Comparison of rheological models for determining dark chocolate viscosity

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Summary Parameters in chocolate rheology, namely shear viscosity and yield stress, are important in manufacture and directly influenced by product particle size distribution (PSD) and composition. The Casson model was the standard confectionery industry strategy to quantify rheological properties of molten chocolate until in 2000, the International Confectionery Association recommended the use of interpolation data to describe viscosity. The two strategies are compared and correlated in defining rheological properties of molten dark chocolates prepared using different PSD, fat and lecithin content. Rheological parameters were determined using a shear rate-controlled rheometer and data examined using correlation, regression and principal component analyses to establish their inter-relationships. Correlation and regression analyses showed high correlation \( r = 0.89–1.00 \) and regression coefficients \( R^2 = 0.84–1.00 \). The newer International Confectionery Association technique gave higher correlation and regression coefficients than the Casson model, but multivariate principal component analysis showed that the two models were highly related and either could effectively quantify dark chocolate viscosity parameters.

Keywords Chocolate composition, particle size distribution, shear viscosity, yield stress.

Introduction The rheological properties of molten chocolate are important for confectionery quality assurance and accurate weight measurements. Molten chocolate behaves as a non-Newtonian liquid, exhibiting non-ideal plastic behaviour with a yield stress, related to amount of energy required to initiate fluid flow, and plastic viscosity, energy required to keep fluid in motion (Beckett, 1999; Ziegler & Hogg, 1999; Afoakwa et al., 2007a). Plastic viscosity relates to pumping characteristics, filling of rough surfaces and coating properties, yield stress to shape retention, pattern holding, inclined surface coating and bubbles in processing (Seguine, 1988). Afoakwa et al. (2007b) concluded that rheological properties are important in chocolate manufacturing for quality-control purposes and can be related to composition, processing strategy and solid particle size distribution. Apparent viscosity in oral aqueous solutions influences flavour attribute perception (Ziegler et al., 2001); thus, rheological parameters often give information related to sensory character in chocolate.

Important models that have been used to characterise chocolate rheology include the Herschel-Bulkley, Casson and Bingham forms (Chevalley, 1999; Beckett, 2000; Sokmen & Gunes, 2006), following the equations:

Herschel-Bulkley:
\[
\tau = \tau_0 + \eta \gamma \gamma^n
\]

Casson:
\[
\sqrt{\tau} = \sqrt{\tau_{CA}} + \eta_{CA} \cdot \sqrt{\gamma}
\]

Bingham:
\[
\tau_B = \tau_0 + \eta_B \cdot \gamma
\]

[\tau, shear stress; \tau_0, yield stress; \eta, plastic (shear) viscosity; \tau_{CA}, Casson yield value; \eta_{CA}, Casson plastic viscosity; \tau_B, Bingham yield value; \eta_B, Bingham plastic viscosity; \gamma, shear rate; \eta, viscosity of the suspension; n, flow viscosity index].

Since 1973, the International Confectionery Association (ICA) has accepted rheological measurement of molten chocolate using rotational viscometers with concentric cylinders (bob and cup geometry) and Casson equation calculation of the parameters (IOCCC (International Office of Cocoa, Chocolate and

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Confectionary), 1973; Bouzas & Brown, 1995). In 2000, ICA recommended measurement of stress and viscosity at shear rates between 2 s⁻¹ and 50 s⁻¹ using up and down curves in shear rate, preceded by a pre-shear at 5 s⁻¹ lasting ≥5 min (ICA, 2000).

The basis for the change in 2000 was the results from an inter-laboratory study (Aeschlimann & Beckett, 2000), which concluded that the Casson’s mathematical model employing only a small set of parameters was limited in accuracy as, at lower shear rates, rheology data do not fit the Casson equation well. The outcome was a low degree of repeatability in inter-laboratory analyses, and ICA thus recommended the use of interpolation data for chocolate viscosity. Servais et al. (2004) noted that this strategy was simple, accurate and readily applicable to different systems, given a basis of relevant information.

