4. SUGAR ALCOHOL IN CHOCOLATE MANUFACTURING

Molten chocolate is illustrated as a suspension of solid materials of sugar, cocoa, and milk powder suspended in a liquid matrix of cocoa butter. This suspension exhibits the non-Newtonian flow behavior and is measured rheologically. Control of rheology or flow during chocolate manufacturing is essential to achieve the desirable texture properties and overall higher quality products (Gotz et al., 2005).

The rheology of molten chocolate as a non-Newtonian fluid is measured as apparent/plastic viscosity and yield value. Plastic viscosity is defined as the required energy to keep the flow of a non-Newtonian liquid after motion has been initiated. It is associated with the ability of a fluid to fill rough surfaces, pumping and coating abilities, also to the sensory properties later on. Yield value is defined as the minimum required energy to start the flow of the matter. It is influenced by the particle size distribution (PSD), specific surface area (SSA), emulsifiers, moisture, and particle-particle interactions (Cikrikci et al., 2017).

The existing experiment studies of polyols as sugar substitutes in chocolate making available are mainly of maltitol, xylitol, and isomalt. In this chapter, the effect of these sugar alcohols in terms of particle size distribution and hygroscopicity (that leads to change in moisture content) to the viscosity and yield value of molten chocolate would be compared to that of control. As each of the experiments had significant difference in terms of the ingredient formulation and processing technique, the comparison of the data is conducted on each experiment between the sweeteners (not between experiments).

Generally, chocolate formulation consists of cocoa components and sweeteners, with tiny amounts of emulsifiers or flavors. The function of an emulsifier in chocolate formulation is to manage the flow properties of molten chocolate. Lecithin and PGPR (polyglycerolpolyricinoleate) are commonly used as emulsifiers in chocolate making (Christiansen, 2014; Atik et al., 2020).

4.1. The Effect of Particle Size to Chocolate Rheology

Particle size and flow properties of chocolate are crucial factors to determine its viscosity and final texture of the product (Shah et al., 2010). Particle size distribution and ingredient composition mainly influence chocolate rheological properties. The viscosity of chocolate suspension can be significantly adjusted by modifying the PSD while sustaining the same solid composition (Aidoo et al., 2013). The effect of maltitol, isomalt, and xylitol as sugar substitutes to the particle size and viscosity is demonstrated in the Table 7.

Table 7. The Effect of Sugar Substitutes to the Particle Size and Viscosity

Type of polyols	Content in formulation (%)	Testing Parameter					Reference
		Mean particle size D[4,3] (µm)	Largest particle size D_{90} (µm)	Specific surface area (cm^3/cm^2)	Yield stress (Pa)	Casson viscosity (Pa.s)	
Control	34	20.156	42.053	5672.4	5.22 – 5.94	2.54 – 2.68	Konar, (2013)
Maltitol	34	20.047	40.636	5515.6	1.60 - 2.98	1.68 – 3.86	
Isomalt	34	20.149	38.155	4945.4	0.27 – 0.33	3.41 – 4.17	
Control	33	27.30	-	-	3.82	1.72	Pirouzian et al., (2016)
Maltitol	33	27.70	-	-	4.14	1.62	
Xylitol	33	35.50	-	-	1.84	2.65	
Control	-	-	-	-	-	-	Oba et al., (2017)
Maltitol	47	19.67 - 21.00	39.03 - 41.67	5096.3 - 5339.4	2.59 - 4.40	1.10 - 1.47	
Isomalt	47	19.77 - 21.11	36.65 - 39.13	4569.3 - 4787.4	3.25 - 4.05	1.91 – 2.47	
Control	33	20.00	38.16	5716.3	0.67	1.60	Rad et al., (2019[a])
Maltitol	33	25.00	41.23	5216.2	2.61	4.91	
Isomalt	33	22.00	40.06	5523.7	2.71	2.78	
Xylitol	33	28.00	42.52	4968.4	6.94	6.11	

The milk chocolate formulations used in Konar (2013) are designed as follows: 24% cocoa butter, 12.45% cocoa mass, 20% whole powdered milk, 9% inulin, 34% sweetener (sucrose as control/maltitol/isomalt), 0.3% soy lecithin, 0.22% PGPR, 0.03% vanilla flavor. At the beginning, 20% of cocoa butter and dry solids were mixed and refined. The remaining fat, flavor, and emulsifiers (lecithin and PGPR) were then added and conched. Total conching time was 270 minutes for different conching temperatures of 50, 55, and 60^oC. In regards to mean particle size (hereinafter referred as MPS) and D_{90} value, maltitol and isomalt-containing formula have lower value if compared to control. At the same time, the trends of SSA are also similar. Control has higher SSA value if compared to maltitol and isomalt-containing formula. The yield stress of each formulation from the lowest to highest is isomalt, maltitol, and control. However, the order of viscosity from lowest is maltitol, control, and isomalt as the highest.

