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Microstructural and rheological characteristics of dark, milk and white chocolate: a comparative study

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Abstract

Three different chocolate types: dark, milk and white were characterized and compared for the microstructural and rheological (fundamental and empirical) characteristics. A light microscope coupled to an image analysis system was employed in order to evaluate the particle size, the network structure and the distance between particles of each matrix. Rheological parameters (yield stress, viscosity, thixotropy) were evaluated by using a stress–strain rheometer, while mechanical properties (consistency and cohesiveness) were analyzed using a texture analyzer. The *Power law*, *Casson* and *Windhab* rheological models were used in order to better explain the rheological behaviour of chocolate samples.

Results showed that white chocolate, with the highest amount of fat in formulation, had the smallest sized particles, the less aggregate structure and the lowest yield stress, viscosity and thixotropic values. Dark chocolate samples instead presented the highest aggregate structure, with less void spaces between particles that involved the highest rheological parameter values. Milk chocolate matrix exhibited intermediate microstructural and rheological characteristics compared to dark and white chocolate ones.

Keywords: chocolate, microstructure, rheology, modelling

1. Introduction

Chocolate is a dispersion of around 70% of fine particles such as cocoa powder, sugar and milk solids in a continuous phase made up of fats, generally cocoa butter and milk fat, depending on the specific formulation (Fernandez et al., 2013). There are three main types of chocolate: dark, milk and white, with notable differences between them (Awad and Marangoni, 2006; Afoakwa et al., 2008; Beckett, 2010). Dark chocolate formulation consists mainly of cocoa liquor, sugar and cocoa butter. Milk chocolate is made up of sugar, cocoa butter, milk solids and cocoa liquor; white chocolate is made up of sugar, cocoa butter and milk solids (Rousseau, 2007). Chocolate can also include emulsifiers such as lecithin and polyglicerol polyricinoleate (PGPR) as well as salt, flavourings or spices. The directives 2000/36/EC, relating to cocoa and chocolate products intended for human consumption define “Dark chocolate”, as the product obtained from cocoa products and sugars, containing not less than 35 % total dry cocoa solids, including not less than 18 % cocoa butter and not less than 14 % of dry non-fat cocoa solids. “Milk chocolate” is defined as the product obtained from cocoa products, sugar and milk or milk products, with not less than 25 % total dry cocoa solids; not less than 14 % dry milk solids (obtained by partly or totally dehydrated full cream milk, semi- or full-skimmed milk, cream, or from partly or completely dehydrated cream, butter or milk fat); not less than 2.5 % dry non-fat cocoa solids; not less than 3.5 % milk fat and not less than 25 % total fat (cocoa butter and milk fat). By the same directive “White chocolate” is defined as the product obtained from cocoa butter, milk or milk products and sugar, containing not less than 20 % cocoa butter and not less than 14 % dry milk solids (obtained by partly or totally dehydrated full cream milk; semi- or full-skimmed milk; cream, or from partly or completely dehydrated cream, butter or milk fat) of which not less than 3.5 % of milk fat (European Council, 2000). During processing, the chocolate composition, in terms of type and amount of each ingredient, plays an important role in obtaining an high quality product (Fang and Zhang, 1997; Granger, et al., 2005). In particular, flow properties of cocoa dispersions, a concentrated lipophilic suspension of solid particles dispersed in a continuous fluid, are strongly influenced by their formulations, in terms of solid fraction, fat composition and amount (Attaie et al., 2003; Franke and Heinzelmann, 2008). Sugar particles are very important in chocolate manufacture, of which crystals of a particular size and shape are required. Moreover, if sugar is present in an amorphous state (due to a bad crystallization or to the presence of water) it tends to trap fat, because of its irregular structure (Stortz and Marangoni, 2013), thus increasing the product viscosity. Milk powders (present in milk and white chocolate), with their own physical characteristics and the inner presence of milk fat and lactose, may have also a significant impact on the chocolate processing conditions and on the physical, rheological and organoleptic properties of the final product (Liang and Hartel, 2004). Emulsifiers, if present in low amount of around 0.3-0.5%, can contribute to reduce particle interactions and therefore the viscosity in the chocolate products (Johansoon and Bergensthal, 1992). As known by literature (Afoakwa et al., 2009; Beckett, 2010; Glicerina et al., 2015a), the structure of chocolate arises both from the various components used in the formulation and from the manufacturing process during the mixing, pre-refining, refining, conching and tempering steps, that strongly determine the different interactions that take place among ingredients. The relationships between all the ingredients present in cocoa dispersions and the continuous phase, influencing the microstructural properties of the final matrix, affect strongly its rheological and textural characteristics in terms of yield stress, apparent viscosity, thixotropy, hardness and consistency (Vavreck, 2004; Schantz and Rohm, 2005). For this reason, microstructure can be considered a fundamental quality parameter for chocolate products. Some authors, in fact, (Braipson-Danthine and Deroanna, 2004; Aguilera, 2005; Varela et al., 2007; Afoakwa et al., 2008) noted that improvements on the quality of existing foods, among which chocolate, and new product formulations require interventions at a microscopic level.

