EFFECT OF THE TEMPERATURE ON THE RHEOLOGICAL PROPERTIES OF COMPOUND COATING

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Short running title: **RHEOLOGICAL PROPERTIES OF COMPOUND COATINGS**

Abstract

Cocoa butter is one of the most valuable components of chocolate, but due to its high world market price, various cocoa butter replacements are increasingly used in the confectionery industry.

The objective of our experiment was to investigate the rheological properties of a compound coating depending on the pre-treatment temperature regimes.

Compound coating samples were measured at six different temperatures with 2°C resolution between 40 and 50°C. The melted samples were measured by RV1 rotational rheometer at the actual melting temperatures. The remaining melted samples were filled into 9x9x9mm cubes molds. These were cooled 24h in freezer and next day the samples were thawed to room temperature for 3 hours with different temperature-combinations. The solid cubes were measured with Texture Profile Analysis (TPA) test by SMS TA-XTplus precision penetrometer at room temperature.

Results show the effect of pre-treatment on the viscosity of the coating. Furthermore significant differences were found among the samples cooled with different cooling methods. Our results stress the importance of the correct handling of the materials for confectioners.

Keywords: Compound coating, temperature, rheology, viscosity, TPA

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Introduction

Chocolate is an important product of the confectionery industry. The fat in chocolate, the cocoa butter, has quite a few interesting properties, but there are some factors that make it not always suitable. The first is its extremely high and constantly fluctuating world market price, and the second is the problems of its processing and storage (tempering, fat bloom, sugar bloom).

As a result, the use of cocoa butter alternatives in the industry has become increasingly popular. They have similar physico-chemical properties as cocoa butter, but are cheaper and do not require much preparation. During production, some or all of the cocoa butter is replaced by vegetable fat, in which case it can no longer be called chocolate (if the added vegetable fat amount is higher than 5% based on the total fat content), instead it is called compound coating or simply coating. Coatings can be used further for sweets, baked goods and other snacks (Talbot, 2009).

There are four types of cocoa butter alternatives: Cocoa Butter Equivalents (CBE), Cocoa Butter Improvers (CBI), Cocoa Butter Replacers (CBR) and Cocoa Butter Substitutes (CBS). The CBS coatings have lauric acid content, they are chemically completely different from cocoa butter, thus they express very low (<5%) compatibility with cocoa butter (Lipp and Anklam, 1998). CBS fats cannot be blended with cocoa butter because their blend forms an eutectic mixture whose crystallization is unpredictable. These fats solidify in different crystalline structures, therefore these two fat-types are incompatible and it is recommended to use degreased cocoa powder in combination with CBS (Lonchampt and Hartel, 2004).

The steps in the manufacturing process are roughly the same for compound coatings as it is for chocolate, but there are differences in temperature regimes. The main difference is that compound coatings do not require tempering, which makes the production easier. In addition to the chemical composition, the crystallization behavior of fat is influenced also by various dynamic factors, such as cooling rate, mixing and crystallization temperature (Metin and Hartel, 2005).

Important characteristics of both chocolate and coating is their rheological properties such as viscosity and yield stress. Viscosity can be considered as internal movement. Because they are not ideal fluids, they have yield stress that require a significant amount of force to start the flow (Beckett, 2008).

The examination of the mechanical parameters of the coatings is also an important point. Generally, hardness, brittleness, particle size, film thickness, and to understand crystallization behavior, relationships between microstructure and macroscopic properties in coatings are used to be determined. (Foubert et al., 2006; Gregersen et al., 2015a, 2015b)

The objective of our experiment was to investigate the rheological properties of a compound coating depending on the pre-treatment temperature regimes in melted and solid condition. Furthermore aim was to predict the melted temperatures and thawing methods based on the TPA parameters which showed the highest significant different.

Materials and methods

Materials

CBS coating used in the experiments was provided by Göteborgs Food Budapest ZRt. The ingredients of the measured compound coating are following: sugar, partially hydrogenated vegetable fat (palm kernel) CBS fat, low-fat cocoa powder, emulsifiers (sunflower lecithin, PGPR), aroma.

