CORVINUS
UNIVERSITY of
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Faculty of Food Science

THESIS OF PH.D. DISSERTATION

CHARACTERIZATION OF RHEOLOGY OF GELATIN BASED CONFECTIONERY PRODUCT

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The applicant met the requirement of PhD regulations of the Corvinus University of Budapest and the thesis is accepted for defense process.

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1. The background of research and the aim of work

The gum candy is a very popular confectionery product. The peoples consume it generally regardless of age, genus or place of living. This is proved well by the fact that gum candy has already offered as a functional food, too.

The quality of candy gum is determined primary by the textural properties. Texture examination in itself is an interesting research field, because not only the description but the modelling of a complex, subjective sense is a difficult task with objective instruments and methods. In the sensory tests the panelists can describe lot of complex mastication properties, which are very complicated to measure with instruments. Whereas the results of sensory evaluation can be transformed with difficulties into the product technology, therefore the objective instrumental measuring of textural properties is a real industrial demand.

The aim of my work was to describe the textural properties of gelatin-based gum candy with objective, rheological methods so, that the results of rheological examination can be compared with the subjective sensory results, too. But the comparison of the measured, instrumental texture properties with sensory evaluation results is not part of my dissertation. Moreover in this dissertation solely the gelatin based gum candies are examined.

Additional goal was to follow up the textural changes in gum candy during storage at various constant temperatures with parameters of Texture Profile Analysis (TPA) and Creep-Recovery Test (CRT) curves. Further aims were to determine the hardness, the cohesiveness and the adhesiveness of gum candy, which sensory properties are easily measured instrumentally as well, and to fit such multi element rheological model, which describes precisely also the creeping and recovering part of CRT curve with same or practically same rheological parameters.

2. Materials and methods

2.1. About the gum candy

For all the experiments the same gelatin based gum candy was used, which has been available in the retail sale. The examined gum cadies were the market leader products of a national subsidiary of a great, multinational confectionery company. Before the experiments the samples were stored in the original and unopened packaging protected from light and at low temperature (in refrigerator). The samples of short and long time storage experiments were also stored in the original and unopened packaging at different, constant temperatures. During the tests I made an effort to open the packaging just before the test.

2.2. The instrument and the measuring methods

For all the experiments a TA-XT.2 texture analyzer (Stable Micro Systems Ltd., Godalming, Surrey, UK) was used with a Ø75 mm diameter cylinder aluminum plunger with plain plunger surface (producer's code: P75). The parameters from the measured curves were calculated with Texture Exponent 1.21., MS© Office® Excel 2003, and Excel 2010 software.

Texture Profile Analysis (TPA) is a widely known, used quasi as a patent measuring method for characterizing the textural properties of different foods. The TPA test contains a compression and a decompression after each other two times, which imitates the mastication process. Several measuring settings can be set optionally. During the TPA test the force (the stress, respectively), the deformation (relative deformation, respectively) and the time data were recorded. The aim of the TPA measuring method is on one hand to determinate objectively the sensed textural properties during the consumption and on the other hand to characterize these textural properties with parameters calculated from the curve. These parameters should be suitable to compare the textural characteristics of different samples with each other. It is very important to know, that the TPA test method give information about the sample structure, but this method is not applicable for modeling the structure, because during the test the perceived textural properties (e.g. chewiness) are recorded, not the rheological parameters (e.g. elastic modulus).

The Creep-Recovery Test (CRT) is a complex rheological test method, which contains a creeping and after it a recovering test. According to this the CRT test contains 4 parts: loading – creeping – unloading – recovery. During the creeping part the loading is fixed on a constant value for a definite time (called creeping time) and during this time the increasing deformation is measured (it is called creeping). In the recovery part the decreasing deformation is measured under zero loading, so the plunger without force touches the sample. The goal of the CRT test method is to determine the rheological properties of the sample from the creeping and recovery curves. This measuring method gives an opportunity for rheological modelling, because the equations of different rheological models can be fitted both on the creeping and on the recovering curves.

2.3. Performed experiments

2.3.1. Effect of storage temperature on the TPA and the CRT curve parameters

The softening/hardening point of gelatin gel depends on the gelatin concentration: at 10 m/m% gelatin concentration the softening point of the gel is about 29°C. Usually the gum candy is exposed to even higher storage temperatures (transportation, storage on shelf in shop or at home, etc.). So the aim of the storage experiments was to examine the effect of storage temperature on rheological properties of the gum candy. The temperatures (14°C, 16°C, 18°C, 20°C, 22°C, 24,5°C, 26°C, 28°C, 30°C, and 32°C respectively) occurring with high probability during the storage were set. Two-two unopened, original sample packages were stored in ten groups at set temperatures for 72 hours at 50%±10% relative humidity. 20-20 samples from each bag were measured with TPA and CRT tests, respectively at room temperature.