In the chocolate manufacture, tempering is an essential step, influencing important product final properties such as colour and hardness and its shelf-life; for this reason the control of process conditions related to this step is of crucial importance for the product final quality and stability (Herrera and Hartel, 2000; Toro-Vazquez et al., 2004; Altimiras, Pyle and Bouchon, 2007; Pérez-

Martínez et al., 2007 and Debaste et al., 2008). Several studies (Gosh et al., 2002; Lee et al., 2002; Afoakwa et al., 2008; Beckett, 2010; Svanberg et al., 2011) were performed in order to evaluate the relationships between tempering step and dark chocolate microstructure, appearance, hardness and stickiness. Results showed that a more dense chocolate structure, obtained through an optimal tempering processing, improves the product quality, giving arise to a less fat bloom phenomena during storage. Moreover, an optimal tempering, evaluated according with Nelson (1999) and Afoakwa et al., (2009) by using a computerized tempermeter, gave rise to a chocolate with less hardness and higher values of lightness and gloss, that are considered positive attributes, very appreciated from consumers (Kulozik et al., 2003).

To our knowledge, no comparative studies between the main types of chocolate (dark, milk and white) are present in literature. The aim of this research was to evaluate the influence of different formulations on the microstructural, rheological and textural properties of dark, milk and white chocolate types obtained in the same industrial plant. Different rheological models were applied in order to study the rheological behaviour of the chocolate samples.

2. Materials and methods

2.1 Materials

Dark (D), milk (M) and white (W) chocolate samples were produced in an Italian confectionery factory by using an industrial plant (Buhler, Malmo, Sweden) equipped to produce 6000 kg of chocolate at every production cycle. All samples were obtained after tempering step, at the end of three different processing cycles. Their formulations, that are the standard recipes normally used by chocolate factories are reported in Table 1. After processing chocolate samples were stored in plastic bucket (1 kg capacity) at room temperature until the analytical determinations. Before performing each analysis the samples were melted in a microwave at 150 W for 10 min (Stortz and Marangoni, 2013; Glicerina, et al., 2015a).

2.2 Methods

2.2.1 Microstructural analysis

Ten micrographs from each chocolate sample were obtained by using a light microscope (Olympus Optical, Tokyo, Japan) at 10× of magnification. One drop of each sample dispersion (previously diluted with hexane) was placed on a glass slide and carefully covered with a glass slip, placed parallel to the plane of the slide and centred to ensure a uniform sample thickness. Micrographs were captured using a digital camera (Model 2.1 Rev 1; Polaroid Corporation, NY, USA) (Glicerina et al., 2015b). The acquired images were subsequently elaborated using the software Image Pro-plus 6.0 (Media Cybernetics Inc., Bethesda, USA). Particles size were measured according with Glicerina et al., (2013), by evaluating the Feret diameter, defined as the distance between two tangent lines to the two opposite sides of the particles (Allen, 1997). The distance between particles was evaluated generating a Euclidian distance map (EDM). The map indicates, for each pixel in the image (black points) of the originally binary picture, the shortest distance between them (Danielsson, 1990; Bayod, 2008). The distance between black points (particles) was expressed as grey values. On the other hand, the white points represented the empty space. For this reason, applying an EDM to the original image it is possible to obtain information about the minimum distance between particles and about the amount and distribution of void spaces (Krislock and Wolkowicz, 2012).

2.2.2 Fundamental rheological analysis

Rheological measurements were carried out at 40 °C using a controlled strain–stress rheometer (MCR 300, Physica/Anton Paar, Ostfildern, Germany) equipped with coaxial cylinders. In steady state conditions, after a pre-shearing of 500 s at 2 s^{-1}, apparent viscosity was measured as a function of increasing shear rate from 2 to 50 s^{-1} (ramp up) within 180 s, then of decreasing from 50 to 2 s (ramp down); within each ramp 18 measurements were taken (ICA, 2000).

In order to study in depth the results of rheological measurements, the obtained flow curves were fitted by using some specific models, normally employed for concentrated suspensions.

