

Influence of some bulk sweeteners on rheological properties of chocolate

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Abstract

Chocolates with reduced calories have become popular among consumers and manufacturers. One way of manufacturing chocolate with reduced calories is to replace sucrose with some alternatives. Effects of different bulk sweeteners (maltitol, isomalt, and xylitol) with different particle size intervals (PSI) (106–53, 53–38 and 38–20 μm) on rheological properties of molten chocolate were investigated. The best model that fit the rheological data was Herschel–Bulkley model. Maltitol resulted in similar rheological properties of chocolate compared to sucrose and thus can be a good alternative. Isomalt resulted in higher plastic viscosity while maltitol resulted in higher yield stress than others. As the particle size increased the plastic viscosity and the yield stress increased. The differences in rheological properties of chocolate with different bulk sweeteners were caused by differences in solid volume fraction and particle size distribution (PSD). A substitute with large particle size should be chosen to replace sucrose for improving rheological properties of chocolate, but the particle size should be small enough to obtain good sensory properties.

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1. Introduction

Molten chocolate is a dense suspension consisting of nonfat particles (sucrose, cocoa, milk) dispersed in cocoa butter as a continuous phase (Chevalley, 1975). Determination of rheological properties of chocolate is important in manufacturing process for obtaining high-quality products with well-defined texture (Servais, Ranc, & Roberts, 2004). Factors such as fat content, particle size distribution (PSD), moisture content, emulsifiers, conching time, and temperature affect rheological properties and the production cost (Tscheuschner & Wünsche, 1979). Flow of molten chocolate is non-Newtonian with an apparent yield stress, and can be described by a number of mathematical models including Bingham, Herschel–Bulkley, and Casson models (Chevalley, 1999; Servais et al., 2004). The International Office of Cocoa, Chocolate and Sugar Confectionery (IOCCC), National Confectioners Association (NCA) and Confectioners Manufacturing Association (CMA) accepted rheological measurement of chocolate in a

shear rate range of $5\text{--}60\text{ s}^{-1}$ using rotational viscometers with concentric cylinders (bob and cup), and Casson equation for calculation of rheological parameters (Bouzas & Brown, 1995).

Increasing solid concentration results in higher viscosity as shown by Servais, Jones, and Roberts (2002). High solid content, interactions of the suspended particles and their interfacial properties affect rheological properties of chocolate (Bouzas & Brown, 1995). Viscosity of suspensions can be greatly modified by changing PSD while maintaining the same solid content (Chevalley, 1975). Smaller particle sizes in chocolate are known to improve sensory properties (Ziegler, Mongia, & Hollender, 2001) but plastic viscosity and yield stress increase due to increased surface area of particles in contact with cocoa butter (Mongia & Ziegler, 2000). The optimum average sugar particle size in chocolate is 30–33 μm with a maximum of 50 μm in the US and 20–23 μm with a maximum of 35–40 μm in Europe (Jeffery, 1993). Optimum particle size is restricted by sensory attributes. It has been reported that chocolate was acceptable if the proportion of particles above 22 μm were less than 20% (Chevalley, 1975). Chocolate with particle size above 35 μm becomes

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gritty or coarse in the mouth resulting in lower acceptability (Servais et al., 2002).

Sucrose-free chocolates have become popular among consumers and manufacturers because they have reduced calorific values, and they are noncariogenic and suitable for diabetics (Olinger, 1994). Sucrose constitutes more than 40–50% of solids dispersed in fat and thus, its functional properties including sweetness, stability, PSD, mouthfeel (texture), and its impact on rheological properties of the product are important for chocolate products (Jeffery, 1993). Bulk sweeteners substituted for sucrose in chocolates should provide these functional properties for an acceptable product. Sugar alcohols such as isomalt, maltitol, and xylitol can be used as bulk sweeteners to manufacture sucrose-free chocolates (Olinger, 1994). These bulk sweeteners that are commonly used in foods, pharmaceuticals, and cosmetics give body, texture, and sweet flavor to products and have reduced calories and noncariogenic character (Kato & Moskowitz, 2001; Olinger & Pepper, 2001; Wijers & Sträter, 2001).