The milk chocolate formulations used in Pirouzian et al. (2016) are designed as follows: 6% cocoa powder, 34.5% cocoa butter substitute, 26% whole powdered milk, 33% sweetener (sucrose as control/maltitol/xylitol), 0.5% lecithin, and 0.01% vanilla flavor. All the ingredients are added and refined at 55^oC for 4 – 5 hour. Maltitol-containing formula generates similar MPS compared to control, whilst xylitol is significantly higher than the two. In terms of viscosity, the same phenomenon could be noted as well. Maltitol-containing formula has only a slight difference compared to control. On the other hand, the xylitol-containing formula is much higher.

The dark chocolate formulations used in Oba et al. (2017) are designed as follows: 17.2% cocoa butter, 35% cocoa mass, 47.5% sweetener (maltitol/isomalt), 0.3% soy lecithin, and 0.2% PGPR. At the beginning, cocoa mass and sweetener is dry-conched at 60^oC for 1 hour. The remaining ingredients are then added and conched altogether at 60^oC for 2 hours. Maltitol and isomalt-containing formulations generate similar MPS, D_{90}, SSA, yield value, and viscosity. MPS, yield value, and viscosity of isomalt-containing formulation are slightly higher if compared with isomalt. On the other hand, the D_{90} value and SSA are higher in the maltitol-containing formula.

The milk chocolate formulations used in Rad et al. (2019[a]) are designed as follows: 27.5% cocoa butter, 13% cocoa mass, 26% whole milk powder, 33% sweetener (sucrose as control/maltitol/isomalt/xylitol), 0.3% sunflower lecithin, 0.2% PGPR, and 0.01% ethyl vanillin. All of the ingredients are added and homogenized at 40°C for 3 hours. Control, maltitol, and isomalt generated similar rheology, whilst xylitol is the most different of all. MPS, D_{90}, yield value, and viscosity listed from the lowest to highest would be control, followed by isomalt, maltitol, and xylitol as the highest. In contrast, SSA if listed from highest to lowest would be as follows: control, isomalt, maltitol, xylitol.

As shown in Table 7, MPS of all formulations fell between the range of 19.67 – 28.00 µm, noted from maltitol-containing formula in Oba et al. (2017) and xylitol in Rad et al. (2019[a]), respectively. Konar (2013) and Obat et al. (2017) showed that isomalt had a higher MPS than maltitol, whilst the experiment by Rad et al. (2019[a]) stated otherwise. Fortunately, these numbers still fall within the favorable PSD range of less than 30 µm (Do et al., 2007; Beckett et al., 2017; McGill & Hartel, 2018). However, the largest particle size (D_{90}) ranged between 36.65 – 42.52 µm. According to Toker et al. (2016) & Do et al. (2007), D_{90} value plays a very critical role in coarseness and texture of the end-product. As D_{90} values of these samples are all above 30 µm, some coarseness/grittiness might be discovered during sensory testing.

In regards to specific surface area (SSA), it can be noticed that SSA and PSD are inversely related. As PSD lowers, the numbers of SSA increases. This phenomenon could be observed especially in the experiment by Rad et al. (2019[a]). According to Pirouzian et al. (2016), MPS and SSA are closely linked to flow properties. Smaller particle size increases the surface area of the dispersed particle, resulting in stronger particle-particle interactions, ensuring higher yield value and viscosity.

Hypothetically, smaller particle size means higher specific surface area that requires more fat to coat each of the particles, thus increasing its viscosity. Therefore, optimizing the particle size distribution (PSD) can significantly improve the viscosity (Do et al., 2007; Pirouzian et al., 2016). However, all of the illustrated data did not fit this model.