The *Casson* model is generally the most used to study the rheological behaviour of chocolate dispersions, however sometimes it does not reflect in accurate way the physical and rheological properties of chocolate, especially for low viscosity values. For this reason, further models were developed such as the *Windhab* model that is recommended for shear rate in the range between 2 and 50 s^{-1} (Ludger and Teixtera, 2007). Another model used for concentrated suspension, especially in the case of high viscosity, is the *Ostwald de Waele* (Bouzas and Brown, 1995).

In preliminary trials the three different models were applied on flow curves obtained from each sample. The applied model for each chocolate type was chosen on the basis of the best goodness of fitting obtained. The model of *Ostwald de Waele*, commonly referred to as the *Power Law* model (Holdsworth, 1993; Hugelsholfer, 2000) is described by the following equation:

$$\tau = K^* \dot{\gamma}^{n} \qquad (1)$$

where τ is the shear stress (Pa), K is consistency index (Pa s^n), $\dot{\gamma}$ is the shear rate (1/s) and n is the dimensionless flow behaviour index.

According to Chevalley (1991), curve points of the *Casson* rheological model represent a better fitting to chocolate data if the exponent is taken as 0.6 rather than 0.5. This model is described by the following equation:

$$\tau^{0.6} = \tau_0^{0.6} + (n_{PL}\ \dot{\gamma})^{0.6} \qquad (2)$$

where τ_0 is the yield stress at the zero point and η_{PL} is the so-called plastic viscosity.

The *Windhab* model, recommended (Ludger and Teixeira, 2007) for shear rates in the range between 2 and 50 s^{-1} at 40 °C, was used to describe the flow behaviour of W chocolate sample. This model is described by the following equation:

$$\tau = \tau_0 + \eta_\infty * \dot{\gamma} + (\tau_1 - \tau_0)\ (1 - e - \dot{\gamma}/\dot{\gamma}^*) \qquad (3)$$

where τ is the shear stress, τ_0 is the shear stress at the zero point, η_∞ is the infinite viscosity, $\dot{\gamma}$ is the shear rate, τ_1 is the hypothetical yield stress and $\dot{\gamma}*$ represents the shear rate corresponding to the infinite viscosity.

By using both the *Casson* and *Windhab* models it is possible to obtain at the same way and immediately the theoretical viscosity values (η). The *Casson* and Infinity viscosities are comparable because the same basic parameters are involved in these models. As known by literature (Rao, 2007) the *Casson* plastic viscosity can be used as the infinite shear viscosity η_∞ of dispersions by considering the limiting viscosity at infinite shear rate.

From the *Power Law* model instead the viscosity values are provided indirectly, for this reason further processing is necessary in order to obtain the theoretical viscosity value. From *Power Law* model apparent viscosity, according to Ludger and Teixteira (2007), was given, by:

$$\eta = \text{shear stress/shear rate} = \eta = \frac{\tau}{\gamma} \qquad (4)$$

So by replacing $K * \dot{\gamma}^n$ (equation 1) into the equation (4) it is possible to obtain the following equation:

$$\eta = \frac{\tau}{\gamma} = \frac{\kappa * \gamma^n}{\gamma} = K * \dot{\gamma}^{n-1} \qquad (5)$$

From the rheological curves of the chocolate samples, the thixotropy values were also obtained. During shearing, the continuous decrease in apparent viscosity and its subsequently recovery, when flow is discontinuous, create an hysteresis loop (Chabbra, 2006). In this research, thixotropy was evaluated according to Servais et al., (2004), from the difference between viscosity measured at 40 s^{-1} during ramp up (from 2 to 50 s^{-1}) and ramp down (from 50 to 2 s^{-1}), multiplied to 40^2. The thixotropy data obtained in this way, in accordance with the method proposed by Servais et al., (2004) and Cheng (2003), very accurately represent the values of the hysteresis area underlying the two curves of flow during the increase and decrease of the shear rate.

