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Influence of Composition and Storage Conditions on Chocolate Hardness and Heat Resistance

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Abstract. The EU Chocolate Directive 2000/36/EC allows the use of the vegetable fats CBEs and CBIs up to a maximum of 5% in chocolate. Manufacturers and users must know how this has an influence on the properties of chocolate. The objective of the work reported here was to find out by systematic investigations, which effect CBEs/CBIs have on the quality parameters, hardness and heat resistance of chocolate. The influence on the hardness was tested also under extreme practical storage conditions. The quality monitoring was performed up to one year. For the determination of the heat resistance the penetrometric method was used in the temperature range 25–32 °C measuring the maximum loading force, occurring during the penetration of a cylindrical probe of 2 mm diameter with 4 mm penetration. The correlation between the average maximum loading force, relevant to the hardness of chocolate, and the temperature can be described by a linear regression at 95% confidence level. Statistical analyses (correlation analysis, residual analysis, Durban-Watson statistic) showed that it is possible to define the heat resistance of solid chocolate in the temperature range of 25–32 °C by the slope and the ordinate intercept of the regression line of the loading force vs. temperature for given parameters (composition, storage, experimental layout, etc.). For the determination of the hardness of the chocolate also the penetrometric method was used to measure the maximum loading force occurring during the penetration of a needle probe with 2 mm deformation. The hardness of the chocolate samples determined with the penetrometric method and statistical analysis (One-Way, Two-Way Analysis of Variance, Dunnett's comparisons) is significantly dependent on the composition and storage conditions, where the storage conditions are the dominant factor. The results show that the differences in hardness between the chocolate samples with CBE/CBI and those without CBE/CBI, both stored in the cellar (cold storage), are marginal. After one week of storage the sample with CBI has nearly the same hardness as the standard sample with CB,

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whereas the sample with CBE was slightly softer. The differences are slightly clearer for the northern storage room (moderate temperature) and for the southern room (warm temperature). After a definite storage time the hardness of all samples increased and was in the case of the southern storage room (warm temperature) up to twice as high. The quality monitoring up to one year showed that the reason for this increase in hardness is not a special storage time but the increasing temperatures with the beginning of the warm season and the cyclic change of the temperature during day and night. So an explanation for this unexpected increase in hardness can be a thermocyclic hardening of the chocolate samples under these storage conditions.

Keywords: chocolate, texture, hardness, composition, storage time, temperature, heat resistance

According to the regulations (Matissek 2000; Codex Alimentarius Hungaricus 2010) the use of certain vegetable fats, such as cocoa butter equivalents (CBE) and cocoa butter improvers (CBI) is permitted for partial replacement of cocoa butter during chocolate production. The amount of these vegetable fats may not exceed 5%.

Tscheuschner and Markov (1986, 1987, 1988, 1991) studied the effect of ingredients on the chocolate structure. They found that the compression hardness of plain dark chocolate that does not contain vegetable fats decreased linearly with the increase of cocoa butter to a certain extent (approx. 60%), then the compression hardness became approximately constant**.**

Hausmann et al. (1994) studied the effect of storage temperature and time on the physical parameters – such as crystallized fat content, compression hardness and melting – of dark and milk chocolates. They found that none of these physical parameters reached a constant value at the end of the three-month storage period. Therefore, the crystallization processes in the chocolate were not finished. The compression hardness increased with the increase of storage time and temperature, while the melting height decreased. They determined that the critical storage temperature of dark chocolate is approximately 18 °C. Above this value sudden quality deterioration occurs.

Kleinert (1997) found that the melting temperature (heat resistance) of dark chocolate increased to 34–35 °C when repeating the precrystallization procedure (cyclothermal precrystallization process) during production. Therefore, the final product became harder because of the mentioned procedure.

Biczó et al. (2005) tested the influence of the storage conditions and chocolate composition on the chocolate quality of samples containing CBE and CBI vegetable fats during long term (one year) storage experiments. The authors found that long term storage under extremely warm conditions increased chocolate hardness because of cyclothermic hardening.

It is very important to produce high quality chocolate. Therefore, one should know the exact influence of the cocoa butter equivalents and improvers on the hardness and heat resistance of solid chocolate during storage under different conditions. However, there were not available statistically approved experimental results in the literature. Generally, the melting characteristics of chocolate were studied on the basis of the melting speed that was in definite relationship with the "melting height" and the elapsed time. The hardness and heat resistance of chocolate have not been determined for the above mentioned parameters.

Consequently, the objective of the work reported here was to determine the influence of chocolate composition and storage conditions on the hardness and heat resistance of chocolate produced under laboratory conditions.

