

## RHEOLOGICAL PARAMETERS OF FRUIT GUMS “HARIBO” GOLD BEARS

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### ABSTRACT

Mechanical hysteresis and force relaxation curves of “Haribo” gold bears consisting of glucose syrup, sucrose, gelatine, dextrose, citric acid, vegetable oils, fruit extracts, were measured with Stable Micro System TA-XT2 texture analyser. Loading-unloading curves were determined at room temperature with probe speed of 0.3, 0.5, 0.7, 0.9 and 1.1 mm/s, and in the temperature range from 5 °C up to 55 °C with 0.1 mm/s probe speed. The maximal deformation was 5 mm. The force-deformation curves had linear character up to about 1 mm deformation and at higher deformations the slope of the curves increased with the increasing of the deformation. The degree of elasticity defined as the ratio of unloading work to loading work decreased at temperatures lower than 20 °C and higher than 40 °C. The degree of elasticity decreased with the increasing of the probe speed. The measured force relaxation curves at constant 5 mm deformation were approached with a three elements generalized Maxwell-model. The relaxation time of all the three components decreased and the amplitude decreased for the two slower components and increased for the quickest component as the probe speed increased.

### INTRODUCTION

It is easy to find connection of physical properties of gummy sweets with relative simple structure and the phase morphology of them (DeMars and Ziegler, 2001). Some suitable rheological parameters can represent the quality of such products (Ziegler and Rizvi, 1989). For example, the degree of fragmentation of food into particles is related to ratio of toughness (work needed

to generate a unit of surface area during fracture) to the Young's modulus ( $E$ , normal stress/normal strain) (Lucas et al., 2004). Gelatine forming thermoreversible gel (Ledward, 1990) has melting point at about 35 °C (Johnston-Banks, 1990) and addition of sugar to gelatine increases the strength of its gels (Kasapis and Al-Marhoobi, 2003). During storage of high sugar content confectioneries the increase of temperature (above 40-45 °C) can cause structural collapse, welding and crystallization (caking) of the product.

The main goal of the present study is to find an appropriate rheological model describing the stress-strain curve and the relaxation curve of fruit gums "Haribo" gold bears of various temperature.

## MATERIALS AND METHODS

"HARIBO" gold bears consisting of glucose syrup, sucrose, gelatine, dextrose, citric acid, vegetable oils, fruit extracts ([www.haribo.com](http://www.haribo.com)) were measured by hysteresis and relaxation methods in temperature series, with Stable Micro Systems TA-XT2 penetrometer. The deformation speed was varied between 0.1 mm/s and 1.1 mm/s with steps of 0.2 mm/s. The diameter of the measure cylinder was 2 mm. For the hysteresis method the deformation was maximized to 5 mm. The load-unload curves were determined in temperature range from 5 °C up to 55 °C. The bears were held in a laboratory oven "Venticell", or in a refrigerator. During the measurements the bears were in a thermally isolated box and their temperature was measured with a termistor. The force relaxation under 5 mm constant deformation was followed 300 s time duration at room temperature only. The Young's modulus was calculated as the slope of the linear part of the loading section in the hysteresis test. The hysteresis work was integrated from the area between the loading and unloading section. The degree of elasticity is defined as the ratio of unloading work to loading work. The measured relaxation curves were approached with three elements generalized Maxwell model

$$F(t) = F_o + F_1 e^{-\frac{t}{T_1}} + F_2 e^{-\frac{t}{T_2}} + F_3 e^{-\frac{t}{T_3}} \quad (1)$$

with successive-residual method (Sitkei, 1986).  $F_o$  is the equilibrium force,  $F_1$ ,  $F_2$  and  $F_3$  contain the elastic modulus of each Maxwell elements, and the  $T_1$ ,  $T_2$  and  $T_3$  are the relaxation times of Maxwell elements.

## RESULTS AND DISCUSSION

The stress-strain curves have linear character at low deformation about up to 1 mm and at higher deformations the slope of curves is increasing with increasing

deformation (Figure 1.A). In the linear region the structure remains intact and in the region of increasing slope there are micro cracks in gel structure (Foegeding, 2007). The increasing probe speed resulted in increasing slope in both linear and non-linear viscoelastic regions. While the loading work greatly, the unload work little increases with increasing test speed (Figure 1.A), therefore the ratio of unload work to load work – the degree of elasticity – is decreasing. This observation also confirms the presence of micro crack in non-linear viscoelastic region.

