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# STRETCHED EXPONENT RHEOLOGICAL MODEL OF GUM CANDY

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Creep-Recovery Tests (CRT) were measured with a Stable Micros Systems TA.XT-2 precision penetrometer with 75 mm diameter cylinder probe and with different loading stress and creeping-recovery times on gelatine-based candy gum samples, purchased from the local market. The loading force changed from 1 N up to 10 N and the creeping time varied from 30 s up to 120 s. The creeping and the recovering part of CRT curves were approached by Burgers-model with stretched exponential function. The two elastic moduli and the two viscosities increased linearly in the function of the applied stress. One elastic modulus and the two viscosities also increased, but another elastic modulus slightly decreased in the function of the creeping time. The stretching exponent β practically linearly decreased as the creeping time increased. Based on theoretical considerations, the Kelvin-Voigt-element of Burgers-model can describe the rheological behaviour of sugar content, and the Maxwell-element of Burgers-model can describe the rheological behaviour of gelatine-mesh.

**Keywords:** gum candy, rheological modelling, Burgers-model, Creep-Recovery Test, stretch exponent

Gum candies have high popularity among consumers. The quality of gum candies after production is determined mainly by conditions of transport and storage. For consumers, the quality is mostly realised by "mouth feel", which is heavily depended on the rheological properties of the food (Foegeding, 2007).

Gum candies contain mainly sucrose and dextrose dissolved in glucose syrup (Burey et al., 2009) and about 8–10% w/w gelatine. During the processing the gelatine forms a spatial mesh (Finer et al., 1975), giving the typical elastic behaviour to gum candy (Mohos, 2010). The structure of gelatine mash in the presence of sugar differs from the pure gelatine mesh, the bindings between polymer chains are strengthened (Kasapis et al., 2003; Burey et al., 2009) and the gel viscosity is decreased (Johnston-Banks, 1990).

The creeping and the recovering periods of CRT are suitable for rheological modelling (Steffe, 1996), for example in different foods: gels and emulsions (Yilmaz et al., 2012) or bread crumbs (Lambertné-Meretei, 2012).

In our earlier works (Vozáry et al., 2011; Csima et al., 2014), the creep period of the CRT curve of gum candies was approached with classical three elements (Poyinting–Thomson) and four elements (Burgers) models, the latter being more accurate. The parameters of models were studied under constant force. Elastic moduli and viscosities increased with increasing stress, demonstrating the structure change – becoming harder and more viscous under constant stress.

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Recently in some articles the "fractional calculus" was used for describing the viscoelastic properties of various materials (Mainardi & Spada, 2011). This method gives stretched exponential relaxation or creep instead of pure exponential functions (Schiessel et al., 1995). The stretched exponent – the measure of stretching of exponential function – can characterize the distribution of the relaxation times.

The aim of this work was to approach both the creeping and the relaxing processes of gum candies by Burgers-model with exponential function and with stretched exponential function, too. The effect of creeping time and stress on the rheological parameters of candies was also studied.

## 1. Materials and methods

### *1.1. Materials*

Gelatine-based gum candies purchased from the local market were used in the experiments. The overall size of candy samples was about 2 cm × 1 cm × 1 cm and the average weight was 2.40 g per pieces.

Candies according to the list on the package contained in range of decreasing weight ratio 50–60% glucose syrup; 20–30% sucrose; 8–10% gelatine; about 5% dextrose; citric acid; aroma-, colour- and taste components from fruit- and vegetable extracts; bee- and carnauba wax; and fructose. The exact composition is manufacturing secret. Generally during the production of gum candies (Mohos, 1993), the sucrose and dextrose are dissolved in glucose syrup preventing the crystallization of sugar (Burey et al., 2009) and providing an amorphous, unsettled, but viscous structure. The swelled gelatine is admixed to this hot mixture, and before moulding, citric acid solution and various fruit- and vegetable extracts are added to this blend. During cooling the gelatine, due to the decrease of temperature (Finer et al., 1975) and pH (Mohos, 1993), creates a spatial mesh (Johnston-Banks, 1990) strengthened by H-bindings and other secondary bindings (Djabourov, 1991) that gives the typical elastic behaviour to gum candy (Mohos, 2010).

All the samples were stored in the original semi-permeable polymer foil package at cool temperature until the measurements at room temperature.