1. Materials and Methods

1.1. Materials

Three types of chocolate were produced for the experiments. One of the samples contained only cocoa butter as fat (later on called CB-sample), while the other two ones contained 5% vegetable fats, either CBE (Cocoa Butter Equivalent), or CBI (Cocoa Butter Improver). Both vegetable fats have chemical and physical properties similar to those of the cocoa butter.

Table 1 shows the composition of the different chocolate samples that were prepared for the experiments.

The final process of chocolate mass production is the so called "conching," which is an essential procedure concerning the development of the final flavour and texture properties of the product. A jacketed cooking cutter type Stephan UMC 12 was used for the conching process with cooling water circulated in the jacket ensuring a temperature range between 55 °C and 65 °C. The first period of conching (dry conching) lasted for one and half hour when the cocoa mass, sugar, half the amount of the cocoa butter and vegetable fat were added. The second period (wet conching) took half an hour and all the remaining ingredients were added in this phase. AASTED - MIKROWERK AMK 10 type continuous process tempering system was used for the precrystallization (tempering) of chocolate mass. The purpose with the three phase tempering method was to obtain appropriate, stable crystal formation of the fats (cocoa butter and cocoa butter alternatives) of the chocolate mass. At the last step of the process the tempered chocolate mass was put into plastic chocolate forms of 6 mm height and then stored in a cooling room for the main crystallization.

Table 1. The composition of the tested chocolate samples [m/m %]

Ingredients	CB-sample, [%]	CBE-sample [%]	CBI-sample [%]
Cocoa mass	46	46	46
Sugar	40	40	40
Cocoa butter	14	9	9
CBE-fat	0	5	0
CBI-fat	0	0	5
Lecithin	0.5	0.5	0.5
Vanillin	0.03	0.03	0.03

The solid samples of chocolates were taken out of the forms, wrapped and transferred to the site of the experiment, either into a climate chamber to be tested as fresh samples, or into the different storage locations for the storage experiments.

1.2. Methods

A Stable Micro Systems (SMS) TA-XT2 type precision texture analyzer was used for the compression tests. The measuring probe was either a stainless steel needle or a stainless steel cylinder, depending on the test type and the sample. With the compression test, the measuring probe attached to the arm of the texture analyzer penetrated into the sample and measured the compression force needed that was the loading force and the time and the deformation. The parameters of the measurement (such as penetration speed, etc.) could be set from the control panel or via the Texture Expert software. As a result, we obtained diagrams showing the changes in the measured variables, either versus the time or versus the deformation. These diagrams were stored and analyzed by a computer. These diagrams represented the loading force versus the deformation. Therefore, we received information on the texture and hardness of the tested materials by processing the specific parameters of these diagrams.

1.2.1. Relationship between hardness and temperature (heat resistance)

The influence of the chocolate temperature on the hardness of the fresh chocolate samples was determined with the SMS TA-XT2 texture analyzer. The data pairs of the loading force and the temperature described the softening of the samples.

Parameters of force measurement

- measurement probe: P202 cylinder, diameter: 2 mm
- speed prior to deformation: 2 mm/s
- test speed: 1 mm/s
- maximum deformation: 4 mm

The sample temperature was increased step by step, where 1 °C meant one step of the fresh sample. The samples were heated to a definite temperature in a high performance climate chamber. The tempered sample lost heat while it was transferred to the measurement locations. When the sample was taken out of the chamber, it was put into a thermo box made of expanded polystyrene-foam sheets and wrapped into aluminium foil to decrease the reduction in the sample temperature.

The hardness of the different samples was measured in a temperature range between 25 and 32 °C with 1 °C intervals for each measurement. We repeated each measurement nine times and calculated the average values for the maximum deformation (4 mm) and the maximum loading force. The maximum loading has to be measured as the function of the temperature; actually this described the hardness, or rather the heat resistance of the tested chocolates.

1.2.2. The influence of chocolate composition and storage conditions on hardness

In order to determine the effect of storage conditions on the texture of chocolate the samples were stored in three different rooms of a building under atmospheric air pressure and different room temperatures, having no air conditioning. The rooms were, as follows:

A) Warm room (southern room): the samples were stored behind the window looking at south where sunshine could heat them. This room was heated in winter when the temperature changed between 20 and 25 °C, the average temperature was 22 °C. During summer, without heating, the temperature changed between 20 and 40 °C, the average temperature was 28 °C.

B) Moderate temperature room (northern room): the samples were stored in shadow, far from the window looking at north. This room was moderately heated during winter when the temperature changed between 18 and 20 °C, the average temperature was 19 °C. During summer, without heating, the temperature changed between 18 and 26 °C, the average temperature was 21°C.

C) Cold room (cellar): the samples were stored in a cellar having no window. The cellar was not heated during winter. The temperature changed between 12 and 14 °C, the average temperature was 13 °C during winter. However, during summer the temperature changed between 14 and 19 °C and the average temperature was 17 °C.