Viscosity measurement of the melted samples

The compound coating were tempered in drying chamber at six different temperatures 40-42-44-46-48-50°C. The shear stress of the sample were measured with Z10 DinTi type conical end stainless steel cylinder by Haake RotoVisco1 rotational viscometer at the actual melted temperature, and the viscosity was determined from the ratio of the shear stress and shear rate. The measurement consisted of 3 period with 100-100s: acceleration section 1-500 1/s, constant speed section at 500 1/s and deceleration section 500-1 1/s shear rate. The viscosity was determined from the constant speed section of the flow curve at the melting temperatures. Each measured groups consisted of 12 samples (N = 72).

TPA measurement of the solid samples

The remaining melted samples were filled into 9x9x9mm cubes molds in case of all melting temperatures. These cubes were held 24h in freezer (-18°C) and next day the samples were thawed to room temperature for 3 hours with different melting regimes, which were as the following: 2 hours refrigerator + 1 hour room temperature, 1 hour refrigerator + 2 hours room temperature, 3 hours room temperature. The temperature and the relative humidity were 8.7±0.6°C and 51.1±9.7 RH% in the refrigerator and 28.1±0.3°C and 28.4±0.7 RH% in the measuring room. The solid cubes were measured with Texture Profile Analysis (TPA) test by TA-XTplus (Stable Micro System, Surrey, UK) precision penetrometer with P/25 type stainless steel cylinder at room temperature. Test setting were as follows: compression with pre-test speed 2 mm/s, test speed 1 mm/s, post-test speed 2 mm/s, strain 10%, count 2, 200pps. A 5kg load cell was used and the hardness, adhesiveness, resilience, cohesion, springiness, gumminess and chewiness parameters were determined from the deformation-time curves. Each measured groups consisted of 10 samples (N=180).

Statistical analysis

The measured rheological properties values were evaluated by SPSS 25.0.2.2 (SPSS, 2018) and R-Studio Version 1.1.414 (R-Studio, 2018). After leaving out the outlier data, a normality test (Kolmogorov-Smirnov and Shapiro-Wilk Test) was run on results of the samples. Two-way ANOVA was used to identify any significant differences between the groups in the case of certain parameters. Where ANOVA indicated TukeyHSD test ($p<0.05$) was used for detecting the significant differences between the groups (Reiczigel et al., 2014). The thawing temperature were predicted based on the results obtained with mechanical tests parameters by the means of PLS regression (Kvalheim, 2009). PLSR models were built based on hardness, gumminess and chewiness parameters obtained by TA.XTPlus to predict the melting temperature and the thawing methods.

Results and discussion

Figure 1. shows the average of the viscosity from the constant speed section of the flow curve at the melting temperatures. Significant difference was found between the 40, 42°C and the other temperatures. However there is no significant difference between the viscosities among the groups of 44°C, 46°C, 48°C and 50°C melting temperatures. Furthermore the viscosity and the standard deviation of the viscosity decreases with the increasing of the temperature, which could be a result of increasing homogeneity in the structure of the samples.

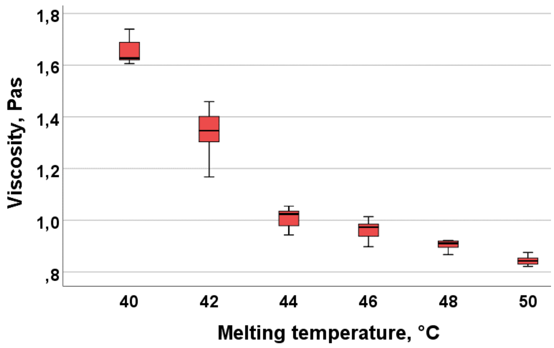

Figure 1. Viscosity in the function of the melting temperature at 95% CI (N=66)

The hardness, adhesion, resilience, cohesion, springiness, gumminess and chewiness parameters were calculated from the deformation-time curve of TPA test. From the rheological parameters the hardness, gumminess and chewiness showed the strongest significant differences among the sample groups. The hardness values at 50°C melting temperature showed significant difference from the other temperatures with more than doubled values.

