INFLUENCE OF EMULSIFIERS ON THE OPTIMIZATION OF PROCESSING PARAMETERS OF REFINING MILK CHOCOLATE IN THE BALL MILL

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Chocolate manufacture is a complex process which includes a large number of technology operations. One of the obligatory phases is milling, called refining, which aims at obtaining the appropriate distribution of particle size, resulting in the chocolate with optimal physical and sensory characteristics.

The aim of this work was to define and optimize the process parameters for the production of milk chocolate by a non-conventional procedure, using the ball mill. The quality of chocolate mass, produced on this way, is determined by measuring the following parameters: moisture, size of the largest cocoa particle, yield flow, and Casson plastic viscosity. A special consideration of this study is the optimization of the types and amounts of emulsifiers, which are responsible for achieving the appropriate rheological and physical characteristics of the chocolate mass. The obtained parameters are compared with those which are typical for the standard procedure.

KEY WORDS: milk chocolate, ball mill, emulsifiers, rheological properties

INTRODUCTION

The traditional way of chocolate manufacture is a complex technological process which consists of a number of technological operations: mixing of raw materials, refining in a five-roll mill, conching, tempering, panning and final crystallization (1). All these processes are necessary for obtaining the optimal physical characteristics and appropriate sensory quality of chocolate. The constitution of chocolate mass, according to raw material composition of chocolate, takes place in a melangeur pan or in a mixing machine. The obtained mass then goes to refining, in order to achieve the optimal distribution of particle size (2). The particle size reduction take place in a five-roll mill and very often with pre-refining in a three-roll refiner. The obtained mass then goes through the next stage of technological process - conching, which can be described as the mechanical working of chocolate, concerning a long-term of chocolate mass mixing at the appropriate

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temperature, in order to get the stable suspension of solid particles in cocoa butter (3). During this stage, the rheological properties of chocolate mass are formed.

The study of chocolate production in the ball mill started from the nineties of the last century. There is a very small number of scientific publications about ball mill application for chocolate production (4, 5). Ball mill is primarily designed for the industry of cement and marble, and many years later it began to be applied in the food industry. The ball mill found wide application in the confectionery industry, for refining of chocolate mass and in the production of cream products and chocolate like products similar. Ball mill is a vertical or a horizontal cylinder with double walls with hot water circulating through (6). In the central part of the cylinder are situated paddle mixers. 60-80% of the cylinder is filled with the medium refining, with balls. The balls can be made of different materials: stainless steel, steel, ceramic or other material that is applied in the food industry. During the refining process, the balls collide with particles of chocolate mass and because of the striking force, friction and shear, particle size reduction occurs. The ball mill is provided with chocolate mass recirculation, and it replaces the two phases in the standard chocolate mass production: refining and conching. Traditional refining and conching could be replaced by a process of 'liquid' refining carried out using a ball mill which can also be combined with a liquefier and a moisture removing device. In order to achieve the adequate rheological characteristics of the chocolate mass, the addition of emulsifiers, as surfactants active substances, is necessary (7-9). Before the panning process, the stable chocolate mass is tempered in order to create the crystal centers of cocoa butter in stable V crystal form (10-12). Cocoa butter can crystallize as a function of trigliyceride composition into six polymorphic forms (I-VI), where form I is the least stable and V, the most desirable form, which can transform to VI, the most stable from in storage (13, 14). These crystals allow a proper panning and solidification of chocolate, as for obtaining the optimal physical and sensory characteristics of the chocolate.

The aim of this paper is to define the optimal parameters of the milk chocolate production, as for optimal mass of the balls and retention time of chocolate mass in the ball mill. At the same time, the influence of the type and concentration of emulsifiers (lecithin and PGPR), are analyzed in order to get a chocolate mass with appropriate rheological properties. Emulsifiers have long been used to modify the flow properties of chocolate masses. Because of their special molecular structure, these surface-active ingredients lower the interfacial tension between the dispersed and the continuous phase and, besides the rheology, affect a number of properties such as the sensitivity to moisture and temperature, and the tempering behaviour (15). Lecithin and PGPR (Polyglycerol polyricinoleate) are the most widely used emulsifiers in the production of chocolate.

