THIXOTROPIC BEHAVIOUR OF KETCHUP

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ABSTRACT

Ketchup is a typical food product, which possesses a thixotropic behaviour. The destroying and the recovery of its structure were monitored by rotational viscometry HAAKE VT 550. The Moore model, which describes the thixotropic behaviour by structural parameter λ, was chosen for fitting the basic rheological curve ($\tau = \tau(\dot{\gamma})$, where τ is the shear stress and $\dot{\gamma}$ is the shear rate) and the stress-time dependences at different shear rates. As a result the relaxation times at different shear rates were calculated. It was shown as well, that the ketchup possesses a spectrum of relaxation times, expresses as stretched exponent parameter β. The changes in thixotropic behaviour during storage were also monitored.

INTRODUCTION

In many industrial materials, the viscosity decreases with time of shearing, but if the shearing is stopped, the viscosity regains the higher value. This behaviour is known as thixotropy and it is found in fluids as well as in semi-solid materials. Thixotropy arises from structural formation due to antiparticle forces acting between dispersed species in a material (Schramm, 1994). It is governed by Brownian motion and shear and leads to the time dependent characteristics.

Ketchup is a typical food product, which possesses a thixotropic behaviour. It is due to agglomeration of fibrous particles and entanglement, which build-up structure at rest, and de-agglomeration and disentanglement under shear.

The main parameters, which affect the rate of structure changes at rest and under shear, are: concentration of the dispersed phase, shape and size of the particles, size distribution, value of shear rate, internal constitution, etc.

The present work shows a method for characterizing the thixotropic behaviour of ketchup by the use of empiric structural model – lumped parameter model.

THEORETICAL BACKGROUND OF THE MODEL

In the λ-model all these parameters, affecting the structure changing, are replaced by one structural parameter, defined as follows (Cheng, 1987):

- For fully build up structure, $\lambda = 1$ and the viscosity is maximal $\eta = \eta_\infty + \mathbf{c}$, where **c** is the viscosity increment;
- When the structure is fully broken down $\lambda = 0$ and $\eta = \eta_\infty$;
- For intermediate structures the viscosity is $\eta = \eta_\infty + \mathbf{c}\lambda$, $0 < \lambda < 1$;
- The break-down rate is a power law function of shear rate and depends also on the current structure:

  $\textbf{break-down rate} = -\mathbf{b}\lambda\dot{\gamma}^{\mathbf{m}}$;
- The build-up rate depends on the amount of structure to be recovered:

  $\textbf{build}-\textbf{up rate} = \mathbf{a}(1-\lambda)$;
- The net rate of change of structure is:

  $\frac{\mathbf{d}\lambda(\mathbf{t})}{\mathbf{dt}} = \mathbf{a}(1-\lambda) - \mathbf{b}\lambda\dot{\gamma}^{\mathbf{m}}$;
- The equation of state (flow curve) is:

$$\tau(\dot{\gamma},\mathbf{t}) = \tau_0 + (\eta_\infty + \mathbf{c}\lambda)\dot{\gamma}^{\mathbf{m}} \qquad (1)$$

$$\tau(\dot{\gamma},\mathbf{t}) = \tau_0 + (\eta_\infty + \mathbf{c}\lambda_{\mathbf{e}})\dot{\gamma} - \mathbf{c}\dot{\gamma}(\lambda_{\mathbf{e}} - \lambda_0)\mathbf{e}^{-(\mathbf{a}+\mathbf{b}\dot{\gamma}^{\mathbf{m}})\mathbf{t}} \qquad (2)$$

where λ_0 gives the structure at time $\mathbf{t}_0 = 0$ and $\lambda_{\mathbf{e}} = \frac{1}{1+\frac{\mathbf{b}}{\mathbf{a}}\dot{\gamma}^{\mathbf{m}}}$ corresponds to the equilibrium structure. When equilibrium structure is achieved

$$\tau(\dot{\gamma},\mathbf{t}) = \tau_0 + (\eta_\infty + \mathbf{c}\lambda_{\mathbf{e}})\dot{\gamma} \qquad (3)$$

MATERIALS AND METHODS

Ketchup trade mark “Olineza” from Bulgarian market has been investigated.

