# Influence of Shearing and Time on the Rheological Properties of Milk Chocolate During Tempering

**J.L. Briggs**[a] **and T. Wang**[b,*]

[a]Thermo Electron Corp., Madison, Wisconsin 53711, and [b]Iowa State University, Ames, Iowa 50011

**ABSTRACT:** The quality of chocolate is highly dependent on proper tempering. During tempering, crystals are formed as the chocolate is subjected to shear. The aim of this work was to evaluate the applicability of traditional rheological techniques to gain a better understanding of the relationship between rheological properties and the degree of shearing and time of tempering. Treatments of two shearing rates (15 and 30 $s^{-1}$) covering four tempering times (0, 400, 600, and 800 s) were investigated. As samples were cooled from a melt temperature of 50°C, the apparent viscosity followed the Arrhenius equation. An induction time, which was affected by shear rate, was observed during tempering, followed by an increase in apparent viscosity, caused by formation of crystalline structures. Various characteristics of the rewarming curve were attributed to polymorphism. Steady-shear constitutive models assessed after rewarming showed that the yield stress was dependent on shear and tempering time. Collectively, findings showed that traditional rheological methods may be used as tools to investigate crystallization and flow properties of molten chocolate indirectly during tempering.

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**KEY WORDS:** Chocolate, rheology, tempering, viscosity.

During the tempering of chocolate, the degree of shearing, time, and temperature play critical roles in the final product quality because these processing parameters affect crystallization. Properly tempered chocolate exhibits high gloss, appropriate melting temperature, adequate snap, and fat-bloom stability (1). In addition, the flow behavior of tempered chocolate has implications for the processing of chocolate after tempering.

The tempering process for chocolate involves: (i) complete melting at 45–50°C; (ii) cooling to 28–29°C in about 20 min to initiate crystallization, and maintaining the chocolate at this temperature for several minutes to permit the development of seed crystals; and (iii) warming to 30–32°C to melt out the unstable crystals but continue forming new stable type V crystals (2). The tempered chocolate is then deposited into molds, where it is cooled to 18°C for crystals to develop and form a brittle, glossy, stable, and homogeneous mass.

Tempering equipment introduces shearing through mixing, which produces a nonuniform shear field or a relatively uniform shear field, as found with a scraped-surface heat exchanger (SSHE). Understanding the crystallization kinetics associated with shearing would assist in process and equipment design and optimization. Studies that have investigated equipment and its influence on the quality and physical properties of chocolate include those performed by Bollinger *et al.* (3) and Loisel and colleagues (4,5). Others have studied and modeled the dynamic and static crystallization of chocolate (6) and developed ultrasonic techniques to study the effect of shear on lipid crystallization (7).

The objective of this study was to investigate the applicability of traditional rheological methods to determine the influences of shearing rate and tempering time on the flow behavior of milk chocolate during the tempering process.

## EXPERIMENTAL PROCEDURES

*Rheological testing conditions.* Rheological studies were conducted on commercially available milk chocolate bars (30.2% fat, 7.0% protein, 58.1% carbohydrate). A Thermo Haake RS-150 controlled-stress rheometer (Madison, WI) equipped with a 35-mm plate and plate sensor was used. Each chocolate sample was melted at 50°C directly on the rheometer plate for 5 min and equilibrated for another 5 min after the lower plate was raised to its testing position of 1 mm. Temperature was controlled using a Peltier system. At 50°C, the sample was subjected to preshearing at 30 $s^{-1}$ for 300 s. After preshearing, the temperature was decreased from 50 to 24°C at a cooling rate of 0.087°C/s and under two shearing rates as described below. Samples were held at various times at 24°C and then rewarmed to 30°C at a heating rate of 0.02°C/s at 30 $s^{-1}$.

*Experimental variables.* Shear rates of 15 or 30 $s^{-1}$ were used for the cooling phase of tempering. After reaching 24°C, the samples were held for 0, 400, 600, or 800 s while maintaining the prescribed shear rate. All samples were then reheated to 30°C, followed by shearing the sample for 90 s prior to steady-shear flow analysis of the chocolate melt.

