NEW RESULTS OF RHEOLOGICAL MODELING OF CANDY GUM

GYÖRGY CSIMA*[1] & ESZTER VOZÁRY[2]

Abstract. The creep-recovery curve of gum candies were measured with a SMS TA.XT-2 precision penetrometer with 75 mm diameter aluminum plane cylinder probe under 1, 2, 5, 7 and 10 N loading force and with 30, 60, 90 and 120 s creep/recovery time. The creeping part of measured curves was approached with the four elements Burgers-model containing stretched exponential function. The elastic modulus and the viscosity of both Maxwell and Kelvin-Voigt elements were determined, the retardation time and the stretched exponent were also obtained. A strong positive linear correlation of the two viscosities and the two elastic moduli with the loading stress were found. The two viscosities were increased as the creeping time is increased. The retardation time practically was independent on the applied stress, but linearly increased with increasing creeping time. The stretching exponent β proved to be independent on loading stress, and decreased linearly as the creeping time increased. These observed changes can suggest while the Maxwell element can describe the rheological behavior of protein mesh, the Kelvin element can characterize the sugar solution.

Keywords:. candy gum; rheology; Burgers-model; stretched exponent; texture analyzer

Introduction

The candy gum is a market leader confectionery product with a characteristic viscoelastic behavior. The candies with various forms, shapes and flavors are one of the most preferred confectionery products independent from gender and age. Nowadays the candy could be a functional food, too, e.g. filled with vitamins and trace elements.

The viscoelastic property of candies is determined by their components (type and ratio of carbohydrate(s) and gelling agent(s)) (MOHOS, 2010) and by the product technology parameters (MOHOS, 1993). The main components of gum candies are carbohydrates, sucrose, glucose-fructose syrup and fructose in an appropriate ratio (MÉ 2-84/03/3). The glucose-fructose syrup ensures that the solved carbohydrates will never crystallize (BUREY et al., 2009). The very high sugar content results sweet taste and viscous behavior (BUREY et al., 2009). Porcine origin gelatin from pig skin (GME, 2015) after an acidic hydrolysis and extraction treatment (SEGTNAN & ISAKSSON, 2004) is the mainly used gelling agent. The

[1] corresponding author Csima.Gyorgy@kertk.szie.hu, +36-1 305-7267; Technical Department, Faculty of Horticultural Sciences, Szent István University

[2] Department of Physics and Control, Faculty of Food Sciences, Szent István University

added gelatin forms a continuous spatial polymer mesh, which is responsible for the characteristic elastic property (ROSS-MURPHY, 1992). The required gelatin concentration for gelling is about 1 w% (SEGTNAN & ISAKSSON, 2004), but usually the ratio of gelatin in candies is about 6-8 w% (MOHOS, 2013).

The material of candy gum is homogenous, it contains one continuous phase, without separations (MARFIL et al., 2012), the spatial mesh of gelatin (DJABOUROV, 1990) is filled with high sugar content solution (KASAPIS et al. 2003).

The Creep-Recovery Test (CRT) is a well-known rheological measuring method, which contains 4 step: loading up to definite force, creeping under this definite loading force for a given time, unloading till zero force, recovering for definite time (see Fig. 1.) (STEFFE, 1996; LAMBERTNÉ-MERETEI, 2012). The creeping and the recovery periods of CRT curves were successfully used for rheological modeling in case of chicken breast meat (MYHAN et al, 2012), low oil content emulsions (DOLZ et al, 2008) and different gels (YILMAZ et al, 2012).

In our earlier work (CSIMA et al. 2014) the creeping and the recovering parts of CRT curves of gum candies were approached with 4 elements viscoelastic Burgers model (SITKEI, 1981; STEFFE, 1996; TÓTH, 2000) containing stretched exponent. We found, that the Maxwell element with high elastic modulus and very high viscosity can describe the rheological behavior of elastic protein polymer mesh, while the Kelvin-Voigt element with one and half times higher firmness and with about ten times lower viscosity can represent the slow, viscous flow of the carbohydrate solution (CSIMA 2015). All the four rheological parameters of the Burgers-model were linearly increased on applied stress (CSIMA & VOZÁRY 2016).