### *1.2. Methods*

The Creep-Recovery Test (CRT) (Bagley, 1983; Tóth, 2000) contains four steps: loading – creeping – unloading – recovery. In loading, the sample is stressed with constant speed until the preset force is reached. In creeping, the deformation is recorded under constant force for the preset creeping time. In unloading, the force is falling to zero with the same speed. In recovery, under zero loading the deformation is recorded for the same time (Fig. 1).

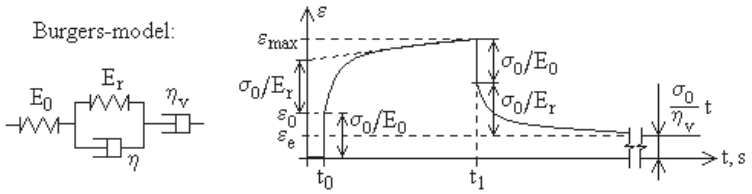


*Fig. 1.* Schematic figure and characteristic curve of Burgers-model in function of relative deformation ($\varepsilon=\Delta L/L_0$). '0': initial value; 'e': equilibrium; 'r': retardation of strain; 'v': residual deformation

The CRT curves of gum candies were measured with a TA.XT-2 precision texture analyzer (Stable Micro Systems, Godalming, Surrey, UK) with the built-in 'relaxation test' program. The samples were pressed with a metal plate cylinder probe of 75 mm diameter and the test speed was 0.2 mm $s^{-1}$, like in our earlier experiments (Csima & Vozáry, 2013). 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, and 120 s). The data acquisition rate was 10 points pro sec and in every setting 20 samples were measured and evaluated (each measurement was executed on new candy). The accuracy of the measurements was 0.001 N in force, 0.001 mm in deformation, and 0.001 s in time.

The recorded force – deformation – time data of CRT curves were handled with Texture Exponent 1.21. and MS® Office Excel 2010 and 2013 software. The data evaluation was practically the same as the method used earlier (Csima et al., 2014), but in the recent work all measured point was used for model fitting with the Solver function of MS® Excel, while in earlier works only a reduced data series (one point from every minutes) were handled with R-Project 3.0.1 software. The relative deformation during the creeping and the recovering periods were approached by Burgers-model with four parameters ($E_0$, $E_r$, $\eta$, $\eta_v$; see Eqs 1–2) according to Sitkei (1981) and by Burgers-model with Kohlrausch's stretch exponent with five parameters ($E_0$, $E_r$, $\eta$, $\eta_v$; $\beta$; see Eqs 3–4):

$$\varepsilon = \frac{\sigma}{E_0} + \frac{\sigma}{E_r} \cdot \left(1 - e^{-\frac{t}{T_r}}\right) + \frac{\sigma}{\eta_v} t \tag{1}$$

$$\varepsilon = \frac{\sigma}{E_r} \cdot \left(1 - e^{-\frac{t_1}{T_r}}\right) \cdot e^{-\frac{t}{T_r}} + \frac{\sigma}{\eta_v} t_1 \tag{2}$$

$$\varepsilon = \frac{\sigma}{E_0} + \frac{\sigma}{E_r} \cdot \left(1 - e^{\left(-\frac{t}{T_r}\right)^{\beta}}\right) + \frac{\sigma}{\eta_v} t \tag{3}$$

$$\varepsilon = \frac{\sigma}{E_r} \cdot \left(1 - e^{\left(-\frac{t_1}{T_r}\right)^{\beta}}\right) \cdot e^{\left(-\frac{t}{T_r}\right)^{\beta}} + \frac{\sigma}{\eta_v} t_1 \tag{4}$$

In the equations $\varepsilon$ is the relative deformation; $\sigma$ 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; $\eta$ and $\eta_v$ are the viscosities; $\beta$ is the stretch exponent between 0 and 1; $T_r$ is the relaxation time at creeping and the retardation time at recovery, $T_r = \eta/E_r$; $t$ is the time; and $t_1$ is the time, which elapsed until the beginning of recovery.

For both creeping and recovery periods the fitted curves were obtained by minimizing the difference between the measured and calculated strain values (the minimizing process was executed with the Solver function of MS®Excel). From the fitted curves the rheological parameters were calculated.

Statistical parameters – $R^2$: determination coefficient; RMSEP: root of mean square error of prediction; D-W: value of Durbin-Watson statistic – were also calculated.

## 2. Results and discussion

Typical fitting of measured creeping and recovery curves with Burgers and with stretched Burgers-model are shown in Fig. 2. The statistical parameters of our model fitting clearly showed that the Burgers-model with stretch exponent gave much better approach for all

measured curves, than the Burgers-model with simple exponent (see the insert boxes in Fig. 2A and B).