Replacement of sucrose with sugar alcohols would affect rheological properties and thus the processing conditions and quality of chocolates. The objective of this study was to investigate effects of different bulk sweeteners (maltitol, isomalt, and xylitol) and their PSDs on rheological properties of molten chocolates.

2. Materials and method

2.1. Materials

Cocoa powder, cocoa butter, and lecithin were obtained from Pelit Chocolate & Pie GmbH (Istanbul, Turkey). Sucrose was obtained from Elit Chocolate and Confectionary GmbH (Istanbul, Turkey). Maltitol and isomalt were obtained from Dora Foreign Trade GmbH. (Istanbul, Turkey). Xylitol was obtained from Perfetti Van Melle Food Industry GmbH (Istanbul, Turkey).

2.2. Fractionation of the bulk sweeteners to different particle size intervals (PSI)

Sucrose, maltitol, isomalt, and xylitol powders were placed on a tier of sieves of decreasing mesh size of: 106, 53, 38, and 20 μm on a shaker (Endecotts, Ltd, London, UK, Model EL 80-030) and sieved for 3 h. The following particle size intervals (PSI) were obtained: PSI 1, 38–20 μm ; PSI 2, 53–38 μm ; PSI 3, 106–53 μm . The PSD parameters ($d(0.1)$, $d(0.5)$, and $d(0.9)$) of the each fraction was measured using a particle size analyser (Malvern Mastersizer 2000S, Malvern Instruments Ltd, Worcestershire, England). The density of the bulk sweeteners were measured using a 50 ml picnometer (Borucam Laboratory products GmbH., Istanbul, Turkey).

2.3. Preparation of chocolate samples

Sucrose, isomalt, xylitol, and maltitol of each PSI were used to manufacture chocolates in our laboratory. In order to manufacture 100 g chocolate samples, cocoa butter (21.89 g.) was melted in an oven at 60 °C. Cocoa powder (23.47 g) and sugar (43.40 g) were added to the melted cocoa butter. The mixture was then conched using a mixer for 3 h in a paraffin bath at 65 °C. Lecithin (0.3 g) and more cocoa butter (10.94 g) were added in the last 30 min of conching. Samples in beaker were then sealed in aluminum foil and stored at room temperature until analysed. Two chocolate samples with each fraction of the bulk sweeteners were prepared independently. The moisture content of chocolate samples was determined using an official gravimetric method (AOAC, 1990).

2.4. Rheological measurements

Rheological properties of the chocolate samples were measured using a shear rate-controlled rheometer (Haake Rotovisco RT 20, Thermo Electron Corp., Karlsruhe, Germany) with a concentric cylinder system (sensor Z40 DIN) according to IOCCC method (Aeschlimann & Beckett, 2000). The ratio of inner radius to outer radius was 0.92 in the concentric cylinder system. Each chocolate sample was incubated at 50 °C for 75 min for melting and transferred to the rheometer cub, sheared at 5 s⁻¹ rate for 10 min at 40 °C in rheometer before the measurement cycles started. Shear stress was measured at 40 °C as function of increasing shear rate from 5 to 60 s⁻¹ (ramp up) within 120 s, then decreasing the shear rate from 60 to 5 s⁻¹ (ramp down), and in each ramp 50 measurements were taken. This measurement cycle was repeated 30 times consecutively until thixotropy in the samples were eliminated. The data from the 30th measurement were applied to Casson, Bingham and Herschel–Bulkley models. Each of the duplicate samples of chocolate was measured once in the rheometer. The best model was selected by statistical analysis and all rheological parameters (viscosity, yield stress, flow behavior index) were calculated using the best model.

2.5. Statistical analysis

Data from rheological measurements were analysed using linear and nonlinear regression analysis for evaluation of different mathematical models using SPSS Release 10.0.1 (SPSS Inc., Chicago, IL). Diagnostic analyses were performed to determine validity of the models according to Neter, Kutner, Nachtsheim, and Wasserman (1996). Plastic viscosity, yield stress and flow behavior index of samples were analysed using GLM procedure to determine effects of bulk sweetener, PSD and interactions between them using Minitab Release 12.2 (Minitab Inc., State College, PA). Tukey multiple comparisons at 5% significance level

were also conducted to determine differences between the levels of each factors.