EXPERIMENTAL

Materials

Raw materials used for the production of milk chocolate mass: medium-grain sugar (Crvenka AD, Serbia), powdered milk (Imlek, Serbia), cocoa butter (Theobroma, Amsterdam), cocoa liquor (Cargill), ethylvanilin (FCC, Norway), soy lecithin with a mini-

mum insoluble content of 65% in acetone (Soyaprotein AD, Serbia), PGPR – Polyglyce-rol polyricinoleate (Malaysia).

Method

Chemical analyses. The basic chemical composition of milk chocolate mass was de-termined using standard AOACC methods (Table 1).

Table 1. Chemical composition of milk chocolate mass

Quality factor	Method/Principle	Values
Moisture [%]	Thermogravimetric	1.10
Total fat [% d.m.]	Determination of the petrol ether extract	32.41
Proteins [% d.m.]	Kjeldahl method	8.76
Carbohydrates [% d.m.]	Polarimetric	52.98
Cocoa components [% d.m.]	Spectrophotometric	30.14
Nonfat cocoa components [% d.m.]	Spectrophotometric	4.74
Saccharose [% d.m.]	Polarimetric	42.67
Lactose [% d.m.]	Iodine metric titration	10.31
Energy value [kcal]	Calculation	538.64
Energy value [kJ]	Calculation	2251.53

Rheological properties of chocolate mass. The rheological properties were determi-ned by rotational viscosimeter Rometar Rheo Stress 600, Haake, according to O.I.C.C.C. method, at $40\pm0.1°C$ (16). The tests were carried using a concentric cylinder system (sensor Z20 DIN) d applying a shear rate varying from 1.0 to 60.0 1/s. The shear rate was increased from 1 1/s to 60 1/s within 240 s, and was then kept constant at a maximum speed of 60 1/s for 60 s. After that, the shear rate was reduced to 1 1/s within 240s.

Size of the largest cocoa particles. The size of the biggest cocoa particles was deter-mined by the microscopic method for determining the greatest linear dimensions of the cocoa particles.

Description of the experiment. The chocolate mass was made in the laboratory ball mill with a homogenizer (capacity of 5 kg), of a domestic make. Raw materials were me-asured and added into the homogenizer at once, where they were blended for 20 minutes at a temperature of $50°C$, at the mixer speed of 50 rpm. Then, the homogeneous mass was transferred into the ball mill. The diameter of balls in the mill was 9.1 mm, and the mixer speed 50 rpm. The ball mill was equipped with a recirculation system, with a speed of 10 kg/h. The internal diameter of the ball mill was 0.250 m, and the height 0.31 m. The volume of the space provided for balls and 5 kg of chocolate mass was 0.0152 m^3.

Plan of the experiment. The experiments were realized according to the plan shown in Table 2.

Table 2. Plan of the experiment

Experiment 1											
M [kg]	25			30				35			
T [min]	120										
Type and amount of emulsifier	A										
Experiment 2											
M [kg]	30										
T [min]	30		60			90			120		
Type and amount of emulsifier	A										
Experiment 3											
M [kg]	30										
T [min]	30		60			90			120		
Type and amount of emulsifier	A	B	C	A	B	C	A	B	C	A	B	C

Experiment 1 = Optimization of the mass of balls in the ball mill
Experiment 2 = Optimization of the time of holding of chocolate mass in the ball mill
Experiment 3 = Optimization of the type and amount of emulsifier
A = 0.5% of lecithin
B = 0.2% of PGPR and 0.3% of lecithin
C = 0.3% of PGPR and 0.2% of lecithin

RESULTS AND DISCUSSION

Optimal mass of mass of the balls in the ball mill

The measured values of yield flow, viscosity, size of the largest cocoa particles and moisture of chocolate mass, in the dependence of the on mass of the balls in the ball mill, are shown in Table 3. In the experiment 1, the mass of the balls was varied at a constant time of refining of 120 minutes. The duration of milling was 30, 60, 90, 120 minutes and the times were selected according to recommendation from the literature (4).

Flow curves of the milk chocolate mass produced by standard procedure and in the ball mill as a function of the mass of the balls are shown in Figure 1.