The destroying and the recovery of the ketchup structure have been monitored by rotational viscometry HAAKE VT 550. Coaxial cylinder sensor SV-DIN has been used, which is recommended for high viscosity materials. The tests have been done at constant temperature 25°C. Two types of tests have been done to investigate the thixotropy and to calculate the parameters of the λ-model:

- *Multistep Steady State Test (MSST)*: This test is designed to determine the equilibrium flow curve. The test is produced over a shear rate range of 0.123 s-1 to 1000 s^{-1}. The maximum waiting time to reach equilibrium was 120 s. For each shear rate 5 repetitions have been done. The yield stress τ_0, the infinite viscosity η_∞, the viscosity increment **c**, the power law parameter **m** and the ratio **b/a** could be calculated from MSST test using equation (3).

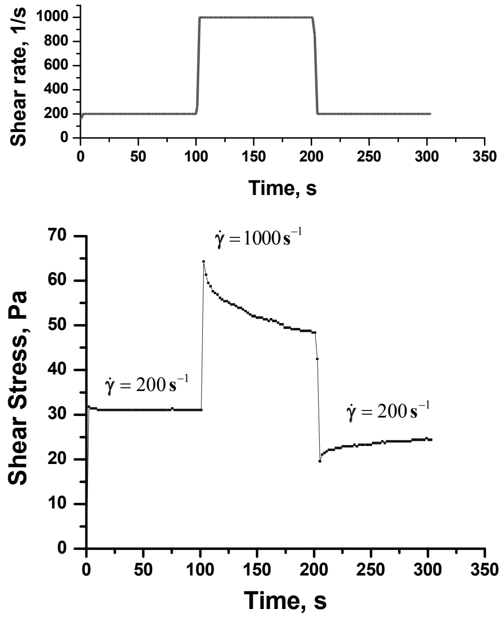
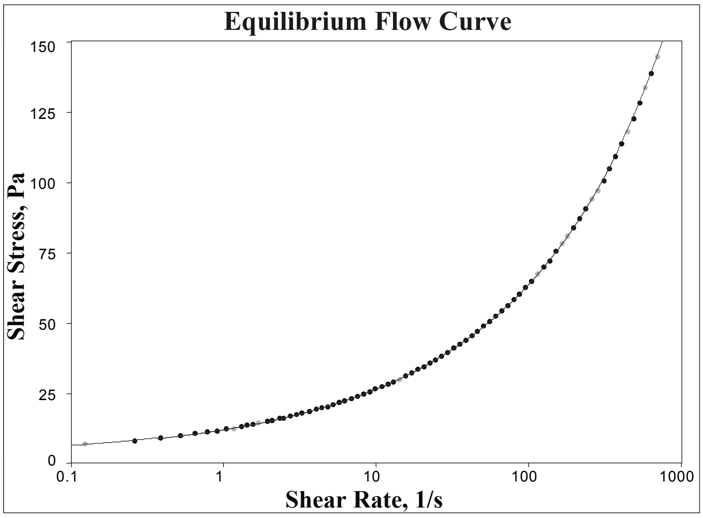


Fig.1 *Time test. Monitoring a build-up and break-down of ketchup structure at constant shear rate*

- *Time test*: The test consists of applying a constant shear rate and monitoring the viscosity and the shear stress as a function of time. This type of test, applied at several sections with different shear rates, is recommended for monitoring the thixotropic behaviour (fig. 1). The relaxation time τ_r and the separate values for **a** and **b** could be get from the time test.

