorphic transformation of cocoa butter has been identified by using a rheometer (Şekeroğlu, 2014; Sonwai and Mackley, 2006; Toro-Vazquez et al., 2005; Toro-Vazquez et al., 2004; Ziegleder, 1985).

Although cooling and shear rates may affect polymorphism, formation of different polymorphs for a given lipid material depends mainly on the temperature at which the crystallization takes place. There are mainly three events in crystallization process: First is the solid phase formation which is called nucleation. The main driving force for nucleation is the difference between the chemical potential of a monomer in crystalline and supercooled liquid states (Mohos,

2010). In other words, nucleation can be defined as the time point where the melt becomes visually cloudy and the temperature increases due to latent heat release (Campos and Marangoni, 2014). The second step is the crystallization or in another words crystal growth and the last one is crystal ripening (Toro-Vazquez et al., 2005). Several authors have investigated the effect of shear and cooling rate on crystallization of cocoa butter and chocolate (Campos and Marangoni, 2014; Fernandez et al., 2013; Mohos, 2010; Dhonsi and Stapley, 2006; Sonwai and Mackley, 2006; Toro-Vazquez et al., 2005; Brunello et al., 2003; Stapley et al., 1999). Many attempts have been made to control of crystallization of cocoa butter to achieve the crystallization in Form V which is the most desirable form (Sato and Koyano, 2001).

In this paper, the effect of shear and cooling-heating rates on the crystallization and melting behavior of cocoa butter has been investigated at different temperatures. First, chemical and physical measurements were done to define the composition and properties of cocoa butter. Rheological analyses were done using a strain/stress controlled rheometer with a temperature controlled unit. The results from this paper will be useful to controlling of crystallization properties of cocoa butter in confectionery and chocolate production.

## **Materials and Methods**

### *Materials*

Cocoa butter was kindly supplied from a local firm in Gaziantep, Turkey. Chromatographic grade and other chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA).

### *Methods*

#### *Physical and chemical analysis*

Free fatty acid content, refractive index, saponification value, iodine value and color value of cocoa butter were done by the directive of Association of Official Analytical Chemists (AOAC, 1995).

#### *Triglyceride analysis*

Triacylglycerol composition of cocoa butter was analyzed using an High Performance Liquid chromatography (HPLC) instrument. It consists of Agilent 1200 series model quadratic pump, temperature controlled automatic injection unit, column heater and refractive index detector (Waldbronn, Germany). The Agilent Chemstation Rev. B.04.01 (Waldbronn, Germany) software program was used to monitor the device and analyze the peaks. Waters Spherisorb S50DS2 (250 x 4.6 mm) (Berkshire, England) column was used for TAG analysis. Mobile phase was a mixture of acetonitrile / acetone (34.6; 65.4) (v:v). A calibration curve was prepared by using HPLC for determining TAG composition. Samples (5ml) were dissolved in acetone (100ml), and filtered using 0.45 µm filters (Econofilters, Agilent Technologies, Waldbronn, Germany). Injection volume was 10 µl. Flow rate was 1.0 ml. min<sup>-1</sup>.

#### *Solid fat content analysis*

Minispec mq-20 model p-NMR (Bruker, Germany) was used to determine the solid fat content (SFC) of cocoa butter, according to AOCS Method Cd 16-81 (1989) (AOCS, 1989). Approximately 3 grams of cocoa butter were placed in glass NMR tubes (1 mm thickness, 180 mm height and 10 mm diameter) and melted at 80°C for 30 minutes and ensured that all the cocoa butter of crystallization has been removed. After the samples were prepared and tempered, a serial temperature profile was applied. Then samples were transferred to water baths set at 0, 5, 10, 15, 20, 25, 30, 35 and 40°C. SFC readings were obtained after 60 minutes of isothermal static crystallization in a water bath. At least three sample tubes were measured at each temperature.

#### *Rheological measurements*

The rheological measurements were performed using a strain/stress controlled rheometer (Mars II-Haake GmbH, Karlsruhe, Germany) with TCP/P peltier temperature controlled system. It was equipped with a cone-

plate configuration using a cone radius of 35 mm and an angle of 1° and a gap of 0.052 mm between the cone and the plate. Each measurement was replicated three times on the same sample.