The milk chocolate mass produced in the ball mill, despite of applied mass of the balls, keeps tixotropy properties, like the mass produced by standard procedure with milling on the five-roll refiner and conching. Increasing the mass of the balls leads to a higher degree of particle size reduction, which results in the increased of yield flow and viscosity of the chocolate mass comparing with the mass produced by standard procedure.

The influence of the ball mill was much more expressed on the viscosity of the milk chocolate mass than on the yield flow. The moisture of the chocolate mass did not change by using the new way of refining, comparing with the standard way. Neither the mass of the balls had influence on this parameter. The chocolate mass produced by milling in the ball mill with the mass of the balls of 30 kg, had the smallest area of tixotropic curve, due to the best arranged internal structure. This chocolate mass showed a lower value of the yield stress then the mass of balls under 30 kg, which is a significant parameter in terms of energy consumption for its flow. The obtained results showed that this was the optimal mass of the balls, so the further experiments were done with this ball mass.

Table 3. Influence of the mass (M [kg]) of the balls in the ball mill on rheological parameters, size of the largest cocoa particles and moisture of milk chocolate mass

M [kg]	τ_0 [Pa]	η [Pas]	P [Pa/s]	D [μm]	V [%]
25	18.49	9.410	6906	66.07	1.11
30	18.82	9.915	4670	64.24	1.13
35	20.23	9.749	5326	55.95	1.08
The mass produced by standard procedure	18.04	5.037	1492	80.00	1.10

τ_0 [Pa] - yield stress
η [Pas] - Casson plastic viscosity
P [Pa/s] - tixotropy area
D [μm] - size of largest cocoa particles
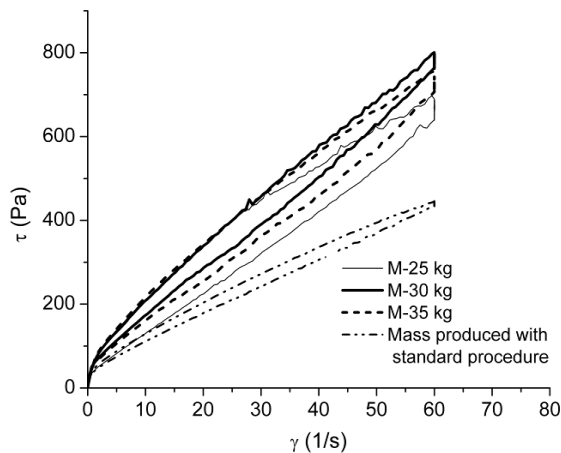V [%] - moisture

Figure 1. Flow curves of the milk chocolate mass produced by standard procedure and in the ball mill as a function of the mass of the balls

Optimal refining time of chocolate mass in the ball mill

The results of flow curves determination are shown in Figure 2. Table 4 shows the rheological parameters, size of the largest cocoa particles and moisture of the milk chocolate mass, depending on the refining time of mass in the ball mill. Experiment 2 was performed with a constant mass of the balls of 30 kg and with emulsifier A, which was involved in the chocolate mass production by standard procedure.

The increase of the refining time led to a significant reduction in the tixotropy surface area, due to a greater stability of the internal structure of the mass.

Optimal retention time in the ball mill was 90 minutes. Further extension of the refining time to 120 minutes resulted in too small cocoa particles, which reduced the efficiency because a greater amount of cocoa butter was required to establish the optimal rheological properties, and on the other hand, additional energy was consumed, which increased the cost of the production process.
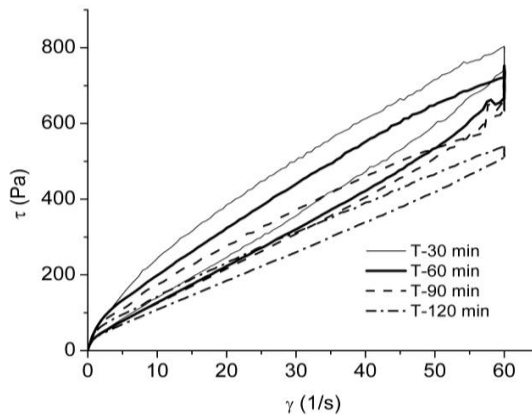