*Steady-shear flow analysis.* To investigate the influence of tempering on the flow behavior of chocolate, a steady-shear flow was analyzed by increasing the shear rate linearly from 0 to 100 $s^{-1}$. Shear stress vs. shear rate data were fit with the Casson and Herschel–Bulkley constitutive equations.

All testing was performed in duplicate.

## RESULTS AND DISCUSSION

In this study, chocolate was evaluated using a parallel-plate sensor. Unlike a cone-and-plate sensor, where the shear is uni-

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*To whom correspondence should be addressed at Iowa State University, 2312 Food Sciences Bldg., Ames, IA 50011. E-mail: tongwang@iastate.edu form across the cone radius for small cone angles, the shear between parallel plates varies linearly with the radius of the plate (Eq. 1),

$$\dot{\gamma} = \frac{\Omega r}{h} \qquad [1]$$

where $\dot{\gamma}$ = shear rate ($s^{-1}$), $\Omega$ = rotational speed (rad/s), $r$ = plate radius (m), and $h$ = separation distance between plates (m). Therefore, the maximum shear is found at the plate rim, where $r = 0.0175$ m for a 35-mm plate. Linear shearing effects were consistent across all treatments, and data collected were comparable. Although the shear rate varied across the radius of the plate, which is a drawback in this type of experiment, this system provided a uniform heating profile across the sample during testing because of the constant distance separating the plates. In addition, the plate-and-plate system produced more reproducible results than the cone-and-plate system in preliminary tests, most likely because of the small separation distance between the lower plate and the truncated cone (0.14 mm in the case of the Thermo Haake 35-mm, 4° cone), which interfered with torque readings during precrystallization.

In rotational rheometry using plate-and-plate and cone-and-plate sensors, the testing material should fill the gap throughout the experimental procedures. During the hold time of testing, a small distance of about 0.5 mm of contraction in the radical direction was observed from the sample. This phenomenon, in turn, would result in slightly lower recorded torques, which would underestimate the shear stress as well as the shear rate values. At the shear rates (15 and 30 $s^{-1}$) and tempering times investigated in this work, the contraction was relatively similar among treatments and was considered to affect all calculated values uniformly. Contraction of the sample was more severe as the shear rate was increased to 45 or 60 $s^{-1}$. In preliminary tests at these higher shear rates, the apparent viscosity increased, followed by a rapid decrease shortly after the tempering segment began, presumably due to increased contraction or slip of the sample (data not shown). Although not undertaken in this experiment, the rheological testing protocol presented here could be used to investigate the implications of contraction on the measured rheological properties, provided the contraction distance is measured as a function of time and a pseudo-plate diameter is substituted into the shear stress and shear rate calculations. The use of optical rheometer would facilitate this measurement, or it could be accomplished by preliminary experiments that would require stopping the measurements at various points during tempering, taking contraction measurements, and repeating the testing procedure with a fresh sample at a different time. Either of these alternatives would require extracting the raw data, torque, and rotational speed, which could be done easily by the software of most commercial instruments. When slip occurs, the use of serrated plates could aid in eliminating this, allowing higher shear rates to be achieved.

*Effect of cooling on rheological properties of milk chocolate.* Apparent viscosity from the cooling segment as the temperature decreased from 50 to 24°C exhibited Arrhenius behavior (Eq. 2):