In the experiment by Konar (2013), it was found that maltitol and isomalt have lower value in all of the parameters, even though quite similar in all values compared to control. In the experiment by Pirouzian et al. (2016), the MPS and viscosity of maltitol is similar to control, whilst the xylitol has the highest and most contrasting value of all. In the experiment of Oba et al. (2017), it can be observed that maltitol and isomalt having similar numbers in all of the parameters. In the experiment by Rad et al. (2019[a]), it can be observed that as MPS and D_{90} increases, the SSA decreases, and the viscosity increases. According to Do et al. (2007), hypothetically, MPS and SSA are inversely related to each other. The smaller the particle size means the higher the surface area is. This resulted in more fat needed to coat each of the particles. With less free fat available in the compound, then viscosity is bound to increase as well.

The difference in all these results could be caused by the influence of many factors, such as the different formulation and processing technique of each experiment. Isomalt and maltitol-containing formula are observed to be quite similar in numbers compared to the control in all different experiments. They also give similar viscosity value to the sucrose. From a sensory point of view, it is important to keep the viscosity of molten chocolate moderate. Too high of viscosity resulted in pasty mouthfeel. Lower viscosity in chocolate is associated with faster melting properties that does not linger in the palate, which is good as for the sensory aspects. However, too low of viscosity could also result in the rise of problems during the handling and moulding process later on (Do et al., 2007; Afoakwa, 2016; Beckett et al., 2017).

4.2. The Effect of Hygroscopicity & Moisture to Chocolate Rheology

Hygroscopicity is defined as the ability of an ingredient to absorb moisture from its surroundings. The hygroscopicity of sugar alcohols are demonstrated in Table 8. The data on this table is acquired by translating qualitative data into rating sequence.

Table 8. Hygroscopicity of Sugar Alcohol

Type of polyols	Hygroscopicity		
	Aidoo et al., (2013)	Afoakwa, (2016)	Selvasekaran & Chidambaram, (2021)
Maltitol	+	+	+
Isomalt	-	-	-
Xylitol	++	++	++

++ : highly hygroscopic
+ : less hygroscopic
- : very low / non hygroscopic

Table 8 shows that by the order of hygroscopicity, isomalt is the very least hygroscopic, followed by maltitol, and xylitol as the most hygroscopic polyols out of the three. The effect of sugar substitutes on the moisture and viscosity is demonstrated in Table 9.

Table 9. The Effect of Moisture Content to Chocolate Rheology

Type of polyols	Content in formulation (%)	Testing Parameter		Reference
		Moisture content (g/100g)	Casson viscosity (Pa.s)	
Control	34	-	2.54 - 2.68	Konar, (2013)
Maltitol	34	-	1.68 - 3.86	
Isomalt	34	-	3.41 - 4.17	
Control	33	0.92	1.72	Pirouzian et al., (2016)
Maltitol	33	0.88	1.62	
Xylitol	33	1.17	2.65	
Control	33	1.02	1.60	Rad et al., (2019[a])
Maltitol	33	1.24	4.91	
Isomalt	33	1.11	2.78	
Xylitol	33	1.37	6.11	
Control	33	0.93	1.54 - 1.67	Rad et al., (2019[b])
Maltitol	33	1.01	5.96 - 6.15	
Isomalt	33	1.10	2.59 - 2.84	
Xylitol	33	1.30	7.74 - 7.92	

The ingredient formulation and processing technique of the experiment by Konar (2013), Pirouzian et al. (2016), and Rad et al. (2019[a]) had already been disclosed in the previous subchapter.

The milk chocolate formulations used in Rad et al. (2019[b]) are designed as follows: 13% cocoa mass, 27.5% cocoa butter, 26% whole powdered milk, 33% sweetener (sucrose as control/maltitol/isomalt/xylitol), 0.3% soy lecithin, 0.2% PGPR, 0.01%

vanilla flavor. At the beginning, one-third of cocoa butter is melted and milled. Then another one-third of the cocoa butter is pre-melted altogether with the cocoa and sugar components, added to the first compound and milled at 40°C for 1 hour. Lecithin, PGPR, and the remaining cocoa butter then pre-melted and put into the compound as well. The refining time took 3 hours in total.