3. Results and discussion

3.1. Physical properties of bulk sweeteners

The PSD parameters of the bulk sweeteners for three different PSI are given in Table 1. Three successfully separated PSI (38–20, 53–38 and 106–53 μm) were obtained although each of these intervals contains some smaller particles that were out of the range. This could be due to agglomeration or plugged pores during sieving. Maltitol contained a higher amount of smaller particles (out of range) as illustrated by its smaller $d(0.1)$, $d(0.5)$, and $d(0.9)$ values compared to other sweeteners (Table 1). The PSI 1 covered the optimum size (20–33 μm) for sensory properties of chocolate samples (Jeffery, 1993). The density of sucrose, maltitol, xylitol, and isomalt were 1.60, 1.63, 1.52, 1.50 g/cm^3 , respectively. Moisture contents of all chocolate samples were similar within the range of 0.60–0.73%.

3.2. Rheological model

The shear rate vs shear stress data from the 30th measurement in all chocolate samples were applied to Casson, Bingham, and Herschel–Bulkley models. Thixotropic behavior of chocolate has been reported (Servais et al., 2004) and we also observed this behavior in the samples. In order to eliminate thixotropy we repeated our measurement cycle until the shear rate-shear stress data was stabilized. We found that thixotropy in all samples was eliminated after 30 consecutive measurements, and thus the data from the 30th measurement for each chocolate samples were used in the analysis.

Statistical evaluations of the models showed that the best model that fit the data was Herschel–Bulkley model ($\tau =$

$\tau_0 + \eta_{\text{pl}} \cdot (\dot{\gamma})^n$) where: τ is shear stress, τ_0 is yield stress, η_{pl} is plastic viscosity, $\dot{\gamma}$ is shear rate, and n is flow behavior index. Casson ($\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta_{\text{pl}} \cdot \sqrt{\dot{\gamma}}}$) and Bingham ($\tau = \tau_0 + \eta_{\text{pl}} \cdot \dot{\gamma}$) models for all chocolate samples resulted in patterns in residual plots (Fig. 1A and B) and nonnormal distribution of residual, which indicate violation of the model assumptions. Residuals in statistical modeling must be random and normally distributed for a valid model, and these assumptions are checked by diagnostic analysis through residual plots and normality tests (Neter et al., 1996). Diagnostic analysis of the Herschel–Bulkley model showed that the model assumptions were valid: no systematic patterns in residual plot was observed (Fig. 1C) and the residuals were normally distributed (data not shown). Therefore, all rheological parameters (plastic viscosity, yield stress, and flow behavior index) were calculated according to Herschel–Bulkley model. Casson model is widely used and recommended by IOCCC to describe flow behavior of chocolate (Bouzas & Brown, 1995). However, the model requires a lower amount of particles than that is present in chocolate, and does not produce acceptable reproducibility (Aeschlimann & Beckett, 2000; Bouzas & Brown, 1995; Servais et al., 2004).

3.3. Plastic viscosity

Xylitol and maltitol in chocolate resulted in similar plastic viscosity to sucrose while the plastic viscosity of chocolate with isomalt was significantly higher (Fig. 2). As the particle size increased plastic viscosity decreased significantly (Fig. 2). Higher particle size results in smaller surface area for a given amount of solids. As the surface area in contact with the continuous fat phase decrease, internal friction and thus, the viscosity decreases. There was a significant interaction between PSI and bulk sweetener type ($P = 0.024$). The higher plastic viscosity caused by isomalt compared to other sweeteners was more apparent at lower particle sizes (PSI 1). When each PSI was evaluated separately, viscosity of chocolate with isomalt was higher than those with xylitol and maltitol in PSI 1, and higher than sucrose and maltitol in PSI 2 ($P < 0.05$). Viscosity of chocolate with sucrose was lower than that with maltitol in PSI 3 ($P < 0.05$). Casson plastic viscosity values for dark chocolate has been reported to be between 2.1 and 3.9 Pa s (Aeschlimann & Beckett, 2000). Plastic viscosities of the chocolate samples in PSI 1 fell in this range, but it was lower for samples with larger particle sizes (PSI 2 and 3).