2.3.2. Long time storage experiment

The aim of the long time storage experiment was to examine the effect of storage conditions (temperature, time) on the rheological properties of the gum candy during the producer guaranteed shelf life. The unopened, original bags were stored in four groups at four different storage temperature (15°C, 20°C, 25°C and 30°C, respectively) for 12 month (from 01.06.2011. to 01.06.2012.) in temperature controlled storage boxes with 10 L volume. At the beginning of each storage month (altogether 13 times) 2-2 bags were taken out from the storage boxes (altogether 4 x 2 = 8 bag per month). In every group 30-30 samples were measured with both TPA and CRT test method, 3120 sample was measured (at the 4 temperatures of the storage with 2 methods 13 times with 30 repetitions = so altogether 3120 sample).

2.3.3. Analysis of measuring settings of CRT method

The aim of the experiment was to determine the most effective setting parameter from loading force; creeping/recovering time and deformation speed in CRT test. Further goal was to find the best setting configuration for gum candy measurements. The experimental tests was featured at room temperature with three repetitions in each configuration (5 loading force x 5 creeping/recovering time x 5 deformation speed x 3 repetition = 375 tests). From the recorded data after a data reduction a 2^3 type full factorial design was evaluated.

2.3.4. Fitting of rheological model

The aim of the experiment was to determine the rheological model of gum candy with usage of CRT test method. Gum candy samples were measured in 5 groups with different loading forces (1 N, 2N, 5N, 7 N and 10 N, respectively) with 20-20 repetitions in every configuration (5 loading force x 20 repetition = 100 test). From the recorded force – deformation – time data the creeping and the recovery part was cut out. Knowing the sample height (parallel size with the loading force) the change of relative deformation (ε) in both creeping and recovery part was calculated. Four different rheological models (Thomson-model with 3 element, Burgers-model with 4 elements and the Kohlrausch's stretched exponent version of both model) were fitted on the relative deformation ($\varepsilon(t)$) curves of both creeping and recovery parts. From the fitting coefficients the rheological parameters were determined (E_0, E_r, η, η_v). The calculated rheological parameter values were compared between the creeping and recovery part of such measuring curve, between the normal and exponential form of such model and between the 3 and the 4 element models.

3. Results

3.1. Effect of storage temperature on TPA and CRT curve parameters

From the TPA parameters the hardness, the adhesiveness and the ratio of force to deformation decreased, the cohesiveness remained quasi constant, the force ratio increased with at higher temperature. From the CRT parameters the ratio of force to deformation decreased with at higher temperatures. The deformation relations under 26°C were constant, over 26°C the ratio E/D_{max} decreased, the ratio P/D_{max} and ratio P/E increased at higher temperatures.

Both the read and the calculated parameters of TPA and CRT test shows, that about 26°C the structure of gelatin based gum candy changes. The temperature dependence of the most parameters (there was two exceptions) both under and over 26°C was characterizable with an Arrhenius-type exponential function. The coefficients of Arrhenius-type exponential function differed significantly under and over 26°C, this fact refers to structure changing (softening/melting point).

3.2. Long time storage experiment

Based on the results of the long time storage experiment it was determined, that the gum candy became harder during the storage (the hardness, the chewiness and the ratio of force to deformation increased), the elastic character decreased (ratio E/D_{max} decreased) and the plasticity of gum candy increased (ratio P/D_{max} and ratio P/E). These processes proceeded slower on low temperatures and faster on high temperatures. The product quality was preserved the best on 15°C storage temperature.

3.3. Analysis of measuring settings of CRT method

From the analysis of test results it was clear, that all the three setting factor of CRT had effect on the majority of CRT test results. It was also clear, that from the main factors the loading force had the most significant effect on the measured results. Contrary of my expectations the deformation speed had the second strongest significant effect on CRT test results against the deformation speed, which has significant effect only on the range of creeping. None of cross effects had significant effect. In case of each examined setting parameter the fitted multivariable regression model proved adequate on α=0.05 confidence level.

3.4. Fitting of rheological model

From the fitted rheological models the stretched exponent Burgers-model with four elements proved the most suitable for characterizing the texture of gelatin based gum candy. The values of rheological parameters calculated from both creeping and recovery part was quasi the same. The value of β = 0.5..0.6 referred to that, the distinctly elastic texture of gum candy was not characterizable with only one retardation and one relaxation time, but only with a time distribution spectrum with more different long retardation and relaxation time. The rheological model parameters (E_0, E_r, η, η_v) depended linearly on the applied loading stress in the examined stress interval (10-40 kPa).