In the United States, the current NCA/Chocolate Manufacturers Association (CMA) method for determining chocolate rheological properties is to extrapolate concentric cylinder flow data using the Casson equation and the vane technique rather than Couette geometry (Baker et al., 2006). This conflicts with the ICA quantification strategy (ICA, 2000). Understanding the relationship between the two strategies for estimating dark chocolate rheological parameters is therefore the objective of this study.

Materials and methods

Materials

Cocoa liquor of Central West African Origin was obtained from Cargill Cocoa Processing Company (York, UK). Sucrose (pure cane extra fine granulated) from British Sugar Company (Peterborough, UK); pure prime pressed cocoa butter and soy lecithin from ADM Cocoa Limited (Koog aan de Zaan, the Netherlands) and Unitechem Company Ltd. (Tianjin, China), respectively.

The production of samples (Table 1) is described elsewhere (Afoakwa et al., 2007b). Refined chocolates were placed in plastic containers and melted under 20–22 °C and moisture and fat contents determined using Karl Fisher and Soxhlet methods (ICA, 1988, 1990), respectively.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>25% Fat</th>
<th>30% Fat</th>
<th>35% Fat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose (%)</td>
<td>58.8</td>
<td>59.0</td>
<td>49.7</td>
</tr>
<tr>
<td>Cocoa liquor (%)</td>
<td>35.9</td>
<td>35.5</td>
<td>45.0</td>
</tr>
<tr>
<td>Cocoa butter (%)</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Lecithin (%)</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 1 Recipes used for the formulation of the dark chocolate

3.5 h at 60 °C. Lecithin and cocoa butter were then added and mixtures conched at high speed for further 30 min for mixing and liquefaction. Samples were kept in sealed plastic containers at ambient temperature (20–22 °C) and moisture and fat contents determined using Karl Fischer and Soxhlet methods (ICA, 1988, 1990), respectively.

Determination of particle size distribution

A MasterSizer® Laser Diffraction Particle Size Analyzer equipped with MS 15 Sample Presentation Unit (Refractive index 1.590) (Malvern Instrument Ltd., Malvern, England) was used. About 0.2 g of refined dark chocolate was dispersed in vegetable oil (refractive index 1.450) at ambient temperature (20 ± 2 °C) until an obscuration of 0.2 was obtained. The sample was then put through ultrasonic dispersion for 2 min to ensure that the particles were independently dispersed and thereafter maintained by stirring during the measurement. Size distribution was quantified as the relative volume of particles in size bands presented as size distribution curves (Malvern MasterSizer® Micro Software v 2.19). Particle size distribution (PSD) parameters were obtained as described previously (Afoakwa et al., 2007b).

Rheological measurements of molten dark chocolate

Rheological behaviour was characterised using steady shear measurements carried out in a shear rate-controlled rheometer [Thermo Haake ViscoTester 550 (VT 550); Thermo Electron Corp., Karlsruhe, Germany]. This used bob and cup (recessed end) geometry (Sensor SAVI and SVII), as for IOCCC method (Aeschlimann & Beckett, 2000) with a ratio of inner to outer radius of 0.92 in the concentric cylinder system. The samples were incubated at 50 °C for 75 min for melting and transferred, pre-sheared at 5 s⁻¹ for 15 min at 40 °C, before measurement cycles. Shear stress was measured at 40 °C as a function of increasing shear rate from 5 to 50 s⁻¹ (ramp up) over 120 s, then decreasing from 50 to 5 s⁻¹ (ramp down); within each ramp, 50 measurements were taken. Temperature was controlled using Haake K20 Thermo-regulator (Thermo Electron Corp.). The mean value and standard deviation of triplicate readings were recorded.

