PHD SCHOOL OF FOOD SCIENCE
DEPARTMENT OF PHYSICS AND CONTROL

INFLUENCE OF COCOA BUTTER EQUIVALENT VEGETABLE FATS AND STORAGE CONDITIONS ON THE RHEOLOGICAL AND ORGANOLEPTIC PROPERTIES OF CHOCOLATE

Thesis of the PhD Dissertation

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1. WORK PREPARATION, OBJECTIVE

For chocolate manufacturing – according to the current legislations considering its main components - a maximum amount of 5% of cocoa butter equivalent vegetable fats could be used. The presence of these cocoa butter equivalent fats could influence the flow parameters, thermal resistance, hardness, shelf life, and the resistance to surface fat separation of chocolate, and last but not least also its organoleptic properties, thus its popularity. Through my research besides the analysis of the above mentioned subjects I dealt with the current as well as tested other alternative measurement method.

Examining the effects of the application of cocoa butter equivalent vegetable fats and storage conditions on the rheological and organoleptic properties of chocolate I set the following tasks to solve as targets:

Rheological measurements

1. The applicability of rotational rheometer parallel plate geometry on the definition of flow parameters of chocolate mass
2. The applicability of oscillation rheometer as a non-destructive method for the examination of rheological parameters of chocolate masses
3. The effect of cocoa butter equivalents on rheological properties of chocolate mass
4. Thermal resistance of chocolate described by mathematic model
5. Hardness change caused by the cocoa butter equivalents present in solid chocolate
6. The effect of tempering degree as a technological parameter on hardness

Storage examinations

7. The effect of storage temperature changes and time on hardness of chocolate
8. Surface fat separation in the function of storage conditions

Organoleptic examinations

9. The effect of cocoa butter equivalent fats on chocolate preference and quality number

High pressure treatment measurements

10. Analysis of crystallisation of chocolate mass as a result of high pressure hydrostatic treatment with hardness measurement

2. MATERIAL AND METHOD

The examined materials

To be able to perform the measurements I manufactured ***dark chocolate mass and solid chocolate bars*** without adding milk powder or any other milk derivatives, and would simplify and refer to as „chocolate" from this point on. Among the five types of chocolate masses I examined the one named *CB-mass* does not contain cocoa butter equivalent fats. Masses named *CBE I* -, *CBE II* -, *CBE III* - and *CBI* contain proportionally less cocoa butter, and according to the legal regulations contain less than 5% of cocoa butter equivalent (CBE I, CBE II, CBE III) and cocoa butter improver (CBI) vegetable fats based on the main components (not considering lecithin and vanillin).

For the preparation of chocolate mass I used a jacketed, water bath temperature controlled and stirrable Stephan UMC 12 type cooker cutter which could be tempered with flowing water between its double walls. I used an AASTED - MIKROWERK AMK 10 type continuous operation tempering device for the pre-crystallisation (tempering) of the given chocolate masses. I dosed the tempered chocolate mass into plastic moulds and placed in a 4°C cooling chamber.

To be able to examine the effect of storage conditions on the texture and organoleptic properties of solid chocolate I placed the samples *under non-regulated circumstances* to the *three adjacent rooms* of a building at *normal room temperature and atmospheric pressure*. The definition of the storage places is determined by the need for the ability to simulate the different, spontaneous storage habits of consumers that are also subject to weather change. For this reason I chose three different locations for the storage.

1. **„southern side"** (extremely hot): temperature range under heated conditions: 20-25°C, with an average of 22°C, temperature range under unheated conditions next to the samples: 20-60 °C, 28°C on average.
2. **„northern side"** (standard): temperature range under heated conditions: 18-20 °C, average of 19°C, temperature range under unheated conditions: 18°C-26°C, average of 21°C.
3. **„cellar"** (extremely cold): temperature range under heated conditions: 12-14°C, average of 13°C, temperature range under unheated conditions: 14-19°C, average of 17°C.

According to the literature the particle size of quality chocolate is a value between 20-30µm. The chocolate samples I produced for the experiments have a particle size of 45-46µm measured by grindometer and micrometer, as the process lacks fine grinding, which is due to the partial inability of the mincing function of the cooking cutter applied. For this reason – as is represented by the title of the thesis – I named the product produced as chocolate model system, however consequently used the denomination „chocolate".

Measurement methods

Rotational rheometry

I used a parallel plate geometry *Rheometric Scientific SR*-5000 type rheometer, a *dynamic stress rheometer (DSR)* and the associated software called *RSI Orchestrator* for the performance of the rotational measurements.

The method is to place the sample on the lower plate of the device (called measurement gap), in which the upper rotating plate induces a shear stress. During the parallel plate measurement the sample is subject to an uneven deformation on the surface of the plates, as the shear speed increases with the radius. The measurement error occuring could be eliminated with a correction.