The SMS TA-XT2 type texture analyzer was fitted with a stainless steel needle probe and it was used for the measurement of chocolate sample hardness. The measurements were performed at 22 °C room temperature. The chocolate samples were transferred from differently tempered storage locations into the test room an hour before the force measurement.

Parameters of force measurement

- measurement probe: P2N needle
- speed prior to deformation: 2 mm/s
- test speed: 1 mm/s
- upwards speed after deformation: 2 mm/s
- maximum deformation, that belongs to the maximum loading force: 2 mm

The loading force was determined as the function of the deformation from the result of the hardness tests of the samples. The maximum loading force was used to describe the hardness of the different chocolate samples and the value of the maximum loading force was calculated as the average of the maximum force of ten compression tests.

2. Results and Discussion

2.1. Relationship between hardness and temperature (heat resistance)

The compression test method was used to determine the relationship between the hardness and the temperature of fresh chocolate. The measuring probe was a stainless steel cylinder of 2 mm diameter with a penetration depth of 4 mm. The maximum loading force was determined and that was used for the evaluation. The tests were performed with 1 °C intervals in the 25–32 °C temperature range.

Fig. 1 represents a rheogram which shows typical relationships between deformation and the loading force for the chocolates. The penetration was carried out on ten pieces of chocolate samples in every measurement. The ten curves of rheogram show that the loading force reached its maximum value at a very low penetration depth and after that it decreased a little bit and remained almost constant, with a slight decrease until the end of the penetration process.

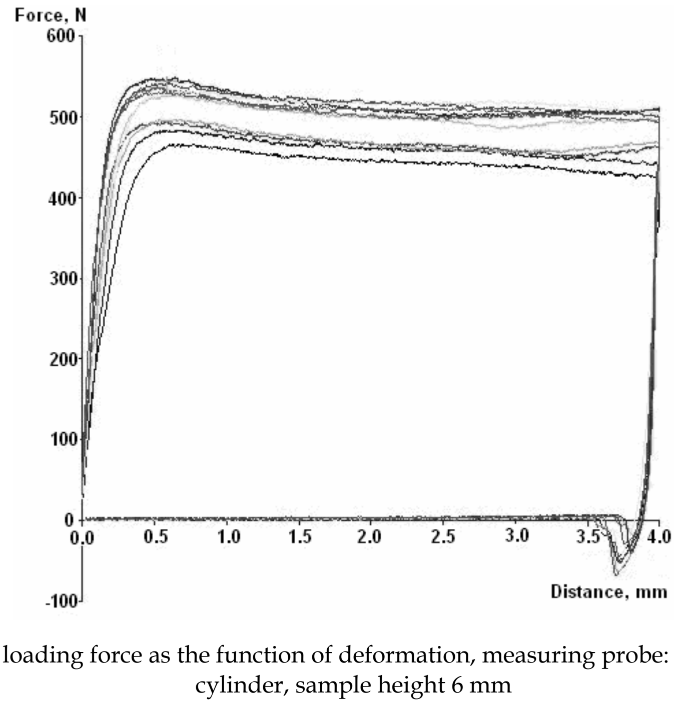

Fig. 1. The loading force as the function of deformation, measuring probe: stainless steel cylinder, sample height 6 mm

Fig. 2 shows the results of the experiments performed with fresh chocolate samples that contained only CB (neither CBE, nor CBI). This figure demonstrates the coefficient of variation and the average of the maximum loading force values for ten parallel measurements versus the temperature.

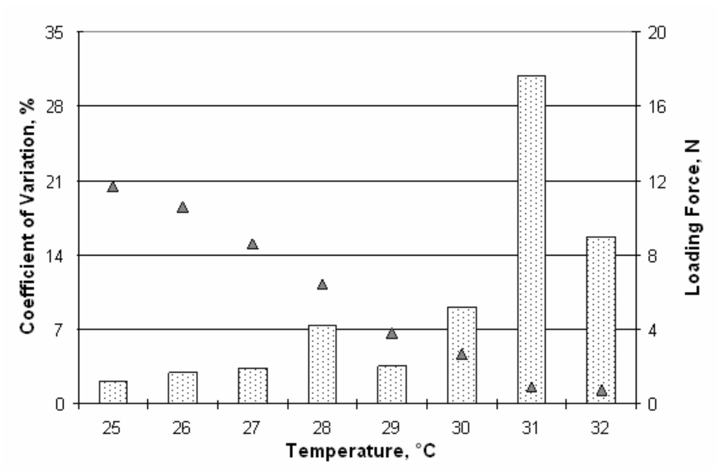

Fig. 2. The coefficient of variation ☐ and the average of maximum values of loading force ▲ for fresh CB-samples of the chocolates versus temperature

When taking into account earlier experience and that chocolate is a multi-component complex system we thought that a coefficient of variation is acceptable if it does not exceed 10%. Values of coefficient of variation varied between 2.13% and 9.09% when the sample temperature was between 25 °C and 30 °C. However, in a higher temperature range (31 °C and 32 °C) the coefficient of variation sharply increased. The cause of this phenomenon was that there is a phase change in the chocolate structure. It is supposed that there is a gradual melting of cocoa butter and, within the solid structure of the sample, these melted parts are present and make its consistency inhomogeneous. The results of this melting process gave high coefficient of variation. The loading force decreased with the increase of the temperature, and above 31 °C it reached a very small value and did not change considerably.