Higher plastic viscosity with isomalt may be associated with its higher solid volume fraction in chocolate because the density of isomalt (1.50 g/cm^3) was slightly lower than that of the other bulk sweeteners (1.60, 1.63, 1.52 g/cm^3 for sucrose, maltitol, xylitol, respectively). Because the sweeteners were added to chocolate mix on a weight basis, chocolate with isomalt had more solids and thus more surface area. Addition of bulk sweeteners on volumetric basis (especially if density of the sweetener is different than

Table 1
The particle size distribution parameters of bulk sweeteners in three different particle size intervals (PSI)

Sugars	PSI	$d(0.1)^a$	$d(0.5)^a$	$d(0.9)^a$
Sucrose	1 (38–20 μm)	3.73	12.51	29.64
	2 (53–38 μm)	4.55	21.52	49.96
	3 (106–53 μm)	11.65	52.68	109.59
Isomalt	1 (38–20 μm)	4.10	13.69	33.22
	2 (53–38 μm)	6.03	25.55	55.14
	3 (106–53 μm)	19.56	60.94	108.08
Xylitol	1 (38–20 μm)	4.12	11.35	26.34
	2 (53–38 μm)	7.13	20.46	56.95
	3 (106–53 μm)	14.54	58.98	108.64
Maltitol	1 (38–20 μm)	2.78	10.60	27.51
	2 (53–38 μm)	3.42	16.65	45.96
	3 (106–53 μm)	5.95	38.57	91.25

^a $d(0.1)$, $d(0.5)$, $d(0.9)$: respectively 10%, 50%, and 90% of all particles had smaller size than given value.