Hygroscopicity of sugar alcohol will affect the moisture content of the suspension, hence also affects the viscosity. Water of crystallization present in the ingredients are released during the conching process. However, hygroscopic ingredients naturally reabsorbed these water particles again, maintaining the moisture content in the compound relatively high. As the presence of excess moisture lowers the availability of free fat that is needed to coat the particle's surface, then the viscosity also increases (Pirouzian et al., 2017; Villa et al., 2019). In the experiment by Konar (2013), it was found that between the control, maltitol, and isomalt, isomalt-containing formula generated the highest viscosity compared to control and maltitol. In this study, maltitol has lower viscosity even when compared to control.

The experiment by Pirouzian et al. (2016) showed similar moisture content and viscosity of maltitol-containing formulation compared to control. The numbers are slightly lower than control, whilst xylitol is the highest of all. In the experiment by Rad et al. (2019[a]) and Rad et al. (2019[b]), the value of moisture content and viscosity accounted from lowest to highest are as follows: control, isomalt, maltitol, and xylitol. All the observed data ranged between 0.88–1.24 g/100 g, which still falls under the acceptable limit of 0.5–1.5% (Pirouzian et al., 2016).

Different hygroscopic behavior of the polyols is one of the major reasons for the difference in viscosity (Pirouzian et al., 2017). The high moisture content and viscosity of xylitol-containing formulas are correlated with the high hygroscopic properties of xylitol. Hydroxyl groups in xylitol preserve moisture in the compound, and absorb some of the moisture released by other ingredients as well, thus maintaining the moisture level relatively high (Pirouzian et al., 2016). Simultaneously, the difference of the ingredients' particle density might also be the cause. Maltitol has a particle density of

1.63 g/cm^3 and xylitol 1.52 g/cm^3, respectively. As xylitol has higher solid volume due to lower particle density, the plastic viscosity also increases (Pirouzian et al., 2017).

From the very same experiment by Pirouzian et al. (2017), it was concluded that formulations containing high components of xylitol demonstrated undesirable rheological properties as it has high moisture content, viscosity, and flow index. At the same time, the addition of xylitol in chocolate formulation is recommended to be not more than 12.1578% as rheological properties declined after this point. On the other hand, formulations containing high concentration of maltitol showed similar rheological properties compared to control. The best combination of maltitol and xylitol used in chocolate formulation are 87.8% and 12.2% respectively. This combination of sweeteners is found to be rheologically similar to control.

4.3. Other Factors Influencing Chocolate Rheology

In the previous subchapter, the effect of PSD and hygroscopicity/moisture of sugar alcohols to chocolate rheology had been discussed. However, there are also many more factors that had to be taken into account while determining chocolate rheology. Fat content, the addition of emulsifiers, and conching time and temperature are also factors that determine chocolate rheology (Pirouzian et al., 2017).

In the experiment by Afoakwa et al. (2008[b]), it was found that fat content had a direct influence on PSD. Increase fat content from 25% to 35% resulted to SSA reduction and increase in all other PSD parameters. Simultaneously, reduction in sugar component with increase in fat content during the refining process influences overall PSD. Fat component also plays an important role in melting characteristics. The characteristics of the fat phase facilitated the perceived taste, flavor, and texture during mastication.

In the study by Atik et al. (2020), it was found that yield stress and viscosity is significantly affected by lecithin and PGPR ratio. Higher content of lecithin induces the formation of β_V polymorph that is desirable in chocolate manufacturing. On the other hand, higher content of PGPR increases the end-product fracturability and hardness. Simultaneously, addition of fat and lecithin during conching reduced interaction between particles, thus causing significant decrease in rheological and textural properties (Glicerina et al., 2013).

Conching is generally a time-consuming process in the chocolate making. However this process is very important as moisture reduction and desirable flavors of chocolate were developed by this process. Conching applied continuous particle size reduction to the compound. At the same time, this process helps to cover the new surfaces with fat, so that desirable flow properties are obtained. Conching for dark chocolate formulation is usually carried out at 70-80^{o}C, and less than 50^{o}C for milk chocolate formulation (Saputro et al., 2016; Beckett et al., 2017). The time used for the conching process may vary according to the experimental condition. Most importantly, sufficient time must be allowed to reach the viscosity equilibrium of the molten chocolate.

Imperfect conching process may resulted in poor fat and solid particles distribution that leads to nonuniform chocolate complex, ensuing the migration of fat and sugar crystals to the surface, unremoved acidic flavor components, and the lack of desirable flavor of chocolate (Aidoo et al., 2014).