Significant difference was found between the temperatures, however there is no significant difference between the 42°C and 44°C in case of each thawing condition (Figure 2.). Furthermore increasing hardness of the compound counting cubes appears to be proportional to the temperature increase.

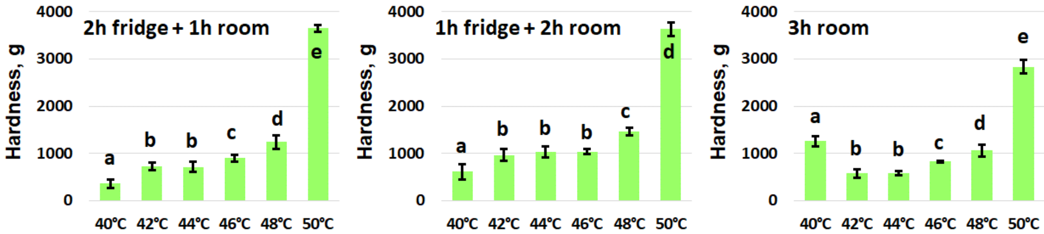

Figure 2. Significant differences of the melting temperatures at different thawing conditions based on hardness (N= 172) (a, b, c, d, e - significant different samples)

The gumminess and chewiness (Figure 3. and 4.) increased with the increase of the melting temperature. The values are also extremely high at 50°C in case of these rheological parameters. Significant difference was found between the temperatures, however the values are closer in the 42-46°C temperature range, and there was no significant difference between the 42-44°C.

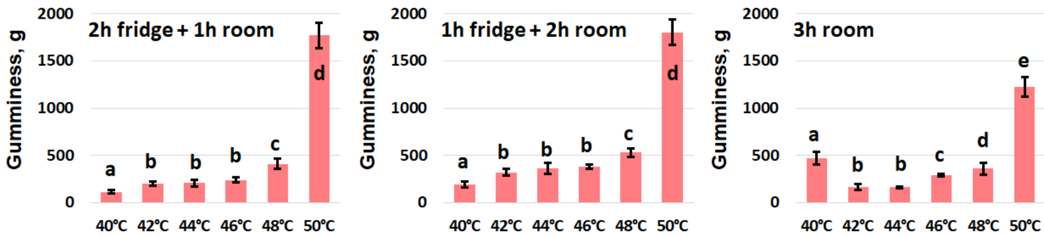

Figure 3. Significant differences among the melting temperatures at different thawing conditions based on gumminess (A) (N= 170) and (a, b, c, d, e - significant different samples)

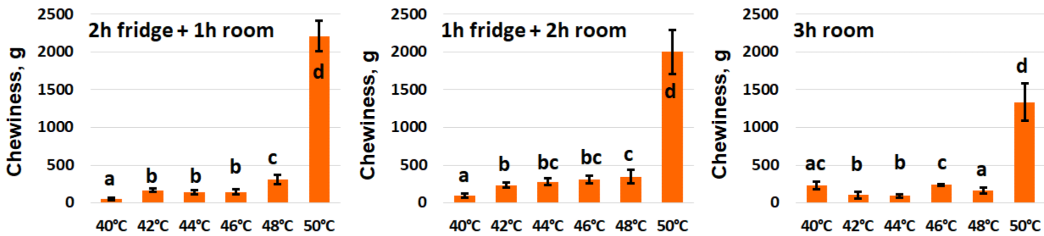

Figure 4. Significant differences among the melting temperatures at different thawing conditions based on and chewiness (B) (N = 165) (a, b, c, d - significant different samples)

TPA rheological parameters of the samples were statistically analyzed grouped by the thawing methods, too. The next figures illustrate these results at the melting temperatures. Significant differences were found among the thawing methods based on the hardness except for 50°C. However the samples only thawed at the room temperature were significantly different from the samples which had been thawed partially in the refrigerator (Figure 5.).