$$\eta = A \exp\left(\frac{E_a}{RT}\right) \qquad [2]$$

where $\eta$ = apparent viscosity (Pa · s), $A$ = Arrhenius constant (Pa · s), $E_a$ = activation energy (cal/g · mol), $R$ = ideal gas constant (1.987 cal/g · mol · K), and $T$ = temperature (K). Data deviated slightly from the predicted curve using the Arrhenius equation at temperatures ranging from 50 to 24°C (Fig. 1). For samples subjected to a shear rate of 30 $s^{-1}$, the average values of $E_a$ and $A$ were 5,660 ± 73 cal/g · mol and 0.000 5 ± 7E-5 P · s, respectively. The value of $A$, 0.0011 ± 6E-5 Pa · s, for samples subjected to 15 $s^{-1}$ was greater than for the samples sheared at 30 $s^{-1}$. This finding was expected due to the shear-thinning characteristic of chocolate; the apparent viscosity was greater at a lower shear rates. $E_a$ for samples sheared at 15 $s^{-1}$ was 5,270 ± 30 cal/g · mol. Wang and Briggs (8) found $E_a$ values of soybean oils to be similar in magnitude to the values obtained in this study.

*Effect of holding time on rheological properties of milk chocolate.* Real-time changes in rheological properties during holding at 24°C showed that both holding time and degree of shearing affected lipid crystallization, as shown in the apparent viscosity change (Fig. 2). Owing to the shear-thinning nature of chocolate, the apparent viscosity values of samples sheared at 15 $s^{-1}$ were greater than in samples sheared at 30 $s^{-1}$, but the general shape of the curves was similar. An induction time was observed, as indicated by a relatively constant apparent viscosity attributable to no apparent crystalline formation. For samples subjected to shear at 30 $s^{-1}$, this time was 450 s. The induction time was increased by 100 to 550 s for samples subjected to shear at 15 $s^{-1}$. This suggests that the crystal formation was faster under higher shear than lower shear. Chaiseri and Dimick (9) also observed an induction time *via* spectrophotometric methods for pure cocoa butter from various origins that had been subjected to shear using a Brabender mixer. In their study, crystallization was tracked as a function of mixing time, but the degree of shearing was not varied. Using a lab-scale SSHE, Loisel *et al.* (5) showed that induction times determined by measuring corresponding torque responses on the SSHE rotor

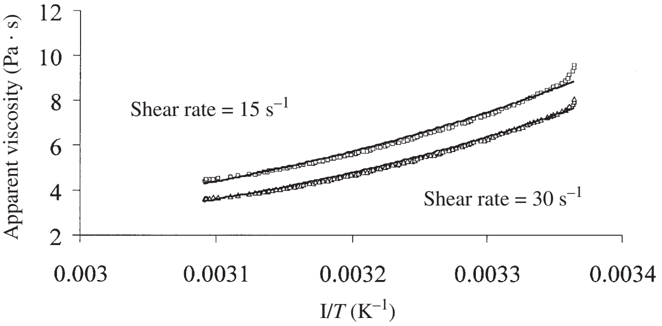

**FIG. 1.** Cooling segment (50–24°C) of chocolate samples subjected to 15 and 30 $s^{-1}$ shear rates.

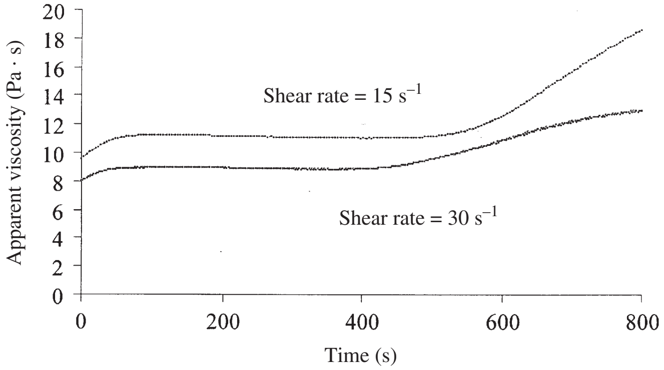

**FIG. 2.** Tempering of chocolate samples (at 24°C) subjected to shear rates of 15 and 30 s$^{-1}$.

were a function of tempering temperatures and minor lipid components.

