SELECTED RHEOLOGICAL PROPERTIES OF SOME TOMATO KETCHUPS

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Abstract
This article is focused on monitoring and evaluation of rheological properties of tomato ketchups. Influence of temperature in range (5 – 30) °C and short storage time was investigated. Dependencies of rheological properties on temperature and storage time were evaluated by the regression equations and the coefficients of determination. Ketchup is a non-Newtonian material, so apparent viscosity was measured using digital rotational viscometer Anton Paar DV-3P. Densities of samples were determined according to definition. Apparent viscosity of samples decreased exponentially with increasing temperature, so the Arrhenius equation is valid. Ketchup's apparent fluidity was increasing exponentially with the temperature. We also found out that apparent viscosity had decreased with storage time and on the other hand apparent fluidity was increasing with storage time, which can be caused by structural changes in samples during storing. Temperature dependencies of ketchup densities were sufficiently characterized by decreasing linear function in measured temperature range.

Key words: *ketchup; rheological parameters; density; temperature, dependency.*

INTRODUCTION

Precise knowledge of physical quantities of materials is required at controlled processes in manufacturing, handling and holding. For the quality evaluation of food materials it is important to know their physical properties particularly, mechanical (*Kubík et al., 2017*), rheological and thermophysical (*Glicerina et al., 2013*). Tomatoes are often consumed in fresh state, but several varieties are processed into various products such as tomato sauce, soup, paste, puree, juice, ketchup and salsa. Authors noted that several studies had investigated the benefits of tomatoes in reducing the risk of heart disease, improving bone health, and decreasing the risk of cancer (*Tan & Kerr, 2015*). The industrial processing of tomatoes leads to a great variety of output products. Some of the most relevant are the following: concentrated tomato products, either as puree or paste depending on the percentage of natural soluble solids; pizza sauce, from peels and seeds; tomato powder, as dehydrated concentrated tomato; peeled tomato, either whole or diced; ketchup, tomato sauce seasoned with vinegar, sugar, salt and some spices, etc. (*Ruiz Celma et al., 2009*). New design of experimental double piston filament stretching apparatus that can stretch fluids to very high extensional strain rates was presented by *Mackley et al. (2017)*. Authors had used high speed photography for determination of filament deformation and breakup profiles of a strategically selected range of fluids including low and higher viscosity Newtonian liquids together with a viscoelastic polymer solution, biological and yield stress fluids at extensional strain rates in excess of 1000 s^{-1}. *Mackley et al. (2017)* had also reported that numerical modelling can be used with the fluids correct rheological characterization to gain physical in-sight into how rheologically complex fluids deform and breakup at very high extensional deformation rates. *Chandrapala et al. (2012)* had stated that ultrasonic pulses in combination with rheological measurements could be used at the solids concentration determination in various highly concentrated and industrial food suspensions (tomato, vegetable and pasta sauces, seafood chowder, strawberry yoghurt, cheese sauce with vegetables). Low intensity ultrasound-based techniques could be used during the detection and identification of foreign bodies in food products (e.g. tomato ketchup) (*Chandrapala et al., 2012*). The rheological behaviour of some food dispersions were investigated and modelled with the Herschel–Bulkley model by *Herrmann et al. (2013)*. Several rheologic parameters were