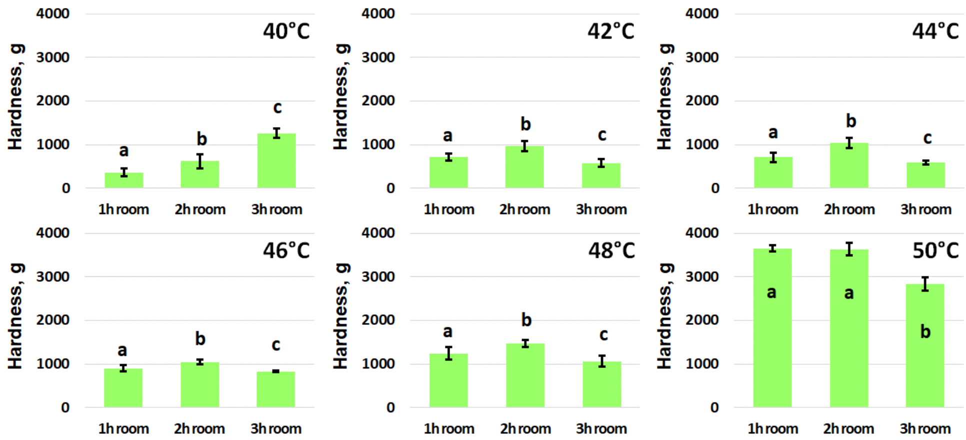

Figure 5. Significant differences among the thawing conditions of the differently melted samples based on hardness (N= 172) (a, b, c - significant different samples)

In the case of the gumminess and chewiness (Figure 6. and 7.) except for 48°C samples the results are same. The groups are separated well by the used melting temperatures. Furthermore significant difference was found between the thawing conditions, the samples thawed only at room temperature are significantly distinguished.

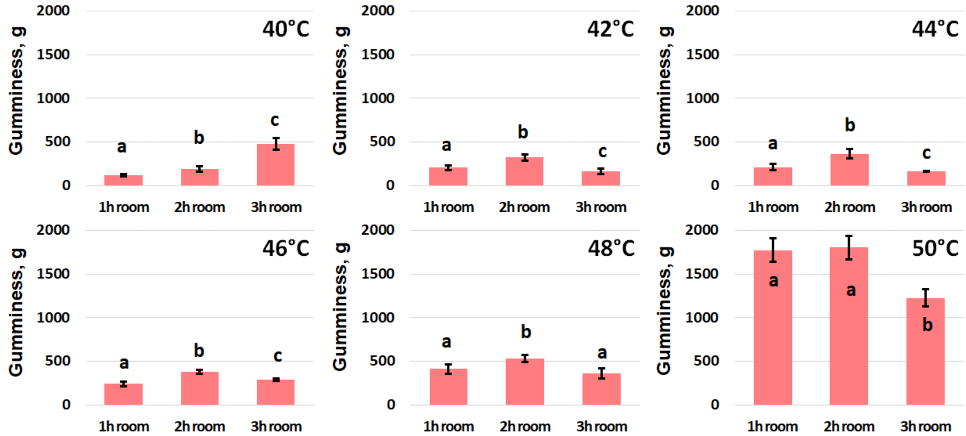

Figure 6. Significant differences of the thawing conditions of the melted-frozen samples based on gumminess (N= 170) (a, b, c - significant different)

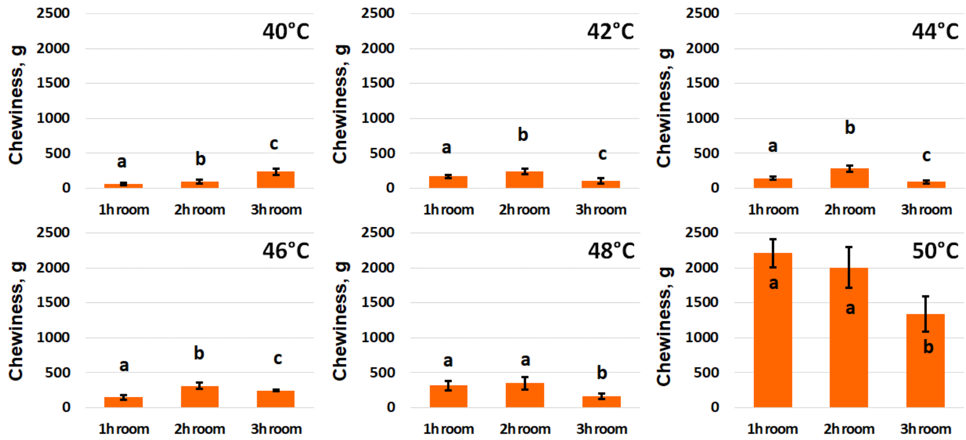

Figure 7. Significant differences of the thawing conditions of the differently melted samples based on chewiness (N= 165) (a, b, c - significant different)