Therefore, it is supposed that the variation of the loading force versus the temperature can be approximated by linear relationship between 25 °C and 30 °C. Regression method was used to get this function between the loading force and the temperature in this definite range *(Fig. 3)*. This figure shows the determination coefficient for the approximation, as well. Naturally, this relationship is valid only for the definite temperature range.

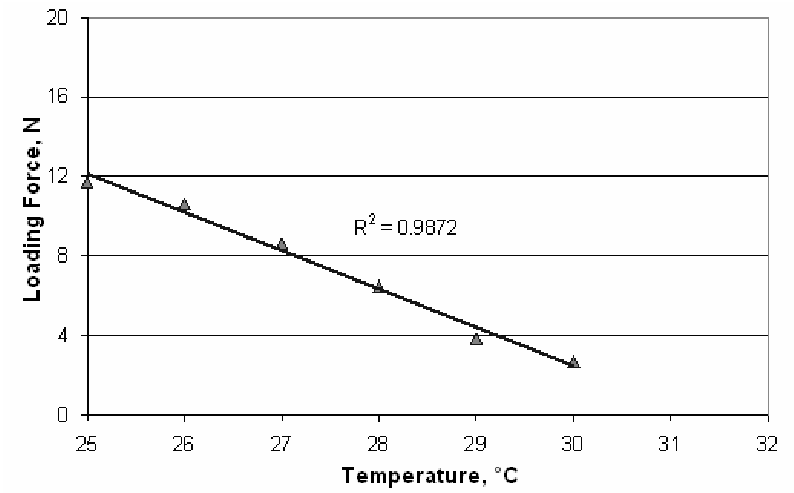

Fig. 3. Loading force versus the temperature for fresh CB-samples

The goodness of the fit of this approximation was checked by three different statistical methods:

1. The correlation analysis showed that the coefficient of determination was R^2 = 0.987; this meant that 98.72% was the influence of the temperature on the loading force. Therefore, the model fitted to the test results really well.
2. Residual analysis *(Fig. 4)*: the position of errors was random, there neither definite tendency, nor outliers were observed. According to the graphical result of the residual analysis, the linear approximation was accepted.
3. Durbin-Watson statistic: According to H_0 hypothesis, there was no autocorrelation found between the two variables. The statistics calculated for the above model and the value of Durbin-Watson value was d = 1.9587. Since 1.9587 > 1.356, therefore we accepted H_0 hypothesis (there was no autocorrelation) according to Durbin-Watson statistics, there was no systematic error and the regression model was suitable for the purpose.

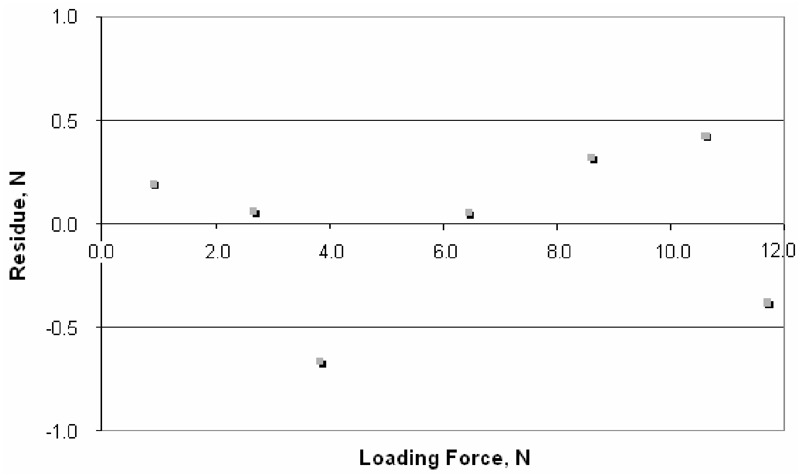

Fig. 4. Distribution of estimation errors versus the loading force with fresh CB-samples of chocolate

The suitability of the linear regression model shown in *Figs. 3* and *4* was confirmed by experiments performed at the end of each month with CB-, CBE- and CBI-samples stored in the warm and the moderate temperature rooms and in the cold cellar.

This linear regression correlation describes the change of loading force that is a specific characteristic of the hardness of chocolate, with 95% confidence level in the definite temperature range.