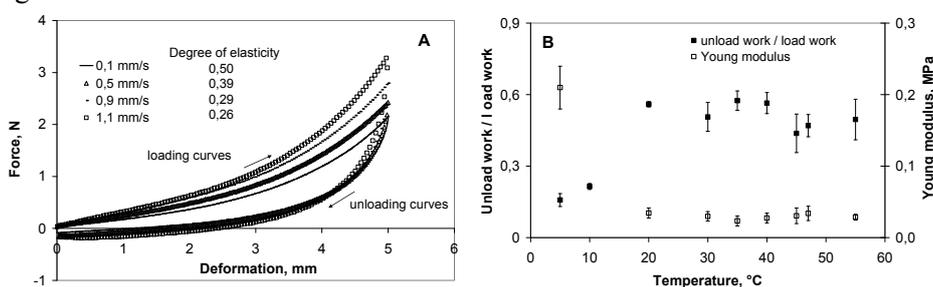


Figure 1.

- A. The loading and unloading stress-strain curves at various test speed.  
 B. The Young modulus and the degree of elasticity at various temperatures.

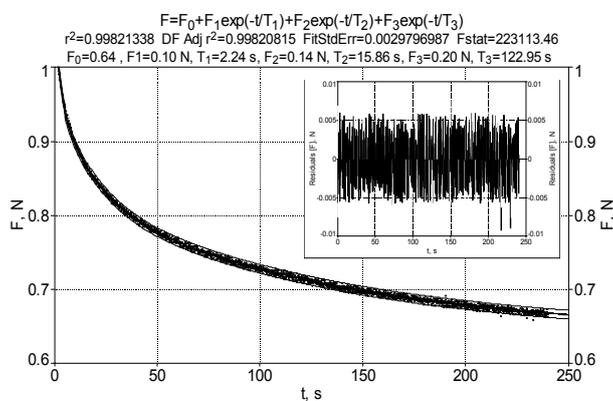


Figure 2.

A typical approach of measured relaxation curve with three element generalized Maxwell model at 5 mm deformation, at temperature of 22 °C. In the insert the residuals can be seen.

At low temperatures the increasing Young modulus (Hayashi 1983) can show on more elastic character of gelatine gel according to gelation processes (Walkenstrom, 1994), but the decrease of degree of elasticity can reflect considerable increase of viscosity (Figure 1.B). The degree of elasticity is the

highest at temperature interval 20-40°C. Further increase of the temperature leads to a decrease in the degree of elasticity. Three-dimensional network forms at temperatures below 30°C, when gelatin crystallization is realized (Zandi, 2007). The segmental mobility of the gelatine molecules is small at temperatures lower than the crystallization temperature and therefore the values of the Young's modulus are higher. The temperature increase leads to more intensive segmental motion expressed in higher degree of elasticity and lower values of the Young's modulus.

It was found that the 3 element Maxwell model fits enough well to the measured relaxation and the residuals are uniform distributed (Figure 2.).

Table 1.

The parameters and their standard deviation of generalized Maxwell model, as a result of successive-residual approaching method. The relaxation of force was followed 300 s at constant, 5 mm, deformation reaching with probe of various speed.

Speed of probe, mm/s	F <sub>0</sub> N	F <sub>1</sub> N	T <sub>1</sub> s	F <sub>2</sub> N	T <sub>2</sub> s	F <sub>3</sub> N	T <sub>3</sub> s
0,1	0,90±0,021	0,21±0,051	3,24±0,625	0,27±0,057	20,5±2,25	0,32±0,012	160±25,2
0,3	0,74±0,102	0,24±0,053	2,57±0,552	0,22±0,031	16,0±0,73	0,30±0,045	138±8,2
0,5	0,71±0,082	0,31±0,045	3,36±0,331	0,21±0,030	20,6±2,50	0,22±0,033	162±20,6
0,7	0,77±0,075	0,35±0,053	2,69±0,246	0,26±0,023	16,9±0,66	0,26±0,015	140±1,5
0,9	0,72±0,065	0,32±0,034	2,03±0,125	0,24±0,032	15,5±0,37	0,25±0,015	140±2,6
1,1	0,74±0,051	0,33±0,015	2,44±0,036	0,24±0,025	17,9±1,06	0,24±0,024	145±5,8

All relaxation time, F<sub>2</sub>, F<sub>3</sub> parameters show slightly decreasing tendency with increasing speed of probe and only F<sub>1</sub> parameter connecting with the modulus of elasticity of the first (the quickest) component increased as the probe speed increased. The observation time – the time requiring to reach the 5 mm deformation – is varied from 4,5 s up to 50 s depending on the probe speed from 1,1 mm/s to 0,1 mm/s. For the first component the ratio of relaxation time to observation time (Deborah number) (Figura and Teixeira, 2007) is increasing from very low value up to about one, and the elastic character can become more expressed. The Deborah number is less than one for the first component and greater than one for the second and third components, so the first component can show mainly viscous properties and the second and third components show more elastic character.

## CONCLUSION

The rheological properties of gummy bears can be described with parameters of generalized Maxwell model. In the experiment it is important to choose the appropriate observation time for investigation the viscoelastic properties. The optimal temperature range for storage of gummy bears is 20-40 °C.

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