2.2.3 Empirical rheological analysis

A TA.HDi 500 Texture Analyzer (Stable Micro System Vienna Court, England) was employed to investigate the textural properties of the three different chocolate types. All measurements were performed using a back extrusion test. Samples were analyzed at room temperature, after melting as explained in the section 2.1. The test was carried out in a back extrusion container (50 mm in diameter), filled to 75% with the sample, using a disk (35 mm) attached to a extension bar, with a load cell of 25 kg. The test parameters used were: a pre-test speed of 1 mm s^{-1}, a test speed of 1 mm s^{-1}, a post-test speed of 1 mm s^{-1} and a distance of 30 mm. The following textural properties of sample structure were obtained: consistency (N s), the positive area up to the maximum force during probe descent and cohesiveness (N), the peak maximum of the negative region during probe return (Glicerina et al., 2013)

2.3 Statistical analysis

The rheological curve fitting was obtained by using the software Rheoplus (v.3.0, Anton Paar, Ostfildern, Germany) based on the ordinary least squares statistical method. The results are reported as the average of at least three determinations for each sample. Analyses of variance (ANOVA) and the test of mean comparison, according to Fisher’s least significant difference (LSD) were applied on all obtained data. Level of significance was $P \leq 0.05$.

The statistical software used was STATISTICA, version 8.0 (StatSoft, Tulsa, Okhlaoma).

3. Result and discussions

3.1 Microstructural properties

In order to study the microstructural properties of chocolate matrices a light microscope was used, since this kind of instrument makes an easy differentiation between particles and void spaces, in relation to the different light diffusion (Kalab et al., 1996). In a conventional bright-field microscope, in fact, illumination is transmitted sequentially through a condenser (the specimen and the objective). Previous researchers (Do et al., 2007; Afoakwa et al., 2008; Afoakwa et al., 2009; Glicerina et al., 2015b) demonstrated the usefulness of this technique to study the particle size, the presence of network and the state of aggregation in dark and white chocolate matrices. In Figure 1 micrographs of D, M and W chocolate samples are shown. On the obtained micrographs the characteristics of particle networks and their distribution in the matrices were evaluated. In order to better highlight the state of aggregation of the different matrices and the presence of particles and empty spaces filled with fat, Euclidean distance maps (EDM) were obtained (Figure 2). By using an EDM it was possible to underline the distribution of particles (black areas) and void spaces (white areas), surrounded with fat, in the different matrices and to evaluate the minimum distance between particles and therefore their state of aggregation related to interactions. In Table 2 the particle Feret diameters and the minimum distance between particles of D, M and W chocolate samples are reported. From samples micrographs (Figure 1) and from data reported in Table 2 it is possible to notice how dark and milk chocolate samples (D and M) have greater particles size compared to white chocolate one (W). As known by literature (Sokmen and Gunes, 2006; Beckett, 2009) specific surface area is inversely correlated with particle size and these parameters in chocolate dispersions are strictly related to the amount of fat content in the sample, necessary to obtain desirable flow properties. So usually, smaller are the particles, bigger will be the specific surface area; this implies the presence of more contact points and more interaction between particles (Chevalley, 1991). For these reasons only considering particle size results we would expect the highest rheological values (in terms of yield stress, viscosity and thixotropy) in white chocolate sample; however microstructural and hence rheological properties of chocolate samples are affected not only by the particle size, but also by other factors, including the amount and distribution of fat, presence of emulsifiers and solid particles, and particles shape. Therefore, in the case of the three different formulations, the quality and quantity of ingredients become very important for the products final characteristics.

In sample W, made up from smallest particles size, a less dense crystalline network and reduced particle-particle interactions are present, parallel to the presence of highest distance between particles filled with fat. According with the studies of Afoakwa et al., (2008), high fat content in a suspension tends to wet the matrix, opening up the fat phase, that fill the voids within the crystal network reducing resistance to flow. Sample M, even if had particles with diameters (Table 2) not statistically different from sample D, showed a less aggregate structure, with more open spaces (filled with fats) than sample D (Figure2), that had the lowest minimum distance value between particles. Milk chocolate sample showed values of this parameter intermediate and significantly different from D and W (Table 2). The fat in the voids derives both from the cocoa butter, present in all chocolate types, and from milk fat presents in milk powders in M and W samples. Moreover, in both M and W chocolate samples, lactose (the major carbohydrate of whole milk powders) if present in crystalline forms (Aguilar et al., 1994; Aguilar and Zieglier, 1995; Koc et al., 2003; Lonchampt and Hartel, 2004), contributes to make available a part of milk fat, normally entrapped in milk powders, so increasing its amount in the final product. The fat quantity of sample M and W was quite similar (Table 1), however, the more aggregated microstructure of M sample compared to W (Figure 1, Table 2) is probably due to the presence of cocoa particles between sugar ones and probably the absence of lecithin in M sample formulation, that usually migrates to sugar/fat interfaces and coats sugar crystals, promoting the dispersion of the latter (Johansoon and Bergensthal, 1992; Vernier, 1998).

As shown by micrographs (Figure 1) it is possible to notice how D and M samples present more evidenced particles with an irregular and flaky shaped than W; sugar particles are mainly evidenced in M sample micrograph.