The parameters of the regression line were estimated by the least squares criteria, the equation is as follows:

$$Y_i^{'} = b_0 + b_1 \cdot X_i$$

where:

$Y_i^{'}$	*Y* value of the *i*-th data pair estimated with the regression line
X_i	*X* value of the *i*-th data pair
b_1	slope
b_0	ordinate intercept

The slope and ordinate intercept were determined by linear regression model. In *Fig. 3* the values of the slope and the intercept at 25 °C are –1.9319 and 12.14, respectively. The slope of the line provides the information on the heat resistance of the chocolates. The greater the slope, the more intense the softening and the smaller the hardness of the chocolate are. According to our experiments, it is possible to characterize the hardness and the heat resistance of chocolate samples by the regression line fitted to the data points of force-temperature relationship with given chocolate compositions.

2.2. The influence of chocolate composition and storage conditions on hardness

The stainless steel needle was used as a measuring probe for the texture analyser to perform experiments for the hardness measurement of solid chocolates to determine the force-deformation relationships for the samples *(Fig 5)*.

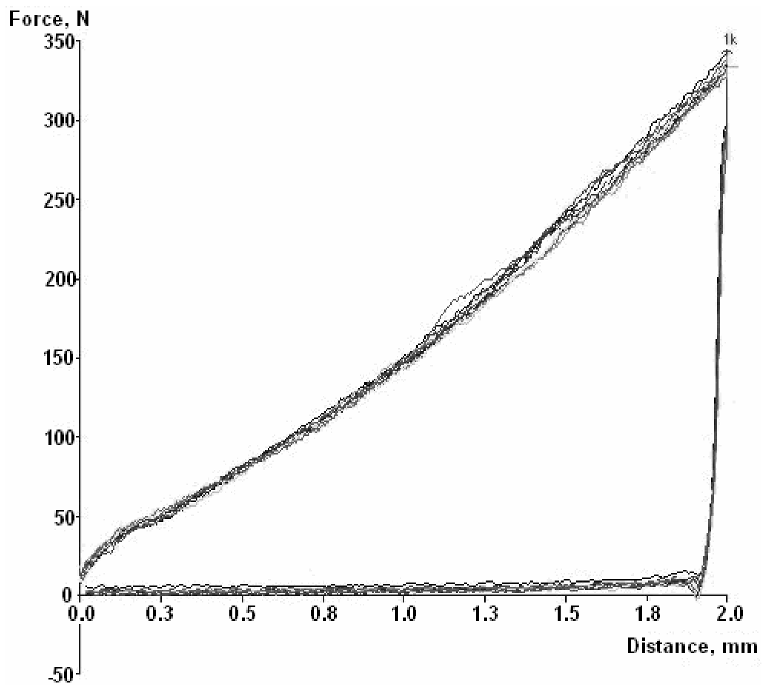

Fig. 5. The loading force as the function of the deformation, measuring probe: stainless steel needle

Fig. 5 represents curves of ten parallel measurements. The value of the loading force continuously increased and reached its maximum at the pre-defined highest deformation value. This maximum value of the loading force was used for the evaluation. Compression tests were performed to analyze the influence of the different storage conditions and that of the compositions of the chocolate samples on the hardness.

The changes in the hardness of chocolate samples containing CB-, CBE- and CBI-fat stored in the warm (southern) and in the moderate temperature (northern) storage rooms and in the cold (cellar) were measured. The tests were performed after one week storage and, after that, at the end of each month *(Figs. 6, 7* and *8).*

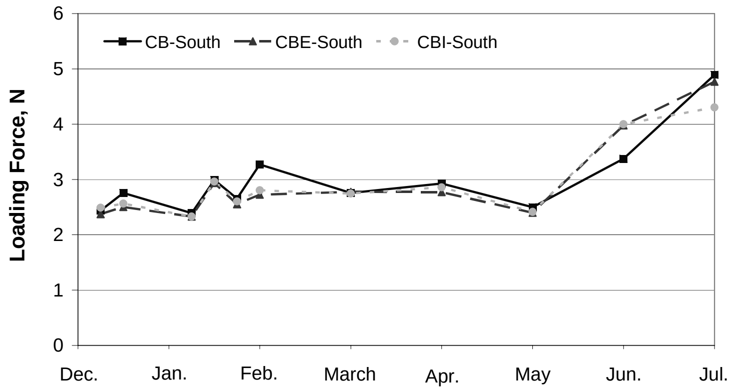

Fig. 6. Loading force of CB-, CBE- and CBI-samples and storage time, the samples were stored in the warm (southern) room