While the gelatin is a mixture of protein molecules with various molecular weight (10.000-200.000 g/mol) depending on the extraction processes (JOHNSTON-BANKS, 1990), the relaxation/retardation of gelatin mesh can be described with a spectrum of relaxation/retardation times (SCHIESSEL et al., 1996). That relaxation/retardation process which contains not only a single relaxation/retardation process can be described with stretched exponential function and the stretching exponent can characterize the distribution of relaxation/retardation times (MAINARDI & SPADA, 2011; ZSIVÁNOVITS, 2007). On the bases of these observations it may seem interesting to investigate the effect of loading stress and creeping time on the retardation time and on the stretched exponent in Burgers-model describing the rheology of gum candies.

In the present work our attention was focused on the changes in retardation time and in the stretched exponent of Burgers model, when the loading force and the creeping time were increased

Materials and methods

The samples, the same gelatin-based gum candies of the same market leader manufacturer were purchased from a local shop. The original packages were stored in fridge. Before the measurements the temperature of gum candies were equilibrated with room temperature.

The creep-recovery curves (Fig. 1.) on the candy samples were measured with a Stable Micros System TA.XT-2 precision penetrometer (Godalming, Surrey, UK) equipped with a 75 mm diameter aluminum plane cylindrical probe. The CRT curves were recorded with various loading forces (1 N, 2 N, 5 N, 7 N, and 10 N) and creeping time values (30 s, 60 s, 90 s, 120 s). The data acquisition rate was 10 points pro seconds. The test speed was 0.2 mm/s. In one adjustment three parallel measurements were carried out.

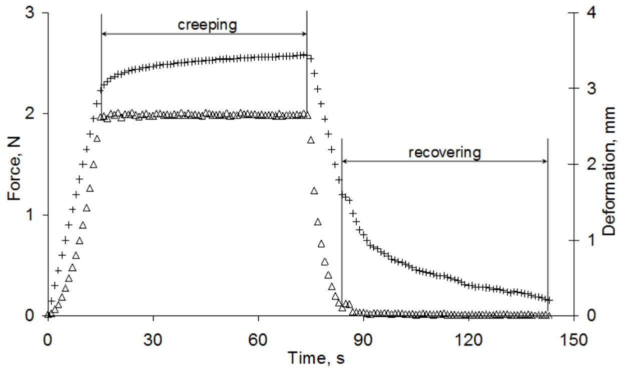

Fig. 1.Typical CRT curve measured on gum candy

(∆: loading force; +: measured deformation)

The measured data was managed with Texture Exponent 1.21. and MS© Excel® 2010 (with Solver function) software. The creeping period of each CRT curve were approached with Burgers-model (Fig. 2) containing stretched exponential (SITKEI 1981).

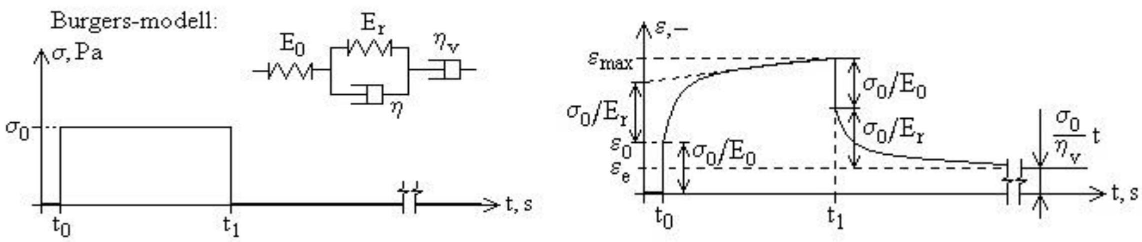

Fig. 2. The four elements Burgers-model and the meaning of model parameters in CRT curve (based on SITKEI (1981))