studied in dependency on composition of various ingredients (fats, carbohydrates, proteins, water). The effects of manothermosonication or thermal treatment on tomato pectic enzymes and tomato paste rheological properties were compared by *Vercet et al. (2002)*. The quality of tomato concentrate was studied by *Fadavi et al. (2018)* using ohmic vacuum, ohmic, and conventional-vacuum heating methods. Authors had indicated that ohmic heating under vacuum condition had a good effect on quality during the concentration of tomato juice and that vacuum condition decreased the time required for processing and heating rate. Small amplitude oscillatory shear (SAOS) and large amplitude oscillatory shear (LAOS) behaviour of tomato paste was investigated by *Duvarci et al. (2017)*. Authors had stated that the semi-empirical Bird-Carreau constitutive model can be used in small amplitude oscillatory shear behaviour of tomato paste. Authors also used Ewoldt-McKinley theory for determination of non-linear rheologic properties in large amplitude oscillatory shear behaviour of tomato paste. This method offered parameters which can be used for better understanding of structural changes which occur at different deformations or time scales (*Duvarci et al., 2017*). Rheological properties of tomato products are considered as one of the most important quality attributes, since they influence product processing parameters, especially flow properties during transport, as well as consumers' acceptability (*Torbica et al., 2016*). Investigation of rheological properties and microstructure of tomato puree using continuous high pressure homogenization was done by *Tan & Kerr (2015)*. Influence of rheological and structural characterization of tomato paste on the quality of ketchup was investigated by *Bayod et al. (2008)*. According to *Sharoba et al. (2005)* ketchup is time-independent, semi-solid non-Newtonian fluid having a definite yield stress. The effect of temperature on viscosity of fluids at a specified shear rate could be described by the Arrhenius equation, in which the apparent viscosity decreases as an exponential function with temperature (*Sharoba et al., 2005*). According to *Bayod et al. (2008)* viscosity of tomato ketchup is a major quality component for consumer acceptance. Several parameters affect the flow behaviour of tomato ketchup, including the quality of the raw material (e.g. tomato paste) and the processing conditions. To achieve a constant and desirable quality in the final product (i.e. ketchup), high quality paste and continuous control and adjustment of the variables for its processing are required (*Bayod et al., 2008*). Tomato ketchup could be presented as concentrated dispersion of insoluble matter in aqueous media, and its complex structure causes that it exhibits non-Newtonian, shear-thinning and time-dependent rheological behaviour with yield stress (*Torbica et al., 2016*). Ketchup can be included into one of the most commonly consumed condiment which is made either from fresh tomatoes or from the concentrates such as tomato purees and tomato pastes (*Mert, 2012*). Effect of temperature and concentration on rheological properties of ketchup–processed cheese mixtures was analysed using steady and dynamic oscillatory shear by *Yilmaz et al. (2011)*. Temperature dependency of the apparent viscosity at a specified shear rate (50 s^{-1}) could be described by the Arrhenius model (*Yilmaz et al., 2011*). *Torbica et al. (2016)* have evaluated nutritional, rheological, and sensory properties of tomato ketchup with increased content of natural fibres made from fresh tomato pomace and compared the results with five commercial products. Authors found out that the rheological properties of the ketchup with increased fibre content depend mostly on total solids and insoluble particles content, but properties remained in the limits for standard tomato products.