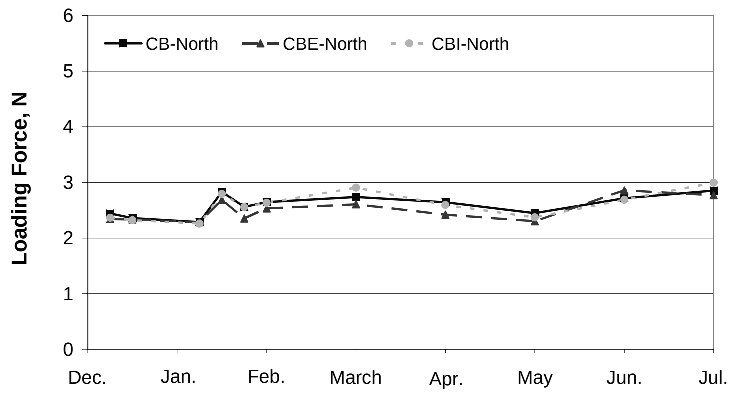

Fig. 7. Loading force of CB-, CBE- and CBI-samples and storage time, the samples were stored in the moderate temperature (northern) room

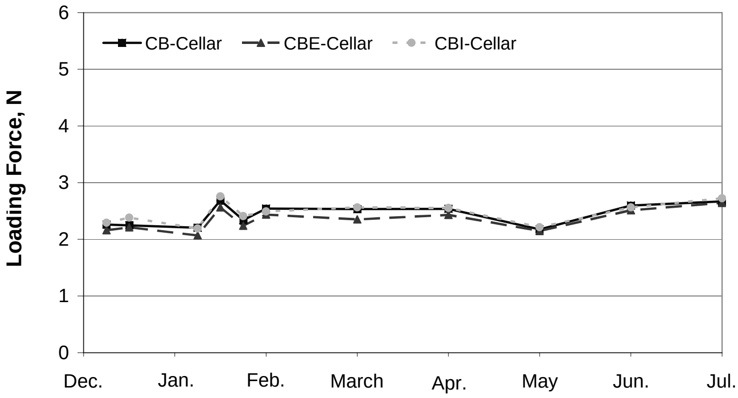

Fig. 8. Loading force of CB-, CBE- and CBI-samples and storage time, the samples were stored in the cold room (cellar)

Figs. 6, 7 and *8* show that the curves for the chocolate samples produced in the first days of December changed only slightly during the first six months of storage. However, after the sixth month, the loading force increased as the function of the storage time. *Fig. 6* shows that the samples stored in the warm (southern) room are the hardest. The chocolate samples stored in the moderate temperature (northern) room show slightly smaller hardness (*Fig. 7*), while the softest chocolate samples are the ones stored in the cold room (cellar) *(Fig. 8)*. The greatest change in hardness can be seen in the results measured at the end of the storage period. The samples stored in the warmest conditions (in the southern room) were harder than the ones stored under cooler conditions (in the northern room and in the cellar).

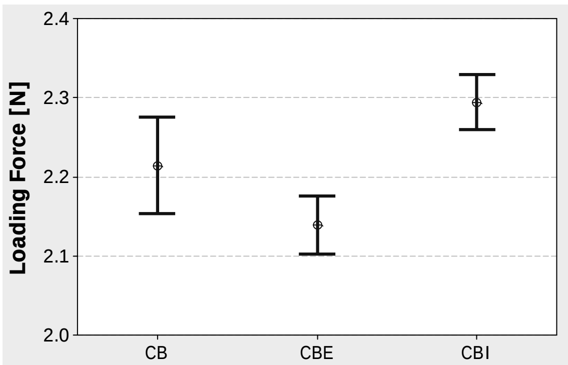

Fig. 9. The mean and the confidence interval of the loading force for CB-, CBE- and CBI-samples after one week storage in the cold room (cellar)

Figs. 9 and *10* illustrate the mean and the confidence interval of the loading force for CB-, CBE- and CBI-samples, after one week storage under different conditions.

Fig. 9 demonstrates the influence of chocolate composition on the hardness after one week storage in the cold room (cellar). The hardest were the CBI-samples and the loading force was the lowest with the CBE-samples. The hardness of the CB-samples was between that of the two other ones. The hardness of the CBI-samples was 4.5% higher and the CBE-samples 2.7% lower than with CB-samples.

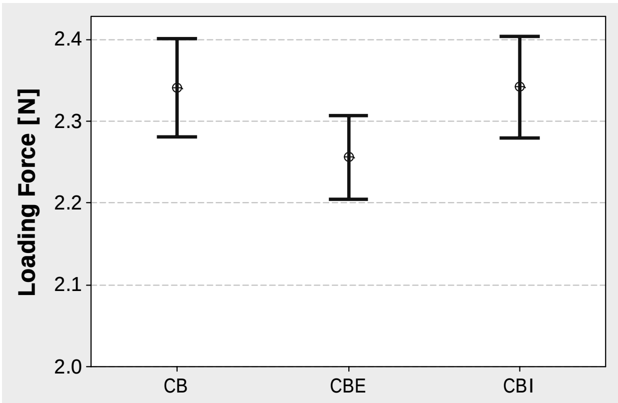

Fig. 10. The mean and the confidence interval of the loading force of CB-, CBE- and CBI-samples after one week storage in the warm (southern) room

Fig. 10 shows the influence of chocolate composition on the hardness after one week storage in the warm (southern) room. In this case, the hardest were the CB- and the CBI-samples and the lowest loading force was found with the CBE-samples. However, the differences were not significant. The hardness of the CBE-samples was 4.5% lower than with CB- and CBI-samples.