3.5. New scientific results (thesis list)

1. During the long time storage of gelatin based gum candies the value of the following parameters of Texture Profile Analysis (TPA) increased linearly: harness (F_1 and F_2), ratios of force to deformation (F_1/D_1 and F_2/D_2) and gumminess ($F_1 \cdot (A_2/A_1)$). The value of TPA parameter cohesiveness (A_2/A_1) decreased linearly in a little range, while the ratio of peak forces (F_2/F_1) was independent from the duration time of storage.

2. During the long time storage of gelatin based gum candies the value of the following parameters of Texture Profile Analysis (TPA) decreased according to an Arrhenius-type exponential function: hardness (F_1, and F_2), ratios of force to deformation (F_1/D_1, and F_2/D_2) and gumminess ($F_1 \cdot (A_2/A_1)$). The value of TPA parameter cohesiveness (A_2/A_1) and force peak ratio (F_2/F_1) increased exponentially on higher storage temperatures.
3. From the Creep Recovery Test (CRT) parameters during the long time storage of gelatin based gum candies the value of the ratios of force to deformation (F/D_1 and F/D_{max}) increased linearly in a little range. The values of deformation ratios (E/D_{max}, P/D_{max}, and P/E respectively) were describable with a sigmoid function curve.
4. From the Creep Recovery Test (CRT) parameters during the long time storage of gelatin based gum candies the value of the ratios of force to deformation (F/D_1 and F/D_{max}) decreased according to an Arrhenius-type exponential function. The values of deformation ratios (E/D_{max}, P/D_{max}, and P/E respectively) were constant under 26°C and changed exponentially according to an Arrhenius-type exponential function over 26°C.
5. In case of gelatin based gum candies a break point was found at 26°C in the temperature dependence, which was explained with a phase transition in the gum candy texture (softening point). Based on the high carbohydrate content of the gum candy the phase transition could be a second order one, presumably. The speed of the change of each parameter of TPA and CRT were twofold-threefold higher over 26°C, than under 26°C storage temperature.
6. From the different rheological model curves, which were fitted, the Burger model with four elements gave significantly better fitting on the creeping and the recovery parts of Creep-Recovery Test (CRT) curves measured on gelatin based gum candies, than the Thomson-model with three elements. The stretched exponential form of both models gave a closer fitting, than the original models. The value of stretched exponent β was 0.5 in case of Thomson-model and 0.64 in case of Burgers-model. The rheological parameters of rheological models, which were calculated from the coefficients of the fitted curves, were quasi the same calculated from the creeping or

the recovery part of CRT curve. Based on these ascertainments, the stretched exponential Burgers model proved to be the most suitable model for the complex rheological characterizing of gelatin based gum candies.

7. In case of the CRT curves measured on gelatin based gum candies, all the rheological parameters (E_0, E_r, η, η_v) depended linearly on the applied loading stress in the examined stress interval. According to this, the Thomson model with three elements was describable with 6(+1) rheological parameter, and the Burgers-model with four elements with 8(+1) rheological parameter. In case of stretched exponential models the stretch exponent β is the +1 rheological parameter

4. Conclusions and recommendations

4.1. Conclusions

- Based on the results of the performed experiments and measurements, the TPA as a dynamic measuring method was proven suitable for characterizing the rheological properties of gelatin based gum candies. Thank to this, the results of the TPA tests are comparable with sensory properties of mastication process and with the results of sensory tests.
- The CRT test, as a static measuring method proved to be suitable for characterizing the rheological behavior of gelatin based gum candies. The read and calculated test results describes the texture changes during storage with various conditions.
- From the applied rheological models the stretched exponential form Burgers model with four elements had the closest correlation both on creep and recovery parts too. So this model proved to be suitable for the complex describe of rheological behavior of gelatin based gum candy.

4.2. Recommendations

- In case of TPA test method it seems expedient to perform further, detailed experiments for examination of temperature and time dependence of result parameters. A new experiment series is required with different size plungers and different deformation speed values for the examination of the effect of ambient temperature on result parameters.