After the induction period was reached, the rate of change in apparent viscosity was greater for samples sheared at 15 s$^{-1}$, as seen with a greater slope than the slope sheared at 30 s$^{-1}$. This may indicate that crystal particles of larger size may have formed during low shearing than those formed under high shearing. The coarse texture and more interparticle friction may result in a higher viscosity of the mass. Bollinger *et al.* (3) precrystallized chocolate with a conventional and an SSHE system. They noted in subsequent rotational viscometry tests that chocolates precrystallized using conventional equipment exhibited an increased rate of change in apparent viscosity compared with samples precrystallized using the SSHE. These results are in agreement with those reported here. It has been reported that crystallization rate is also dependent on fat components and composition (10,11), but since the same material was used for all treatments in this experiment, this variable did not influence our test.

*Effect of rewarming on the rheological properties of milk chocolate.* At the end of the holding stage, rewarming was started, and apparent viscosity was recorded as the temperature was increased from 24 to 30°C (Fig. 3). The objective of reheating during the tempering process is to convert the possible metastable structure of the crystals formed at 24°C holding to the more stable crystalline forms. As shown, samples tempered for 600 and 800 s at a shear rate of 30 s$^{-1}$ exhibited two distinct segments of apparent viscosity. Of these samples, a plateau region showing relatively constant apparent viscosity was observed as the temperature was increased from 24 to 26°C. This indicates that under conditions of higher shearing and longer holding time, relatively stable crystals were formed that did not undergo polymorphism at the beginning stage of rewarming. The second region of apparent viscosity at temperature >26°C shows a linear decrease in apparent viscosity. This may have been caused by partial melting of the less stable form of the crystals with the temperature increase. Slopes of the linear portion of samples sheared at 15 s$^{-1}$ for 800 s and 30 s$^{-1}$ for 600 and 800 s were statistically different at $P < 0.05$ (Table 1), which suggests that different forms or amounts of the metastable forms of the crystal may have formed under different treatment conditions. The sample treated with a 15 s$^{-1}$ shear rate for 800 s showed an initial decrease in viscosity, indicating that the lower shearing produced not only relatively large crystalline particles, but also a relatively unstable form of crystal.

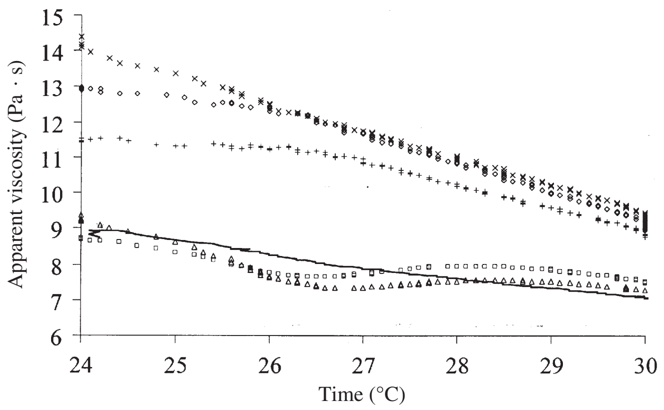

**FIG. 3.** Rewarming of chocolate samples subjected to holding times (at 24°C) of (◇) 800 s at 30 s$^{-1}$; (×) 800 s at 15 s$^{-1}$; (+) 600 s at 30 s$^{-1}$; (□) 400 s at 30 s$^{-1}$; (△) 400 s at 15 s$^{-1}$; (–) no holding at 30 s$^{-1}$.

Samples sheared for 400 s at shear rates of 15 or 30 s$^{-1}$ exhibited different rheological behavior. They had much lower apparent viscosity owing to the shorter holding time and less or no crystal formation compared with those having longer holding times. Between temperatures of 25.5 and 28°C, a trough characterized by a decrease and subsequent slight rise in apparent viscosity was observed, but only for samples that were sheared for 400 s. Regarding the behavior shown in Figure 2, the two samples held for 400 s should not have crystals formed, but their behavior during rewarming was significantly different from the sample without any holding. Holding had apparently influenced the material in a certain way, but we are unable to explain how.