Figs. 11 and *12* illustrate the mean and the confidence interval of the loading force for CB-, CBE- and CBI-samples after eight months storage under different conditions.

Fig. 11 shows the influence of chocolate composition on the hardness after eight months storage in the cold room (cellar). The hardest were the CBE-samples and the softest were the CBI-samples. However, there were not significant differences between the samples.

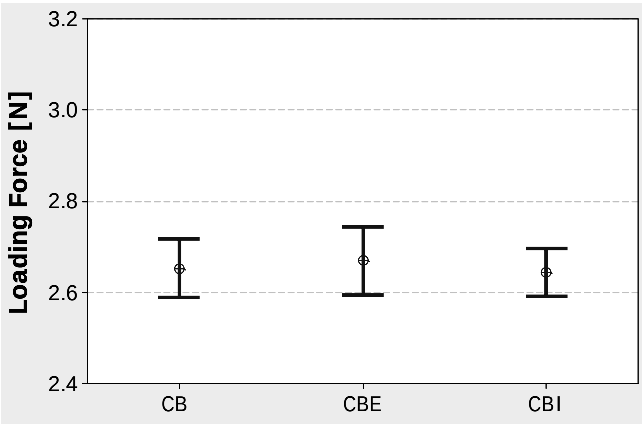

Fig. 11. The mean and the confidence interval of the loading force of CB-, CBE- and CBI-samples after eight months storage in the cold room (cellar)

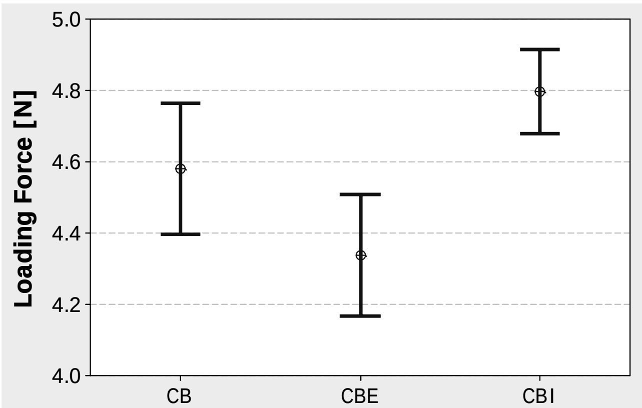

Fig. 12. The mean and the confidence interval of the loading force of CB-, CBE- and CBI-samples after eight months storage in the warm (southern) room

Fig. 12 demonstrates the influence of chocolate composition on the hardness after eight months storage in the warm (southern) room. The hardest were the CBI-samples and the lowest force was found with the CBE-samples. The CBI-samples were significantly harder than the CBE-samples. The hardness of the CB-samples was between the two other ones. The hardness of the CBE-samples was 5.24% lower and the CBI-samples 4.80% higher than with CB-samples.

Figs. 13, 14 and *15* illustrate a comparison of the mean hardness values depending on the influence of the different chocolate compositions and the storage conditions after one week and eight months of storage.

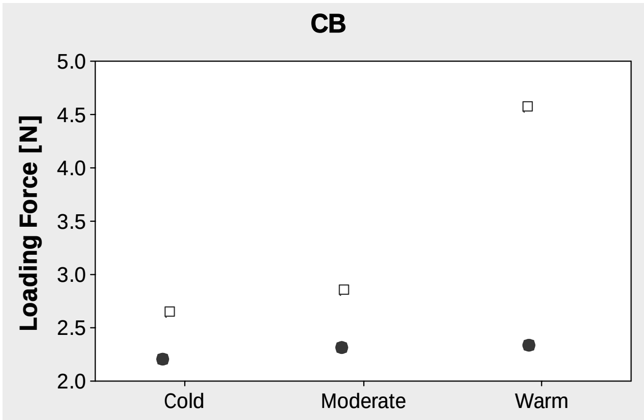

Fig 13. The mean hardness values of the CB-samples stored for one week ● and eight months □ under different storage conditions

Fig. 13 shows the mean hardness values of CB-samples stored for one week and eight months depending on the storage conditions. The hardness of the CB-samples stored for eight months was a little bit higher than the samples stored only for one week. However, the hardness of the CB-samples was definitely the biggest after eight months when stored under warm conditions in the southern room (approximately 100% increase), where the temperature changed in a very wide range because of the sunshine. Probably the reason for this phenomenon is the thermocyclic hardening.