In the equations ε is the strain (relative deformation); σ is the normal stress calculated from preset loading force and the contact surface area of the sample; E_0 and E_r are the elastic moduli; η and η_v are the viscosities (Fig. 1.); β is the stretch exponent between 0 and 1; T_r is the retardation time at creeping, $T_r = \eta/E_r$; t is the time. In approaching process the rheological parameters were calculated for creeping period.

$$\varepsilon = \frac{\sigma}{E_0} + \frac{\sigma}{E_r}\left(1 - e^{\left(-\frac{t}{T_r}\right)^{\beta}}\right) + \frac{\sigma}{\eta_v} t \quad \rightarrow \quad \varepsilon = a + b\left(1 - e^{\left(-\frac{t}{c}\right)^{\beta}}\right) + dt \qquad \text{(Eq. 1.)}$$

From the fitted curve parameters (a, b, c, d) the rheological parameters (E_0, E_r, η, η_v, T_r) were calculated. The average and standard deviation of rheological parameters and of β were obtained in each measuring set.

Results

The all rheological parameter, E_0, E_r, η, η_v were linearly increased as the loading stress was increased (not shown) as it was presented in our earlier work (CSIMA & VOZÁRY 2016). The two viscosities, η, η_v, were increased at all loading force when the creeping time was increased. The E_r parameter a little decreased as the creeping time increased. The retardation time, $T_r = \eta/E_r$, practically was independent on the applied loading force (Fig. 3.) in range from 1 N up to 10N at all creeping time. T_r increased as the creeping time increased in range of 30 – 120 s (Fig, 4.), This linear function essentially was the same for all loading stress.

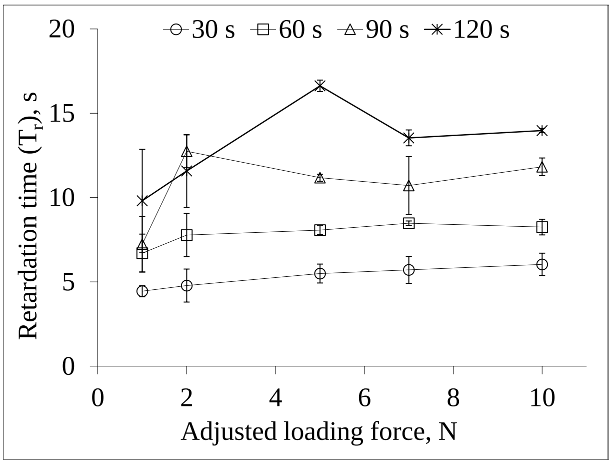

Fig. 3. Change of retardation time (average T_r with standard deviation) of four elements Burgers model with stretched exponent as the function of loading force

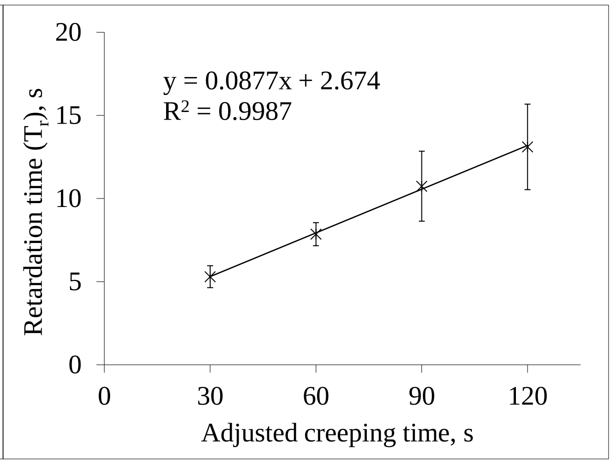

Fig. 4. Change of retardation time (average T_r with standard deviation) of four elements Burgers-model with stretched exponent as the function of creeping time

The stretch exponent, β, also did not depend on the applied loading force (Fig. 5.) at each creeping time. The value of β was about 0,6. The stretch exponent decreased when the creeping time was increased (Fig. 6.). Similar linear function was obtained for all loading force.