3.2 Fundamental rheological properties

In Figure 3 the flow curves of dark, milk and white chocolate samples are reported. As shown, viscosity values decreased with the increase of the shear rate in all samples, underlining the presence of a shear thinning behaviour (Izidoro et al., 2008). All chocolate samples exhibited a 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) typical of a non-newtonian liquid (Ziegler and Hogg, 1999; Afoakwa et al., 2008; Beckett, 2010).

In particular, sample D showed the highest apparent viscosity (Figure 3) with an initial value of around 7 Pa s, followed by sample M with initial apparent viscosity values of around 5 Pa s; sample W had the lowest apparent viscosity value. In order to better highlight differences between the three chocolate samples, yield stress and plastic viscosity were obtained from flow curves, respectively at 5 s^{-1} and 30 s^{-1} of shear rate, according with ICA (2000) and Servais et al., (2004). Obtained values are reported in Table 3. Dark chocolate (D) showed the significantly highest yield stress and viscosity values ($p<0.05$) compared to M and W samples. This means that the amount of energy needed to start flow was the highest in the former. These results are in agreement with those obtained from the microstructural analysis, sample D in fact showed a more aggregate matrix than the others (Figure 2), having the lowest amount of cocoa butter in formulation (Table 1). Sample M had intermediate values of yield stress and viscosity, between those of D and W. M chocolate had in formulation more fat than D; the lubricating effect of fat (Beckett, 2010) is the cause of its lower rheological parameters. The lowest viscosity and yield stress values of sample W can be attributed both to the highest quantity of fat (from cocoa butter and milk fat) and to the presence of lecithin in its formulation, that, as known by literature (Vernier, 1998; Afoakwa et al., 2008; Beckett, 2010), contributes to reduce particle-particles interaction. Moreover, as mentioned before in the microstructural section, the presence of crystalline lactose in M and W samples must be considered as a factor that could have influenced their lower viscosity values, promoting the release of entrapped milk-fat. Rheological behaviour of chocolate flow curves was further studied by applying different rheological models. In particular, D sample flow curves were well fitted by applying the *Ostwald de Waele* model (Rao, 2007); M chocolate curves by using the *Casson* model (ICA, 1973), modified by Chevalley (1991) and W chocolate curves by using the *Windhab* model (IOCCC, 2000). The fitted constants of each rheological model are reported in Table 4.

Very high coefficients of determinations ($R^2 = 0.99$) were obtained in all cases, demonstrating that the chosen models for each chocolate sample fit well the related data. In Table 5, the obtained apparent viscosity values for each sample are reported. Also in this case, and in agreement with the previous reported results, D chocolate sample had the highest apparent viscosity value (9.62 Pa s). Chevalley (1991) and Afoakwa, Paterson, Fowler & Vieira (2007) reported that higher viscosity values are related with more aggregate matrices with less voids space between particles, probably due to a low amount of fat that promotes particle-particle interactions.

The highest value of thixotropy showed by sample D (Figure 4) demonstrates further the more aggregate structure of this kind of chocolate compared to the M and W ones. High thixotropic values in fact are due to the high damage of the structure, highlighted immediately after the stress removal, which can be attributed (Aguilera and Stanley, 1999; Afoakwa et al., 2008) to a high level of matrix aggregation, which undergoes to an irreversible break. Sample M showed an intermediate thixotropic value between D and W ones. As expected, W chocolate, having the highest amount of fat and hence a more fluid matrix and a less aggregate structure, showed the less intense thixotropic behaviour, being able to recovery most part of its initial structure.

3.3 Empirical properties

The textural parameters of consistency and cohesiveness were chosen being the most related to the sensory mechanical properties of chocolate during consumption (Beckett, 2010). The consistency and cohesiveness values of chocolate samples, obtained by using a *back extrusion* test, are reported in Table 6. D chocolate sample presented the highest and significantly different values of both textural parameters; these results further confirm that this sample was characterized by a very aggregate and dense structure, that makes more resistance to the probe return during the back extrusion test. M and W chocolate samples showed the lowest consistency and cohesiveness values, underling the presence of a structure with weaker interactions between particles.

4. Conclusions

The obtained results showed how different ingredients in chocolate recipes affect in strong way microstructural and rheological properties of the final product. In particular, different amount of fat involves changes in the particle-particle interaction, in terms of distance between particles and their distribution, as well as, the solid fat and non-fat particles. The presence of lecithin and crystalline lactose, can also influence the final product properties.