The experimental parameters were chosen based on industrial chocolate tempering and cooling processes, types and properties of cocoa butter polymorphs and storage conditions. Two different cooling-heating rate values were applied to understand the effect of rapid and slow cooling/heating processes during industrial chocolate manufacture. In this context, rheological measurements were done after holding of cocoa butter at 70°C for 10 min to delete the crystal memory of cocoa butter. Then, sample was cooled from 70°C to 45°C with a 15 °C.min<sup>-1</sup> cooling rate. Crystallization was performed by cooling of cocoa butter from 45°C to critical temperatures (20, 22 and 24°C) at the rates of cooling of 1 and 10 °C.min<sup>-1</sup> with different shear rates (25, 50 and 100 s<sup>-1</sup>) and then viscosity change was measured. Viscosity change of cocoa butter during heating and cooling processes between 70-20-70°C was measured again after holding of cocoa butter 10 min at 70°C. These measurements were repeated for 1, 5 and 10 °C.min<sup>-1</sup> cooling rates and 25, 50 and 100 s<sup>-1</sup> shear rates.

The equation which was the viscosity versus temperature function of (crystal free) cocoa butter was obtained from using Arrhenius equation from the temperature region between 30-70°C.

Arrhenius equation can be denoted as (Toro-Vazquez et al., 2001),

$$\eta = A \exp\left[\frac{E_a}{RT}\right] \quad (1)$$

Here  $\eta$  is the viscosity in Pa.s,  $T$  is the absolute temperature in Kelvin,  $E_a$  is the activation energy,  $A$  is the pre-exponential factor and  $R$  is the Universal gas constant.

### Statistical analysis

Analysis of variance was performed by the Statgraphics version plus 5.1 (Statistical Graphics Corp.). Duncan's multiple range test was used to obtain comparisons among sample means. Evaluations were based on a 5% significance level ( $P < 0.05$ ). All experiments and measurements were done in triplicate.

## Results and Discussion

### Physical and chemical properties of cocoa butter

Table 1 shows physical and chemical properties of cocoa butter used in this study. The chemical composition of cocoa butter was similar to other cocoa butters in literature and used in manufacturing of chocolate (Beckett, 2006; Van-Langevelde et al., 2001; Lipp and Anklam, 1998a).

Table 1. Physical and chemical properties of cocoa butter<sup>1</sup>

Properties	Value
Saponification Value (mg KOH/g fat)	188 ± 1.03
Iodine Value (Wijs)	25.81 ± 0.57
Free Fatty Acid (% weight, as oleic acid)	1.73 ± 0.02
Refractive Index Value (40°C)	1.467 ± 0.008
Color Value:	
YI (Yellowness Index)	58.68 ± 0.32
L*	76.75±0.10
a*	-3.19±0.08
b*	37.08 ± 0.14

<sup>1</sup>Values are based on triplicate analysis (Mean ± SD)

### Solid fat content

Figure 1 shows changes in SFC of cocoa butter found by NMR. Melting profile of cocoa butter was obtained by plotting the SFC as a function of temperature. The similar results for cocoa butter were found in literature (Perez-Martinez et al., 2007; Hartel, 2001). SFC value decreased when the temperature was increased, and complete melting of cocoa butter occurred between 35 and 40°C. This melting profile has a great importance to evaluate the suitability of cocoa butter for chocolate and confectionery products (Afoakwa et al., 2007; Beckett, 2006; Schenk and Peschar, 2004). SFC values mostly depend on the composition and origin of cocoa butter. The determination of SFC values at various temperatures is very useful when creating

product physical attributes and predicting final product behavior (Torbica et al., 2005). For example, the physical properties of chocolate are affected by the SFC values of cocoa butter. Also,

the result shows how the temperature affects the change in the SFC values and textural properties of chocolate.