- Fitting of stretched exponential form Burgers-model on the creeping and recovery parts of recorded CRT curves of long time storage experiment is suggested. From the fitted curves the change of rheological parameters (E_0, E_r, η, η_v) during storage is determinable. So the temperature and time dependence of rheological parameters of gelatin based gum candies is describable.
- In case of rheological modeling, the application of fractional calculus (differential equation with fractional exponent) can give more precise model fitting on measured curves. With the obtained equations the rheological model of gelatin based gum candy could be refined.
- At all events a detailed structure examination is required for the proving of noticed processes and changes under modeling and storage. On one hand DSC calorimetry measurements are needed, on the other hand applying of imaging techniques (X-ray diffraction, electron microscope, etc.) is suggested.
- It is strongly recommended to extend the research field for candy gums with other contents (e.g. combined gels with starch, pectin or other gelation components next the gelatin). It is considered to examine the structure of any semi solid or semi liquid food gel.

5. Publication list (related to the topic of the field)

Peer reviewed international journal articles:

- Gy. Csima & E. Vozáry (2015): New results in rheological modeling of gum candy. accepted for publication: 2015.05.07., expected presence: *Acta Alimentaria 45 (3)*, DOI: 10.1556/AAlim.2015.5555. ($IF_{2013/2014}$: 0,427)
- Gy. Csima, L.D. Dénes & E. Vozáry (2014): A possible rheological model of gum candies. *Acta Alimentaria 43* (Suppl. 1), pp. 36-44.
DOI: http://dx.doi.org/10.1556/AAlim.43.2014.Suppl.6 ($IF_{2013/2014}$: 0,427)

International conference full papers:

- Gy. Csima, E. Várvölgyi & E. Vozáry (2014): Effect of non-ideal storage conditions on candy gum quality. *International Conference of Agricultural Engineering - AgEng 2014 Zürich*. Paper C0482. (ISBN:978-0-9930236-0-6); http://www.geyseco.es/geystiona/adjs/comunicaciones/304/C04820001.pdf, http://www.geyseco.es/geystiona/adjs/comunicaciones/304/P04820002.pdf
- Gy. Csima, E. Vozáry, T.I. Yorov & Marudova, M. (2014): Rheological model of gum candy. *International Scientific-Practical Conference "Food, Technologies & Health"*. Proceedings Book, pp. 150-155.
- Gy. Csima & E. Vozáry (2014): Effect of Measure Settings on Creep-Recovery Test Results of Candy Gums. *3rd International Conference of CIGR Hungarian National Committee and Szent István University, Faculty of Mechanical Engineering*. In: L. Magó, Z. Kurják, I. Szabó (Eds.): Synergy 2013 - CD of Full Papers: Paper N06-4-180. (ISBN:978-963-269 359-0)
- Gy. Csima & E. Vozáry (2013): Modelling the Rheological Behavior of Candy Gums. *Food Science Conference 2013 - With research for the success of Darányi Program*.: I. Dalmadi, T. Engelhardt, Zs. Bogó-Tóth, L. Baranyai. J. Bús-Pap, Cs. Mohácsi-Farkas (Eds.): Food Science Conference 2013 - With research for the success of Darányi Program: Book of proceedings. pp. 64-67. (ISBN:978-963-503-550-2)
- Gy. Csima, T. Kaszab & A. Fekete (2011): Relationship between Mechanical-Rheological and Sensory Attributes of Foods. *Synergy 2011 – II. International Conference of the CIGR Hungarian National Committee, the Faculty of Mechanical Engineering of the Szent István University, and the Agricultural Engineering*. In: Magó, Z. Kurják, I. Szabó (eds.): CD of Full Papers, Paper Working Session I. Food Engineering (S2) (ISBN:978-963-269-250-0)
- T. Kaszab, Gy. Csima, A. Lambert-Meretei & A. Fekete (2011): Food Texture Profile Analysis by Compression Test. *CNEUCOOP International Conference 2011*. In:

CNEUCOOP International Conference 2011. Paper session 3; http://korny.uni-corvinus.hu/cneucoop_fullpapers/s3/gyorgycsima.pdf

- E. Vozáry, Á.O. Krisán & Gy. Csima (2011): Rheological Properties of Gummy Confections. *PRAE 2011 Physics - Research - Applications - Education: Proceedings of Scientific Works*. In: M. Božiková, Z. Hlaváčová, P. Hlaváč, F. Adamovský (Eds.): 2011 Physics - Research - Applications - Education: Proceedings of Scientific Works 2011. pp. 150-154.
- Gy. Csima, V. Biczó, T. Kaszab & A. Fekete (2010): Methods for the assessment of candy gum elasticity. *XVIIth World Congress of the International Commission of Agricultural and Biosystems Engineering (CIGR)*. In: Paper p. 101167.
- Gy. Csima, T. Kaszab & A. Fekete (2010): Influence of storage condition on candy gum quality. *International Conference on Agricultural Engineering*. In: R. Genet (Eds.): International Conference on Agricultural Engineering. Paper REF478.