Casson plastic viscosity and Casson yield values were calculated from interpolation data using ThermoHaake RheoWin Pro 297 Software by the least squares method. Other rheological parameters (yield stress, apparent viscosity and thixotropy) were deduced from data as recommended by ICA (2000) and Servais et al. (2004) with some modifications. Value of stress at a shear rate of 5 s⁻¹ represented yield stress, viscosity at

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a shear of 30 s\(^{-1}\), apparent viscosity, and difference between yield stresses at 5 s\(^{-1}\) during ramp up and down, thixotropy.

Experimental design and statistical analysis

A 4 × 3 × 2 factorial experimental design was used with principal factors: particle size distribution \((D_{90})\): 18, 25, 35 and 50 μm; fat content: 25%, 30% and 35% (w/w); lecithin content: 0.3% and 0.5% (w/w). Other variables, including refiner temperature and pressure, conching time and temperature, and cocoa butter [5% (w/w)], were held constant.

Statgraphics Plus 4.1 (Graphics Software System, STCC, Inc, Rockville, USA) examined Casson plastic viscosity and yield values, apparent viscosity, yield stress and thixotropy using two-way analysis of variance (ANOVA) and multiple range tests to determine the effect of PSD, fat and lecithin contents and their interactions. Regression, correlation and principal component analyses were used to evaluate the relationships between the two rheological models. Tukey multiple comparisons at 95% significance level were conducted to determine the differences between the factor levels.

Results and discussion

Particle size distribution of dark chocolates

Wide variations in PSD were observed for 18, 25, 35 and 50 μm (Fig. 1) using \(D_{90}\) values (>90% finer) that relate to chocolate character (Beckett, 2000; Afoakwa et al., 2007b). Figure 1 shows volume histograms of samples with size distributions of narrow unimodal distribution for 18 μm PS, wide unimodal distribution for the 25 μm PS, narrow bimodal distribution for 35 μm PS, and a wide bimodal distribution for 50 μm (Fig. 1). Such PSD, ranging from fine (18 μm) to coarse particles (50 μm), cover optimal minima and maxima (Ziegler & Hogg, 1999; Beckett, 2000). Data from the PSD (Afoakwa et al., 2007b) showed variations in specific surface area and mean particle diameter \([D(4,3)]\) with increasing \(D_{90}\) particle sizes. These findings have been discussed previously (Afoakwa et al., 2007b).

Increasing fat content led to significant \((P < 0.001)\) reductions in specific surface area and increase in all other PSD parameters (Table 2), suggesting that fat content at refining has a direct influence on PSD parameters. Beckett (1999) concluded largest particle size and solid-specific surface area are the two key parameters for chocolate manufacture. The former determines chocolate coarseness and textural character, while the latter evaluates chocolate desirable flow properties. Specific surface area is inversely correlated with the various components of PSD (Beckett, 1999; Ziegler & Hogg, 1999; Sokmen & Gunes, 2006; Afoakwa et al., 2007b). The fat contents were 25 ± 1, 30 ± 1 and 35 ± 1%; moisture within the range 0.80–0.98%.

Relationships between Casson model and International Confectionery Association recommendations

Multivariate correlation, regression and principal component analyses evaluated relationships between Casson plastic viscosity and Casson yield value and the newly recommended yield stress, apparent viscosity and thixotropy (ICA, 2000; Servais et al., 2004). Effects of PSD and composition on dark chocolate rheology using both models have been reported (Afoakwa et al., 2007b).

Correlation and regression analyses conducted on the data revealed high regression and correlation coefficients among all rheological parameters (Table 3). Relationships were calculated using correlation analysis between Casson plastic viscosity and Casson yield value, apparent viscosity and yield stress. High correlation coefficients \((r \sim 0.95, P < 0.001)\) were observed between Casson plastic viscosity and apparent viscosity, and between Casson yield value and yield stress \((r \sim 0.98, P < 0.001)\).