Apparent viscosity is defined as ratio of shear stress and corresponding shear rate and its physical unit is (Pa·s). Viscosity changes with temperature, for most of the liquids decreases with increasing temperature. According to Eyering theory molecules of liquids continuously move into the vacancies (*Bird et al., 1960*). The temperature effect on viscosity can be described by an Arrhenius type equation

$$\eta = \eta_0 \, e^{-\frac{E_A}{RT}} \quad (1)$$

where η_0 is reference value of viscosity, E_A is activation energy, *R* is gas constant and *T* is absolute temperature (*Figura & Teixeira, 2007*). Density of material ρ is defined as a ratio between mass of material *m* and its volume *V*

$$\rho = \frac{m}{V} \quad (2)$$

The definition is valid for solids, liquids, gases and disperses (*Figura & Teixeira, 2007*). The standard SI unit of density is ($kg \cdot m^{-3}$). Reciprocal value of apparent viscosity η is called apparent fluidity φ and unit of apparent fluidity is ($Pa^{-1}.s^{-1}$) (*Figura & Teixeira, 2007*).

$$\varphi = \frac{1}{\eta} \quad (3)$$

Almost all parameters are influenced by temperature, so mainly these effects were analysed as a main aim in this article.

MATERIALS AND METHODS

Measurements were performed in laboratory settings on four samples of tomato ketchup, purchased in local market (Heinz tomato ketchup, soft ketchup Hellmann´s, sweet ketchup Hamé and soft ketchup Snico). As ketchup is not Newtonian material, apparent viscosity had to be measured. Density (Eq. 2) and apparent fluidity (Eq. 3) were also determined. The measurements of all samples were carried out under the same conditions in approximate temperature range (5 – 30) °C. Measuring of apparent viscosity was performed by digital rotational viscometer Anton Paar (DV-3P). First measurements were performed at the beginning of storing, second measurements were done after three weeks of storing and last measurements were realised after four weeks of storing. There were constructed dependencies of rheological properties on temperature and storage time and evaluated by the regression equations and the coefficients of determination. Temperature dependencies of apparent viscosity can be described by decreasing exponential function (4), in the case of temperature dependencies of apparent fluidity can be used increasing exponential function (5), and temperature dependencies of density were described by decreasing linear function (6).

$$\eta = A e^{-B\left(\frac{t}{t_o}\right)}; \quad \varphi = E e^{F\left(\frac{t}{t_o}\right)}; \quad \rho = -G\left(\frac{t}{t_0}\right) + H \qquad (4, 5, 6)$$

where t is temperature (°C), t_0 is 1 °C, A, B, E, F, G, H are constants dependent on kind of material, and on ways of processing and storing .

RESULTS AND DISCUSSION

On Fig. 1 are presented temperature dependencies of ketchup apparent viscosity. It is possible to observe from Fig. 1 that apparent viscosity of ketchups is decreasing with increasing of temperature. The progress can be described by decreasing exponential function, which is in accordance with Arrhenius equation (1). Comparable rheological results for ketchup were reported by *Sharoba et al. (2005)*. It is also visible on Fig. 1 that highest apparent viscosities were obtained for sample of Ketchup Snico, and lowest values for Ketchup Hamé, which could be caused by different composition of ketchups.

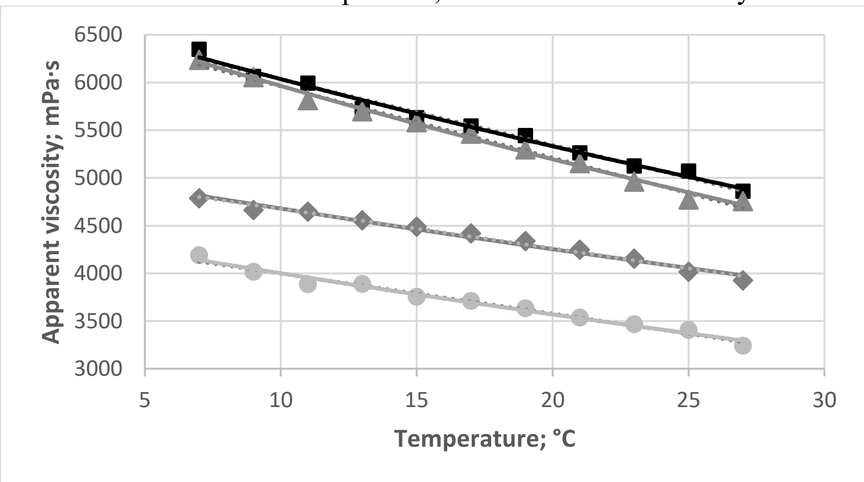

Fig. 1 Relations of ketchup apparent viscosity to the temperature Snico (■), Hellmanns (▲), Heinz (♦), Hamé (●)

Temperature dependencies of ketchup density are shown on Fig. 2. It can be seen that values of density are decreasing with increasing temperature for all samples of ketchup. Similar decreasing progress was found for different samples by *Kumbár & Nedomová (2015)*. In this temperature range was used linear decreasing function. Same type of dependency was used also by *Thomas et al. (2015)* and *Kelkar et al. (2015)*. Highest density values were obtained for Ketchup Snico and on the contrary lowest values for Ketchup Hamé. Apparent fluidity dependencies on temperature are presented on Fig. 3. Increasing exponential character of dependency was used for all samples. Due to the fact that apparent fluidity is defined as reciprocal value of apparent viscosity, highest fluidities were found for Ketchup Hamé and lowest for Ketchup Snico. Regression coefficients and coefficients of determination for all dependencies are shown in Tab. 1.