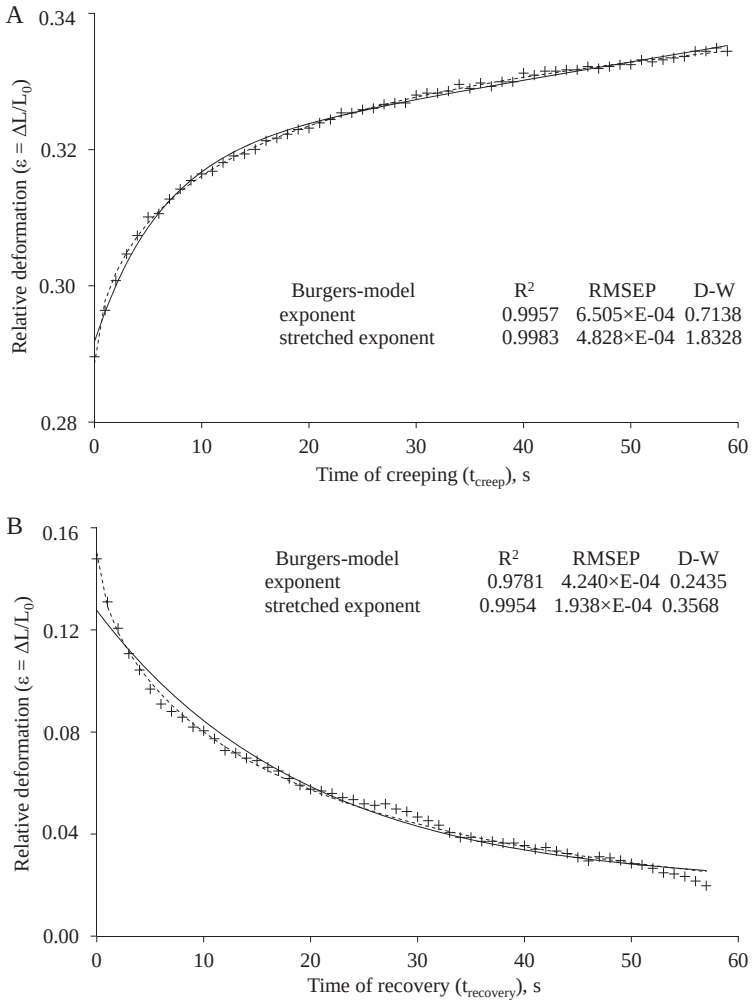


*Fig. 2.* Typical fitted model curves on measured strain data of creeping (A) and recovery (B) period of Burgers-model.
+: measured strain; ——: Burgers-model; - - - - : stretched exponent Burgers-model

The rheological parameters (elastic moduli and viscosities) calculated from both creeping and recovery part of measured curves with creeping time of 60 s had about the same values (Table 1). All four parameters showed increasing tendency as the constant stress during creeping period increased. This increasing tendency can be described by linear function with a high $R^2$ statistical parameter (Table 1).

Dependence of rheological parameters on the applied stress is explained with change of gum candies structure under stress. In reality, below 0.1 strain there is linear function between stress and strain (Mitchell, 1980; Vozáry et al., 2011), but at higher strain the secondary, non-covalent bonds of polymer mesh are damaged (Foegeding, 2007) but the non-crystallized, viscous carbohydrate content bear the deformation (Burey et al., 2009), so the texture changes, becomes more concise and firm (Mitchell, 1980). The elastic modulus increases with loading stress because of compaction and hardening of texture (Mioche & Peyron, 1995). The carbohydrate content flows out from the protein polymer mash, and this change leads to higher viscosity.

The lower value of elastic moduli and viscosities in recovery part is explained by the fact that in recovery part the stress is zero on the samples in contrary of creeping part when there is a constant stress on the samples. In creeping part the structure is changed by constant force, while in recovery part it is relaxing to the initial structure.