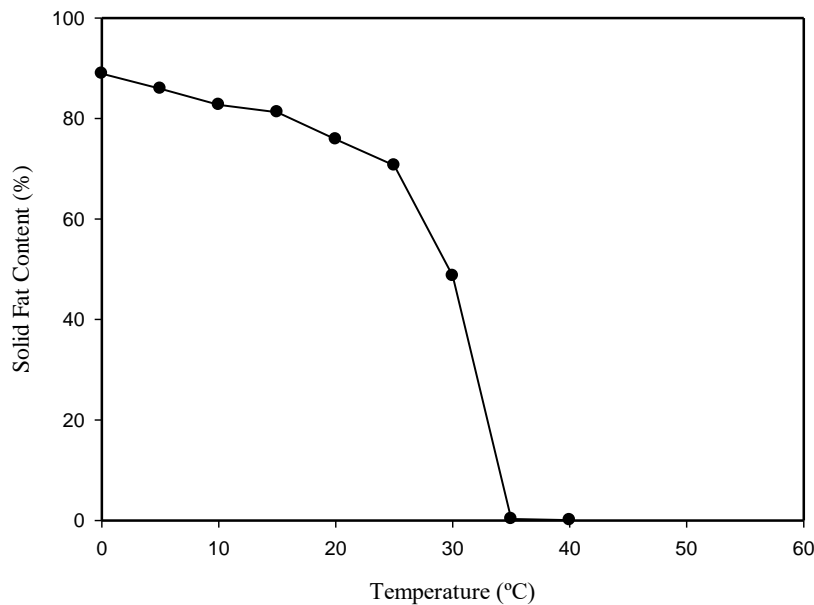


Figure 1. Solid fat content of cocoa butter obtained by NMR measurements

#### TAG composition

TAG composition for cocoa butter was calculated as % area by using HPLC and found as POP:  $19.09 \pm 0.08$ , SOS:  $32.71 \pm 0.57$  and POS:  $48.19 \pm 0.63$ . Natural cocoa butter contains 0.35% phospholipids, 1.71% mono and di-glycerides and 97-98% triglyceride. Total amount of triglycerides, SOS (stearic-oleic-stearic), POS (palmitic-oleic-stearic) and POP (palmitic-oleic-palmitic) were 85% in cocoa butter, so they were the most important ones and properties of cocoa butter were directly related to these three TAG (Fessas et al., 2005; Toro-Vazquez et al., 2004; Lipp and Anklam, 1998a; Loisel, et al., 1998). Dimick and Manning (1987) observed that the first visible crystals of cocoa butter contain POP, POS and SOS under static crystallization at 26 and 32°C. Foubert et al. (2006) found that the composition of cocoa butter is important during isothermal crystallization of cocoa butter and differences in the chemical composition of fat phases cause differences in the crystallization kinetics.

#### Rheological analysis

Flow curve of cocoa butter was obtained and

viscosity of cocoa butter was calculated from the slope of this curve at each temperature. Finally, viscosity change with temperature was presented in Table 2.

Table 2. Viscosity change of cocoa butter with temperature<sup>1</sup>

Temperature (°C)	Viscosity (Pa.s)
70	$0.0124 \pm 0.0002$
60	$0.0190 \pm 0.0002$
50	$0.0262 \pm 0.0003$
40	$0.0377 \pm 0.0004$
30	$0.0571 \pm 0.0006$

<sup>1</sup>(Mean  $\pm$  SD)

The Equation 2 which was the viscosity versus temperature function of (crystal free) cocoa butter was obtained from using the Equation 1 from the temperature region between 30-70°C,

$$\eta = 1.838 \times 10^{-7} \exp\left[\frac{3833}{T}\right] \quad (2)$$

Viscosity results of cocoa butter are similar and in a good agreement with the results reported by Landfeld et al. (2000). It is obviously stated that

the progress of crystallization from the melt is controlled mainly by the removal of heat of crystallization. Viscosity determines the induction period and nucleation which consists of combination effect of cooling rate and super cooling (Toro-Vazquez et al., 2001).