Lower cocoa butter concentrations, parallel to high fraction of solid particles, such as in the dark chocolate formulation, promote particle-particle interactions, involving higher values of rheological characteristics. On the other hand, higher cocoa butter amount, even if in presence of higher amount of non fat particles (sugar), together with the presence of milk fat (from milk powders), reduce resistance to flow. This effect was shown in white chocolate sample, made up of smallest particles having the highest distance between them. Moreover, the synergistic effect of the lecithin, that promotes the reduction of particles inter-forces, involves a further reduction in the yield stress, viscosity and thixotropic values.

The influence of each single ingredient, in terms of type and amount, must be taken into account in order to improve or modify the micro- and macrostructure characteristics and hence the final quality of chocolate products.

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Table 1. Dark, milk and white chocolate formulations.

Ingredient	Dark chocolate (%)	Milk chocolate (%)	White chocolate (%)
Sugar	39.52	47.00	47.00
Cocoa liquor	53.00	7.00	–
Cocoa butter (further added)	7.00	25.00	31.00
Full cream milk powder	–	21.00	21.50
Lecithin	0.30	–	0.49
Sodium carbonate	0.15	–	–
Vanilla extract	0.03	–	0.01

Table 2. Particles dimension (Feret diameter) and minimum distance between particles of dark (D), milk (M) and white (W) chocolate samples.

Samples	Feret diameter (µm)	Minimum distance between particles (µm)
D	20.16 ± 2.17^{a}	12.64 ± 2.67^{c}
M	19.30 ± 2.32^{a}	16.25 ± 1.92^{b}
W	14.27± 2.29^{b}	23.46± 2.34^{a}

Values (mean±standard deviation) in the same column followed by different letters differ significantly at $p<0.05$ level

Table 3. Yield stress and viscosity values, calculated respectively at 5s^{-1} and 30 s^{-1} of shear rates, of dark (D), milk (M) and white (W) chocolate samples**.**

Samples	**Yield stress** **(Pa s)**	**Apparent Viscosity** **(Pa s)**
D	33.07±0.15^{a}	6.87±0.03^{a}
M	14.56±1.78^{b}	1.32±0.12^{b}
W	11.50±0.14^{c}	0.98±0.02^{c}

Values (mean±standard deviation) in the same column followed by different letters differ significantly at $p<0.05$ level

Table 4. Rheological constants of dark, milk and white chocolate samples obtained respectively from Power law, Casson and Windhab models.

Rheological models	Dark chocolate (D)	Milk chocolate (M)	White chocolate (W)
Power Law			
Consistency Index (k), Pa s^n	4.78±0.22		
Flow behaviour Index (n)	0.45±0.04		
**Determination coefficient* (R^2)	0.99		
Casson			
Yield stress (τ_0), *Pa*		3.68±0.15	
Plastic viscosity (η_{PL}), *Pa s*		0.68±0.04	
**Determination coefficient* (R^2)		0.99	
Windhab			
Yield stress at zero point (τ_0), *Pa*			0.00±0.00
Infinite viscosity (η_∞), *Pa s*			0.59±0.07
Hypotetical yield stress (τ_1), *Pa*			8.32±0.18
Shear rate of infinity viscosity (γ), s^{-1}			1.04±0.01
**Determination coefficient* (R^2)			0.99

$^*p \leq 0.01$

Values are means of three replicate experiments ± standard error (SE)

Table 5. Apparent viscosity of dark (D), milk (M) and white (W) chocolate samples, evaluated by applying respectively *Power Law*, *Casson* and *Windhab* models.

Samples	**Viscosity** **(Pa s)**
D	9.62±0.38^{a}
M	1.55±0.33^{b}
W	0.59 ±0.23^{c}

Values (mean±standard deviation) in the same column followed by different letters differ significantly at $p<0.05$ level

Table 6. Consistency and cohesiveness index of dark (D), milk (M) and white (W) chocolate samples.