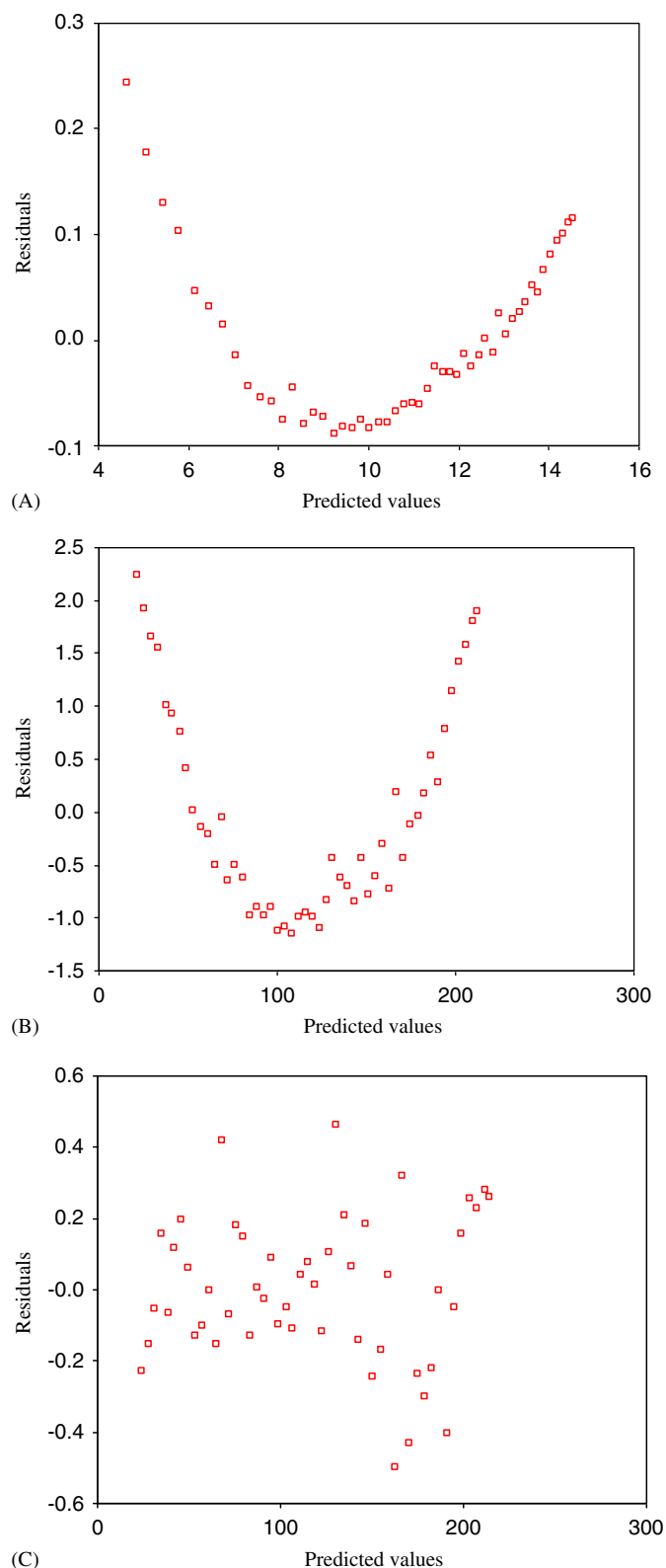


Fig. 1. Residual plots obtained from regression analysis of rheological data (isomalt PSI 1) to fit Casson (A), Bingham (B), and Herschel–Bulkey (C) models.

that of sucrose) may eliminate variation in total surface area in formulations and thus may reflect the effect of sweeteners on rheological properties more accurately.

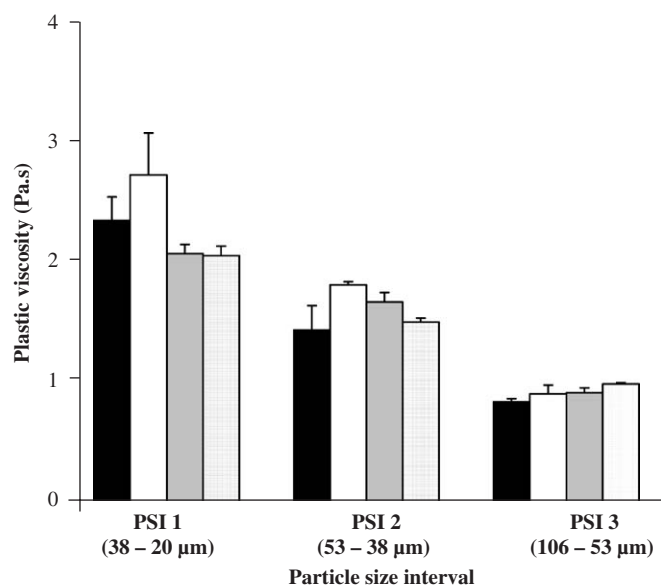


Fig. 2. Herschel–Bulkey plastic viscosity of chocolate samples manufactured with sucrose (■), isomalt (□), xylitol (▒), and maltitol (░) in different particle size intervals (PSI). Error bars represent standard deviations.

Higher plastic viscosity with isomalt was apparently not related with its PSD parameters. PSD parameters of isomalt were larger than that of other bulk sweeteners (Table 1) and thus lower viscosity would be expected. Differences among the PSD of the bulk sweeteners within each PSI fraction make it difficult to interpret the bulk sweetener effects and thus, better control of PSD is required for these types of experiments. Moisture contents of all chocolate samples were similar between 0.60% and 0.73%, and not associated with the differences in viscosities. Higher plastic viscosity caused by isomalt may be associated with its other physical properties such as specific surface area, crystallinity and hygroscopicity that were not evaluated in this study.

Viscosity of chocolate changes with conching temperature and duration, as the conching temperature decreased viscosity of chocolate decreased (Olinger, 1994). It has been shown that isomalt in chocolate resulted in higher viscosity than maltitol, sucrose, and xylitol after 18 h conching at 50 °C but lower viscosity than xylitol when conched at 60 °C (Olinger, 1994). As a result Olinger (1994) suggested different conching temperatures for chocolates with different sugar alcohols. Although the conching process was different (at 65 °C for 3 h) in our study, we also found a higher viscosity caused by isomalt.

Similar results where viscosity decreased as particle size increased have been reported in literature. For example, 1.2–2 times higher plastic viscosity for chocolate with finer particle size has been reported (Chevalley, 1975). Viscosity can double as the solid content increases by a few percent for high amounts of solid containing suspensions (Servais et al., 2002). Keogh, Murray, and O’Kennedy (2003) found a significant correlation between particle size and viscosity of milk chocolate. They reported that viscosity increased as

the particle size after refining increased, and this was attributed to the increase in fat content upon refining.