Table 2 Analysis of variance (ANOVA) summary of F-ratios from particle size distribution

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Specific surface area</th>
<th>(D(v,0.1))</th>
<th>(D(v,0.5))</th>
<th>(D(3,2))</th>
<th>(D(4,3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Particle size ((D_{90}))</td>
<td>302.77*</td>
<td>455.54*</td>
<td>1007.84*</td>
<td>546.01*</td>
<td>8388.61*</td>
</tr>
<tr>
<td>B: Fat</td>
<td>115.88*</td>
<td>312.87*</td>
<td>311.17*</td>
<td>228.10*</td>
<td>23.21*</td>
</tr>
<tr>
<td>A × B</td>
<td>4.37*</td>
<td>6.63*</td>
<td>2.59*</td>
<td>3.52*</td>
<td>2.08*</td>
</tr>
</tbody>
</table>

*Significant F-ratios at \(P \leq 0.05\).
\(D(v,0.1), D(v,0.5), D(3,2)\) and \(D(4,3)\) represent 10%, 50%, Sauter mean diameter and mean particle diameter of all particles finer than this size, respectively.
Regression analyses (Figs 2 and 3) showed that Casson plastic viscosity and apparent viscosity, and Casson yield value and yield stress were very closely related. Contrary to the findings of Servais et al. (2004), Casson plastic viscosity and Casson yield value were highly correlated ($r \approx 0.89$, $P < 0.001$), with a high and significant regression coefficient, $R^2 = 0.84$ (Table 3).

The regression model is as shown on Fig. 4. Similarly, yield stress and apparent viscosity were highly correlated ($r \approx 0.99$, $P < 0.001$), with regression coefficient, $R^2 = 0.99$ (Table 3). Fig. 5 shows the regression model for yield stress and apparent viscosity.

Thixotropy is exhibited in chocolates if its apparent viscosity or shear stress decreases with time when sheared at a constant rate, and relates to degree of conching as well-conched chocolate should not be thixotropic (Beckett, 2000). Both interpolation and extrapolation data are used to characterize thixotropy but no certified method has been denoted (ICA, 2000; Cheng, 2003; Chhabra, 2007). Servais et al. (2004) suggested that practically, thixotropy can be obtained by: (i) area differences between ramp up and ramp down in flow curves; (ii) calculating analytically area differences in Casson models between 2 and 50 s$^{-1}$; (iii) stress

**Table 3** Regression and correlation analyses between rheological parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Analysis</th>
<th>Casson plastic viscosity</th>
<th>Casson yield value</th>
<th>Apparent viscosity</th>
<th>Yield stress</th>
<th>Thixotropy (YS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casson plastic viscosity</td>
<td>Regression</td>
<td>1</td>
<td>0.8368*</td>
<td>0.9053*</td>
<td>0.8919*</td>
<td>0.9021*</td>
</tr>
<tr>
<td>Correlation</td>
<td>1</td>
<td></td>
<td>0.8903*</td>
<td>0.9467*</td>
<td>0.9349*</td>
<td>0.9447*</td>
</tr>
<tr>
<td>Casson yield value</td>
<td>Regression</td>
<td>–</td>
<td>1</td>
<td>0.9582*</td>
<td>0.9694*</td>
<td>0.9665*</td>
</tr>
<tr>
<td>Correlation</td>
<td>–</td>
<td></td>
<td>1</td>
<td>0.9786*</td>
<td>0.9844*</td>
<td>0.9823*</td>
</tr>
<tr>
<td>Apparent viscosity</td>
<td>Regression</td>
<td>–</td>
<td>–</td>
<td>1</td>
<td>0.9898*</td>
<td>0.9955*</td>
</tr>
<tr>
<td>Correlation</td>
<td>–</td>
<td></td>
<td>–</td>
<td>1</td>
<td>0.9941*</td>
<td>0.9977*</td>
</tr>
<tr>
<td>Yield stress</td>
<td>Regression</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1</td>
<td>0.9939*</td>
</tr>
<tr>
<td>Correlation</td>
<td>–</td>
<td></td>
<td>–</td>
<td>–</td>
<td>1</td>
<td>0.9957*</td>
</tr>
<tr>
<td>Thixotropy (AP)</td>
<td>Regression</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.9527*</td>
</tr>
<tr>
<td>Correlation</td>
<td>–</td>
<td></td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.9761*</td>
</tr>
</tbody>
</table>

* Significant at $P < 0.001$.  