Samples that were not held for any length of time at 24°C, but were subjected only to a temperature decrease from 50 to 24°C and immediately rewarmed to 30°C, showed no plateau region. The characteristic curve from rewarming was linear, which suggests that no crystallization or polymorphism changes had taken place, but rather partial reduction of viscosity with the temperature increase. Stapley *et al.* (12) noted a lack of detectable crystal formation, as determined by DSC, for milk chocolate when sheared for less than 200 s. They found that increasing the tempering time, which was dependent on the shear rate, to a critical value shifted the exothermic peak upon cooling, indicating the formation of crystals.

**TABLE 1**
**Slope of the Linear Portion of the Rewarming Curve**

| Holding time (s) | $\dot{\gamma}$ (s$^{-1}$) | Ave. (Pa · s/°C) | SD |
|---|---|---|---|
| None | 30 | –0.312 | 0.0007 |
| 600 | 30 | –0.659 | 0.0262 |
| 800 | 15 | –0.773 | 0.0035 |
| 800 | 30 | –0.826 | 0.0042 |

It is worth mentioning that the temperature change (from 24 to 30°C) itself may affect the apparent viscosity. Therefore, the observed viscosity change could be an overlaid effect of temperature and the dynamics of crystallization and polymorphism.

The work of Stapley *et al.* (12) initially inspired this study. Our primary motivation was to determine whether rheological studies could provide convenient, direct, and quantitative measurement during the crystallization of chocolate. The rheological rewarming data presented in Figure 3 suggest that traditional rheological techniques are sensitive enough to detect rheological differences caused by varying treatments of time and degree of shearing. Therefore, a rheometer can be used not only to measure viscosity and possible crystalline form changes, but also as a tool to optimize tempering conditions to obtain desirable products.

The shear rates used in this experiment are much lower (due to the experimental limitations discussed) than those used in commercial tempering equipment where the shear rates can be between 500 and 12,000 $s^{-1}$ (12). As discussed, shearing has a major effect on crystallization kinetics: It induces a faster and more homogeneous crystallization and produces more stable crystal forms with a refined grain size. Nevertheless, its effect is not yet fully understood. A study conducted by Rousset and Rappaz (6) also showed that the effect of shearing on crystallization onset time is temperature-dependent. A critical shear rate existed, and when the rate exceeded this value, the onset time decreased with an increase of shear. These critical rates were between 10 and 100 $s^{-1}$ for the temperatures used.

*Steady flow behavior of the molten chocolate.* After rewarming to 30°C, the rheological behavior was characterized using the Casson model (Eq. 3) and the Herschel–Bulkley model (Eq. 4) over the shear rate range of 0 to 70 $s^{-1}$,

$$\sigma^{0.5} = K_1 (\dot{\gamma})^{0.5} + \sigma_o^{0.5} \qquad [3]$$

$$\sigma = K (\dot{\gamma})^n + \sigma_o \qquad [4]$$

where $\sigma$ = shear stress (Pa), $K_1$ = Casson viscosity $[(\text{Pa} \cdot \text{s})^{0.5}]$, $\dot{\gamma}$ = the shear rate ($s^{-1}$), $\sigma_o$ = yield stress (Pa), $K$ = the consistency coefficient ($\text{Pa} \cdot \text{s}^n$), and $n$ = the flow behavior index (dimensionless). At rates above 70 $s^{-1}$, a plateau was observed in plots of shear stress vs. shear rate. These data were neglected in curve fitting because the origin of this observation was unclear (whether the plateau was characteristic of the data or whether it was an artifact of either contraction or potential slip at these higher shear rates). Tables 2 and 3 summarize the rheological parameters from Equations 3 and 4.

The Casson model is the standard constitutive model in the chocolate industry (13,14). Based on a linear regression of the data, the yield stress ranged from 13.1 to 15.4 Pa. In a survey of the rheological properties of chocolate, Wilson *et al.* (15) reported similar yield stress values for chocolate. The Casson viscosity ranged from 3.8 to 5.3 $(\text{Pa} \cdot \text{s})^{0.5}$. The best-fit line predicted small differences in yield stress between the various treatments. A slight increase in Casson viscosity of about 1.3 $(\text{Pa} \cdot \text{s})^{0.5}$ occurred as tempering time increased from 0 to 800 s.