The change in viscosity as a function of temperature, shear, heating and cooling rates between 70-20°C (cooling) and 20-70°C (heating) are presented in Figure 2. It was clearly seen that, the viscosity change was lower when the cooling rate was higher. When the cooling rate was 1 °C.min<sup>-1</sup>, viscosity reached the highest value of 0.6 Pa.s with a shear rate of 25 s<sup>-1</sup>. Viscosity started to increase below 30°C with the order of rate as 10>5>1 °C.min<sup>-1</sup>, viscosity increased rapidly below 22°C at 1 °C.min<sup>-1</sup> rate. The viscosity of cocoa butter increased towards end of cooling step (around 20°C) then the viscosity continued to increase at the beginning of heating cycle to a certain temperature then it tended to decrease and approached to melting viscosity value approximately at 30°C. This behavior of cocoa butter was observed under all rates studied in this study.

The fall in viscosity occurred rapidly during heating cycle because of low heating rate (Figure 2a), but when the heating rate was increased, viscosity proceeded to increase and it followed a transition temperature at which rate of crystallization and melting were in equilibrium, and viscosity value remained nearly constant for a short time, then it decreased due to heating effect (Figure 2c).

Viscosity values of cocoa butter were always found higher at 25 s<sup>-1</sup> shear rates on both melting and crystallization rheograms. As a result, shear was important to occurring of crystals or polymorphic transformation but after a certain limit, it has a melting effect acting like a thinning agent and occurring crystals are deforming under the high shear. Another interesting result was the change in viscosity while increasing temperature during the initial stage of the heating cycle. It can be explained that, after nucleation, crystals continue to grow after a certain time even though temperature increases.

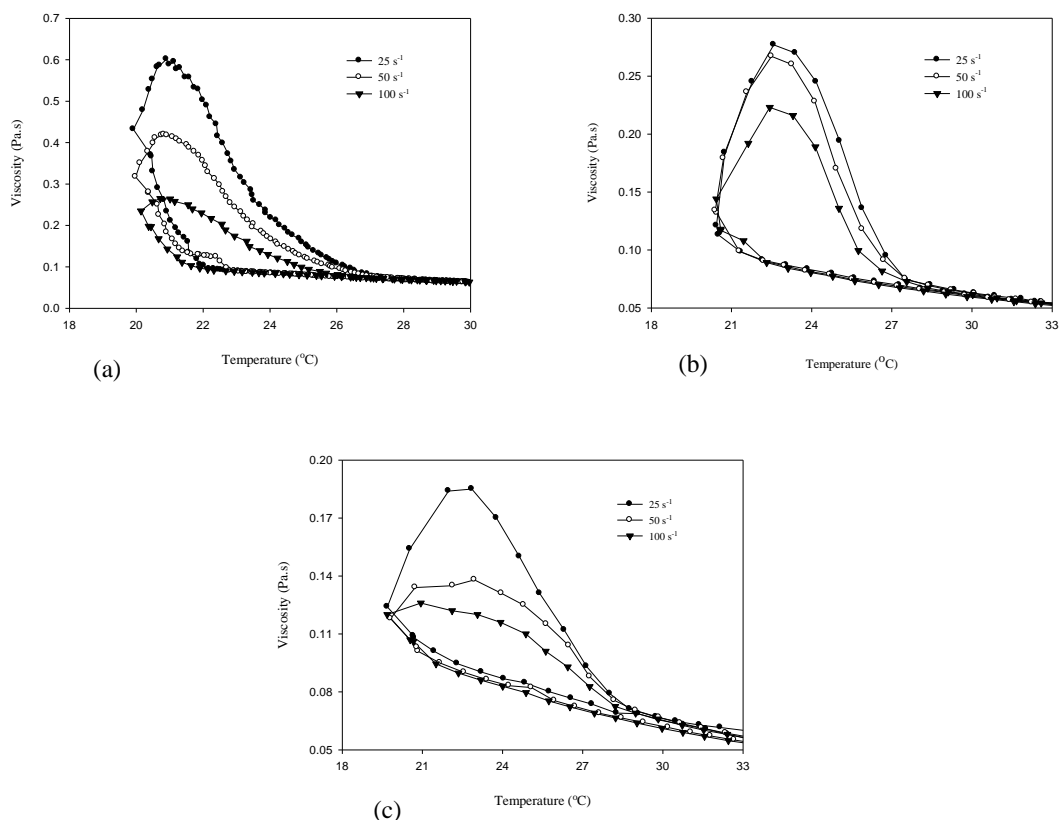


Figure 2. Effect of cooling – heating rates and shear rates on viscosity of cocoa butter (a) 1 °C.min<sup>-1</sup> (b) 5 °C.min<sup>-1</sup> (c) 10 °C.min<sup>-1</sup>