Oscillation rheometry

I performed the dynamic rheological measurements with the so called A*nnular Pumping Rig* measuring device of the recently developed by *Stable Micro Systems (SMS) TA-XT2 type precision penetrometer (texture analyser).* Annular Pumpig Rig consists of a jacketed, water tempered, *cylindrical and ribbed sample holder* (vessel) and a *cylindrical ribbed probe body*.

The plastic probe attached to the arm of the device immersed into the center of the sample induces low amplitude oscillation vibrations, sine-waves, and the load cell placed in the arm of the texture analyser is measuring the deformation force resulting from the resistance in the material. During the measurement *Texture Expert software* records the force needed for deformation and we obtain the so called *Sine Wave Test* specific to the material. Of these parameters force, amplitude and phase difference could be determined by cross correlation, and of these parameters the basic rheological properties (viscous, elastic characteristics) could be calculated.

Penetrometric measurements

I used the same precision penetrometer I applied for the oscillometric measurements, *Stable Micro Systems (SMS) TA-XT2 type (texture analyser).* For measuring body I used a *stainless steel needle* and a *stainless steel cylinder* depending on the type of measurement.

According to the theory of the method, the measuring head fixed to the arm of the device penetrates into the sample and provides information on the force occuring during deformation, which is the deformation force. As a result of the measurement we obtain rheograms, which we can store and analyse with a computer. These diagrams show the deformation force over the penetrating depth. Through the definition of the specific parameters of these diagrams (i.e.: maximum deformation force, apparent modulus) we could get information on the structure and hardness of the examined material.

Organoleptic measurements

I performed the organoleptic measurements based on the sensory panel methods set in Germany at Food Technology Department of Fachhochschule Fulda.

During *preference tests* the chocolate samples had to be analysed through an assessment (re-tasting was allowed), and had to be ranked in the hedonic scale results. Samples could get the same ranking.

According to the German *DLG assessment method*, the organoleptic categories of the given samples were scored on the criteria present at a 5-point scale. The scores of the categories were multiplied by the the given factor numbers (weighted), and the results obtained divided by the sum of the weighting factors provides the quality number of the given sample.

High hydrostatic pressure treatment

High pressure treatment of chocolate was performed by a *STANSTED Mini Foodlab FBG 5620 type high hydrostatic pressure equipment*. I melted the chocolate samples on 50°C, and put them into plastic sample vessels. I treated the samples on 800 MPa pressure for 5 minutes. I examined the resulting crystallization process caused by high pressure with hardness test.

3. RESULTS

New scientific results

1. ***I described the heat resistance of solid chocolate model systems between the 25°C and 30°C temperature range with mathematical parameters (regression coefficient and regression constant).***

   For the definition of heat resistance ability I performed penetrometric measurements with 2mm diameter stainless steel cylinder at 4mm deformation on different chocolate models in composition and storage conditions (only containing cocoa butter: CB-, containing cocoa butter equivalent vegetable fats: CBE- and CBI-). During the experiment I set the maximum deformation force versus the temperature and set a regression line to the data pairs in the 25-30°C temperature range.

   With mathematical methods and statistical analysis (correlation analysis, Durbin-Watson trial) I proved with 95% confidence that both for the chocolate model system samples containing different composition, and the samples stored under different conditions, *deformation force and temperature dependence in the 25-30°C temperature range could be well described with the regression equation*. Furthermore I stated, that in this temperature range the deformation force and temperature steepness curve (regression coefficient) proved to be -

2,7738 and -1,8261 and its intercept (regression constant) at x=25°C changed between 11,52 and 16,94, those representing the heat stability of the product.

2. ***I stated, that the hardness of solid chocolate model systems subjected to high temperature fluctuation (even over 40°C) determined by minimal deformation force doubles during the 8 month uncontrolled storage conditions (spontaneous cyclothermic crystallization).***

   I verified with statistical methods (one- and two way analysis of variance, Dunett's comparisons) at a 95% confidence level with penetrometric method (stainless steel measuring needle and 2mm deformation), that *there is a considerable hardness increase in the samples stored at the extremely hot location* (southern side: temperature range under heated conditions: 20-25°C, with an average of 22°C, temperature range under unheated conditions next to the samples: 20-60 °C) which I considered to be an evidence of the *cyclothermic crystallization*. Samples stored for a longer period of time (8,9 11 and 12 months) subjected to the extreme heat alterations especially in the summertime (even over 40°C) and direct sunlight I observed that chocolate samples melt in daily cycles, and spontaneously re-crystallizes again.