RESULTS AND DISCUSSION

When the time tests at two different shear rate values are applied to the ketchup, its thixotropic behaviour could be demonstrated (fig. 1.) To analyze this thixotropic behaviour, a six parameter λ-model has been used (equation 2). The equilibrium flow curve has been successfully fitted to the model and 5 of the parameters have been determined (fig. 2). The values, received for the yield stress and the infinite viscosity are in good agreement with the data in the literature.



$$\tau(\dot{\gamma},t) = \tau_0 + (\eta_\infty + c\lambda_e)\dot{\gamma} - c\dot{\gamma}(\lambda_e - \lambda_0)e^{-(a+b\dot{\gamma}^m)t}$$

Parameters:

τ_0=2.97 Pa

η_∞=0.02 Pa.s

c=210.21 Pa.s

m=0.60

b/a=22.27 s

Fig.2. Multistep Steady State Test (MSST)

The λ-model propose just one relaxation time. The experimental curve from Time test could not be well fitted to the exponential model with one relaxation time (fig. 3.). The presence of spectrum of relaxation times makes the parameter calculations more difficult, because the distribution function is not known. Therefore a stretched exponential model has been suggested (Lindsey and Patterson, 1980). The relaxation spectrum is characterized by the parameter **β**, which values vary in the range **0<β<1**. As higher the β, the closer the spectrum distribution. Introducing the β parameter to the λ-model, the average (imaginary) relaxation time could be calculated from the dependence:

$$\tau(\dot{\gamma} = \mathbf{const}, \mathbf{t}) = \mathbf{A}(\dot{\gamma}) + \mathbf{B}(\dot{\gamma})\mathbf{e}^{-\left[\left(\mathbf{a}+\mathbf{b}\dot{\gamma}^{\mathbf{m}}\right)\mathbf{t}\right]^{\beta}}, \qquad (4)$$

where

$$\mathbf{A}(\dot{\gamma}) = \tau_0 + \left(\eta_\infty + \frac{\mathbf{c}}{1 + \frac{\mathbf{b}}{\mathbf{a}}\dot{\gamma}^{\mathbf{m}}}\right)\dot{\gamma} = \mathbf{const} \text{ and } \mathbf{B}(\dot{\gamma}) = \mathbf{c}\dot{\gamma}(\lambda_e - \lambda_0) = \mathbf{const}.$$

The values of the model parameters are shown in fig. 4. The values of β-parameter practically do not depend on the shear rate and are the same for break-down and build-up state. They indicate relatively wide distribution of relaxation times.

The average relaxation time decreases with increasing the shear rate. It is one decay smaller in case of break-down state.

The a- and b-parameters increase when the shear rate increase. It could be interpreted as faster change in the structure.