3.4. Yield stress

Yield stress of chocolate samples with maltitol was significantly higher than that with isomalt while no difference was detected among other pairs of samples (Fig. 3). As the particle size increased the yield stress decreased significantly (Fig. 3). The interaction between the PSI and the bulk sweetener type was significant ($P = 0.001$). Within PSI 1 sucrose caused higher yield stress than isomalt and xylitol; and maltitol caused higher yield stress than isomalt and xylitol ($P < 0.05$). Within PSI 2, yield stress with sucrose was higher than others; and yield stress with isomalt was lower than xylitol ($P < 0.05$). Within PSI 3, maltitol caused greater yield stress than others while isomalt caused lower yield stress than sucrose and xylitol ($P < 0.05$).

Yield stress is important in keeping small solid particles in suspension and in the coating of solid surfaces (Yoo & Rao, 1995). Casson yield values for dark chocolate has been reported to be between 4 and 32 Pa (Aeschlimann & Beckett, 2000). The yield values obtained in our study fell in this range. It has been reported that yield value changed with conching temperature and higher values were obtained with xylitol compared to isomalt and maltitol (Olinger, 1994). The author suggested different conching temperatures for each sugar alcohols to obtain acceptable yield values. Our results are in agreement with Olinger's (1994), that maltitol had higher yield value than isomalt, but disagree with that xylitol caused higher yield value compared to other sweeteners. Higher yield value of

chocolate with maltitol found in our study may be explained by maltitol's PSD, which contained more amounts of smaller particles (out of range) than the other sucrose substitutes.

3.5. Flow behavior index

Flow behavior index (n) of all chocolate samples were in the range from 0.991 to 1.05 (Fig. 4). Although the n values are close to 1 (as in the Bingham model) the deviations were important because Bingham model was not adequately fitting the data. The average flow behavior index for each bulk sweeteners were 1.006, 1.003, 1.011, and 1.033 for sucrose, maltitol, isomalt, and xylitol, respectively. These n values higher than 1 indicates slight shear thickening behavior above the yield stresses. Overall, xylitol caused higher flow behavior index than others ($P < 0.05$). Chocolates manufactured with the first and the second PSI of xylitol and the first PSI of isomalt had higher flow behavior index ($P < 0.05$). As the particle size decreased the flow behavior index increased ($P < 0.005$).

3.6. Apparent viscosity

Apparent viscosity of chocolates prepared with different bulk sweeteners were determined at 30 s^{-1} shear rate as shown in Table 2. Overall, isomalt caused higher apparent viscosity than sucrose and maltitol. The effect of bulk sweeteners on apparent viscosity was dependent on particle size: no effect was seen with larger PSI while the effect became apparent with finer particles (Table 2). As the particle size decreased the apparent viscosity increased substantially. The result with apparent viscosity is in agreement with plastic viscosity results: isomalt resulted in higher apparent and plastic viscosity.

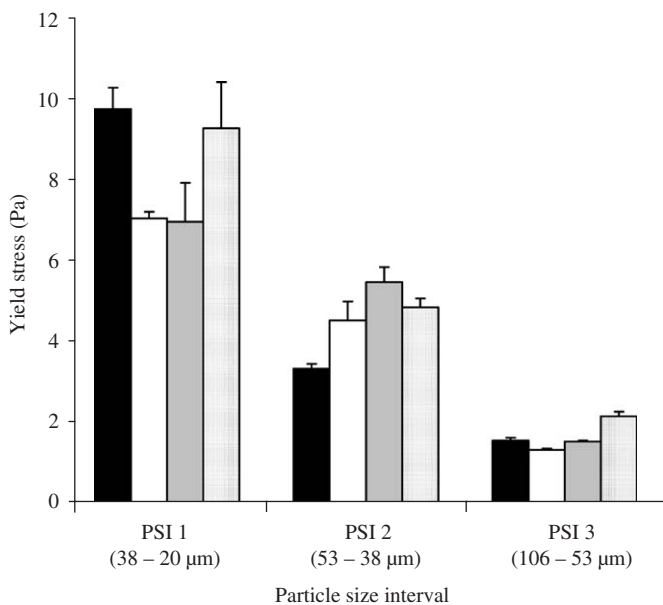


Fig. 3. Herschel–Bulkley plastic yield stress of chocolate samples manufactured with sucrose (■), isomalt (□), xylitol (▒), and maltitol (▨) in different particle size intervals (PSI). Error bars represent standard deviations.