*Table 1.* Rheological parameters of stretched Burgers-model and their stress-dependence calculated from creep and recovery period of CRT curve at 60 s creeping time (mean±standard deviation of 20–20 measurements)

| Rheological parameters calculated from creeping period | | | | | |
|---|---|---|---|---|---|
| $\sigma_0$, kPa | $E_0$, kPa | $E_r$, kPa | η, MPa×s | $\eta_v$, MPa×s | β |
| 11.70 | 62.82±6.765 | 245.8±19.58 | 1.468±0.177 | 62.90±11.31 | 0.668±0.0404 |
| 13.95 | 50.92±2.796 | 318.2±16.48 | 2.306±0.192 | 83.35±10.27 | 0.631±0.0237 |
| 25.00 | 64.74±2.631 | 565.2±28.19 | 4.729±0.429 | 140.1±16.20 | 0.635±0.0197 |
| 29.95 | 69.38±2.223 | 699.5±43.46 | 6.307±0.447 | 181.0±17.98 | 0.629±0.0138 |
| 38.10 | 84.50±3.297 | 875.9±48.64 | 7.625±0.493 | 209.0±13.45 | 0.648±0.0096 |
| Rheological parameters calculated from recovery period | | | | | |
| $\sigma_0$, kPa | $E_0$, kPa | $E_r$, kPa | η, MPa×s | $\eta_v$, MPa×s | β |
| 11.70 | non calculable | 102.1±10.77 | 1.227±0.192 | 63.53±47.23 | 0.651±0.0574 |
| 13.95 | | 114.3±13.55 | 1.365±0.151 | 69.25±47.61 | 0.640±0.0491 |
| 25.00 | | 175.4±20.05 | 2.691±0.294 | 107.9±49.76 | 0.629±0.0559 |
| 29.95 | | 196.0±17.93 | 3.311±0.536 | 140.9±65.49 | 0.642±0.0477 |
| 38.10 | | 247.7±30.91 | 4.110±0.748 | 132.5±40.28 | 0.671±0.0554 |

| Parameter | from creeping period | | from recovery period | |
|---|---|---|---|---|
| | σ: applied stress, kPa | $R^2$ | σ: applied stress, kPa | $R^2$ |
| $E_0$, kPa | $E_0$=1.360×σ+31.01 | 0.9837 | non calculable | |
| $E_r$, kPa | $E_r$=23.73×σ–22.40 | 0.9987 | $E_r$=5.432×σ+38.14 | 0.9977 |
| η, MPa×s | η=0.2348×σ–1.086 | 0.9977 | η=0.1126×σ–0.1315 | 0.9976 |
| $\eta_v$, MPa×s | $\eta_v$=5.602×σ+2.299 | 0.9976 | $\eta_v$=3.020×σ+31.12 | 0.8833 |
| β | β=0.642±0.016 | | β=0.647±0.016 | |

The elements of Burgers-model correspond to the components of gum candy. The rheological properties of carbohydrates are described by relative high elastic modulus, $E_r$, and by relative low viscosity, η, which means the Kelvin-Voigt-element of Burgers-model. The texture of carbohydrate inside of gelatine gel is semi fluid similar to the fluid crystals

(Burey et al., 2009). The Maxwell-element of Burgers-model represents the gelatine polymer mash, which is very elastic ($E_0 \approx 0.1–0.2E_r$) and has a very high viscosity ($\eta_v \approx 20–40\eta$). The sugar content has a solidification effect on gelatine gel. That means, the gelatine deforms very fast and elastic according to the gel structure (Djabourov, 1991; Segtnan & Isaksson, 2004; Burey et al., 2009), but only under very high stress shows flowing.

The outlying high value of $E_0$ at the smallest stress (see Table 1 first row) is caused by the inaccuracy of measurement of contact area. The high standard deviation of $\eta_v$ in recovery period (see Table 1 second part) is caused by the different range recovery of different range structure damage under creeping.

The value of β exponent was practically the same in both creeping and recovering period and was independent from the applied stress (see Table 1) at 60 sec creeping time. This indicates that the distribution of relaxation times does not depend on the stress (Mainardi & Spada, 2011).

Values of $E_0$, η, and $\eta_v$ parameters increased but $E_r$ parameter slightly decreased as the creeping time increased (Fig. 3). The larger deformation caused by longer creeping time results more damage in the structure and the polymer mesh becomes harder and more viscous. Under larger deformation, the carbohydrate texture (a semi-solid fluid) becomes softer and more viscous. The investigated range of stress and creeping time were relative narrow, therefore the various functions in Figure 3 were linear.