This result showed that temperature, shear and cooling rates influence the nucleation and crystal growth of cocoa butter. High shear rate has effect of breaking the solid fat crystals and uniformly distributing them. In addition, it provides heat and energy which increase the rate in which the more unstable crystals can change to more stable Form V (Beckett, 2006; Mazzanti et al., 2004). However, there is a major problem with high shear rates at which they can generate too much heat and results melting of all the crystals formed. Mostly cocoa butter is crystallized under shear in industrial chocolate and candies processes because mixing promotes heat transfer and helps to build a homogeneous product (Mazzanti et al., 2003).

The necessary shear rate and temperature during chocolate production can be achieved by using an instrument, tempermeter (Le Révérend, et al., 2009). The formation of true forms can be adjusted depending on the temper index value. Stapley et al. (1999) sheared the chocolate with a concentric cylinder and discovered that up to  $27 \text{ s}^{-1}$  shear rates, a peak crystallization temperature of  $13^\circ\text{C}$  was observed and this was the typical untempered chocolate. Campos and Marangoni (2014) studied the static and dynamic crystallization of cocoa butter and it was reported that the crystalline structure of cocoa butter cooled under the shear resulted in a high melting stable  $\beta$  form. They also reported that the influence of high shear (400 rpm) on the crystallization of cocoa butter is more significant than any cooling rate effect. Also, MacMillan et al. (2002) demonstrated that temperature plays an important role in the formation of individual cocoa butter polymorphs. They also reported that forms III and IV were obtained under static conditions so shear was necessary to obtain the desired form V. The crystallization of chocolate under high shear has been investigated by Windhab et al. (1993) and with increasing shear stress, lower viscosities and significantly shorter solidification times were found by them.

The influence of shear (between  $0\text{-}500 \text{ s}^{-1}$ ) on the crystallization of CB was also investigated by

Sonwai and Mackley (2006) at a single temperature of  $20^\circ\text{C}$ . They reported that shear influences crystallization kinetics and polymorphic structure of cocoa butter. It was also reported that at first, the viscosity increased slowly and much more rapidly at a later stage due to a second phase crystallization of fat phases under the influence of shear (Sonwai and Mackley, 2006).

The change in viscosity values of cocoa butter both during cooling and isothermal conditions was illustrated in Figure 3. Temperature plot was also added to rheograms because viscosity started to increase during cooling at low temperatures so this change was also important. The nucleation of crystals led to an increase in viscosity that occurred during the cooling stage. Similar behaviors had been observed in the crystallization of cocoa butter at  $18.5^\circ\text{C}$  and palm stearin/sesame oil blends at a cooling rate of  $1 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  (Toro-Vazquez et al., 2004).

The effect of shear and cooling rates was more evident as the temperature decreased. (Figures 3a and 3b). As expected the viscosity increased towards the end of the isothermal holding period and the increases in cooling and shear rates resulted in shorter induction periods. Dhonsi and Stapley (2006) and Toro-Vazques et al. (2004) also reported that an increase in the applied shear rate resulted a shorter induction time. The effect of shear was found to be more pronounced at low cooling rates. In the present study, the longest induction period was obtained at  $24^\circ\text{C}$ .

There was an interesting situation during isothermal holding period at  $20^\circ\text{C}$ . Viscosity increased rapidly as soon as isothermal step started, then the viscosity remained approximately constant at  $1 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  cooling rate because in this region, shear had an effect to melt unstable crystals formed during cooling and initial stage of isothermal period. Then transformation rate of unstable forms to stable ones increased with increasing shear rate as seen rapid change in viscosity at  $100 \text{ s}^{-1}$  (Figure 3a). However, a remarkably decrease in viscosity was seen at  $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  cooling rate. So, after this intermediate

region viscosity increased rapidly. This can be explained that small sized unstable crystals which

formed during rapid cooling easily melted by the effect of shear.