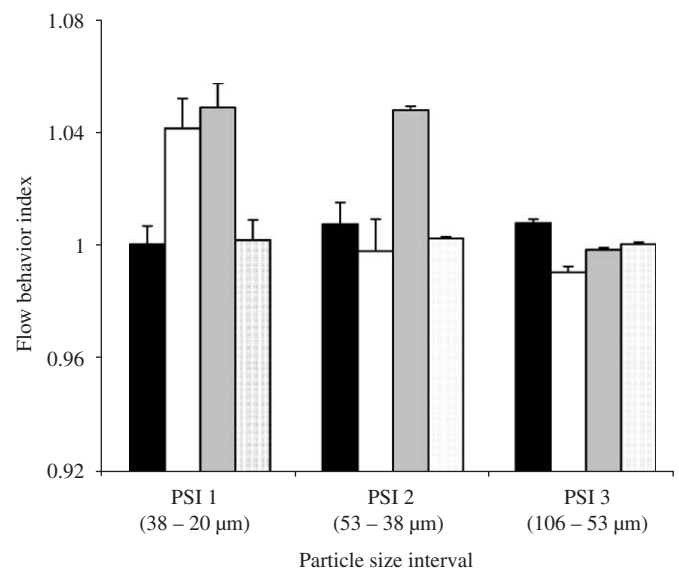


Fig. 4. Flow behavior index of chocolate samples manufactured with sucrose (■), isomalt (□), xylitol (▒), and maltitol (▨) in different particle size intervals (PSI). Error bars represent standard deviations.

Table 2

Effects of bulk sweeteners with different particle size interval (PSI) on apparent viscosity (Pa·s) of chocolate samples measured at 30 s^{-1} shear rate

Bulk sweetener	PSI 1 (20–38 μm)	PSI 2 (38–53 μm)	PSI 3 (53–106 μm)
Sucrose ^a	2.68 ^{ab}	1.60 ^a	0.93 ^a
Maltitol ^a	2.40 ^a	1.70 ^a	1.08 ^a
Isomalt ^b	3.40 ^b	1.98 ^{ab}	0.94 ^a
Xylitol ^{ab}	2.71 ^{ab}	2.18 ^b	0.98 ^a

Different letters within each column indicates significant difference ($P < 0.05$).

Isomalt, maltitol, and xylitol can be used in manufacturing of sucrose-free chocolates. These sweeteners have advantages and disadvantages compared to each other. For example, cooling effect observed in xylitol is absent in isomalt and maltitol (Kato & Moskowitz, 2001; Olinger & Pepper, 2001; Wijers & Sträter, 2001). However, sweetness of isomalt is only 40% of sucrose, so intense sweeteners must be used along with isomalt in chocolate (Wijers & Sträter, 2001). Lower conching temperature is suggested due to isomalt's high content of water of crystallization that result in agglomeration during conching (Olinger, 1994). On the other hand, sweetness of maltitol and xylitol are close to that of sucrose and no additional intense sweeteners may be needed (Kato & Moskowitz, 2001; Olinger & Pepper, 2001). Maltitol has also an advantage due to its low hygroscopic character allowing the refining of the chocolate under the same conditions as sucrose and conching at temperatures up to $80\text{ }^{\circ}\text{C}$ (Olinger, 1994). Consumers may reject chocolate containing xylitol due to xylitol's intense cooling effect in mouth, although this effect can be improved by addition of other bulk sweeteners (Olinger, 1994).

4. Conclusions

Herschel–Bulkley model was the best model that fit the rheological data of chocolate samples. Maltitol resulted in similar rheological properties of chocolate to sucrose, and thus it may be recommended as a good alternative to sucrose in chocolate formulations. Chocolate with isomalt resulted in higher plastic viscosity while xylitol resulted in higher flow behavior index. Addition of bulk sweeteners on volumetric basis (especially if density of the sweetener is different than that of sucrose) may reflect the effect of sweeteners on rheological properties more accurately. Plastic viscosity and yield value of chocolates increased with decreasing particle size of bulk sweeteners. Large particle size would result in better rheological properties for manufacturing process, but it may adversely affect sensory properties. Further experiments with better control of PSD of bulk sweeteners and chocolate mix, and varying conching conditions should be conducted to determine the

effects of bulk sweeteners on physical and sensory properties of chocolates.

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