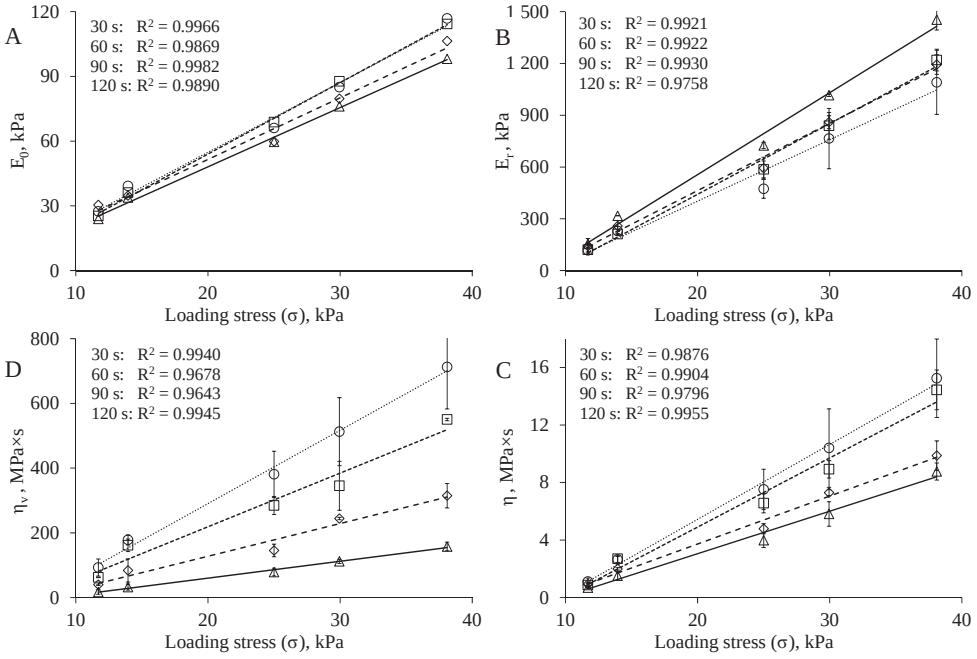


*Fig. 3.* Change of rheological parameters of Burgers-model with stretch exponent (calculated from creeping period) as the function of loading stress and creeping time.
A: $E_0$ elastic modulus; B: $E_r$ elastic modulus; C: η viscosity; D: $\eta_v$ viscosity
△: 30 s; ◇: 60 s; □: 90 s; ○: 120 s

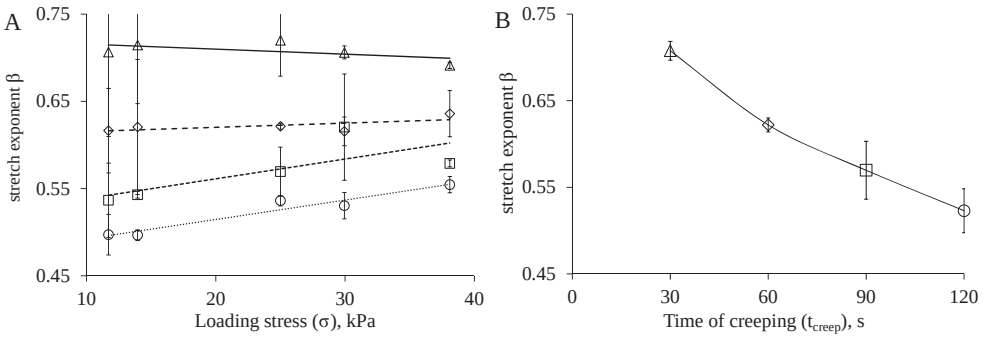


*Fig. 4*. Change of stretch exponent β of Burgers-model with stretch exponent as function of applied stress (A) and creeping time (B).
△: 30 s; ◇: 60 s; □: 90 s; ○: 120 s

The β stretching exponent was practically independent of the applied stress, but depended on the applied creeping time in the 30–120 s range (Fig. 4). Averages of β values at various creeping times show a decreasing tendency at increasing creeping time. At longer creeping time longer relaxation times appear and the distribution of relaxation time becomes wider causing lower stretching exponent value (Sitkei, 1981; Zsivánovits & Marudova-Zsivanovits, 2009; Marudova-Zsivanovits et al., 2010). Zsivánovits and co-workers (2004) found the β around 0.6 in case of pectin gels, similarly to our results.

## 3. Conclusions

It can be stated that the creeping and recovery parts of a CRT curve can be used for determination of rheological parameters of gum candies. Approaching the measured strain by Burgers-model with stretching exponent gave an accurate curve fitting. The elastic moduli and viscosity were linearly depended on the loading force – in range from 1 N to 10 N – and on the creeping time – in range from 30 s to 120 s. The rheological parameters can represent the elastic modulus and the viscosity of the polymer mesh and the carbohydrate part of gum candies. These parameters in the future can be used for characterizing the change in the quality of gum candies for example during storage.

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