**Figure 2** Relationship between Casson plastic viscosity and apparent viscosity using bob and cup (reference) geometry. Data points (squares); linear regression (solid line); minimum and maximum tolerance intervals (both outer lines); Casson plastic viscosity $= 0.477564 + 0.31802 \times$ apparent viscosity.

**Figure 3** Relationship between Casson yield value and yield stress using bob and cup (reference) geometry. Data points (squares); linear regression (solid line); minimum and maximum tolerance intervals (outer lines); Casson yield value $= -11.9953 + 18.4325 \times$ Casson plastic viscosity.

**Figure 4** Relationship between Casson yield value and Casson plastic viscosity using bob and cup (reference) geometry. Data points (squares); linear regression (solid line); minimum and maximum tolerance intervals (outer lines); Casson yield value $= 11.9953 + 18.4325 \times$ Casson plastic viscosity.
differences at 5 s\(^{-1}\) from ramps up and down; (iv) viscosity differences at 40 s\(^{-1}\) from ramps up and down. Using data from four Swiss dark chocolates, they calculated the viscosity differences at 40 s\(^{-1}\) from ramps up and down in shear rates multiplied by 1600 (s\(^{-2}\)) to represent thixotropy. However, we recommend that, provided there are sufficient data points, interpolation data give more robust information, and the use of extrapolation data and multiplication factors should be avoided as they give erroneous results.

Correlation and regression analyses (Fig. 6) determined relationships between thixotropy from differences in yield stress at 5 s\(^{-1}\) and from calculating the difference between apparent viscosities at 30 s\(^{-1}\), in each case comparing ramps up and down. Significant correlation coefficients of \(r \sim 0.98\) (\(P < 0.001\)); and regression coefficient of determination of \(R^2 \sim 0.95\) (\(P < 0.001\)), among the two methods (Table 3), suggested that both yield stress and apparent viscosity could be used as reliable interpolation data to measure thixotropy. In contrast, the use of extrapolation data from Casson parameters should be avoided, as this gave lower coefficients of determination (Table 3).

The principal component analysis (PCA) product space (Fig. 7) explained 95.2% variance (74.2%, 13.7% and 7.3%) (eigen value > 1) and showed that all the rheological parameters were very closely related to the PSD, fat and lecithin content as their key influencing factors. This PCA (Fig. 7) product space for Casson parameters (plastic viscosity and yield value) and ICA recommended parameters (apparent viscosity and yield stress) were closely related, suggesting that both techniques could be used independently to evaluate the rheological properties of dark chocolates.

**Conclusion**

The complexity of behaviour combined with the nature of chocolate flow often is an issue when choosing a representation or equation for evaluating the rheological properties of chocolates. Given sufficient data points, the use of interpolation data usually poses no difficulty, but extrapolation should be avoided. The Casson reference parameters (yield value and plastic viscosity) and newer ICA recommendations (yield stress and apparent viscosity) for evaluating chocolate viscosity are very closely related, and could be used independently. The ICA method is relatively more efficient than the Casson model, which has limitations with chocolates with wide variations in viscosity. Both rheological models are dependent on PSD, fat and lecithin, as key factors under controlled processing conditions. For routine manufacturing, use of the calculation of Casson reference parameters, where the product history is known,
could be justified, while the ICA is better suited for research purposes with wide variations in component viscosity.

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References