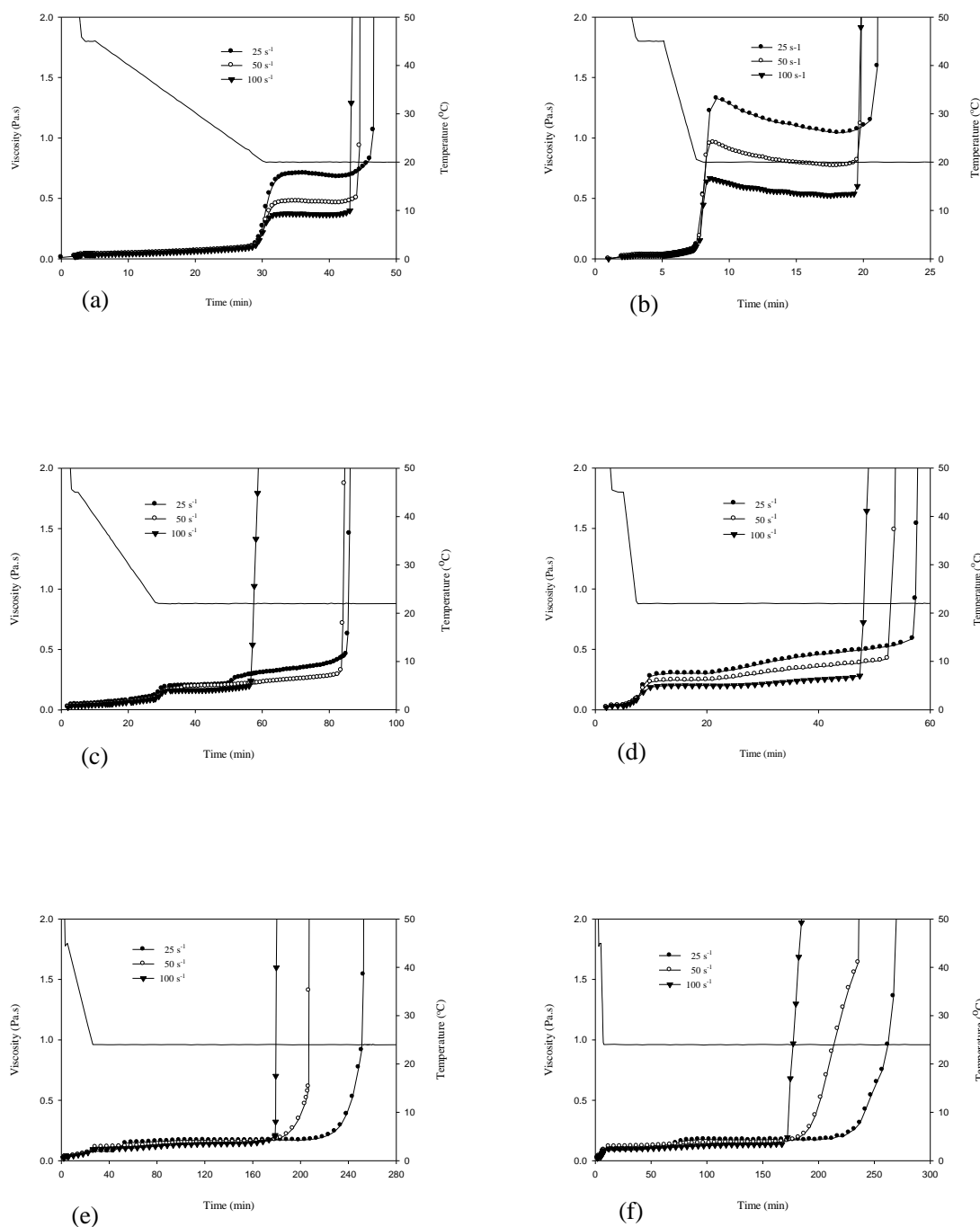


Figure 3. Change of viscosity of cocoa butter with temperature, shear and cooling rate (a)  $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  at  $20^{\circ}\text{C}$ , (b)  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  at  $20^{\circ}\text{C}$ , (c)  $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  at  $22^{\circ}\text{C}$ , (d)  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  at  $22^{\circ}\text{C}$ , (e)  $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  at  $24^{\circ}\text{C}$  (f)  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  at  $24^{\circ}\text{C}$