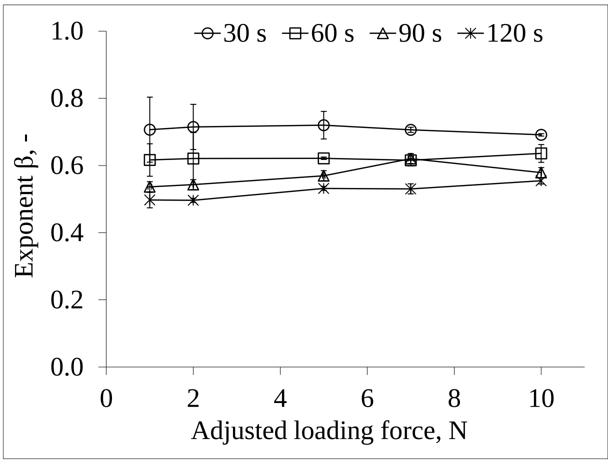

Fig. 5. Change of stretch exponent (average β with standard deviation) of four elements Burgers-model as the function of loading force

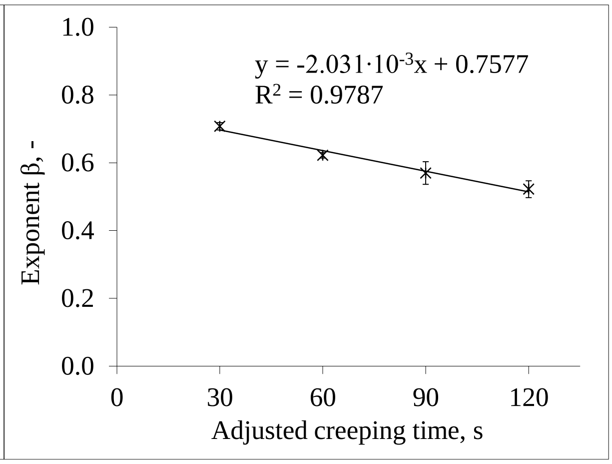

Fig. 6. Change of stretch exponent (average β with standard deviation) of four elements-Burgers model as the function of creeping time

Discussion

The retardation time, $T_r = \eta/E_r$, is the ratio of linearly increasing, η, viscosity and the linearly increasing, E_r, elastic modulus. This ratio at relatively high force becomes constant. These parameters can characterize the high concentration sugar solution inside of gelatin mesh according to our earlier results (CSIMA & VOZÁRY 2016).

Applying higher loading force the spatial mesh of gelatin is squeezed in higher range according to its elastic behavior, but this process requires more time. The slowly flowing non-crystallizing carbohydrate solution in the gelatin mesh can brake the elastic contraction of gelatin mesh (CSIMA et al., 2014). At higher creeping times, longer retardation processes can be appeared and they can cause a widening in retardation time spectra.

The stretch exponent β was independent from loading force and was about 0.6,. That means, the structure of gum candy has a concrete relaxation/retardation time spectra, which is determined primary by the properties of gelatin (extraction properties, gel strength, gelation time, etc.) (SEGTNAN & ISAKSSON, 2004). Considering that the gelatin is a complex mix of a protein with various molecule weights, chain lengths (BUREY, 2009; KASAPIS et al. 2003), the distribution of retardation times has to be a broad spectrum.

The spatial mesh of gelatin is responsible for characteristic elastic property of candy. The larger the load, the greater the squeeze in the spatial mesh and the candy becomes firmer. The range of elasticity depends on the gelatin concentration (MOHOS, 2010).

In the case of short creeping times, only the short retardation times can be appeared. But if the creeping time becomes longer and longer, the longer and longer retardation time values (Fig. 4.) causes the wider retardation spectrum, which can be characterized with lower β values (Fig. 6.).

Further measurements are required to decide, that the squeeze of the gelatin mesh is the same or not on the surface and in the interior of the mesh. If the outer layer of mesh packs in higher range that could explain the intensive hardening of candy under compression (E_0 and E_r are increasing by higher loading stress).

Conclusions

The retardation time and the stretch exponent characterizing the distribution of retardation times can be used for describing the effect of increasing creeping time in the structure of gum candies.

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