Samples	Consistency (N s)	Cohesiveness (N)
D	110.14±13.96^a	16.07±1.25^a
M	1.22±0.16^b	3.16±0.53^b
W	0.87±0.06^b	1.83±0.37^b

Values (mean±standard deviation) in the same column followed by different letters differ significantly at $p<0.05$ level

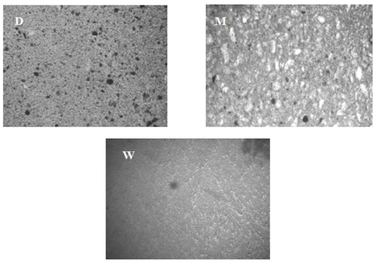
Figure Captions

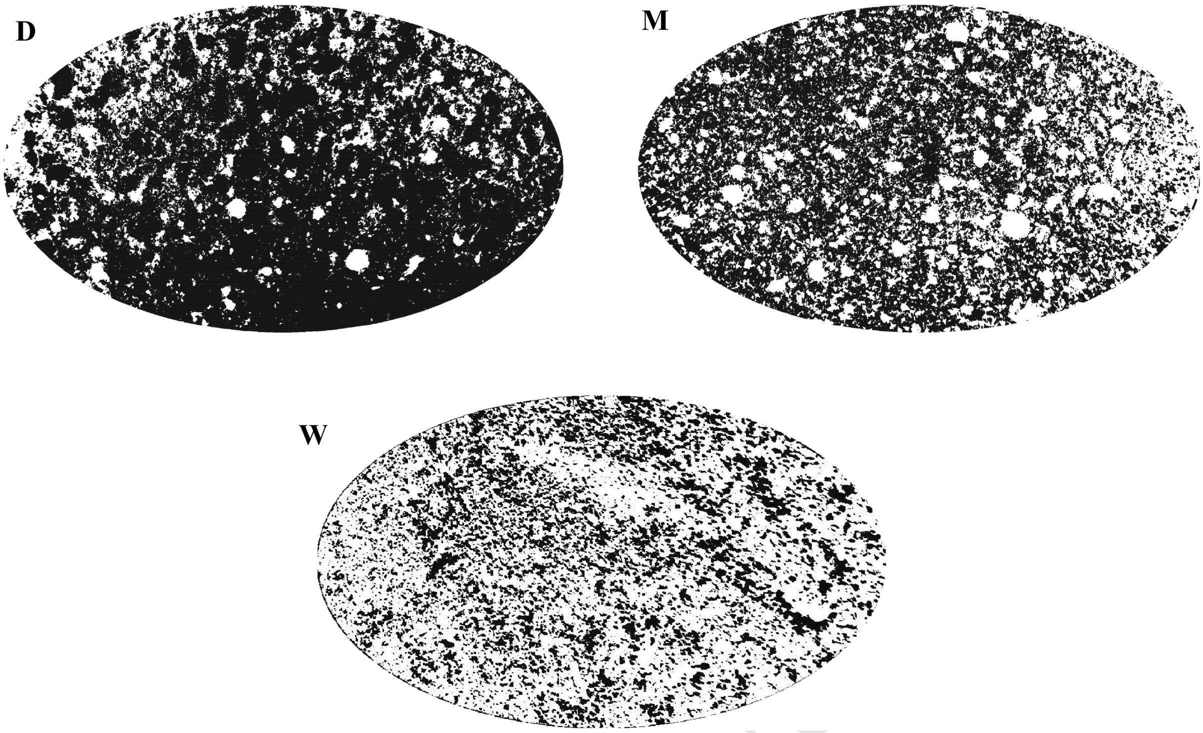
Fig. 1 Micrographs of chocolate samples: dark (D), milk (M) and white (W).

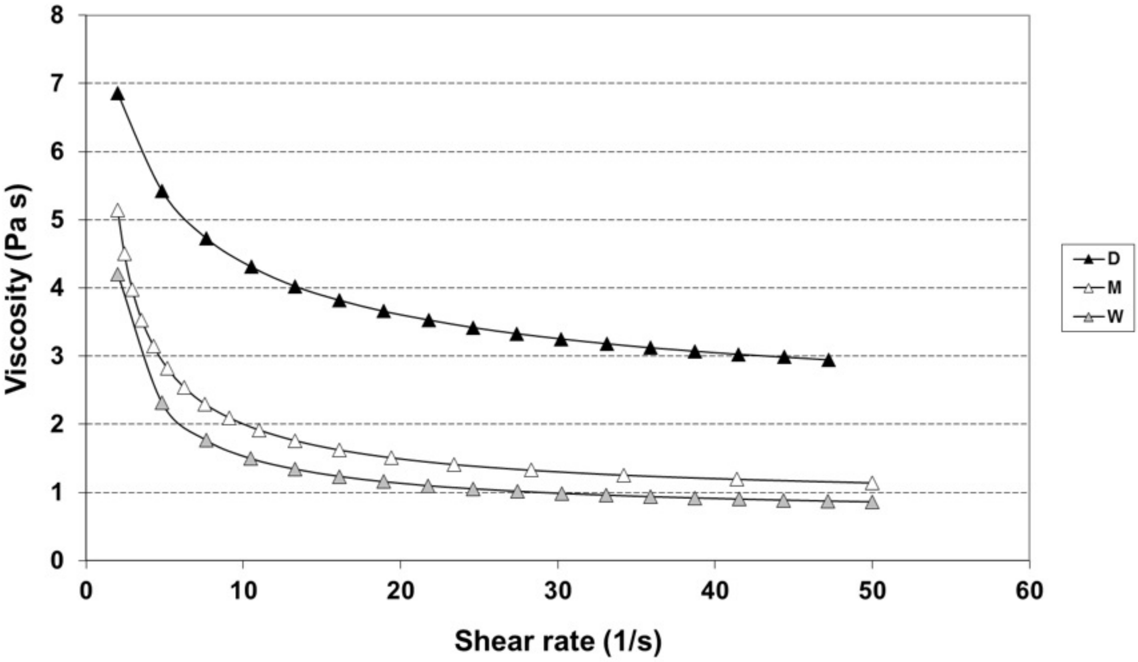
Fig. 2 Euclidean Map of chocolate samples: dark (D), milk (M) and white (W).