3. ***I verified that the 5% application of cocoa butter equivalent CBE- vegetable fats significantly reduced the hardness of chocolate model systems stored for 8 month at high temperatures, and did not change at a lower storage point. The 5% application of CBI – fats did not result a change in hardness of chocolate model system samples stored at high temperatures, and reduced hardness significantly on samples stored at a lower temperature.***

   I stated the hardness of hardness of chocolate with penetrometric method (stainless steel measuring needle and 2mm deformation). According to my results based on statistical calculations (one way analysis of variance, Dunett's comparisons, 95% confidence level) *CBE – fats applied in 5% at higher temperatures* (southern side: temperature range under heated conditions: 20-25°C, with an average of 22°C, temperature range under unheated conditions next to the samples: 20-60 °C, 28°C on average) *reduced the hardness of the stored samples significantly*. At *lower temperature* locations (northern side: temperature range under heated conditions: 18-20 °C, average of 19°C, temperature range under unheated conditions: 18°C-26°C, average of 21°C) however *it did not change the hardness significantly*.

   The application of 5% *CBI - fat* at samples stored under warmer circumstances (southern side: average temperature unheated and heated time period: 22°C and 28°C, temperature range: 20-60°C) *did not change the hardness of chocolate significantly*. The samples stored on the *colder side* (northern side: temperature average unheated and heated time periods:

19°C and 21°C, temperature range: 18-26°C) the fat *significantly reduced the hardness* of the chocolate.

4. ***I stated that after 9 months of storage the hardness of undertempered chocolate model systems was significantly (6%) less, while the hardness of overtempered chocolate model systems was significantly (6%) more than the ones tempered under normal conditions.***

   I measured with penetrometric method (stainless steel measuring needle and 2mm deformation) and statistical analyses (one- and two way analysis of variance, Dunett's comparisons at a 95% confidence level) and verified that after 9 months of storage the *undertempered samples were softer, while the overtempered samples were harder than the normally tempered ones.*

   Furthermore I stated that role of tempering on hardness is determined by the contents of the chocolate mass to be tempered, and that this phenomenon occurs especially at undertempered samples. The *undertempered samples containing 5% of CBE vegetable fat proved to be significantly softer than the standard undertempered samples not containing cocoa butter equivalent vegetable fats.* The reason of this is that the composition of the fat content of the two samples are different – the fat phase of CB – chocolate consists of cocoa butter, while the CBE – chocolate contains 5% cocoa butter equivalent vegetable fat, and this projects the two different samples to crystallize differently under same parameters.

5. ***There is no significant difference between the organoleptic parameters, preference numbers and quality numbers of the chocolate model system samples containing 5% of foreign vegetable fat and the ones not containing vegetable fats after 6 weeks, 4 months and 6 months of storage.***

   I performed sensory assessments with trained assessors (preference test and DLG method) and examined the results on 95% confidence level with statistical methods (Friedman test, pair significant difference). I stated that there is no significant difference between the organoleptic properties of the chocolate model systems legally containing foreign vegetable fat and the ones not containing foreign fats, and this fact would not change with any storage conditions (northern side: temperature average unheated and heated time periods: 19°C and 21°C, temperature range: 18-26°C).

4. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Rheological examinations

1. The rotational rheometer *parallel plate system geometry* could be applicable for rheological parameter measurements of chocolate mass (time dependent average viscosity, flow curve, thixotropy, temperature dependence of viscosity), and the measurement is *well reproducible*.
   The advantage of the parallel plate geometry compared to the coaxial cylinders widely used in the industry today, is that it *requires much less amount of sample, and provides quicker sample change*.
   It was not an explicit goal of this work to cover heat dependence of viscosity of chocolate mass, however it is already visible of the low amount of samples that the *viscosity vs. 1/T* relation referring to the Arrhenius-equation could be considered linear. This corresponds to the relevant results found in the literature.

2. The parameters of time dependent, non-destructive oscillation methods, constant moduli and complex constant viscosity could be applicable for the rheological description of the structure of chocolate mass in the range of loading force with low deformation force.
   Apart from the viscous properties, chocolate mass also has elastic properties, the *loss modulus (G") referring to its viscous behaviour is twice the storage modulus (G') referring to the elastic behaviour.*

3. Confidence interval estimation proved that the viscosity curves of *CBE – and CBI - masses differ significantly* with a 5% probability of failure from the *viscosity curve* of the standard *CB - mass* not containing cocoa butter equivalent vegetable fats.
   The shear rate dependent viscosity of CBE – mass is less, the viscosity of CBI - mass is more than the viscosity of CB - mass.