Figure 2. Flow curves of milk chocolate mass as a function of the retention time of the mass in the ball mill (refining time)

Table 4. Influence of the retention time of the balls in the ball mill on the yield stress, viscosity, size of the largest cocoa particles and moisture of milk chocolate mass

T [min]	τ_0 [Pa]	η [Pas]	P [Pa/s]	D [μm]	V [%]
30	12.98	12.17	8080	94.05	1.13
60	16.58	9.722	6787	88.76	1.10
90	17.57	7.715	3326	70,04	1.10
120	17.16	6.197	2994	68.05	1.00

Optimal type and amount of emulsifiers

During the refining process, a significant increase of the specific boundary of surfaces occurred between the solid particles and the cocoa butter. Because of that, it was necessary to add a sufficient amount of emulsifiers as surface active substances. A correct choice of the type and quantity of emulsifier is of great importance for establishment of appropriate rheological characteristics of the chocolate mass, as well as for obtaining the optimum product quality.

The experimental values of rheological parameters, size of the largest cocoa particles and moisture of chocolate, for various types and quantity of emulsifier and the retention time in the ball mill are shown in Table 5.

Table 5. Influence of the emulsifier and retention time of the mass in the ball mill on the yield flow, viscosity, tixotropy area, size of the largest cocoa particles and moisture of milk chocolate mass

T [min]	30			60			90			120		
Type and amount of emulsifier	A	B	C	A	B	C	A	B	C	A	B	C
τ_0 [Pa]	12.98	13.45	10.20	16.58	8.26	5.48	17.57	9.46	5.81	17.16	9.68	5.51
η [Pas]	12.17	7.40	8.73	9.72	9.82	12.71	7.71	9.57	11.91	6.20	9.40	11.96
P [Pa/s]	8080	4336	5918	6787	5657	7145	3326	4228	6046	2994	5502	5859
D [µm]	94.05	117.0	112.3	88.76	102.4	85.31	70.04	87.9	81.05	68.05	66.8	65.2
V [%]	1.13	1.28	1.00	1.10	1.29	1.25	1.10	1.24	1.21	1.00	1.20	1.12

A = 0.5% of lecithin
B = 0.2% of PGPR and 0.3% of lecithin
C = 0.3% of PGPR and 0.2% of lecithin
* The amount of emulsifiers is calculated on the total mass of raw materials

The obtained results show that the influence of PGPR, on rheological properties and yield flow of the chocolate mass is significant. The addition of smallest amount of this emulsifier (0.2%) at the refining time of 30 to 60 minutes lead to the reduction of yield flow of the chocolate mass from 16.58 Pa to 8.26 Pa (50.2%) in dependence of the mass with only lecithin added. The addition of 0.3% PGPR at the same refining time led to a 68% reduction. The results are in accordance with the published data for milk chocolate produced by classical method (15). At longer times of refining (to 90 and 120 minutes), the impact of the emulsifier composition on the yield flow was weaker. Under the same conditions of the experiment, PGPR emulsifier had a similar effect on the increase in the viscosity of the chocolate mass. The addition of bigger share of lecithin decreased the yield stress and viscosity proportional to the refining time.

The flow curves of chocolate mass produced using the ball mill have a larger tixotropy areas comparing with the mass produced by standard procedure. The chocolate mass with lecithin added has the smallest tixotropy area, while the addition of PGPR emulsifier leads to the increase in this area and the increase in the disorder and complexity of the system for 90 and 120 minutes. The most stable system with arranged inner structure obtained for the refining time of 90 minutes, shows the smallest increase of tixotropy area compared to the one which is characteristic for standard chocolate production.

Addition of 0.2 % PGPR influenced the increase of moisture of chocolate mass compared to the mass of chocolate with lecithin added, regardless of the refining time. The addition of PGPR in the amount of 0.2% along with the refining time of 90 minutes is optimal because the value of yield stress is significantly smaller compared to the mass of chocolate with lecithin. The size of the largest cocoa particles are approximately the same as in the chocolate mass produced using standard procedure and the relatively low value of viscosity is measured.

The obtained experimental results were statistically analyzed in order to study the correlation between the refining time and quality parameters of chocolate mass (viscosity, particle size and moisture content) for various type of emulsifier (A, B, C), Table 6.