Similar studies were done by Dhonsi and Stapley (2006) for cocoa butter and Loisel et al. (1998) for dark chocolate. They applied extremely low shear,  $1\text{ s}^{-1}$  for cocoa butter. They observed crystallization in two steps or in other words, viscosity started to increase at the beginning and then an intermediate plateau region shown under this shear effect. They suggested that this two-step crystallization region may be arisen

fractionation effect of fats. It was also known that, agitation of the seed crystals leads to secondary nucleation and it is an important phenomena especially in fractionation of fats (Hartel, 2001). It is observed clearly at low temperature and high shear rates in this study (Figure 3a, 3b). These results are consistent with literature findings where shear has been found to promote the formation of higher polymorphs.



MacMillan et al. (2002) and Ziegleder (1985) sheared cocoa butter at 20°C and MacMillan et al. (2002) observed that Form IV was produced at 20°C without shear but formation of Form V was possible when a shear applied. Padar et al. (2009) investigated cocoa butter crystal formation and phase transition caused under the shear and they concluded that the initial form was  $\alpha$  and the transformation into the Form V ( $\beta V$ ) was confirmed up to 24°C.

Furthermore, it has been known for a long time that shear induces the formation of Form V. Application of shear also helps the formation of Form V directly from Form III, bypassing Form IV. Another important effect of shear force is on the orientation of crystal lattice surfaces (or systems) that leads to phase transitions (Mazzanti et al., 2003). Ramel et al. (2018) studied on crystallization and form transition properties of different cocoa butter samples which were statically and dynamically cooled. They observed that transition into more stable forms (Form V) was found to be higher than dynamically cooled cocoa butter samples (Ramel et. al., 2018).

## Conclusions

Cocoa butter is more complex phenomena and known six polymorphs are involved. The forming and transformation of phases are quite sophisticated. There are a lot of factors that affect the solidification and melting properties of cocoa butter. Some of them are composition of cocoa butter especially TAG's amount and process conditions. The results described here, both cooling and shear rates affect the crystallization behavior of cocoa butter. The rate of cooling was important. A rapid rate of cooling generally led to nucleation at a lower temperature than for slow cooling. Slower cooling rates generally led to nucleation at higher temperatures. Results showed that shear promoted Form V crystallization and induction times for crystallization reduced with an increase in shear rate. TAG have enough time to organize in the liquid state in lamellae structures while

decreasing the temperature to achieve isothermal conditions and an increase in viscosity was observed with low cooling rate ( $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ ). Effect of cooling rate was more significant at lower temperatures ( $P < 0.05$ ). It was indicated that applying shear promotes a solid to a solid transformation of fats from unstable to more stable polymorphic forms.

Knowledge of the cooling and isothermal phase behavior of cocoa butter under different cooling and shear rates is important to optimize production processes and to maintain product quality. Chocolate's rheological properties are important in the manufacturing process to achieve high-quality products with a desired textural and sensory properties and cocoa butter is responsible for this as the main ingredient.

Tempering and cooling are the most critical steps in chocolate manufacture and these steps are strongly linked with fat migration and fat bloom of chocolate. Temperature and shear control are important correct crystallization of cocoa butter during tempering process. The degree of molecular packing of cocoa butter crystals network can be controlled using shear, resulting in improved cooling protocols in the processing of chocolate. The output of this study would be useful to understand the effects of cooling and shear rates on crystallization of cocoa butter which are the critical aspects that influenced the stability of chocolate products. It is also important for prevention of fat bloom of chocolate products.

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**Author Contributions :** Gülten Şekeroğlu and

Ahmet Kaya designed the study, evaluated the data and wrote the article and Gülten Şekeroğlu carried out the experiments. Both authors read and approved the final manuscript.

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