4. The *thermal behaviour of the maximum deformation force* relevant to the hardness of chocolate samples in the given 25-30°C thermal range is described by a *linear regression* at 95% confidence level.
   According to my experiments *it is possible to characterize the heat stability* or softening of chocolate samples in the thermal range of 25-30°C with the *coefficient and constant of the regression line* fitted to the data points of temperature and deformation force at given parameters (contents, storage, experimental layout, etc.)

5. Statistical methods proved that *hardness* of chocolate *is significantly changed* with the application of 5% of *CBE - and CBI – fats* depending on the storage conditions and temperature.

6. *Tempering degree* as a processing parameter has a *significant effect on the hardness* of chocolate – undertempered samples are softer, overtempered samples are harder than the normally tempered samples. Furthermore the *composition and tempering combined together also influences hardness*.

Storage tests

7. The alteration of storage temperature has a significant effect on the hardness of chocolate, *samples exposed to extreme high temperature variations showed considerable increase in hardness similar to cyclothermal pre-crystallization process*.

8. *Storage temperature alterations have a crucial role* in surface fat formation, the fat content of samples stored at extremely hot places started to appear on the surface after 2 months of storage causing a color change of the product.
   There was no difference in the surface fat formation process of cocoa butter only and the samples containing 5% of cocoa butter equivalent vegetable fat.

Organoleptic measurements

9. The legally permitted *5% presence of cocoa butter equivalent vegetable fats does not change* the *preference* of the chocolate, nor in inflicts the *quality number* and organoleptic profile.

High pressure treatments

10. Treatment performed with *high hydrostatic pressure on chocolate mass is not reproducible*, hardness of identically treated and hardened chocolate samples differ significantly.

Recommendations

- To be able to define practical applicability of parallel plate geometry I recommend the validation of the measurements with coaxial measurement system.
- It is advised to perform the examination of viscosity-temperature dependence of chocolate mass – with a constant shear rate – with a low rate of temperature increase (1-2°C).

- If there is a statistically proven, strong interdependence between the results of oscillation rheometry and rotational rheometry, it is a possibility to examine whether it is possible to extend this relation to a bigger deformation range.
- I recommend to measure heat resistance in a wider temperature range and define deformation force over temperature relations under 25°C.
- I did not perform statistical analysis on the change of hardness in time over storage temperature, this could be done with storage tests performed under regulated circumstances and constant storage temperatures.
- New information could be gathered on the organoleptic parameters of the different chocolate samples with performing difference tests.
- I recommend to use digital picture analysis as a method to express the surface fat formation in numbers or percentage of the total surface of chocolate.

5. ESSENTIAL PUBLICATIONS RELATED TO THE DISSERTATION

Publications in journals

IF publications

Biczó-Kabai V., Fekete A., Scherer, R. (2011): Influence of composition and storage conditions on chocolate hardness and heat resistance. *Acta Alimentaria* (in press)

Non-IF publications in foreign language

Biczó V., Scherer R., Schaefer R., Fekete A. (2005): Kakaobutteräquivalente (CBEs) in der praktischen Anwendung. *Getreidetechnologie*, 59 (2) 114-118. p.

Non-IF publications in Hungarian

Biczó V. (2003): A csokoládé tulajdonságai és mérési módszerei. *Édesipar*, XLIX (3) 2-8. p.

Biczó V. (2003): A csokoládészelet keménysége. *Édesipar*, XLIX (4) 1-5. p.

Publications in conference proceedings

In Hungarian (full text)

Biczó V. (2004): Édes kísértés – A csokoládé. Pro Scientia Aranyérmesek VII. konferenciája, Gödöllő 159-162. p.

International conferences (full text)

Biczó V., Scherer R., Fekete A. (2005): Measurement methods for the viscosity of chocolate mass. *Proceedings of Research and Teaching of Physics in the Context of University Education*, Nitra, Slovak Republic, ISBN: 80-8069-528-8, 198-201. p.

Biczó V., Fekete A., Scherer R., Schaefer R. (2006): Rheological properties of chocolate mass measured by different methods. *ASABE Annual International Meeting*, Portland, Oregon, Paper No: 066108 1-11. p.

In Hungarian (abstract)

Biczó V. (2003): A csokoládé mérési módszerei. Lippay János - Ormos Imre - Vas Károly Tudományos Ülésszak, Budapest 216. p.

International conferences (abstract)

Biczó V., Scherer R., Schaefer R., Fekete A. (2004): A new measurement method for the viscosity of chocolate: Annual pumping rig., *The 6th International Conference on Food Physics and Dairy Sciences*, Pécs Hungary 61-62. p.

Biczó V., Scherer R., Schäfer R., Fekete A. (2004): Kakaobutteräquivalente (CBEs) in der praktischen Anwendung. *55. Tagung für Bäckerei-Technologie mit „Konditorei-Technologie”*, Detmold, Deutschland 14-15. p.