**TABLE 2**
**Rheological Parameters of the Casson Model for Tempered Milk Chocolate ($T$ = 30°C)**

| Time (s) | $\dot{\gamma}$ ($s^{-1}$) | $\sigma_o$ (Pa) | $K_1$ $[(\text{Pa} \cdot \text{s})^{0.5}]$ |
|---|---|---|---|
| None | 30 | 13.1 | 3.8 |
| 400 | 30 | 15.1 | 4.4 |
| 600 | 30 | 13.5 | 5.1 |
| 800 | 30 | 14.1 | 5.2 |
| 400 | 15 | 13.8 | 4.3 |
| 800 | 15 | 15.4 | 5.3 |

The standard model used in the chocolate industry to describe the rheological behavior of chocolate is that established by the International Office of Cocoa, Chocolate, and Sugar Confectionery, yet this has changed lately. The Casson model also has its limitations (16). Two more reproducible and significant parameters are used instead: Shear stress at 5 $s^{-1}$ is taken as an indication of the yield stress, and viscosity at 40 $s^{-1}$ is taken as an indication of viscosity.

Observing the shear-thinning characteristics of the samples, we also fit data with the Hershel–Bulkley equation. The yield stress determined by linear regression increased threefold between samples that were subjected to no or 800 s of hold time. Yield stress remained relatively constant as the tempering time increased from 600 to 800 s for samples sheared at 30 $s^{-1}$. Reducing the shear rate from 30 to 15 $s^{-1}$ had a negligible effect on the yield stress.

The consistency coefficient from the Herschel–Bulkley equation decreased slightly as the shearing time increased, whereas the flow behavior index increased. In terms of apparent viscosity, $K$ and $n$ are linked through Equation 5:

$$\eta = K (\dot{\gamma})^{n-1} + \frac{\sigma_o}{\dot{\gamma}} \qquad [5]$$

With no tempering, the chocolate showed more shear thinning after rewarming ($n$ = 0.77) than samples that were subjected to tempering. For samples subjected to a shearing rate of 30 $s^{-1}$ and a tempering time of 800 s, $n$ increased to 0.89. We suspect that these differences in $n$ were due to the presence of more crystals in the chocolate, which caused more difficulty in crystal alignment during the process. Although the Herschel–Bulkley model is not commonly used to study

**TABLE 3**
**Rheological Parameters of the Herschel–Bulkley Model for Tempered Milk Chocolate ($T$ = 30°C)**

| Time (s) | $\dot{\gamma}$ ($s^{-1}$) | $\sigma_o$ (Pa) | $K$ ($\text{Pa} \cdot \text{s}^n$) | $n$ (–) |
|---|---|---|---|---|
| None | 30 | 10.6 | 14.2 | 0.77 |
| 400 | 30 | 19.4 | 13.8 | 0.81 |
| 600 | 30 | 31.7 | 11.0 | 0.89 |
| 800 | 30 | 32.8 | 11.3 | 0.89 |
| 400 | 15 | 20.3 | 12.4 | 0.83 |
| 800 | 15 | 127.0 | 13.7 | 0.85 |

the rheology of chocolate (13), the trend of decreasing shear-thinning behavior found in this study is interesting, and further investigation of its applicability in the chocolate industry may be warranted.

In summary, rheological data may be used to infer the influence of shear rate and shearing time on the crystallization of chocolate indirectly through changes in apparent viscosity. By using the method described in this study, it is possible to evaluate chocolate melting characteristics, which would be difficult with a two-step process of tempering chocolate and transferring the chocolate to the viscometer. The practical limitations of implementing traditional rheological methods in studying shear-induced crystallization may be excessive contraction, which, in the case of this study, occurred at shear rates above 45 $s^{-1}$. Based on the findings of this work, the Herschel–Bulkley constitutive model shows potential for describing the steady-state flow behavior of tempered chocolate.

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