Table 6. Correlation between the parameters of production and quality of produced chocolate mass

	Regression equation	Coefficient of determination R^2	Slope
η [Pas]			
A	$\eta_{CA} = -0.071t + 19.075$	0.99	$-0.077 < \text{slope} < -0.066$
B	$\eta_{CA} = 0.017t + 11.630$	0.64	$-0.023 < \text{slope} < 0.058$
C	$\eta_{CA} = 0.009t + 14.620$	0.30	$-0.033 < \text{slope} < 0.051$
D [µm]			
A	$D = -0.318t + 103.825$	0.918	$-0.607 < \text{slope} < -0.030$
B	$D = -0.485t + 122.385$	0.922	$-0.916 < \text{slope} < -0.055$
C	$D = -0.550t + 134.790$	0.990	$-0.714 < \text{slope} < -0.386$
V [%]			
A	$V = -0.001t + 1.180$	0.786	$-0.003 < \text{slope} < 0.001$
B	$V = -0.007t + 1.145$	0.931	$-0.013 < \text{slope} < -0.001$
C	$V = -0.001t + 1.310$	0.769	$-0.001 < \text{slope} < 0.001$

A = 0.5% of lecithin
B = 0.2% of PGPR and 0.3% of lecithin
C = 0.3% of PGPR and 0.2% of lecithin
* The amount of emulsifiers is calculated on the total mass of raw materials

It is shown that in the presence of lecithin (A) there is a statistically significant linear correlation between the quality parameters (mass viscosity, particle size and moisture) and refining time (high coefficient of correlation and a small interval of confidence for the slope that does not include 0). The corresponding linear equations are shown in Table 6. The addition of PGPR (B and C) such a strong linear correlation is retained only for the particle size. This conclusion is made because of the values obtained for the confidence interval of the slope, which in the case of such non-linear relations include zero, regardless of the relatively high value of the coefficient of determination. The results are in accordance with published data about milk chocolate produced by classical method (15).

CONCLUSIONS

The aim of this paper was to define the optimal parameters of the milk chocolate production in the ball mill. At the same time, the selection of the type and concentration of emulsifiers (lecithin and PGPR), was discussed in view of the appropriateness is of rheological properties of chocolate mass.

Based on the results it can be concluded that there is a full justification of chocolate production by the new procedure, using the ball mill. Flow curves of the obtained samples of chocolate mass are very similar to those obtained by conventional way of production. The addition of PGPR emulsifier resulted in a lower yield stress, as the important parameter of mass flow, compared to the one in the traditional process of production. Optimal conditions of laboratory production of chocolate mass in the ball mill with a capacity of 5 kg, which provide the adequate rheological parameters are: mass of balls of 30 kg, refining time of mass in the ball mill of 90 minutes and addition of the combination of 0.2% PGPR emulsifier and 0.3% of lecithin, on the total raw material mass basis.

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УТИЦАЈ ЕМУЛГАТОРА НА ДОБИЈАЊЕ ОПТИМАЛНИХ ПАРАМЕТАРА ПРОИЗВОДЊЕ МЛЕЧНЕ ЧОКОЛАДЕ У КУГЛИЧНОМ МЛИНУ

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Производња чоколаде је сложен процес који обухвата велики број технолошких операција. Процес млевења је једна од неизоставних фаза у производњи чоколаде, која има за циљ добијање одговарајуће расподеле честица по величини, што условљава добијање чоколаде оптималних физичких и сензорних карактеристика.

Циљ овог рада је дефинисање и оптимизација параметара процеса млевења током производње млечне чоколаде на неконвенционалан начин, односно у кугличном млину. Квалитет овако добијене млечне чоколаде је одређен мерењем следећих параметара: влага, величина најкрупније какао честице, приносно протицање, вискозитет по Cassonu. Посебан аспект овог рада је оптимизација врсте и количине емулгатора, неопходних за постизање одговарајућих реолошких и физичких карактеристика чоколадне масе. Добијени резултати су упоређени са истим параметрима производње млечне чоколадне масе добијене стандардним поступком.

Кључне речи: млечна чоколада, куглични млин, емулгатори, реолошке особине