The melting temperature and thawing conditions were used in an estimation model based on the *hardness*, *gumminess* and *chewiness* parameters by Texture Analyzer. Results were used in the PLS regression (Table 1.). Acceptable correlation was found between the estimated and measured parameters based on the correlation of the cross – validation at hardness, gumminess and chewiness, the estimation showed the highest correlation based on the hardness and gumminess.

Table 1. PLS calibration and cross-validation (leave one out (LOO)) to predict the properties of melting temperature and thawing conditions based on the results of the hardness, gumminess and chewiness

Property	LV (number)	calibration		cross validation	
		R^2	RMSEC*	R^2	RMSEP**
Melting temperature [A]	3	0.5207	2.361	0.5106	2.386
Melting temperature [B]	2	0.6016	2.153	0.5925	2.177
Melting temperature [C]	2	0.5912	2.181	0.5811	2.208
Thawing condition [A]	3	0.1317	0.7630	0.1046	0.7748
Thawing condition [B]	2	0.06938	0.7899	0.04139	0.8017
Thawing condition [C]	2	0.09389	0.7794	0.0686	0.7902

* root mean square error of calibration; ** root mean square error of prediction. [A] estimation based on hardness, gumminess and chewiness. [B] estimation based on hardness and gumminess. [C] estimation based on hardness and chewiness. LV: latent variable

Figure 8. shows the results of the prediction of the melting temperature and thawing conditions properties of the samples based on the data of experiment. The diagrams contain also the parameters of calibration and leave one out (LOO) cross - validation.

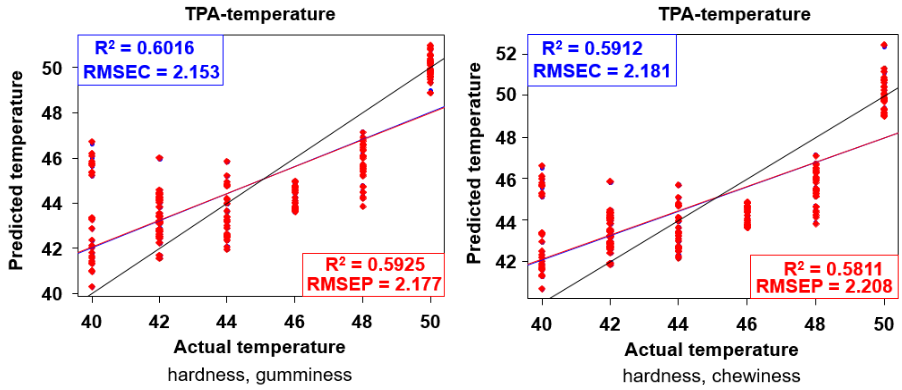

Figure 8. PLSR Results of the prediction of the melting temperature of measurement based on the hardness, gumminess and chewiness

Conclusion

The objective of our experiment was to investigate the rheological properties of a compound coating depending on the pre-treatment temperature regimes in melted and solid conditions. Furthermore aim was to predict the melted temperatures and thawing conditions based on those TPA parameters which showed the highest significant different.

From the determined rheological parameters the hardness, gumminess and chewiness showed the strongest significant differences among the samples. These parameters are suitable to describe the differences between the groups based on the melting temperatures and the thawing conditions. The measuring parameters were the same at all melting temperatures. The maximum melting temperature - by the manufacturer recommended- is 50°C. It can be assumed that the coating mass has a different behavior at this temperature and its spectacular effect can be seen in the parameters examined during the experiment. This assumption is confirmed by the BC Cook Articulation Committee (2015) that temperatures above 50° C can be a problem for coatings because the crystalline structure formed earlier will be destroyed and the viscosity of the mass will be reduced, thereby impairing the coating ability.

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