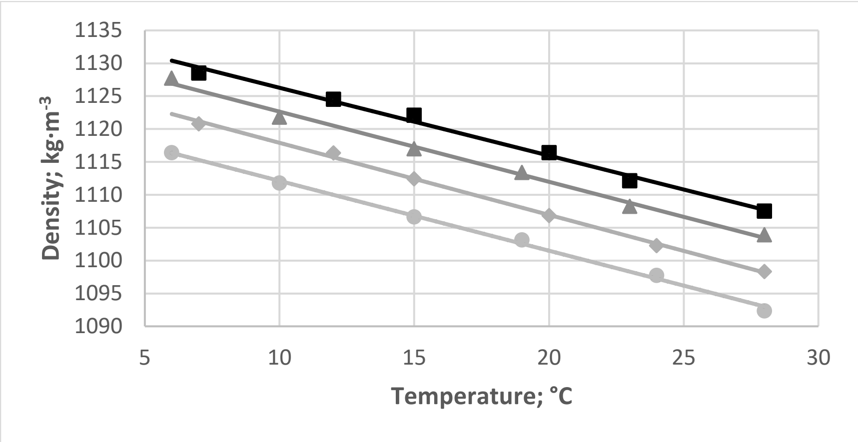

Fig. 2 Relations of ketchup density to the temperature Snico (■), Hellmanns (▲), Heinz (♦), Hamé (●)

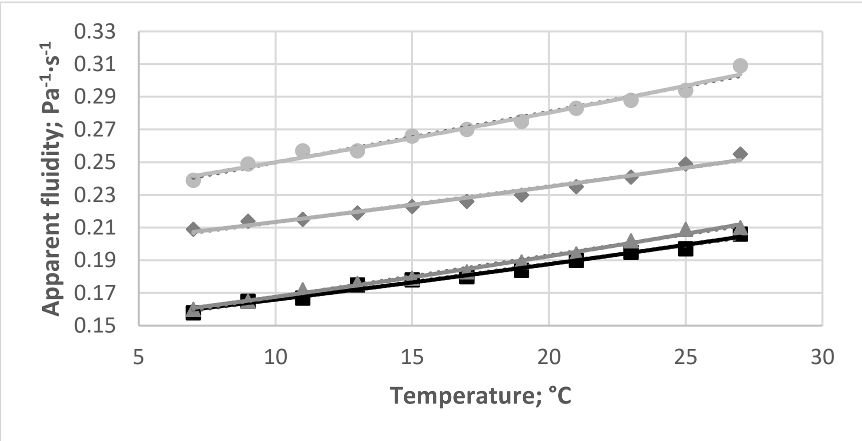

Fig. 3 Relations of ketchup apparent fluidity to the temperature Snico (■), Hellmanns (▲), Heinz (♦), Hamé (●)