Fig. 14 shows the mean hardness values for CBE-samples stored for one week and eight months under different storage conditions. The hardness of the samples stored for eight months was higher than the ones stored only for one week. However, the hardness of the CBE-samples was definitely the highest after eight months when stored under warm conditions in the southern room (approximately 92.5% increase) where the temperature changed in a very wide range because of the sunshine. Probably the reason for this phenomenon is thermocyclic hardening.

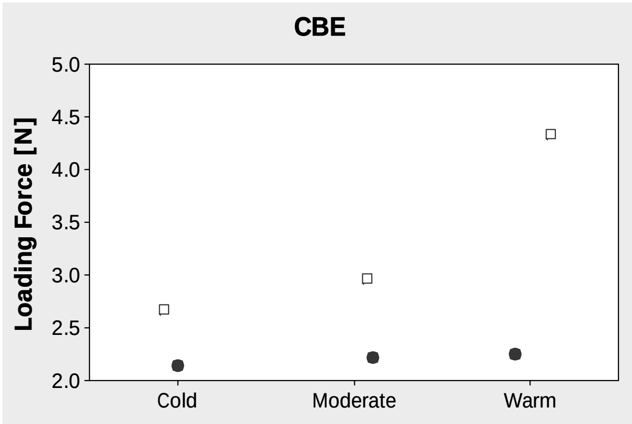

Fig. 14. The mean hardness values of the CBE-samples stored for one week ● and eight months □ under different storage conditions

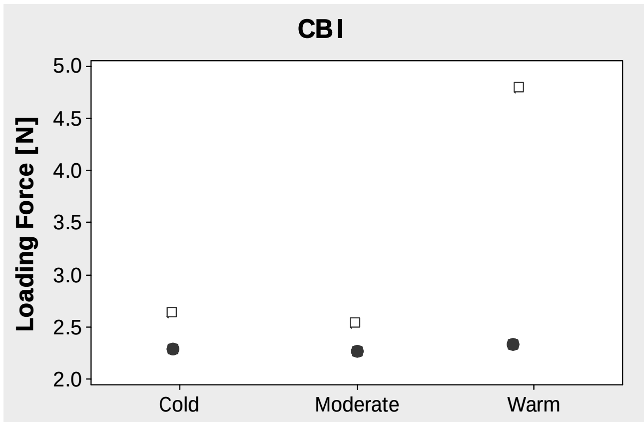

Fig. 15. The mean hardness values of the CBI-samples stored for one week ● and eight months □ under different storage conditions

Fig. 15 illustrates the mean hardness values for CBI-samples stored for one week and eight months under different storage conditions. In this case the result is similar to the other two compositions, because the hardness of the samples stored for eight months was higher than the ones stored only for one week. But the hardness of the CBI-samples was the highest after eight months when stored under warm conditions in the southern room (approximately 109.51% increase) where the temperature changed in a very wide range because of the sunshine. Probably this phenomenon can be explained by thermocyclic hardening that was similar to the two other samples.

First it was surprising that the hardness of the samples increased with beginning of the warm season in the storage rooms as one would expect a softening, due to the higher storage temperatures. This increase in hardness was especially high in the samples stored in the warm (southern) room and led to hardness values that were even more than twice as high. The quality monitoring up to eight months showed that the reason for this increase in hardness was not a special storage time, but the increasing temperatures with the beginning of the warm season and the cyclic change of the temperature during day and night. So an explanation for this unexpected increase in hardness can be the thermocyclic hardening of the chocolate samples under these storage conditions.

3. Conclusions

A texture analyser was fitted either with a needle or a cylindrical probe to measure the hardness and the heat resistance of chocolate samples of different compositions. These probes were approved to be appropriate for the purpose.

Statistical calculations gave the result that the loading force describes the changes in hardness and heat resistance of chocolate by a linear regression correlation at 95% confidence level in the temperature range between 25 and 30 °C. So the hardness and the heat resistance of solid chocolate can be determined by the slope and ordinate intercept of the regression line for the compression force – temperature relationship.

In systematic investigations over a time of up to eight months, the influence of the use of CBE/CBI in chocolate and the influence of the storage conditions (also extreme) on hardness and heat resistance of chocolate were tested. The results show that the differences in hardness between the chocolate samples with CBE/CBI and those without CBE/CBI, both stored in the cellar (cold storage), are marginal. The differences are slightly clearer for the other two storage rooms. After a definite storage time the hardness of all samples increased, in the case of the southern room to a value up to twice as high. An unexpected increase in hardness occured by the storage during the warm season by the cyclic change in temperature between day and night.

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