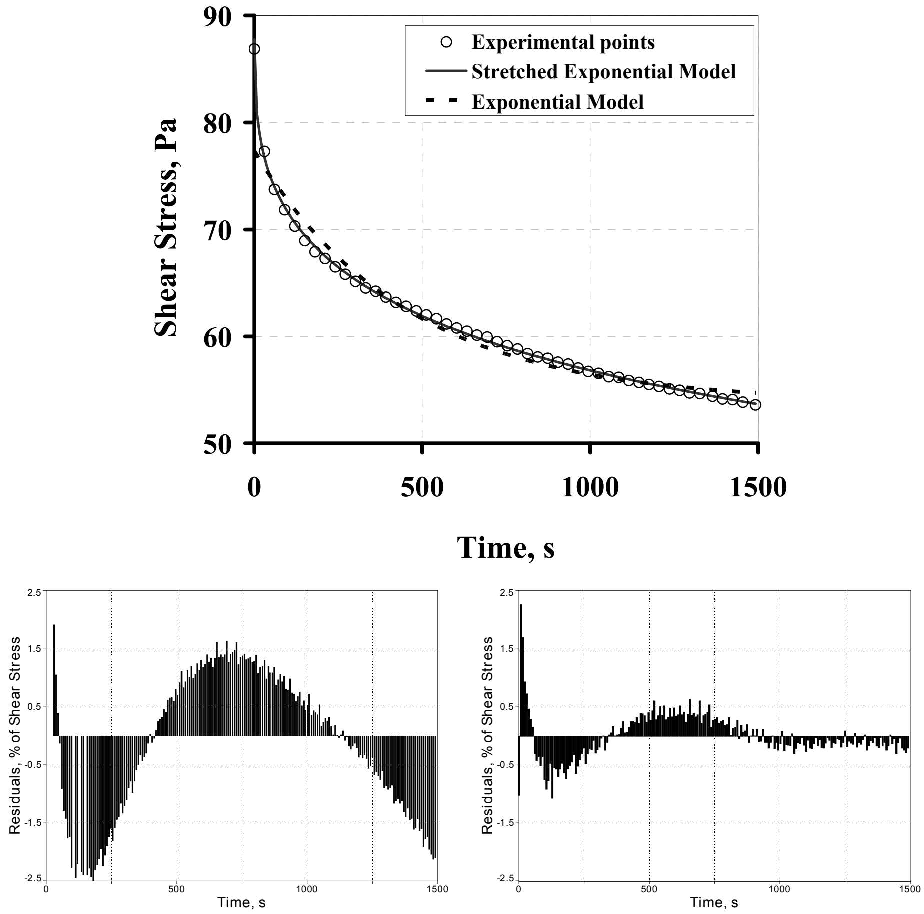


Fig.3 Exponential and stretched exponential models for structure relaxation

CONCLUSIONS

- The λ-model well interprets the thixotropic behaviour of ketchup;
- A spectrum of relaxation times is observed during the relaxation of the ketchup structure. It could be analyzed by stretched exponential model by the β-parameter.
- The parameters in the λ-model indicate faster changes in the ketchup structure, when the shear rate increases.

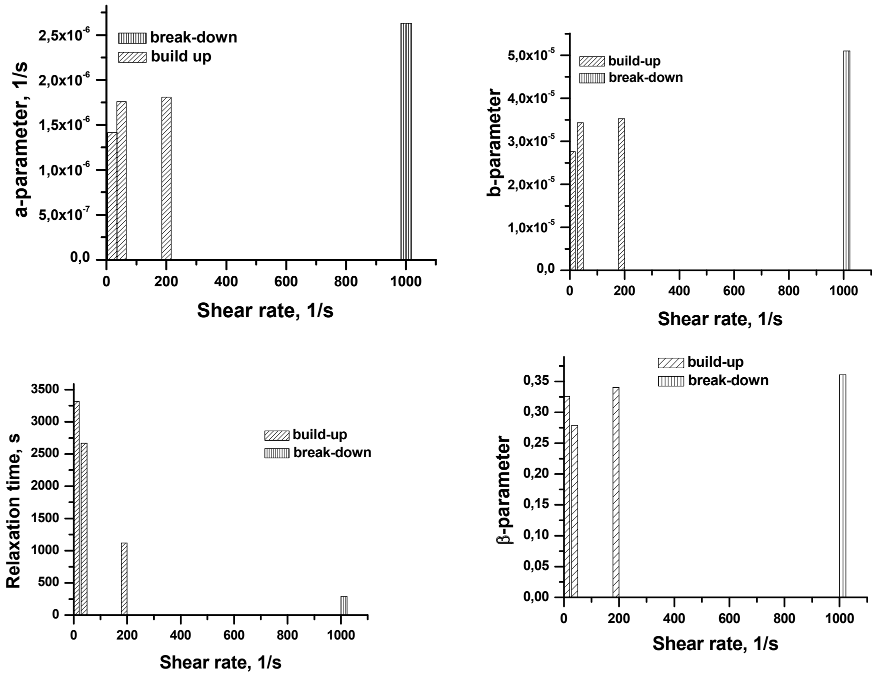


Fig. 4 Effect of the shear rate on the model parameters

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