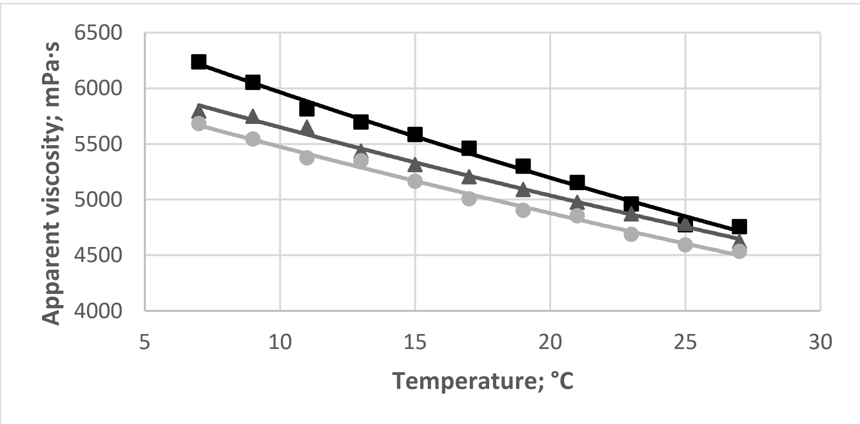

Fig. 4 Relations of ketchup Hellmann´s apparent viscosity to the temperature: first measurement (■), next measurement (▲), last measurement (●)

Influence of storage time for sample of Ketchup Hellmann´s could be seen on Fig. 4. It is clear from Fig. 4 that highest apparent viscosity values were obtained in the beginning of storage, lower values were after three weeks of storing and lowest values after four weeks of storing. This proportion could be caused by structural changes in sample during storing. Similar results were found for other three samples of ketchup. It can be seen from Tab. 1 that coefficients of determination reached very high values in the approximate range (0.980 – 0.998).

Tab. 1 Coefficients A, B, E, F, G and H of regression equations (4 – 6) and coefficients of determinations (R^2)

	Coefficients of regression equations (4 – 6)		
Sample of ketchup	A mPa·s	B -	R^2
Snico	6 832.3	0.012	0.988 4
Hellmann´s	6846.7	0.014	0.992 2
Heinz	5 147.8	0.010	0.980 3
Hamé	4 482.6	0.011	0.981 4
Sample of ketchup	E $Pa^{-1}\cdot s^{-1}$	F -	R^2
Snico	0.146 8	0.012 3	0.987 1
Hellmann´s	0.146 0	0.013 8	0.9919
Heinz	0.193 9	0.009 6	0.978 4
Hamé	0.223 0	0.011 4	0.982 7
Sample of ketchup	G $kg\cdot m^{-3}$	H $kg\cdot m^{-3}$	R^2
Snico	1 136.6	1.031 3	0.991 9
Hellmann´s	1 133.3	1.066 6	0.994 2
Heinz	1 128.9	1.095 6	0.998 2
Hamé	1 122.7	1.061 8	0.997 1
Ketchup Hellmann´s/ measurement	A mPa·s	B -	R^2
First	6 846.7	0.014	0.992 2
Next	6 337.1	0.011	0.994 0
Last	6 143.7	0.012	0.992 6

CONCLUSIONS

Composition of food materials is different so their physical properties are very complex. Physical properties of food materials depend on the manipulation, external conditions and other factors, which determine their behaviour. Rheological properties of tomato ketchups were measured and analysed in this paper. Apparent viscosity is relevant for non-Newtonian materials. Effect of temperature and storing time on measured samples of tomato ketchups was searched and comparison of used samples was made. We found out that apparent viscosity of samples decreased exponentially with increasing temperature, so the Arrhenius equation is valid. Comparable rheological results for ketchup were reported by *Sharoba et al. (2005)*. Proportion of the curves in Fig. 1 could be caused by different composition of analysed samples. Ketchup's apparent fluidity was increasing exponentially with the temperature. Apparent viscosity had decreased with storage time and on the other hand apparent fluidity had increased with storage time, which can be caused by structural changes in samples during storing. Temperature dependencies of ketchup densities were sufficiently characterized by decreasing linear function in measured temperature range, which is in accordance with authors (*Kumbár & Nedomová, 2015*; *Thomas et al., 2015*; *Kelkar et al., 2015*; etc.). The calculated rheological characteristics can be used for designing of technological equipment or containers for distribution of the product to the final users. The knowledge of flow behaviour is also important for the development of new recipes and direct qualitative assessment of the products.

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