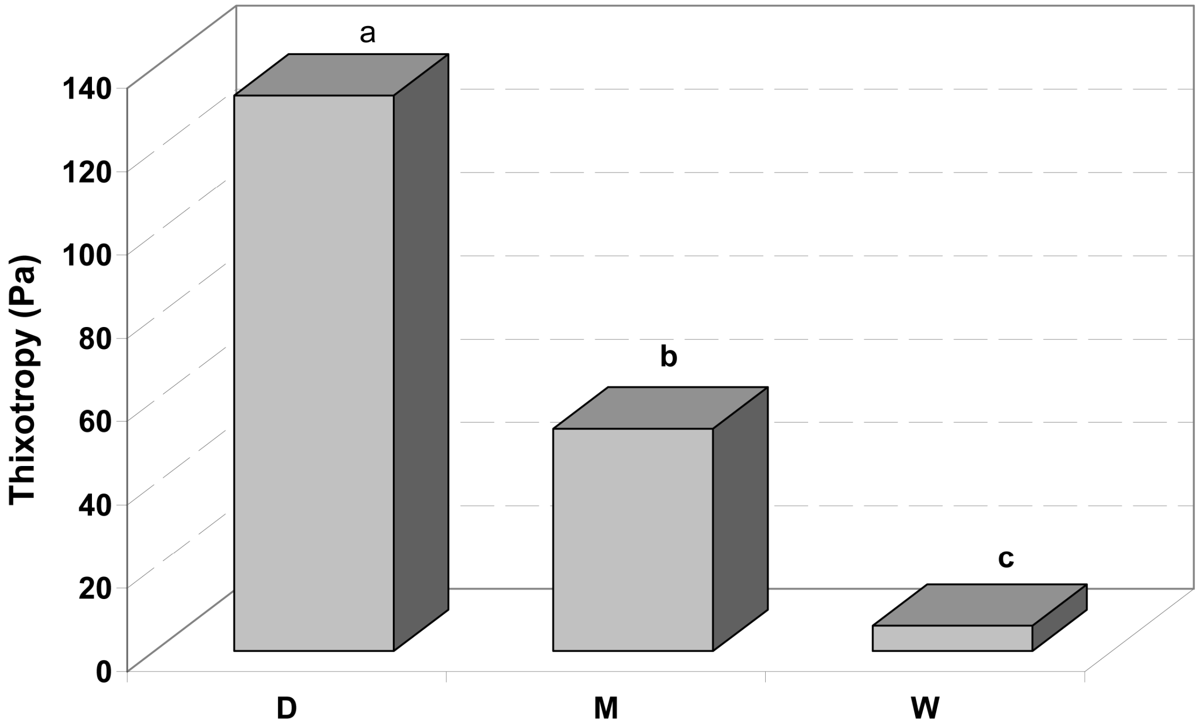
Fig. 3 Flow curves of chocolate samples: dark (D), milk (M) and white (W).

Fig. 4 Thixotropy of chocolate samples: dark (D), milk (M) and white (W).


D
M
W


D
M
W


Viscosity (Pa s)
8
7
6
5
4
3
2
1
0
Shear rate (1/s)
0
10
20
30
40
50
60
D
M
W


Thixotropy (Pa)
0
20
40
60
80
100
120
140
a
b
c
D
M
W

Highlights

- Formulation influences dark, milk and white chocolate characteristics
- Power law, Casson and Windhab models successfully fit rheological data
- Microstructural and rheological analysis well discriminated chocolate types